CHAPTER 2

ATOMIC STRUCTURE AND INTERATOMIC BONDING

PROBLEM SOLUTIONS

Fundamental Concepts
Electrons in Atoms

2.1 *Cite the difference between atomic mass and atomic weight.*

Solution

Atomic mass is the mass of an individual atom, whereas atomic weight is the average (weighted) of the atomic masses of an atom's naturally occurring isotopes.

2.2 *Silicon has three naturally occurring isotopes: 92.23% of* ^{28}Si*, with an atomic weight of 27.9769 amu, 4.68% of* ^{29}Si*, with an atomic weight of 28.9765 amu, and 3.09% of* ^{30}Si*, with an atomic weight of 29.9738 amu. On the basis of these data, confirm that the average atomic weight of Si is 28.0854 amu.*

Solution

The average atomic weight of silicon $(\bar{A}_{\mathrm{Si}})$ is computed by adding fraction-of-occurrence/atomic weight products for the three isotopes—i.e., using Equation 2.2. (Remember: fraction of occurrence is equal to the percent of occurrence divided by 100.) Thus

$$\bar{A}_{\mathrm{Si}} = f_{^{28}\mathrm{Si}} A_{^{28}\mathrm{Si}} + f_{^{29}\mathrm{Si}} A_{^{29}\mathrm{Si}} + f_{^{30}\mathrm{Si}} A_{^{30}\mathrm{Si}}$$

$$= (0.9223)(27.9769) + (0.0468)(28.9765) + (0.0309)(29.9738) = 28.0854$$

2.3 *Zinc has five naturally occurring isotopes: 48.63% of* ^{64}*Zn with an atomic weight of 63.929 amu; 27.90% of* ^{66}*Zn with an atomic weight of 65.926 amu; 4.10% of* ^{67}*Zn with an atomic weight of 66.927 amu; 18.75% of* ^{68}*Zn with an atomic weight of 67.925 amu; and 0.62% of* ^{70}*Zn with an atomic weight of 69.925 amu. Calculate the average atomic weight of Zn.*

Solution

The average atomic weight of zinc $\bar{A}_{\text{Zn}}$ is computed by adding fraction-of-occurrence—atomic weight products for the five isotopes—i.e., using Equation 2.2. (Remember: fraction of occurrence is equal to the percent of occurrence divided by 100.) Thus

$$\bar{A}_{\text{Zn}} = f_{^{64}\text{Zn}} A_{^{64}\text{Zn}} + f_{^{66}\text{Zn}} A_{^{66}\text{Zn}} + f_{^{67}\text{Zn}} A_{^{67}\text{Zn}} + f_{^{68}\text{Zn}} A_{^{68}\text{Zn}} + f_{^{70}\text{Zn}} A_{^{70}\text{Zn}}$$

Including data provided in the problem statement we solve for $\bar{A}_{\text{Zn}}$ as

$$\bar{A}_{\text{Zn}} = (0.4863)(63.929\ \text{amu}) + (0.2790)(65.926\ \text{amu})$$

$$+ (0.0410)(66.927\ \text{amu}) + (0.1875)(67.925\ \text{amu}) + (0.0062)(69.925)$$

$$= 65.400\ \text{amu}$$

2.4 *Indium has two naturally occurring isotopes:* ^{113}*In with an atomic weight of 112.904 amu, and* ^{115}*In with an atomic weight of 114.904 amu. If the average atomic weight for In is 114.818 amu, calculate the fraction-of-occurrences of these two isotopes.*

Solution

The average atomic weight of indium $(\bar{A}_{\text{In}})$ is computed by adding fraction-of-occurrence—atomic weight products for the two isotopes—i.e., using Equation 2.2, or

$$\bar{A}_{\text{In}} = f_{^{113}\text{In}} A_{^{113}\text{In}} + f_{^{115}\text{In}} A_{^{115}\text{In}}$$

Because there are just two isotopes, the sum of the fracture-of-occurrences will be 1.000; or

$$f_{^{113}\text{In}} + f_{^{115}\text{In}} = 1.000$$

which means that

$$f_{^{113}\text{In}} = 1.000 - f_{^{115}\text{In}}$$

Substituting into this expression the one noted above for $f_{^{113}\text{In}}$, and incorporating the atomic weight values provided in the problem statement yields

$$114.818 \text{ amu} = f_{^{113}\text{In}} A_{^{113}\text{In}} + f_{^{115}\text{In}} A_{^{115}\text{In}}$$

$$114.818 \text{ amu} = (1.000 - f_{^{113}\text{In}}) A_{^{113}\text{In}} + f_{^{115}\text{In}} A_{^{115}\text{In}}$$

$$114.818 \text{ amu} = (1.000 - f_{^{115}\text{In}})(112.904 \text{ amu}) + f_{^{115}\text{In}} (114.904 \text{ amu})$$

$$114.818 \text{ amu} = 112.904 \text{ amu} - f_{^{115}\text{In}} (112.904 \text{ amu}) + f_{^{115}\text{In}} (114.904 \text{ amu})$$

Solving this expression for $f_{^{115}\text{In}}$ yields $f_{^{115}\text{In}} = 0.957$. Furthermore, because

$$f_{^{113}\text{In}} = 1.000 - f_{^{115}\text{In}}$$

then

$$f_{^{113}\text{In}} = 1.000 - 0.957 = 0.043$$

2.5 *(a) How many grams are there in one amu of a material?*

(b) Mole, in the context of this book, is taken in units of gram-mole. On this basis, how many atoms are there in a pound-mole of a substance?

Solution

(a) In order to determine the number of grams in one amu of material, appropriate manipulation of the amu/atom, g/mol, and atom/mol relationships is all that is necessary, as

$$\#\text{g/amu} = \left(\frac{1\ \text{mol}}{6.022 \times 10^{23}\ \text{atoms}}\right)\left(\frac{1\ \text{g/mol}}{1\ \text{amu/atom}}\right)$$

$$= 1.66 \times 10^{-24}\ \text{g/amu}$$

(b) Since there are 453.6 g/lb_m,

$$1\ \text{lb-mol} = (453.6\ \text{g/lb}_\text{m})(6.022 \times 10^{23}\ \text{atoms/g-mol})$$

$$= 2.73 \times 10^{26}\ \text{atoms/lb-mol}$$

2.6 *(a) Cite two important quantum-mechanical concepts associated with the Bohr model of the atom.*

(b) Cite two important additional refinements that resulted from the wave-mechanical atomic model.

Solution

(a) Two important quantum-mechanical concepts associated with the Bohr model of the atom are (1) that electrons are particles moving in discrete orbitals, and (2) electron energy is quantized into shells.

(b) Two important refinements resulting from the wave-mechanical atomic model are (1) that electron position is described in terms of a probability distribution, and (2) electron energy is quantized into both shells and subshells--each electron is characterized by four quantum numbers.

2.7 *Relative to electrons and electron states, what does each of the four quantum numbers specify?*

Solution

The n quantum number designates the electron shell.

The l quantum number designates the electron subshell.

The m_l quantum number designates the number of electron states in each electron subshell.

The m_s quantum number designates the spin moment on each electron.

2.8 *Allowed values for the quantum numbers of electrons are as follows:*

$$n = 1, 2, 3, \ldots$$

$$l = 0, 1, 2, 3, \ldots, n-1$$

$$m_l = 0, \pm 1, \pm 2, \pm 3, \ldots, \pm l$$

$$m_s = \pm \frac{1}{2}$$

The relationships between n and the shell designations are noted in Table 2.1. Relative to the subshells,

l = 0 corresponds to an s subshell

l = 1 corresponds to a p subshell

l = 2 corresponds to a d subshell

l = 3 corresponds to an f subshell

For the K shell, the four quantum numbers for each of the two electrons in the 1s state, in the order of nlm_lm_s, *are* $100(\frac{1}{2})$ *and* $100(-\frac{1}{2})$. *Write the four quantum numbers for all of the electrons in the L and M shells, and note which correspond to the s, p, and d subshells.*

Answer

For the *L* state, $n = 2$, and eight electron states are possible. Possible l values are 0 and 1, while possible m_l values are 0 and ±1; and possible m_s values are $\pm\frac{1}{2}$. Therefore, for the *s* states, the quantum numbers are $200(\frac{1}{2})$ and $200(-\frac{1}{2})$. For the *p* states, the quantum numbers are $210(\frac{1}{2})$, $210(-\frac{1}{2})$, $211(\frac{1}{2})$, $211(-\frac{1}{2})$, $21(-1)(\frac{1}{2})$, and $21(-1)(-\frac{1}{2})$.

For the *M* state, $n = 3$, and 18 states are possible. Possible l values are 0, 1, and 2; possible m_l values are 0, ±1, and ±2; and possible m_s values are $\pm\frac{1}{2}$. Therefore, for the *s* states, the quantum numbers are $300(\frac{1}{2})$, $300(-\frac{1}{2})$, for the *p* states they are $310(\frac{1}{2})$, $310(-\frac{1}{2})$, $311(\frac{1}{2})$, $311(-\frac{1}{2})$, $31(-1)(\frac{1}{2})$, and $31(-1)(-\frac{1}{2})$; for the *d* states they are $320(\frac{1}{2})$, $320(-\frac{1}{2})$, $321(\frac{1}{2})$, $321(-\frac{1}{2})$, $32(-1)(\frac{1}{2})$, $32(-1)(-\frac{1}{2})$, $322(\frac{1}{2})$, $322(-\frac{1}{2})$, $32(-2)(\frac{1}{2})$, and $32(-2)(-\frac{1}{2})$.

2.9 *Give the electron configurations for the following ions:* P^{5+}, P^{3-}, Sn^{4+}, Se^{2-}, I^{-}, *and* Ni^{2+}.

Solution

The electron configurations for the ions are determined using Table 2.2 (and Figure 2.8).

P^{5+}: From Table 2.2, the electron configuration for an atom of phosphorus is $1s^22s^22p^63s^23p^3$. In order to become an ion with a plus five charge, it must lose five electrons—in this case the three $3p$ and the two $3s$. Thus, the electron configuration for a P^{5+} ion is $1s^22s^22p^6$.

P^{3-}: From Table 2.2, the electron configuration for an atom of phosphorus is $1s^22s^22p^63s^23p^3$. In order to become an ion with a minus three charge, it must acquire three electrons—in this case another three $3p$. Thus, the electron configuration for a P^{3-} ion is $1s^22s^22p^63s^23p^6$.

Sn^{4+}: From the periodic table, Figure 2.8, the atomic number for tin is 50, which means that it has fifty electrons and an electron configuration of $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^2$. In order to become an ion with a plus four charge, it must lose four electrons—in this case the two $4s$ and two $5p$. Thus, the electron configuration for an Sn^{4+} ion is $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}$.

Se^{2-}: From Table 2.2, the electron configuration for an atom of selenium is $1s^22s^22p^63s^23p^63d^{10}4s^24p^4$. In order to become an ion with a minus two charge, it must acquire two electrons—in this case another two $4p$. Thus, the electron configuration for an Se^{2-} ion is $1s^22s^22p^63s^23p^63d^{10}4s^24p^6$.

I^{-}: From the periodic table, Figure 2.8, the atomic number for iodine is 53, which means that it has fifty three electrons and an electron configuration of $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^5$. In order to become an ion with a minus one charge, it must acquire one electron—in this case another $5p$. Thus, the electron configuration for an I^{-} ion is $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^6$.

Ni^{2+}: From Table 2.2, the electron configuration for an atom of nickel is $1s^22s^22p^63s^23p^63d^84s^2$. In order to become an ion with a plus two charge, it must lose two electrons—in this case the two $4s$. Thus, the electron configuration for a Ni^{2+} ion is $1s^22s^22p^63s^23p^63d^8$.

2.10 *Potassium iodide (KI) exhibits predominantly ionic bonding. The* K^+ *and* I^- *ions have electron structures that are identical to which two inert gases?*

Solution

The K^+ ion is just a potassium atom that has lost one electron; therefore, it has an electron configuration the same as argon (Figure 2.8).

The I^- ion is a iodine atom that has acquired one extra electron; therefore, it has an electron configuration the same as xenon.

2.11 *With regard to electron configuration, what do all the elements in Group IIA of the periodic table have in common?*

Solution

Each of the elements in Group IIA has two *s* electrons.

2.12 *To what group in the periodic table would an element with atomic number 112 belong?*

Solution

From the periodic table (Figure 2.8) the element having atomic number 112 would belong to group IIB. According to Figure 2.8, Ds, having an atomic number of 110 lies below Pt in the periodic table and in the right-most column of group VIII. Moving two columns to the right puts element 112 under Hg and in group IIB.

This element has been artificially created and given the name Copernicium with the symbol Cn. It was named after Nicolaus Copernicus, the Polish scientist who proposed that the earth moves around the sun (and not vice versa).

2.13 *Without consulting Figure 2.8 or Table 2.2, determine whether each of the following electron configurations is an inert gas, a halogen, an alkali metal, an alkaline earth metal, or a transition metal. Justify your choices.*

(a) $1s^22s^22p^63s^23p^5$

(b) $1s^22s^22p^63s^23p^63d^74s^2$

(c) $1s^22s^22p^63s^23p^63d^{10}4s^24p^6$

(d) $1s^22s^22p^63s^23p^64s^1$

(e) $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^55s^2$

(f) $1s^22s^22p^63s^2$

<u>Solution</u>

(a) The $1s^22s^22p^63s^23p^5$ electron configuration is that of a halogen because it is one electron deficient from having a filled *p* subshell.

(b) The $1s^22s^22p^63s^23p^63d^74s^2$ electron configuration is that of a transition metal because of an incomplete *d* subshell.

(c) The $1s^22s^22p^63s^23p^63d^{10}4s^24p^6$ electron configuration is that of an inert gas because of filled 4*s* and 4*p* subshells.

(d) The $1s^22s^22p^63s^23p^64s^1$ electron configuration is that of an alkali metal because of a single *s* electron.

(e) The $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^55s^2$ electron configuration is that of a transition metal because of an incomplete *d* subshell.

(f) The $1s^22s^22p^63s^2$ electron configuration is that of an alkaline earth metal because of two *s* electrons.

2.14 *(a) What electron subshell is being filled for the rare earth series of elements on the periodic table?*

(b) What electron subshell is being filled for the actinide series?

Solution

(a) The 4*f* subshell is being filled for the rare earth series of elements.

(b) The 5*f* subshell is being filled for the actinide series of elements.

Bonding Forces and Energies

2.15 Calculate the force of attraction between a Ca^{2+} and an O^{2-} ion whose centers are separated by a distance of 1.25 nm.

Solution

To solve this problem for the force of attraction between these two ions it is necessary to use Equation 2.13, which takes on the form of Equation 2.14 when values of the constants *e* and ε_0 are included—that is

$$F_A = \frac{(2.31 \times 10^{-28}\ \text{N-m}^2)\left(|Z_1|\right)\left(|Z_2|\right)}{r^2}$$

If we take ion 1 to be Ca^{2+} and ion 2 to be O^{2-}, then $Z_1 = +2$ and $Z_2 = -2$; also, from the problem statement $r = 1.25$ nm $= 1.25 \times 10^{-9}$ m. Thus, using Equation 2.14, we compute the force of attraction between these two ions as follows:

$$F_A = \frac{(2.31 \times 10^{-28}\ \text{N-m}^2)\left(|+2|\right)\left(|-2|\right)}{(1.25 \times 10^{-9}\ \text{m})^2}$$

$$5.91 \times 10^{-10}\ \text{N}$$

2.16 *The atomic radii of* Mg^{2+} *and* F^- *ions are 0.072 and 0.133 nm, respectively.*

(a) Calculate the force of attraction between these two ions at their equilibrium interionic separation (i.e., when the ions just touch one another).

(b) What is the force of repulsion at this same separation distance.

Solution

This problem is solved in the same manner as Example Problem 2.2.

(a) The force of attraction F_A is calculated using Equation 2.14 taking the interionic separation r to be r_0 the equilibrium separation distance. This value of r_0 is the sum of the atomic radii of the Mg^{2+} and F^- ions (per Equation 2.15)—that is

$$r_0 = r_{\mathrm{Mg^{2+}}} + r_{\mathrm{F^-}}$$

$$= 0.072 \text{ nm} + 0.133 \text{ nm} = 0.205 \text{ nm} = 0.205 \times 10^{-9} \text{ m}$$

We may now compute F_A using Equation 2.14. If was assume that ion 1 is Mg^{2+} and ion 2 is F^- then the respective charges on these ions are $Z_1 = Z_{\mathrm{Mg^{2+}}} = +2$, whereas $Z_2 = Z_{\mathrm{F^-}} = -1$. Therefore, we determine F_A as follows:

$$F_A = \frac{(2.31 \times 10^{-28} \text{ N-m}^2)\left(|Z_1|\right)\left(|Z_2|\right)}{r_0^2}$$

$$= \frac{(2.31 \times 10^{-28} \text{ N-m}^2)\left(|+2|\right)\left(|-1|\right)}{(0.205 \times 10^{-9} \text{ m})^2}$$

$$= 1.10 \times 10^{-8} \text{ N}$$

(b) At the equilibrium separation distance the sum of attractive and repulsive forces is zero according to Equation 2.4. Therefore

$$F_R = -F_A$$

$$= -(1.10 \times 10^{-8} \text{ N}) = -1.10 \times 10^{-8} \text{ N}$$

2.17 *The force of attraction between a divalent cation and a divalent anion is 1.67 × 10^{-8} N. If the ionic radius of the cation is 0.080 nm, what is the anion radius?*

Solution

To begin, let us rewrite Equation 2.15 to read as follows:

$$r_0 = r_C + r_A$$

in which r_C and r_A represent, respectively, the radii of the cation and anion. Thus, this problem calls for us to determine the value of r_A. However, before this is possible, it is necessary to compute the value of r_0 using Equation 2.14, and replacing the parameter *r* with r_0. Solving this expression for r_0 leads to the following:

$$r_0 = \sqrt{\frac{(2.31 \times 10^{-28}\ \text{N-m}^2)\left(|Z_C|\right)\left(|Z_A|\right)}{F_A}}$$

Here Z_C and Z_A represent charges on the cation and anion, respectively. Furthermore, inasmuch as both ion are divalent means that $Z_C = +2$ and $Z_A = -2$. The value of r_0 is determined as follows:

$$r_0 = \sqrt{\frac{(2.31 \times 10^{-28}\ \text{N-m}^2)\left(|+2|\right)\left(|-2|\right)}{1.67 \times 10^{-8}\ \text{N}}}$$

$$= \mathbf{0.235 \times 10^{-9}\ m = 0.235\ nm}$$

Using the version of Equation 2.15 given above, and incorporating this value of r_0 and also the value of r_C given in the problem statement (0.080 nm) it is possible to solve for r_A:

$$r_A = r_0 - r_C$$

$$= \mathbf{0.235\ nm - 0.080\ nm = 0.155\ nm}$$

2.18 *The net potential energy between two adjacent ions,* E_N*, may be represented by the sum of Equations 2.9 and 2.11; that is,*

$$E_N = -\frac{A}{r} + \frac{B}{r^n} \qquad (2.17)$$

Calculate the bonding energy E_0 *in terms of the parameters A, B, and n using the following procedure:*

1. Differentiate E_N *with respect to r, and then set the resulting expression equal to zero, since the curve of* E_N *versus r is a minimum at* E_0*.*

2. Solve for r in terms of A, B, and n, which yields r_0*, the equilibrium interionic spacing.*

3. Determine the expression for E_0 *by substitution of* r_0 *into Equation 2.17.*

Solution

(a) Differentiation of Equation 2.17 yields

$$\frac{dE_N}{dr} = \frac{d\left(-\frac{A}{r}\right)}{dr} + \frac{d\left(\frac{B}{r^n}\right)}{dr}$$

$$= \frac{A}{r^{(1+1)}} - \frac{nB}{r^{(n+1)}} = 0$$

(b) Now, solving for r (= r_0)

$$\frac{A}{r_0^2} = \frac{nB}{r_0^{(n+1)}}$$

or

$$r_0 = \left(\frac{A}{nB}\right)^{1/(1-n)}$$

(c) Substitution for r_0 into Equation 2.17 and solving for E (= E_0) yields

$$E_0 = -\frac{A}{r_0} + \frac{B}{r_0^n}$$

$$= -\frac{A}{\left(\frac{A}{nB}\right)^{1/(1-n)}} + \frac{B}{\left(\frac{A}{nB}\right)^{n/(1-n)}}$$

2.19 *For a* $Na^+–Cl^−$ *ion pair, attractive and repulsive energies* E_A *and* E_R*, respectively, depend on the distance between the ions r, according to*

$$E_A = -\frac{1.436}{r}$$

$$E_R = \frac{7.32 \times 10^{-6}}{r^8}$$

For these expressions, energies are expressed in electron volts per $Na^+–Cl^−$ *pair, and r is the distance in nanometers. The net energy* E_N *is just the sum of the preceding two expressions.*

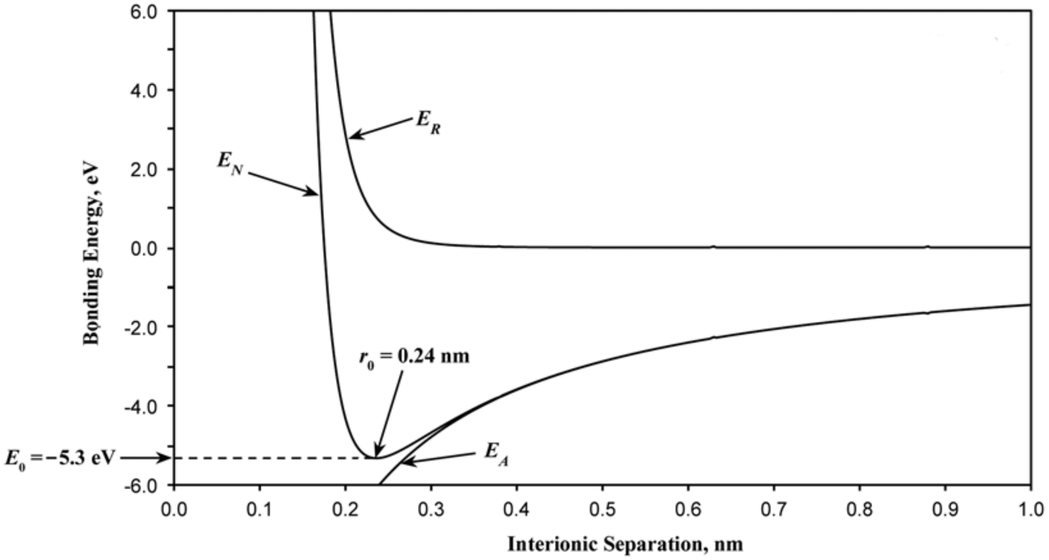
(a) Superimpose on a single plot E_N*,* E_R*, and* E_A *versus r up to 1.0 nm.*

(b) On the basis of this plot, determine (i) the equilibrium spacing r_0 *between the* Na^+ *and* $Cl^−$ *ions, and (ii) the magnitude of the bonding energy* E_0 *between the two ions.*

(c) Mathematically determine the r_0 *and* E_0 *values using the solutions to Problem 2.18, and compare these with the graphical results from part (b).*

Solution

(a) Curves of E_A, E_R, and E_N are shown on the plot below.



(b) From this plot:

$r_0 = 0.24$ nm

$E_0 = –5.3$ eV

(c) From Equation 2.17 for E_N

$$A = 1.436$$

$$B = 7.32 \times 10^{-6}$$

$$n = 8$$

Thus,

$$r_0 = \left(\frac{A}{nB}\right)^{1/(1-n)}$$

$$= \left[\frac{1.436}{(8)(7.32 \times 10^{-6})}\right]^{1/(1-8)} = \mathbf{0.236\ nm}$$

and

$$E_0 = -\frac{1.436}{\left[\dfrac{1.436}{(8)(7.32 \times 10^{-6})}\right]^{1/(1-8)}} + \frac{7.32 \times 10^{-6}}{\left[\dfrac{1.436}{(8)(7.32 \times 10^{-6})}\right]^{8/(1-8)}}$$

$$= -5.32\ \text{eV}$$

2.20 *Consider a hypothetical* X^+*–*Y^- *ion pair for which the equilibrium interionic spacing and bonding energy values are 0.38 nm and –5.37 eV, respectively. If it is known that n in Equation 2.17 has a value of 8, using the results of Problem 2.18, determine explicit expressions for attractive and repulsive energies* E_A *and* E_R *of Equations 2.9 and 2.11.*

Solution

(a) This problem gives us, for a hypothetical X^+-Y^- ion pair, values for r_0 (0.38 nm), E_0 (– 5.37 eV), and n (8), and asks that we determine explicit expressions for attractive and repulsive energies of Equations 2.9 and 2.11. In essence, it is necessary to compute the values of A and B in these equations. Expressions for r_0 and E_0 in terms of n, A, and B were determined in Problem 2.18, which are as follows:

$$r_0 = \left(\frac{A}{nB}\right)^{1/(1-n)}$$

$$E_0 = -\frac{A}{\left(\frac{A}{nB}\right)^{1/(1-n)}} + \frac{B}{\left(\frac{A}{nB}\right)^{n/(1-n)}}$$

Thus, we have two simultaneous equations with two unknowns (viz. A and B). Upon substitution of values for r_0 and E_0 in terms of n, the above two equations become

$$0.38\ \text{nm} = \left(\frac{A}{8B}\right)^{1/(1-8)} = \left(\frac{A}{8B}\right)^{-1/7}$$

and

$$-5.37\ \text{eV} = -\frac{A}{\left(\frac{A}{8B}\right)^{1/(1-8)}} + \frac{B}{\left(\frac{A}{8B}\right)^{8/(1-8)}}$$

$$= -\frac{A}{\left(\frac{A}{8B}\right)^{-1/7}} + \frac{B}{\left(\frac{A}{10B}\right)^{-8/7}}$$

We now want to solve these two equations simultaneously for values of A and B. From the first of these two equations, solving for $A/8B$ leads to

$$\frac{A}{8B} = (0.38\ \text{nm})^{-7}$$

Furthermore, from the above equation the A is equal to

$$A = 8B(0.38\ \text{nm})^{-7}$$

When the above two expressions for $A/8B$ and A are substituted into the above expression for E_0 (– 5.37 eV), the following results

$$-5.37\ \text{eV} == -\frac{A}{\left(\frac{A}{8B}\right)^{-1/7}} + \frac{B}{\left(\frac{A}{10B}\right)^{-8/7}}$$

$$= -\frac{8B(0.38\ \text{nm})^{-7}}{\left[(0.38\ \text{nm})^{-7}\right]^{-1/7}} + \frac{B}{\left[(0.38\ \text{nm})^{-7}\right]^{-8/7}}$$

$$= -\frac{8B(0.38\ \text{nm})^{-7}}{0.38\ \text{nm}} + \frac{B}{(0.38\ \text{nm})^{8}}$$

Or

$$-5.37\ \text{eV} == -\frac{8B}{(0.38\ \text{nm})^{8}} + \frac{B}{(0.38\ \text{nm})^{8}} = -\frac{7B}{(0.38\ \text{nm})^{8}}$$

Solving for B from this equation yields

$$B = 3.34 \times 10^{-4}\ \text{eV-nm}^{8}$$

Furthermore, the value of A is determined from one of the previous equations, as follows:

$$A = 8B(0.38\ \text{nm})^{-7} = (8)(3.34 \times 10^{-4}\ \text{eV-nm}^{8})(0.38\ \text{nm})^{-7}$$

$$= 2.34\ \text{eV-nm}$$

Thus, Equations 2.9 and 2.11 become

$$E_A = -\frac{2.34}{r}$$

$$E_R = \frac{3.34 \times 10^{-4}}{r^{8}}$$

Of course these expressions are valid for r and E in units of nanometers and electron volts, respectively.

2.21 *The net potential energy* E_N *between two adjacent ions is sometimes represented by the expression*

$$E_N = -\frac{C}{r} + D\exp\left(-\frac{r}{\rho}\right) \qquad (2.18)$$

in which r is the interionic separation and C, D, and ρ are constants whose values depend on the specific material.

(a) Derive an expression for the bonding energy E_0 *in terms of the equilibrium interionic separation* r_0 *and the constants D and ρ using the following procedure:*

(i) Differentiate E_N *with respect to r, and set the resulting expression equal to zero.*

(ii) Solve for C in terms of D, ρ, and r_0.

(iii) Determine the expression for E_0 *by substitution for C in Equation 2.18.*

(b) Derive another expression for E_0 *in terms of* r_0*, C, and ρ using a procedure analogous to the one outlined in part* (a).

Solution

(a) Differentiating Equation 2.18 with respect to *r* yields

$$\frac{dE}{dr} = \frac{d\left(-\frac{C}{r}\right)}{dr} - \frac{d\left[D\exp\left(-\frac{r}{\rho}\right)\right]}{dr}$$

$$= \frac{C}{r^2} - \frac{D\exp\left(-\frac{r}{\rho}\right)}{\rho}$$

At $r = r_0$, $dE/dr = 0$, and

$$\frac{C}{r_0^2} = \frac{D\exp\left(-\frac{r_0}{\rho}\right)}{\rho} \qquad (2.18a)$$

Solving for *C* yields

$$C = \frac{r_0^2 D\exp\left(-\frac{r_0}{\rho}\right)}{\rho}$$

Substitution of this expression for *C* into Equation 2.18 yields an expression for E_0 as

$$E_0 = -\frac{\dfrac{r_0^2 D \exp\left(-\dfrac{r_0}{\rho}\right)}{\rho}}{r_0} + D \exp\left(-\frac{r_0}{\rho}\right)$$

$$= -\frac{r_0 D \exp\left(-\dfrac{r_0}{\rho}\right)}{\rho} + D \exp\left(-\frac{r_0}{\rho}\right)$$

$$= D\left(1 - \frac{r_0}{\rho}\right)\exp\left(-\frac{r_0}{\rho}\right)$$

(b) Now solving for *D* from Equation 2.18a above yields

$$D = \frac{C\rho \exp\left(\dfrac{r_0}{\rho}\right)}{r_0^2}$$

Substitution of this expression for *D* into Equation 2.18 yields an expression for E_0 as

$$E_0 = -\frac{C}{r_0} + \left[\frac{C\rho \exp\left(\dfrac{r_0}{\rho}\right)}{r_0^2}\right]\exp\left(-\frac{r_0}{\rho}\right)$$

$$= -\frac{C}{r_0} + \frac{C\rho}{r_0^2}$$

$$E_0 = \frac{C}{r_0}\left(\frac{\rho}{r_0} - 1\right)$$

Primary Interatomic Bonds

2.22 *(a) Briefly cite the main differences among ionic, covalent, and metallic bonding.*

(b) State the Pauli exclusion principle.

Solution

(a) The main differences between the various forms of primary bonding are:

Ionic--there is electrostatic attraction between oppositely charged ions.

Covalent--there is electron sharing between two adjacent atoms such that each atom assumes a stable electron configuration.

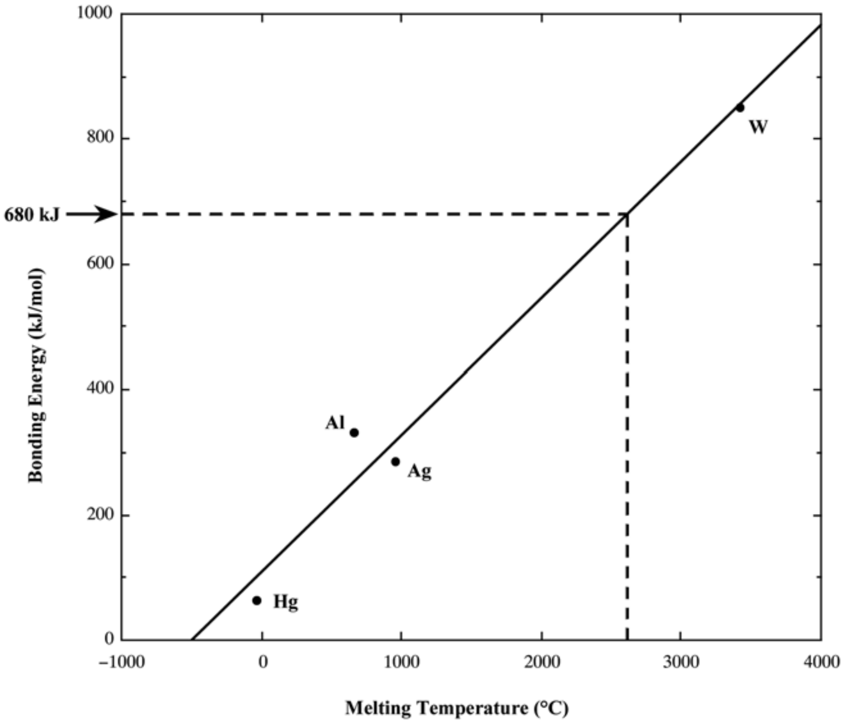
Metallic--the positively charged ion cores are shielded from one another, and also "glued" together by the sea of valence electrons.

(b) The Pauli exclusion principle states that each electron state can hold no more than two electrons, which must have opposite spins.

2.23 *Make a plot of bonding energy versus melting temperature for the metals listed in Table 2.3. Using this plot, approximate the bonding energy for molybdenum, which has a melting temperature of 2617°C.*

Solution

Below is plotted the bonding energy versus melting temperature for these four metals. From this plot, the bonding energy for molybdenum (melting temperature of 2617°C) should be approximately 680 kJ/mol. The experimental value is 660 kJ/mol.



Secondary Bonding or van der Waals Bonding

2.24 *Explain why hydrogen fluoride (HF) has a higher boiling temperature than hydrogen chloride (HCl) (19.4 vs. –85°C), even though HF has a lower molecular weight.*

Solution

The intermolecular bonding for HF is hydrogen, whereas for HCl, the intermolecular bonding is van der Waals. Since the hydrogen bond is stronger than van der Waals, HF will have a higher melting temperature.

Mixed Bonding

2.25 *Compute the %IC of the interatomic bond for each of the following compounds: MgO, GaP, CsF, CdS, and FeO.*

Solution

The percent ionic character is a function of the electron negativities of the ions X_A and X_B according to Equation 2.16. The electronegativities of the elements are found in Figure 2.9.

For MgO, X_{Mg} = 1.3 and X_{O} = 3.5, and therefore,

$$\%\mathrm{IC} = \left[1 - \exp(-0.25)(3.5 - 1.3)^2\right] \times 100 = 70.1\%$$

For GaP, X_{Ga} = 1.8 and X_{P} = 2.1, and therefore,

$$\%\mathrm{IC} = \left[1 - \exp(-0.25)(2.1 - 1.8)^2\right] \times 100 = 2.2\%$$

For CsF, X_{Cs} = 0.9 and X_{F} = 4.1, and therefore,

$$\%\mathrm{IC} = \left[1 - \exp(-0.25)(4.1 - 0.9)^2\right] \times 100 = 92.3\%$$

For CdS, X_{Cd} = 1.5 and X_{S} = 2.4, and therefore,

$$\%\mathrm{IC} = \left[1 - \exp(-0.25)(2.4 - 1.5)^2\right] \times 100 = 18.3\%$$

For FeO, X_{Fe} = 1.7 and X_{O} = 3.5, and therefore,

$$\%\mathrm{IC} = \left[1 - \exp(-0.25)(3.5 - 1.7)^2\right] \times 100 = 55.5\%$$

2.26 *(a) Calculate %IC of the interatomic bonds for the intermetallic compound* Al_6Mn. *(b) On the basis of this result what type of interatomic bonding would you expect to be found in* Al_6Mn*?*

Solution

(a) The percent ionic character is a function of the electron negativities of the ions X_A and X_B according to Equation 2.16. The electronegativities for Al and Mn (Figure 2.9) are 1.5 and 1.6, respectively. Therefore the percent ionic character is determined using Equation 2.16 as follows:

$$\%\mathrm{IC} = \left[1 - \exp(-0.25)(1.6 - 1.5)^2\right] \times 100 = 0.25\%$$

(b) Because the percent ionic character is exceedingly small (0.25%) and this intermetallic compound is composed of two metals, the bonding is completely metallic.

Bonding Type-Material Classification Correlations

2.27 *What type(s) of bonding would be expected for each of the following materials: solid xenon, calcium fluoride (CaF_2), bronze, cadmium telluride (CdTe), rubber, and tungsten?*

Solution

For solid xenon, the bonding is van der Waals since xenon is an inert gas.

For CaF_2, the bonding is predominantly ionic (but with some slight covalent character) on the basis of the relative positions of Ca and F in the periodic table.

For bronze, the bonding is metallic since it is a metal alloy (composed of copper and tin).

For CdTe, the bonding is predominantly covalent (with some slight ionic character) on the basis of the relative positions of Cd and Te in the periodic table.

For rubber, the bonding is covalent with some van der Waals. (Rubber is composed primarily of carbon and hydrogen atoms.)

For tungsten, the bonding is metallic since it is a metallic element from the periodic table.

Fundamentals of Engineering Questions and Problems

2.1FE *The chemical composition of the repeat unit for nylon 6,6 is given by the formula* $C_{12}H_{22}N_2O_2$*. Atomic weights for the constituent elements are* $A_C = 12$*,* $A_H = 1$*,* $A_N = 14$*, and* $A_O = 16$*. According to this chemical formula (for nylon 6,6), the percent (by weight) of carbon in nylon 6,6 is most nearly:*

(A) 31.6%
(B) 4.3%
(C) 14.2%
(D) 63.7%

Solution

The total atomic weight of one repeat unit of nylon 6,6, A_{total}, is calculated as

$$A_{total} = (12 \text{ atoms})(A_C) + (22 \text{ atoms})(A_H) + (2 \text{ atoms})(A_N) + (2 \text{ atoms})(A_O)$$

$$= (12 \text{ atoms})(12 \text{ g/mol}) + (22 \text{ atoms})(1 \text{ g/mol}) + (2 \text{ atoms})(14 \text{ g/mol}) + (2 \text{ atoms})(16 \text{ g/mol}) = 226 \text{ g/mol}$$

Therefore the percent by weight of carbon is calculated as

$$\text{C(wt\%)} = \frac{(12 \text{ atoms})(A_C)}{A_{\text{total}}} \times 100$$

$$= \frac{(12 \text{ atoms})(12 \text{ g/mol})}{226 \text{ g/mol}} \times 100 = 63.7\%$$

which is answer D.

2.2FE *Which of the following electron configurations is for an inert gas?*

(A) $1s^2 2s^2 2p^6 3s^2 3p^6$

(B) $1s^2 2s^2 2p^6 3s^2$

(C) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

(D) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$

Solution

The correct answer is A. The $1s^2 2s^2 2p^6 3s^2 3p^6$ electron configuration is that of an inert gas because of filled 3*s* and 3*p* subshells.

2.3FE *What type(s) of bonding would be expected for bronze (a copper-tin alloy)?*

(A) Ionic bonding

(B) Metallic bonding

(C) Covalent bonding with some van der Waals bonding

(D) van der Waals bonding

<u>Solution</u>

The correct answer is B. For bronze, the bonding is metallic because it is a metal alloy.

2.4FE *What type(s) of bonding would be expected for rubber?*

(A) Ionic bonding

(B) Metallic bonding

(C) Covalent bonding with some van der Waals bonding

(D) van der Waals bonding

Solution

The correct answer is C. For rubber, the bonding is covalent with some van der Waals bonding. (Rubber is composed primarily of carbon and hydrogen atoms.)

CHAPTER 3

THE STRUCTURE OF CRYSTALLINE SOLIDS

PROBLEM SOLUTIONS

Fundamental Concepts

3.1 *What is the difference between atomic structure and crystal structure?*

Solution

Atomic structure relates to the number of protons and neutrons in the nucleus of an atom, as well as the number and probability distributions of the constituent electrons. On the other hand, crystal structure pertains to the arrangement of atoms in the crystalline solid material.

Unit Cells

Metallic Crystal Structures

3.2 *If the atomic radius of lead is 0.175 nm, calculate the volume of its unit cell in cubic meters.*

Solution

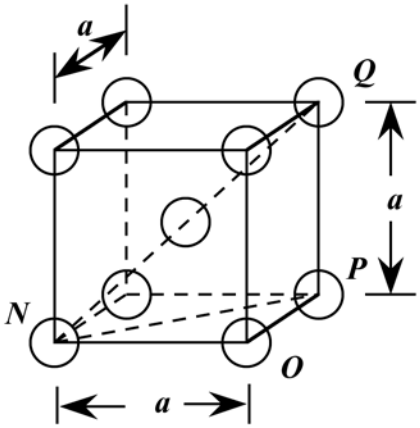
Lead has an FCC crystal structure and an atomic radius of 0.1750 nm (Table 3.1). The FCC unit cell volume may be computed from Equation 3.6 as

$$V_C = 16R^3\sqrt{2} = (16)(0.1750 \times 10^{-9}\ \mathrm{m})^3(\sqrt{2}) = 1.213 \times 10^{-28}\ \mathrm{m}^3$$

3.3 *Show for the body-centered cubic crystal structure that the unit cell edge length a and the atomic radius R are related through* $a = 4R/\sqrt{3}$.

Solution

This problem calls for a demonstration of the relationship $a = \frac{4R}{\sqrt{3}}$ for BCC. Consider the BCC unit cell shown below



From the triangle *NOP*

$$(\overline{NP})^2 = a^2 + a^2 = 2a^2$$

And then for triangle *NPQ*,

$$(\overline{NQ})^2 = (\overline{QP})^2 + (\overline{NP})^2$$

But $\overline{NQ}$ = 4*R*, *R* being the atomic radius. Also, $\overline{QP}$= *a*. Therefore,

$$(4R)^2 = a^2 + 2a^2$$

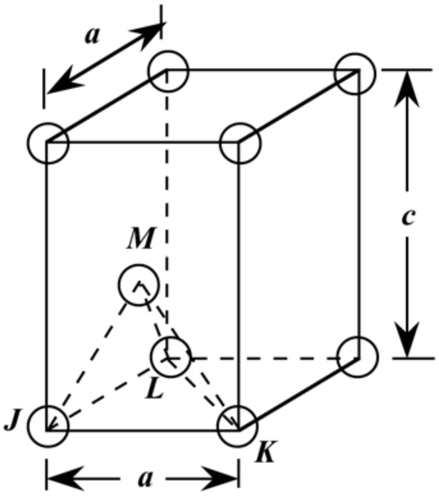
And solving for *a*:

$$a = \frac{4R}{\sqrt{3}}$$

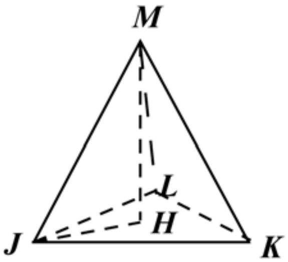
3.4 *For the HCP crystal structure, show that the ideal c/a ratio is 1.633.*

Solution

We are asked to show that the ideal *c/a* ratio for HCP is 1.633. A sketch of one-third of an HCP unit cell is shown below.



Consider the tetrahedron labeled as *JKLM*, which is reconstructed as follows:



The atom at point *M* is midway between the top and bottom faces of the unit cell--that is $\overline{MH} = c/2$. And, since atoms at points *J*, *K*, and *M*, all touch one another,

$$\overline{JM} = \overline{JK} = 2R = a$$

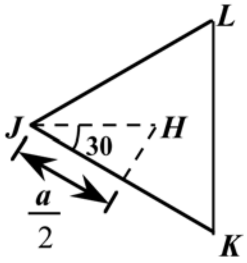
where *R* is the atomic radius. Furthermore, from triangle *JHM*,

$$(\overline{JM})^2 = (\overline{JH})^2 + (\overline{MH})^2$$

or

$$a^2 = (\overline{JH})^2 + \left(\frac{c}{2}\right)^2$$

Now, we can determine the $\overline{JH}$ length by consideration of triangle *JKL*, which is an equilateral triangle,



From this triangle it is the case that the angle subtended between the lines $\overline{JK}$ and $\overline{JH}$ is 30°, and

$$\cos 30^\circ = \frac{a/2}{JH} = \frac{\sqrt{3}}{2}$$

which reduces to the following:

$$\overline{JH} = \frac{a}{\sqrt{3}}$$

Substitution of this value for $\overline{JH}$ into the above expression yields

$$a^2 = \left(\frac{a}{\sqrt{3}}\right)^2 + \left(\frac{c}{2}\right)^2 = \frac{a^2}{3} + \frac{c^2}{4}$$

And when we solve for *c/a*

$$\frac{c}{a} = \sqrt{\frac{8}{3}} = 1.633$$

3.5 *Show that the atomic packing factor for BCC is 0.68.*

Solution

The atomic packing factor is defined as the ratio of sphere volume (V_S) to the total unit cell volume (V_C), or

$$\mathbf{APF} = \frac{V_S}{V_C}$$

Because there are two spheres associated with each unit cell for BCC

$$V_S = 2(\text{sphere volume}) = 2\left(\frac{4\pi R^3}{3}\right) = \frac{8\pi R^3}{3}$$

Also, the unit cell has cubic symmetry, that is $V_C = a^3$. But a depends on R according to Equation 3.4, and

$$V_C = \left(\frac{4R}{\sqrt{3}}\right)^3 = \frac{64R^3}{3\sqrt{3}}$$

Thus,

$$\mathbf{APF} = \frac{V_S}{V_C} = \frac{8\pi R^3/3}{64R^3/3\sqrt{3}} = 0.68$$

3.6 *Show that the atomic packing factor for HCP is 0.74.*

Solution

The APF is just the total sphere volume-unit cell volume ratio—i.e., (V_S / V_C). For HCP, there are the equivalent of six spheres per unit cell, and thus

$$V_S = 6\left(\frac{4\pi R^3}{3}\right) = 8\pi R^3$$

The unit cell volume (V_C) for the HCP unit cell was determined in Example Problem 3.3 and given in Equation 3.7b as

$$V_C = 6R^2 c\sqrt{3}$$

And because $c = 1.633a = 2R(1.633)$

$$V_C = (6R^2\sqrt{3})(2)(1.633R) = 12\sqrt{3}(1.633)R^3$$

Thus,

$$\text{APF} = \frac{V_S}{V_C} = \frac{8\pi R^3}{12\sqrt{3}\,(1.633)\,R^3} = 0.74$$

Density Computations

3.7 *Molybdenum* (*Mo*) has *a BCC crystal structure, an atomic radius of 0.1363 nm, and an atomic weight of 95.94 g/mol. Compute and compare its theoretical density with the experimental value found inside the front cover of the book.*

Solution

This problem calls for a computation of the density of molybdenum. According to Equation 3.8

$$\rho = \frac{nA_{\mathrm{Mo}}}{V_C N_{\mathrm{A}}}$$

For BCC, n = 2 atoms/unit cell. Furthermore, because $V_C = a^3$, and $a = \frac{4R}{\sqrt{3}}$ (Equation 3.4), then

$$V_C = \left(\frac{4R}{\sqrt{3}}\right)^3$$

Thus, realizing that A_{Mo} = 95.94 g/mol, using the above version of Equation 3.8, we compute the theoretical density for Mo as follows:

$$\rho = \frac{nA_{\mathrm{Mo}}}{\left(\frac{4R}{\sqrt{3}}\right)^3 N_{\mathrm{A}}}$$

$$= \frac{(2 \text{ atoms/unit cell})(95.94 \text{ g/mol})}{\left[(4)(0.1363 \times 10^{-7} \text{ cm})^3 / \sqrt{3}\right]^3 / (\text{unit cell})(6.022 \times 10^{23} \text{ atoms/mol})}$$

$$= 10.22 \text{ g/cm}^3$$

The value given inside the front cover is 10.22 g/cm^3.

3.8 *Strontium (Sr) has an FCC crystal structure, an atomic radius of 0.215 nm and an atomic weight of 87.62 g/mol. Calculate the theoretical density for Sr.*

Solution

According to Equation 3.8

$$\rho = \frac{nA_{\mathrm{Sr}}}{V_C N_{\mathrm{A}}}$$

For FCC, n = 4 atoms/unit cell. Furthermore, because $V_C = a^3$, and $a = 2R\sqrt{2}$ (Equation 3.1), then

$$V_C = \left(2R\sqrt{2}\right)^3$$

Thus, realizing that A_{Sr} = 87.62 g/mol, using the above version of Equation 3.8, we compute the theoretical density of Sr as follows:

$$\rho = \frac{nA_{\mathrm{Sr}}}{\left(2R\sqrt{2}\right)^3 N_{\mathrm{A}}}$$

$$= \frac{(\text{4 atoms/unit cell})(\text{87.62 g/mol})}{\left[(2)(0.215 \times 10^{-7}\ \text{cm})^3\sqrt{2}\right]^3/(\text{unit cell})(6.022 \times 10^{23}\ \text{atoms/mol})}$$

$$= 2.59\ \text{g/cm}^3$$

The experimental density for Sr is 2.54 g/cm^3.

3.9 *Calculate the radius of a palladium (Pd) atom, given that Pd has an FCC crystal structure, a density of 12.0 g/cm^3, and an atomic weight of 106.4 g/mol.*

Solution

We are asked to determine the radius of a palladium atom, given that Pd has an FCC crystal structure. For FCC, n = 4 atoms/unit cell, and $V_C = 16R^3\sqrt{2}$ (Equation 3.6). Now, the density of Pd may be expressed using a form of Equation 3.8 as follows:

$$\rho = \frac{nA_{\text{Pd}}}{V_C N_{\text{A}}}$$

$$= \frac{nA_{\text{Pd}}}{(16R^3\sqrt{2})N_{\text{A}}}$$

Solving for R from the above expression yields

$$R = \left(\frac{nA_{\text{Pd}}}{16\rho N_{\text{A}}\sqrt{2}}\right)^{1/3}$$

Incorporation into this expression values for A_{Pd} , n, and ρ leads to the following value of R:

$$= \left[\frac{(4\text{ atoms/unit cell})(106.4\text{ g/mol})}{(16)(12.0\text{ g/cm}^3)(6.022\times 10^{23}\text{ atoms/mol})(\sqrt{2})}\right]^{1/3}$$

$$= 1.38 \times 10^{-8}\text{ cm} = 0.138\text{ nm}$$

3.10 *Calculate the radius of a tantalum (Ta) atom, given that Ta has a BCC crystal structure, a density of 16.6 g/cm^3, and an atomic weight of 180.9 g/mol.*

Solution

It is possible to compute the radius of a Ta atom using a rearranged form of Equation 3.8. For BCC, $n = 2$ atoms/unit cell. Furthermore, because $V_C = a^3$ and $a = \frac{4R}{\sqrt{3}}$ (Equation 3.4) an expression for the BCC unit cell volume is as follows:

$$V_C = \left(\frac{4R}{\sqrt{3}}\right)^3 = \frac{64R^3}{3\sqrt{3}}$$

For Ta, Equation 3.8 takes the form

$$\rho = \frac{nA_{\text{Ta}}}{V_C N_{\text{A}}}$$

$$= \frac{nA_{\text{Ta}}}{\left(\frac{64R^3}{3\sqrt{3}}\right)N_{\text{A}}}$$

Solving for R in this equation yields

$$R = \left(\frac{3\sqrt{3}nA_{\text{Ta}}}{64\rho N_{\text{A}}}\right)^{1/3}$$

Upon incorporation of values of n, A_{Ta}, and ρ into this equation leads to the atomic radius of Ta as follows:

$$R = \left[\frac{(3\sqrt{3})(2\text{ atoms/unit cell})(180.9\text{ g/mol})}{(64)(16.6\text{ g/cm}^3)(6.022 \times 10^{23}\text{ atoms/mol})}\right]^{1/3}$$

$$= 1.43 \times 10^{-8}\text{ cm} = 0.143\text{ nm}$$

3.11 *A hypothetical metal has the simple cubic crystal structure shown in Figure 3.3. If its atomic weight is 74.5 g/mol and the atomic radius is 0.145 nm, compute its density.*

Solution

For the simple cubic crystal structure (Figure 3.3), the value of n in Equation 3.8 is unity since there is only a single atom associated with each unit cell. Furthermore, for the unit cell edge length, $a = 2R$ (Figure 3.3); this means that the unit cell volume $V_C = a^3 = (2R)^3$. Therefore, Equation 3.8 takes the form

$$\rho = \frac{nA}{V_C N_A} = \frac{nA}{(2R)^3 N_A}$$

and incorporating values for R and A given in the problem statement, the density is determined as follows:

$$\rho = \frac{(1\ \text{atom/unit cell})(74.5\ \text{g/mol})}{\left\{\left[(2)(1.45 \times 10^{-8}\ \text{cm})\right]^3/\text{unit cell}\right\}(6.022 \times 10^{23}\ \text{atoms/mol})}$$

5.07 g/cm^3

3.12 *Titanium (Ti) has an HCP crystal structure and a density of 4.51 g/cm*^{3}.

(a) What is the volume of its unit cell in cubic meters?

(b) If the c/a ratio is 1.58, compute the values of c and a.

Solution

(a) The volume of the Ti unit cell may be computed using a rearranged form of Equation 3.8 as

$$V_C = \frac{nA_{\text{Ti}}}{\rho N_{\text{A}}}$$

For HCP, n = 6 atoms/unit cell, and the atomic weight for Ti, A_{Ti} = 47.9 g/mol. Thus,

$$V_C = \frac{(\text{6 atoms/unit cell})(\text{47.9 g/mol})}{(4.51\ \text{g/cm}^3)(6.022 \times 10^{23}\ \text{atoms/mol})}$$

$$= 1.058 \times 10^{-22}\ \text{cm}^3\text{/unit cell} = 1.058 \times 10^{-28}\ \text{m}^3\text{/unit cell}$$

(b) From Equation 3.7a, for HCP the unit cell volume for is

$$V_C = \frac{3\sqrt{3}\,a^2 c}{2}$$

since, for Ti, $c = 1.58a$, then

$$V_C = \frac{3\sqrt{3}(1.58)a^3}{2} = 1.058 \times 10^{-22}\ \text{cm}^3\text{/unit cell}$$

Now, solving for a

$$a = \left[\frac{(2)(1.058 \times 10^{-22}\ \text{cm}^3)}{(3)(\sqrt{3})(1.58)}\right]^{1/3}$$

$$= 2.96 \times 10^{-8}\ \text{cm} = 0.296\ \text{nm}$$

And finally, the value of c is

$$c = 1.58a = (1.58)(0.296\ \text{nm}) = 0.468\ \text{nm}$$

3.13 *Magnesium (Mg) has an HCP crystal structure and a density of 1.74 g/cm^3.*

(a) What is the volume of its unit cell in cubic centimeters?

(b) If the c/a ratio is 1.624, compute the values of c and a.

Solution

(a) The volume of the Mg unit cell may be computed using a rearranged form of Equation 3.8 as

$$V_C = \frac{nA_{\mathrm{Mg}}}{\rho N_{\mathrm{A}}}$$

Now, for HCP, n = 6 atoms/unit cell, and the atomic weight for Mg, A_{Mg} = 24.3 g/mol. Thus,

$$V_C = \frac{(6\ \text{atoms/unit cell})(24.3\ \text{g/mol})}{\left(1.74\ \text{g/cm}^3\right)\left(6.022 \times 10^{23}\ \text{atoms/mol}\right)}$$

$$= 1.39 \times 10^{-22}\ \text{cm}^3/\text{unit cell} = 1.39 \times 10^{-28}\ \text{m}^3/\text{unit cell}$$

(b) From Equation 3.7a, for HCP the unit cell volume for is

$$V_C = \frac{3\sqrt{3}\,a^2 c}{2}$$

but, since, for Mg, $c = 1.624a$, then

$$V_C = \frac{3\sqrt{3}(1.624)a^3}{2} = 1.39 \times 10^{-22}\ \text{cm}^3/\text{unit cell}$$

Now, solving for a

$$a = \left[\frac{(2)\left(1.39 \times 10^{-22}\ \text{cm}^3\right)}{(3)\left(\sqrt{3}\right)(1.624)}\right]^{1/3}$$

$$= 3.21 \times 10^{-8}\ \text{cm} = 0.321\ \text{nm}$$

And finally, the value of c is

$$c = 1.624a = (1.624)(0.321\ \text{nm}) = 0.521\ \text{nm}$$

3.14 *Using atomic weight, crystal structure, and atomic radius data tabulated inside the front cover of the book, compute the theoretical densities of aluminum (Al), nickel (Ni), magnesium (Mg), and tungsten (W), and then compare these values with the measured densities listed in this same table. The c/a ratio for magnesium is 1.624.*

Solution

This problem asks that we calculate the theoretical densities of Al, Ni, Mg, and W.

Since Al has an FCC crystal structure, n = 4, and $V_C = 16R^3\sqrt{2}$ (Equation 3.6). From inside the front cover, for Al, R = 0.143 nm (1.43 × 10^{-8} cm) and A_{Al} = 26.98 g/mol. Employment of Equation 3.8 yields

$$\rho = \frac{nA_{\mathrm{Al}}}{V_C N_{\mathrm{A}}}$$

$$= \frac{(4\ \text{atoms/unit cell})(26.98\ \text{g/mol})}{\left\{\left[(16)(1.43 \times 10^{-8}\ \text{cm})^3(\sqrt{2})\right]/(\text{unit cell})\right\}(6.022 \times 10^{23}\ \text{atoms/mol})}$$

$$= 2.71\ \text{g/cm}^3$$

The value given in the table inside the front cover is 2.71 g/cm^3.

Nickel also has an FCC crystal structure and R = 0.125 nm (1.25 × 10^{-8} cm) and A_{Ni} = 58.69 g/mol. (Again, for FCC, FCC crystal structure, n = 4, and $V_C = 16R^3\sqrt{2}$.) Therefore, we determine the density using Equation 3.8 as follows:

$$\rho = \frac{(4\ \text{atoms/unit cell})(58.69\ \text{g/mol})}{\left\{\left[(16)(1.25 \times 10^{-8}\ \text{cm})^3(\sqrt{2})\right]/(\text{unit cell})\right\}(6.022 \times 10^{23}\ \text{atoms/mol})}$$

$$= 8.82\ \text{g/cm}^3$$

The value given in the table is 8.90 g/cm^3.

Magnesium has an HCP crystal structure, and from Equation 3.7a,

$$V_C = \frac{3a^2c\sqrt{3}}{2}$$

And, since $c = 1.624a$ and $a = 2R$ = 2(1.60 × 10^{-8} cm) = 3.20 × 10^{-8} cm, the unit cell volume is equal to

$$V_C = \frac{(3\sqrt{3})(1.624)(3.20 \times 10^{-8}\ \text{cm})^3}{2} = 1.38 \times 10^{-22}\ \text{cm}^3/\text{unit cell}$$

Also, there are 6 atoms/unit cell for HCP. Therefore the theoretical density is calculated using Equation 3.8 as

$$\rho = \frac{nA_{\text{Mg}}}{V_C N_{\text{A}}}$$

$$= \frac{(6\ \text{atoms/unit cell})(24.31\ \text{g/mol})}{(1.38 \times 10^{-22}\ \text{cm}^3/\text{unit cell})(6.022 \times 10^{23}\ \text{atoms/mol})}$$

$$= 1.75\ \text{g/cm}^3$$

The value given in the table is 1.74 g/cm^3.

Tungsten has a BCC crystal structure for which $n = 2$ and $a = \frac{4R}{\sqrt{3}}$ (Equation 3.4); also $A_{\text{W}} = 183.84$ g/mol and $R = 0.137$ nm. Therefore, employment of Equation 3.8 (and realizing that $V_C = a^3$) yields the following value for the density:

$$\rho = \frac{(2\ \text{atoms/unit cell})(183.84\ \text{g/mol})}{\left\{\left[\frac{(4)(1.37 \times 10^{-8}\ \text{cm})}{\sqrt{3}}\right]^3 /(\text{unit cell})\right\}(6.022 \times 10^{23}\ \text{atoms/mol})}$$

$$= 19.3\ \text{g/cm}^3$$

The value given in the table is 19.3 g/cm^3.

3.15 *Niobium (Nb) has an atomic radius of 0.1430 nm and a density of 8.57 g/cm*^{3}*. Determine whether it has an FCC or a BCC crystal structure.*

Solution

In order to determine whether Nb has an FCC or a BCC crystal structure, we need to compute its density for each of the crystal structures. For FCC, n = 4, and a = $2R\sqrt{2}$ (Equation 3.1). Also, from Figure 2.8, its atomic weight is 92.91 g/mol. Thus, for FCC (employing Equation 3.8)

$$\rho = \frac{nA_{\text{Nb}}}{V_C N_{\text{A}}} = \frac{nA_{\text{Nb}}}{a^3 N_{\text{A}}} = \frac{nA_{\text{Nb}}}{(2R\sqrt{2})^3 N_{\text{A}}}$$

$$= \frac{(\text{4 atoms/unit cell})(\text{92.91 g/mol})}{\left\{\left[(2)(1.43 \times 10^{-8}\,\text{cm})(\sqrt{2})\right]^3/(\text{unit cell})\right\}(6.022 \times 10^{23}\,\text{atoms/mol})}$$

$$= 9.33\ \text{g/cm}^3$$

For BCC, n = 2, and a = $\dfrac{4R}{\sqrt{3}}$ (Equation 3.4), thus

$$\rho = \frac{nA_{\text{Nb}}}{V_C N_{\text{A}}} = \frac{nA_{\text{Nb}}}{a^3 N_{\text{A}}} = \frac{nA_{\text{Nb}}}{\left(\dfrac{4R}{\sqrt{3}}\right)^3 N_{\text{A}}}$$

$$\rho = \frac{(\text{2 atoms/unit cell})(\text{92.91 g/mol})}{\left\{\left[\dfrac{(4)(1.43 \times 10^{-8}\,\text{cm})}{\sqrt{3}}\right]^3/(\text{unit cell})\right\}(6.022 \times 10^{23}\,\text{atoms/mol})}$$

$$= 8.57\ \text{g/cm}^3$$

which is the value provided in the problem statement. Therefore, Nb has the BCC crystal structure.

3.16 *The atomic weight, density, and atomic radius for three hypothetical alloys are listed in the following table. For each, determine whether its crystal structure is FCC, BCC, or simple cubic and then justify your determination.*

Alloy	***Atomic Weight (g/mol)***	***Density (g/cm³)***	***Atomic Radius (nm)***
A	*43.1*	*6.40*	*0.122*
B	*184.4*	*12.30*	*0.146*
C	*91.6*	*9.60*	*0.137*

Solution

For each of these three alloys we need, by trial and error, to calculate the density using Equation 3.8, and compare it to the value cited in the problem. For SC, BCC, and FCC crystal structures, the respective values of n are 1, 2, and 4, whereas the expressions for a (since $V_C = a^3$) are $2R$, $2R\sqrt{2}$, and $\frac{4R}{\sqrt{3}}$.

For alloy A, let us calculate ρ assuming a BCC crystal structure.

$$\rho = \frac{nA_A}{V_C N_A}$$

$$= \frac{nA_A}{\left(\frac{4R}{\sqrt{3}}\right)^3 N_A}$$

$$= \frac{(2\text{ atoms/unit cell})(43.1\text{ g/mol})}{\left\{\left[\frac{(4)(1.22 \times 10^{-8}\text{ cm})}{\sqrt{3}}\right]^3 /(\text{unit cell})\right\}(6.022 \times 10^{23}\text{ atoms/mol})}$$

$$= 6.40\text{ g/cm}^3$$

Therefore, its crystal structure is BCC.

For alloy B, let us calculate ρ assuming a simple cubic crystal structure.

$$\rho = \frac{nA_B}{(2a)^3 N_A}$$

$$= \frac{(1\ \text{atom/unit cell})(184.4\ \text{g/mol})}{\left\{\left[(2)(1.46\ \times\ 10^{-8}\ \text{cm})\right]^3/(\text{unit cell})\right\}(6.022\ \times\ 10^{23}\ \text{atoms/mol})}$$

$$= 12.3\ \text{g/cm}^3$$

Therefore, its crystal structure is simple cubic.

For alloy C, let us calculate ρ assuming a BCC crystal structure.

$$\rho = \frac{nA_C}{\left(\frac{4R}{\sqrt{3}}\right)^3 N_A}$$

$$= \frac{(2\ \text{atoms/unit cell})(91.6\ \text{g/mol})}{\left\{\left[\frac{(4)(1.37 \times 10^{-8}\ \text{cm})}{\sqrt{3}}\right]^3/(\text{unit cell})\right\}(6.022\ \times\ 10^{23}\ \text{atoms/mol})}$$

$$= 9.60\ \text{g/cm}^3$$

Therefore, its crystal structure is BCC.

3.17 *The unit cell for uranium (U) has orthorhombic symmetry, with a, b, and c lattice parameters of 0.286, 0.587, and 0.495 nm, respectively. If its density, atomic weight, and atomic radius are 19.05 g/cm^3, 238.03 g/mol, and 0.1385 nm, respectively, compute the atomic packing factor.*

Solution

In order to determine the APF for U, we need to compute both the unit cell volume (V_C) which is just the product of the three unit cell parameters, as well as the total sphere volume (V_S) which is just the product of the volume of a single sphere and the number of spheres in the unit cell (n). The value of n may be calculated from a rearranged form of Equation 3.8 as

$$n = \frac{\rho V_C N_A}{A_U}$$

$$= \frac{(19.05 \text{ g/cm}^3)(2.86)(5.87)(4.95)(\times 10^{-24} \text{ cm}^3)(6.022 \times 10^{23} \text{ atoms/mol})}{238.03 \text{ g/mol}}$$

= 4.01 atoms/unit cell

Therefore, we determine the atomic packing factor using Equation 3.3 as

$$\text{APF} = \frac{V_S}{V_C} = \frac{(4)\left(\frac{4}{3}\pi R^3\right)}{(a)(b)(c)}$$

$$= \frac{(4)\left[\frac{4}{3}(\pi)(1.385 \times 10^{-8} \text{ cm})^3\right]}{(2.86)(5.87)(4.95)(\times 10^{-24} \text{ cm}^3)}$$

= 0.536

3.18 *Indium (In) has a tetragonal unit cell for which the a and c lattice parameters are 0.459 and 0.495 nm, respectively.*

(a) If the atomic packing factor and atomic radius are 0.693 and 0.1625 nm, respectively, determine the number of atoms in each unit cell.

(b) The atomic weight of indium is 114.82 g/mol; compute its theoretical density.

<u>Solution</u>

(a) For indium, and from the definition of the APF

$$\mathrm{APF} = \frac{V_S}{V_C} = \frac{n\left(\frac{4}{3}\pi R^3\right)}{a^2 c}$$

we may solve for the number of atoms per unit cell, *n*, as

$$n = \frac{(\mathrm{APF})a^2 c}{\frac{4}{3}\pi R^3}$$

$$= \frac{(0.693)(4.59)^2(4.95)(10^{-24}\ \mathrm{cm}^3)}{\frac{4}{3}\pi(1.625 \times 10^{-8}\ \mathrm{cm})^3}$$

= 4.0 atoms/unit cell

(b) In order to compute the density, we just employ Equation 3.8 as

$$\rho = \frac{nA_{\mathrm{In}}}{a^2 c N_{\mathrm{A}}}$$

$$= \frac{(4\ \text{atoms/unit cell})(114.82\ \text{g/mol})}{\left[(4.59 \times 10^{-8}\ \text{cm})^2(4.95 \times 10^{-8}\ \text{cm})/\text{unit cell}\right](6.022 \times 10^{23}\ \text{atoms/mol})}$$

= 7.31 g/cm^3

3.19 *Beryllium (Be) has an HCP unit cell for which the ratio of the lattice parameters c/a is 1.568. If the radius of the Be atom is 0.1143 nm, (a) determine the unit cell volume, and (b) calculate the theoretical density of Be and compare it with the literature value.*

Solution

(a) We are asked to calculate the unit cell volume for Be. The volume of an HCP unit cell is provided by Equation 3.7b as follows:

$$V_C = 6R^2c\sqrt{3}$$

But, $c = 1.568a$, and $a = 2R$, or $c = (1.568)(2R) = 3.136R$. Substitution of this expression for c into the above equation leads to

$$V_C = (6)(3.14)\ R^3\sqrt{3}$$

$$= (6)(3.14)(\sqrt{3})\left[0.1143 \times 10^{-7}\ \text{cm}\right]^3 = 4.87 \times 10^{-23}\ \text{cm}^3/\text{unit cell}$$

(b) The theoretical density of Be is determined, using Equation 3.8, as follows:

$$\rho = \frac{nA_{\text{Be}}}{V_C N_{\text{A}}}$$

For HCP, n = 6 atoms/unit cell, and for Be, A_{Be} = 9.01 g/mol (as noted inside the front cover)—and the value of V_C was determined in part (a). Thus, the theoretical density of Be is

$$\rho = \frac{(6\ \text{atoms/unit cell})(9.01\ \text{g/mol})}{\left(4.87 \times 10^{-23}\ \text{cm}^3/\text{unit cell}\right)\left(6.022 \times 10^{23}\ \text{atoms/mol}\right)}$$

$$= 1.84\ \text{g/cm}^3$$

The literature value is 1.85 g/cm^3.

3.20 *Magnesium (Mg) has an HCP crystal structure, a c/a ratio of 1.624, and a density of 1.74 g/cm*^{3}. *Compute the atomic radius for Mg.*

Solution

This problem calls for us to compute the atomic radius for Mg. In order to do this we must use Equation 3.8, as well as the expression that relates the atomic radius to the unit cell volume for HCP—Equation 3.7b—that is

$$V_C = 6R^2c\sqrt{3}$$

In this case $c = 1.624a$, but, for HCP, $a = 2R$, which means that

$$V_C = 6R^2(1.624)(2R)\sqrt{3} = (1.624)(12\sqrt{3})R^3$$

And from Equation 3.8, the density is equal to

$$\rho = \frac{nA_{\text{Mg}}}{V_C N_{\text{A}}} = \frac{nA_{\text{Mg}}}{(1.624)(12\sqrt{3})R^3 N_{\text{A}}}$$

And, solving for R from the above equation leads to the following:

$$R = \left[\frac{nA_{\text{Mg}}}{(1.624)(12\sqrt{3})\,\rho N_{\text{A}}}\right]^{1/3}$$

For the HCP crystal structure, $n = 6$ and from the inside cover, the atomic weight of Mg is 24.31 g/mol. Upon incorporation of these values as well as the density of Mg provided in the problem statement, we compute the Mg's atomic radius as follows:

$$= \left[\frac{(6\text{ atoms/unit cell})(24.31\text{ g/mol})}{(1.624)(12\sqrt{3})(1.74\text{ g/cm}^3)(6.022\times 10^{23}\text{ atoms/mol})}\right]^{1/3}$$

$$= 1.60 \times 10^{-8}\text{ cm} = 0.160\text{ nm}$$

3.21 *Cobalt (Co) has an HCP crystal structure, an atomic radius of 0.1253 nm, and a c/a ratio of 1.623. Compute the volume of the unit cell for Co.*

Solution

This problem asks that we calculate the unit cell volume for Co, which has an HCP crystal structure. In order to do this, it is necessary to use Equation 3.7b—an expression for the volume of an HCP unit cell in terms of the atomic radius R and the lattice parameter –that is

$$V_C = 6R^2c\sqrt{3}$$

The problem states that $c = 1.623a$; also, it is the case for HCP that $a = 2R$. Making these substitutions into the previous equation yields

$$V_C = (1.623)\left(12\sqrt{3}\right)R^3$$

And incorporation of the value of R provided in the problem statement leads to the following value for the unit cell volume:

$$V_C = (1.623)\left(12\sqrt{3}\right)(1.253 \times 10^{-8}\ \text{cm})^3 = 6.64 \times 10^{-23}\ \text{cm}^3 = 6.64 \times 10^{-2}\ \text{nm}^3$$

Polymorphism and Allotropy

3.22 *Iron (Fe) undergoes an allotropic transformation at 912°C: upon heating from a BCC (α phase) to an FCC (γ phase). Accompanying this transformation is a change in the atomic radius of Fe—from R_{BCC} = 0.12584 nm to R_{FCC} = 0.12894 nm—and, in addition a change in density (and volume). Compute the percent volume change associated with this reaction. Does the volume increase or decrease?*

Solution

To solve this problem let us first compute the density of each phase using Equation 3.8, and then determine the volumes per unit mass (the reciprocals of densities). From these values it is possible to calculate the percent volume change.

The density of each phase may be computed using Equation 3.8—i.e.,

$$\rho = \frac{nA_{\mathrm{Fe}}}{V_C N_{\mathrm{A}}}$$

The atomic weight of Fe will be the same for both BCC and FCC structures (55.85 g/mol); however, values of *n* and V_C will be different.

For BCC iron, n = 2 atoms/unit cell, whereas the volume of the cubic unit cell is the cell edge length *a* cubed--$V_C = a^3$. However, *a* and the atomic radius (R_{BCC}) are related according to Equation 3.4—that is

$$a = \frac{4R_{\mathrm{BCC}}}{\sqrt{3}}$$

which means that

$$V_C = a^3 = \left(\frac{4R_{\mathrm{BCC}}}{\sqrt{3}}\right)^3$$

The value of R_{BCC} is given in the problem statement as 0.12584 nm = 1.2584×10^{-8} cm. It is now possible to calculate the density of BCC iron as follows:

$$\rho_{\mathrm{BCC}} = \frac{nA_{\mathrm{Fe}}}{\left(\frac{4R_{\mathrm{BCC}}}{\sqrt{3}}\right)^3 N_{\mathrm{A}}}$$

$$= \frac{(2 \text{ atoms/unit cell})(55.85 \text{ g/mol})}{\left[\dfrac{(4)(1.2584 \times 10^{-8} \text{ cm})}{\sqrt{3}}\right]^3 (6.022 \times 10^{23} \text{ atoms/mol})}$$

$$= 7.5572 \text{ g/cm}^3$$

For FCC iron, n = 4 atoms/unit cell, $V_C = 16\sqrt{2}R_{\text{FCC}}^3$ (Equation 3.6), and, as noted in the problem statement, R_{FCC} = 0.12894 nm = 1.2894×10^{-8} cm. We now calculate the density of FCC iron as follows:

$$\rho_{\text{FCC}} = \frac{nA_{\text{Fe}}}{\left(16\sqrt{2}R_{\text{FCC}}^3\right)N_{\text{A}}}$$

$$= \frac{(4 \text{ atoms/unit cell})(55.85 \text{ g/mol})}{\left[(16)(\sqrt{2})(1.2894 \times 10^{-8} \text{ cm})^3\right](6.022 \times 10^{23} \text{ atoms/mol})}$$

$$= 7.6479 \text{ g/cm}^3$$

Because we are interested in volumes of these two phases, for each we take the reciprocal of it density, which is equivalent to volume per unit mass (or specific volume), v. The percent volume change $\bar{v}$ experienced by iron during this phase transformation, upon heating is equal to

$$\bar{v} = \frac{v_{\text{BCC}} - v_{\text{FCC}}}{v_{\text{BCC}}} \times 100$$

$$= \frac{\dfrac{1}{7.5572 \text{ g/cm}^3} - \dfrac{1}{7.6479 \text{ g/cm}^3}}{\dfrac{1}{7.5572 \text{ g/cm}^3}} \times 100$$

$$1.19\%$$

The volume decreases because $v_{\text{FCC}} < v_{\text{BCC}}$ –i.e., since $\rho_{\text{FCC}} > \rho_{\text{BCC}}$.

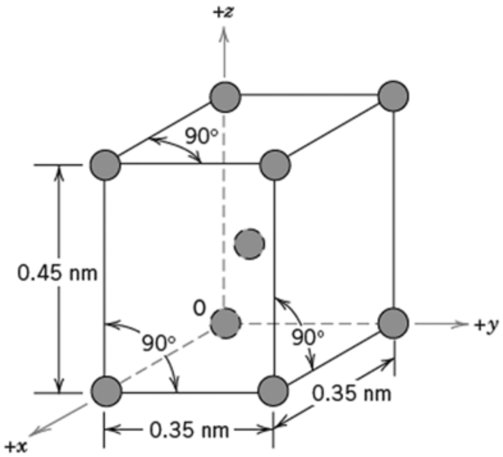
Crystal Systems

3.23 *The accompanying figure shows a unit cell for a hypothetical metal.*

(a) To which crystal system does this unit cell belong?

(b) What would this crystal structure be called?

(c) Calculate the density of the material, given that its atomic weight is 141 g/mol.



Solution

(a) The unit cell shown in the problem statement belongs to the tetragonal crystal system since $a = b = 0.35$ nm, $c = 0.45$ nm, and $\alpha = \beta = \gamma = 90°$.

(b) The crystal structure would be called *body-centered tetragonal*.

(c) As with BCC, $n = 2$ atoms/unit cell. Also, for this unit cell

$$V_C = (3.5 \times 10^{-8}\ \text{cm})^2(4.5 \times 10^{-8}\ \text{cm})$$

$$= 5.51 \times 10^{-23}\ \text{cm}^3/\text{unit cell}$$

Thus, using Equation 3.8, the density is equal to

$$\rho = \frac{nA}{V_C N_A}$$

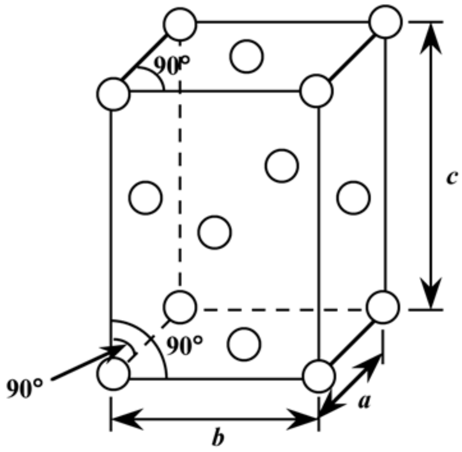
$$= \frac{(2\ \text{atoms/unit cell})(141\ \text{g/mol})}{(5.51 \times 10^{-23}\ \text{cm}^3/\text{unit cell})(6.022 \times 10^{23}\ \text{atoms/mol})}$$

$$= 8.49\ \text{g/cm}^3$$

3.24 *Sketch a unit cell for the face-centered orthorhombic crystal structure.*

Solution

A unit cell for the face-centered orthorhombic crystal structure is presented below.



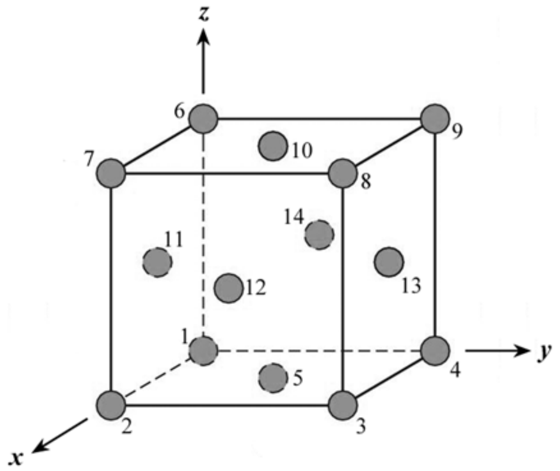
For the orthorhombic crystal system, $a \neq b \neq c$, and $\alpha = \beta = \gamma = 90°$. Also, for the face-centered orthorhombic crystal structure, atoms will be located at the centers of all 6 faces (in addition to all 8 corners).

Point Coordinates

3.25 *List the point coordinates for all atoms that are associated with the FCC unit cell (Figure 3.1).*

Solution

This problem asks that we list the point coordinates for all of the atoms associated with the FCC unit cell. The reduced-sphere FCC unit cell, Figure 3.1b, is shown below on which is superimposed an *x*-*y*-*z* coordinate axis system. Also, each atom in the unit cell is labeled with a number. Of course, because the unit cell is cubic, the unit cell edge length along each of the *x*, *y*, and *z* axes is *a*.



Coordinates for each of these points is determined in a manner similar to that demonstrated in Example Problem 3.6. For the atom labeled 1 in the FCC unit cell, we determine its point coordinates by using rearranged forms of Equations 3.9a, 3.9b, and 3.9c as follows:

The lattice position referenced to the *x* axis is $0a = qa$

The lattice position referenced to the *y* axis is $0a = ra$

The lattice position referenced to the *x* axis is $0a = sa$

Solving these expressions for the values of *q, r,* and *s* leads to

$q = 0$ $\qquad r = 0$ $\qquad s = 0$

Therefore, the *q r s* coordinates for point 1 are 0 0 0.

For point 10, which lies at the middle of the top unit cell face, its lattice position indices referenced to the *x*, *y*, and *z* axes are, respectively, *a/*2, *a*/2, and *a*, and

The lattice position referenced to the *x* axis is $a/2 = qa$

The lattice position referenced to the *y* axis is $a/2 = ra$

The lattice position referenced to the x axis is $a = sa$

Thus, values for the three point coordinates are

$q = 1/2$ $r = 1/2$ $s = 1$

and this point is $\frac{1}{2}\frac{1}{2}1$.

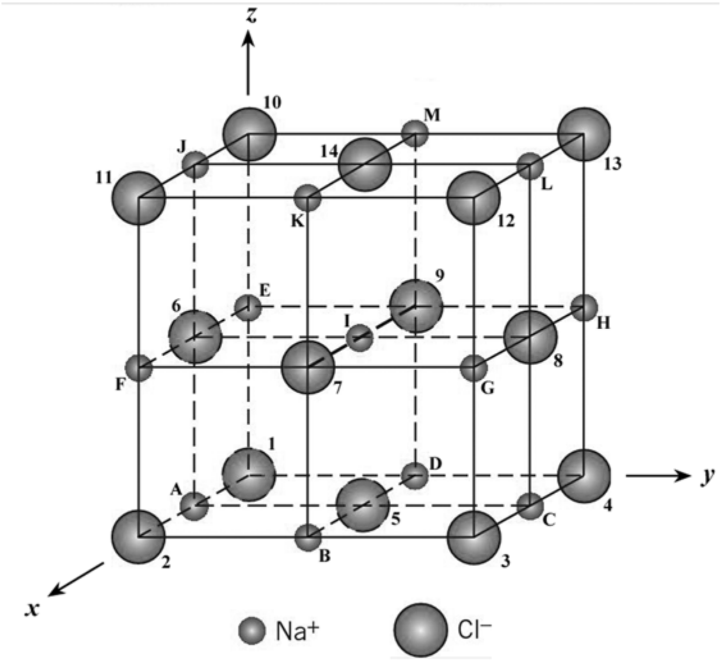
This same procedure is carried out for the remaining the points in the unit cell; indices for all fourteen points are listed in the following table.

Point number	q	r	s
1	0	0	0
2	1	0	0
3	1	1	0
4	0	1	0
5	$\frac{1}{2}$	$\frac{1}{2}$	0
6	0	0	1
7	1	0	1
8	1	1	1
9	0	1	1
10	$\frac{1}{2}$	$\frac{1}{2}$	1
11	$\frac{1}{2}$	0	$\frac{1}{2}$
12	1	$\frac{1}{2}$	$\frac{1}{2}$
13	$\frac{1}{2}$	1	$\frac{1}{2}$
14	0	$\frac{1}{2}$	$\frac{1}{2}$

3.26 *List the point coordinates of both the sodium (Na) and chlorine (Cl) ions for a unit cell of the sodium chloride (NaCl) crystal structure (Figure 12.2).*

Solution

This problem asks that we list the point coordinates for all sodium and chlorine ion associated with the NaCl unit cell. The NaCl unit cell, Figure 12.2, is shown below on which is superimposed an *x*-*y*-*z* coordinate axis system. Also, each Na ion in the unit cell is labeled with an uppercase letter; Cl ions are labeled with numbers. Of course, because the unit cell is cubic, the unit cell edge length along each of the *x*, *y*, and *z* axes is *a*.



Coordinates for each of these points is determined in a manner similar to that demonstrated in Example Problem 3.6. For the Cl ion labeled 5, we determine its point coordinates by using rearranged forms of Equations 3.9a, 3.9b, and 3.9c as follows:

The lattice position referenced to the x axis is $a/2 = qa$

The lattice position referenced to the y axis is $a/2 = ra$

The lattice position referenced to the x axis is $0a = sa$

Solving these expressions for the values of q, r, and s leads to

$$q = \frac{1}{2} \qquad r = \frac{1}{2} \qquad s = 0$$

Therefore, the $q\ r\ s$ coordinates for this point are $\frac{1}{2}\frac{1}{2}\mathbf{0}$.

The Na ion labeled L, has lattice position indices referenced to the *x*, *y*, and *z* axes of *a*/2, *a*, and *a*, respectively. Therefore,

The lattice position referenced to the *x* axis is $a/2 = qa$

The lattice position referenced to the *y* axis is $a = ra$

The lattice position referenced to the *x* axis is $a = sa$

Thus, values for values of *q*, *r*, and *s* are as follows:

$q = 1/2$ $r = 1$ $s = 1$

and the coordinates for the location of this ion are $\frac{1}{2}\mathbf{1}\,\mathbf{1}$.

This same procedure is carried out for determine point coordinates for both Na and Cl ions in the unit cell. Indices for all these points are listed in the following two tables.

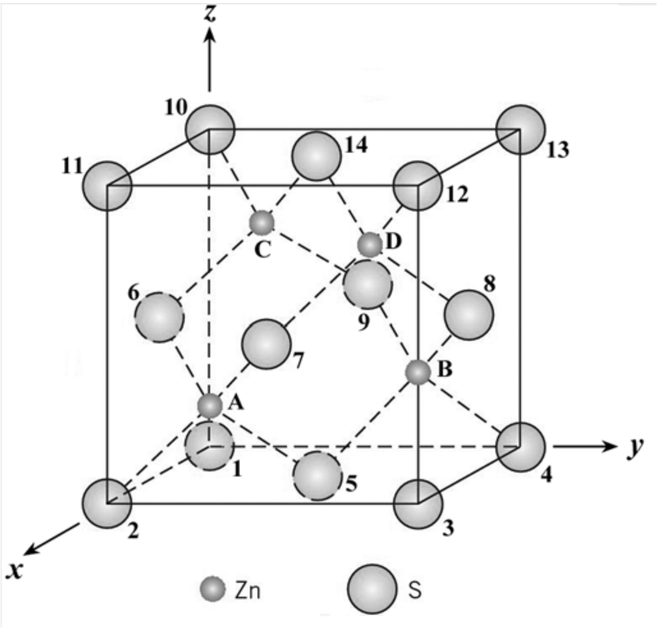
Cl ion point number	*q*	*r*	*s*
1	0	0	0
2	1	0	0
3	1	1	0
4	0	1	0
5	$\frac{1}{2}$	$\frac{1}{2}$	0
6	$\frac{1}{2}$	0	$\frac{1}{2}$
7	1	$\frac{1}{2}$	$\frac{1}{2}$
8	$\frac{1}{2}$	1	$\frac{1}{2}$
9	0	$\frac{1}{2}$	$\frac{1}{2}$
10	0	0	1
11	1	0	1
12	1	1	1
13	0	1	1
14	$\frac{1}{2}$	$\frac{1}{2}$	1

Na ion point letter	q	r	s
A	$\frac{1}{2}$	0	0
B	1	$\frac{1}{2}$	0
C	$\frac{1}{2}$	1	0
D	0	$\frac{1}{2}$	0
E	0	0	$\frac{1}{2}$
F	1	0	$\frac{1}{2}$
G	1	1	$\frac{1}{2}$
H	0	1	$\frac{1}{2}$
I	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
J	$\frac{1}{2}$	0	1
K	1	$\frac{1}{2}$	1
L	$\frac{1}{2}$	1	1
M	0	$\frac{1}{2}$	1

3.27 *List the point coordinates of both the zinc (Zn) and sulfur (S) atoms for a unit cell of the zinc blende (ZnS) crystal structure (Figure 12.4).*

Solution

The ZnS unit cell, Figure 12.4, is shown below on which is superimposed an *x*-*y*-*z* coordinate axis system. Also, each Zn atom in the unit cell is labeled with an uppercase letter; S atoms are labeled with numbers. Of course, because the unit cell is cubic, the unit cell edge length along each of the *x*, *y*, and *z* axes is *a*.



Coordinates for each of these points is determined in a manner similar to that demonstrated in Example Problem 3.6. For the S atom labeled 7, we determine its point coordinates by using rearranged forms of Equations 3.9a, 3.9b, and 3.9c as follows:

The lattice position referenced to the x axis is $a = qa$

The lattice position referenced to the y axis is $a/2 = ra$

The lattice position referenced to the x axis is $a/2 = sa$

Solving these expressions for the values of q, r, and s leads to

$$q = 1 \qquad r = \frac{1}{2} \qquad s = \frac{1}{2}$$

Therefore, the $q\ r\ s$ coordinates for this point are $1\frac{1}{2}\frac{1}{2}$.

The S atom labeled C, has lattice position indices referenced to the *x*, *y*, and *z* axes of *a*/4, *a*/4, and 3*a*/4, respectively. Therefore,

The lattice position referenced to the *x* axis is $a/4 = qa$

The lattice position referenced to the *y* axis is $a/4 = ra$

The lattice position referenced to the *x* axis is $3a/4 = sa$

Thus, values for values of *q*, *r*, and *s* are as follows:

$q = 1/4$ $r = 1/4$ $s = 3/4$

and the coordinates for the location of this atom are $\frac{1}{4}\frac{1}{4}\frac{3}{4}$.

This same procedure is carried out for determine point coordinates for both Zn and S atoms in the unit cell. Indices for all these points are listed in the following two tables.

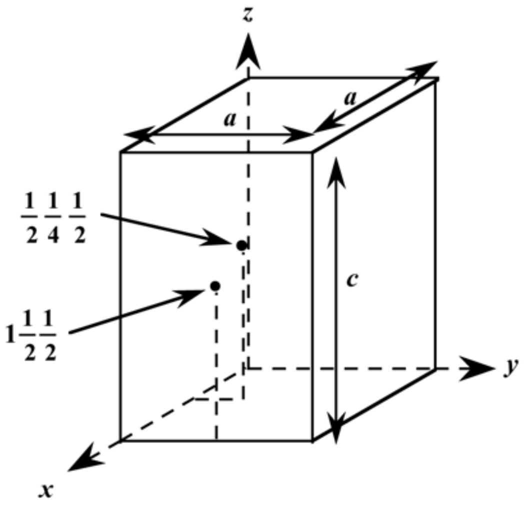
S atom point number	*q*	*r*	*s*
1	0	0	0
2	1	0	0
3	1	1	0
4	0	1	0
5	$\frac{1}{2}$	$\frac{1}{2}$	0
6	$\frac{1}{2}$	0	$\frac{1}{2}$
7	1	$\frac{1}{2}$	$\frac{1}{2}$
8	$\frac{1}{2}$	1	$\frac{1}{2}$
9	0	$\frac{1}{2}$	$\frac{1}{2}$
10	0	0	1
11	1	0	1
12	1	1	1
13	0	1	1
14	$\frac{1}{2}$	$\frac{1}{2}$	1

Zn atom point letter	q	r	s
A	$\frac{3}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
B	$\frac{1}{4}$	$\frac{3}{4}$	$\frac{1}{4}$
C	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{3}{4}$
D	$\frac{3}{4}$	$\frac{3}{4}$	$\frac{3}{4}$

3.28 *Sketch a tetragonal unit cell, and within that cell indicate locations of the* $1\frac{1}{2}\frac{1}{2}$ *and* $\frac{1}{2}\frac{1}{4}\frac{1}{2}$ *point coordinates.*

Solution

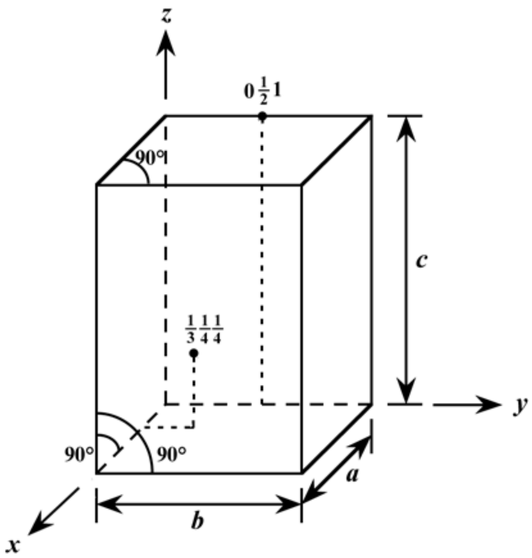
A tetragonal unit in which are shown the $1\frac{1}{2}\frac{1}{2}$ and $\frac{1}{2}\frac{1}{4}\frac{1}{2}$ point coordinates is presented below.



3.29 *Sketch an orthorhombic unit cell, and within that cell indicate locations of the* $\boldsymbol{0\ \frac{1}{2}\ 1}$ *and* $\boldsymbol{\frac{3}{4}\frac{1}{4}\frac{1}{4}}$*point coordinates.*

Solution

An orthorhombic unit in which are shown the $\mathbf{0\frac{1}{2}1}$ and $\mathbf{\frac{1}{3}\frac{1}{4}\frac{1}{4}}$ point coordinates is presented below.



3.30 *Using the Molecule Definition Utility found in the "Metallic Crystal Structures and Crystallography" and "Ceramic Crystal Structures" modules of VMSE, located on the book's web site [www.wiley.com/college/callister (Student Companion Site)], generate (and print out) a three-dimensional unit cell for β tin (Sn), given the following: (1) the unit cell is tetragonal with a =0.583 nm and c =0.318 nm, and (2) Sn atoms are located at the following point coordinates:*

0 0 0
1 0 0
1 1 0
0 1 0
0 0 1
1 0 1
1 1 1

0 1 1
$\frac{1}{2}\ 0\ \frac{3}{4}$
$\frac{1}{2}\ 1\ \frac{3}{4}$
$1\ \frac{1}{2}\ \frac{1}{4}$
$0\ \frac{1}{2}\ \frac{1}{4}$
$\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$

Solution

First of all, open the "Molecule Definition Utility"; it may be found in either of "Metallic Crystal Structures and Crystallography" or "Ceramic Crystal Structures" modules.

In the "Step 1" window, it is necessary to define the atom type, a color for the spheres (atoms), and specify an atom size. Let us enter "Sn" as the name of the atom type (since "Sn" the symbol for tin). Next it is necessary to choose a color from the selections that appear in the pull-down menu—for example, "LtBlue" (light blue). In the "Enter size (nm)" window, it is necessary to enter an atom size. In the instructions for this step, it is suggested that the atom diameter in nanometers be used. From the table found inside the front cover of the textbook, the atomic radius for tin is 0.151 nm, and, therefore, the atomic diameter is twice this value (i.e., 0.302 nm); therefore, we enter the value "0.302". Now click on the "Register Atom Type" button. A small sphere having the color you selected will appear to the right of the white Molecule Definition Utility box.

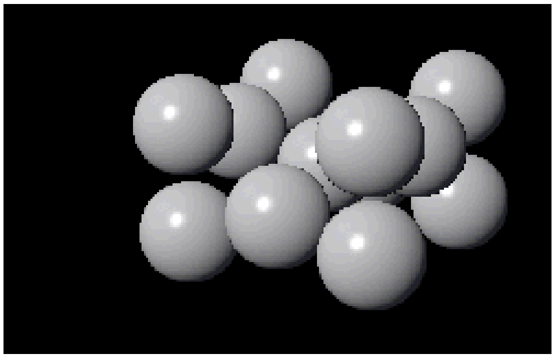
In the "Step 2" window we specify positions for all of the atoms within the unit cell; their point coordinates are specified in the problem statement. It is first necessary to select the Sn atom in order to specify its coordinates. This is accomplished by clicking on the small sphere that appeared in Step 1. At this time it is necessary to enter the X, Y, and Z coordinates for one of the Sn atoms. For example, the point coordinates for the first Sn atom in the list are 000; therefore, we enter a "0" (zero) in each of the "X", "Y", and "Z" atom position boxes, and then click on "Register Atom Position." An atom will be displayed at this position within the X-Y-Z coordinate axis system to the right of the white box. We next, enter the coordinates of another Sn atom—e.g., 1, 0, and 0. Inasmuch as this atom is located a distance of *a* units along the X-axis, the value of "0.583" is entered in the "X" atom position box (since this the value of *a* given in the problem statement); zeros are entered in each of "Y" and "Z" position boxes. Upon clicking on "Register Atom Position" this atom is also displayed within the coordinate system. This same procedure is repeated for all 13 of the point coordinates specified in the problem statement. For the atom having point coordinates of “111” respective values of “0.583”, “0.583”, and “0.318” are entered in the X, Y, and Z atom position boxes, since the unit cell edge length along the Y and Z axes are *a* (0.583) and *c* (0.318 nm), respectively. For fractional point coordinates, the appropriate *a* or *c* value is multiplied by the fraction. For example, the second point coordinate set in the right-hand column, $\frac{1}{2}\mathbf{0}\frac{3}{4}$, the X, Y, and Z atom positions are $\frac{1}{2}(\mathbf{0.583})$ = 0.2915, 0, and $\frac{3}{4}(\mathbf{0.318})$ = 0.2385, respectively. The X, Y, and Z atom position entries for all 13 sets of point coordinates are as follows:

0, 0, and 0
0.583, 0, and 0
0.583, 0.583, and 0
0, 0.583, and 0
0, 0, and 0.318
0.583, 0, and 0.318
0.583, 0.583, and 0.318

0, 0.583, and 0.318
0.2915, 0, and 0.2385
0.2915, 0.583, and 0.2385
0.583, 0.2915, and 0.0795
0, 0.2915, 0.0795
0.2915, 0.2915, and 0.159

In Step 3, we may specify which atoms are to be represented as being bonded to one another, and which type of bond(s) to use (single, double, triple, dashed, and dotted are possibilities), as well as bond color (e.g., light gray, white, cyan); or we may elect to not represent any bonds at all. If it is decided to show bonds, probably the best thing to do is to represent unit cell edges as bonds.

Your image should appear as



Finally, your image may be rotated by using mouse click-and-drag.

[Note: Unfortunately, with this version of the Molecular Definition Utility, it is not possible to save either the data or the image that you have generated. You may use screen capture (or screen shot) software to record and store your image.]

Crystallographic Directions

3.31 *Draw an orthorhombic unit cell, and within that cell a* $[2\bar{1}1]$ *direction.*

Solution

This problem calls for us to draw a $[2\bar{1}1]$ direction within an orthorhombic unit cell ($a \neq b \neq c$, $\alpha = \beta = \gamma =$ 90□). Such a unit cell with its origin positioned at point *O* is shown below. This direction may be plotted using the procedure outlined in Example Problem 3.8, with which rearranged forms of Equations 3.10a-3.10c are used. Let us position the tail of the direction vector at the origin of our coordinate axes; this means that tail vector coordinates for this $[2\bar{1}1]$ direction are

$u = 2$
$v = -1$
$w = 1$

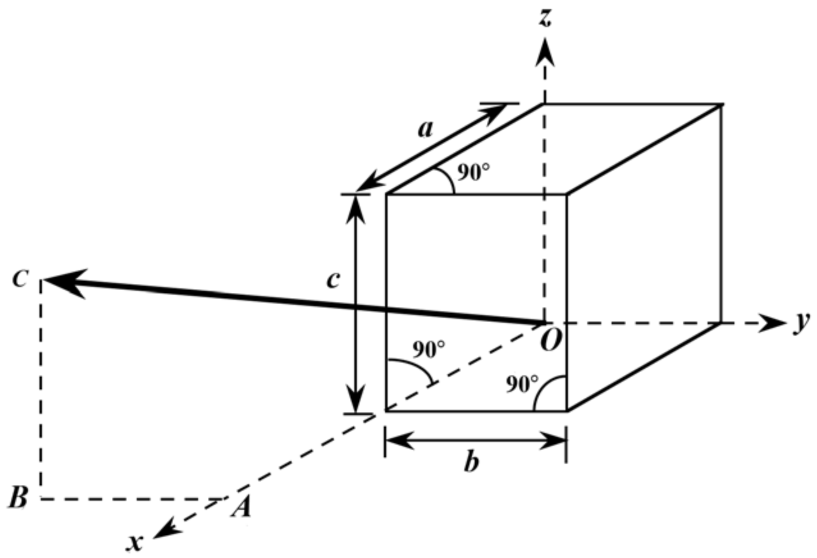
Because the tail of the direction vector is positioned at the origin, its coordinates are as follows:

$x_1 = 0a$
$y_1 = 0b$
$z_1 = 0c$

Head coordinates are determined using the rearranged forms of Equations 3.10a-3.10c, as follows:

$$x_2 = ua + x_1 = (2)a + 0a = 2a$$
$$y_2 = vb + y_1 = (-1)b + 0b = -b$$
$$z_2 = wc + z_1 = (1)c + 0c = c$$

Therefore, coordinates for the vector head are 2*a*, –*b*, and *c*. To locate the vector head, we start at the origin, point *O*, and move along the +*x* axis 2*a* units (from point *O* to point *A*), then parallel to the +*y*-axis –*b* units (from point *A* to point *B*). Finally, we proceed parallel to the *z*-axis *c* units (from point *B* to point *C*). The $[2\bar{1}1]$ direction is the vector from the origin (point *O*) to point *C* as shown.


z
a
90°
c
c
O
y
90°
90°
b
B
A
x

3.32 *Sketch a monoclinic unit cell, and within that cell a $[\bar{1}01]$ direction.*

Solution

This problem asks that a $[\bar{1}01]$ direction be drawn within a monoclinic unit cell ($a \neq b \neq c$, and $\alpha = \beta = 90° \neq \gamma$). Such a unit cell with its origin positioned at point *O* is shown below. This direction may be plotted using the procedure outlined in Example Problem 3.8, with which rearranged forms of Equations 3.10a-3.10c are used. Let us position the tail of the direction vector at the origin of our coordinate axes; this means that vector head indices for this $[\bar{1}01]$ direction are

$u = -1$

$v = 0$

$w = 1$

Because the tail of the direction vector is positioned at the origin, its coordinates are as follows:

$x_1 = 0a$

$y_1 = 0b$

$z_1 = 0c$

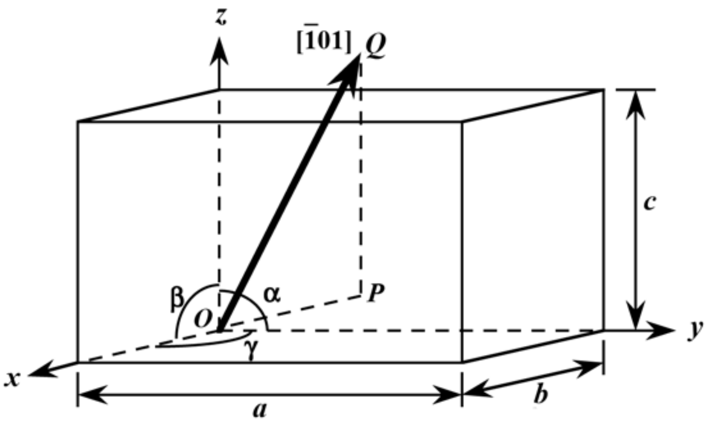
Head coordinates are determined using the rearranged forms of Equations 3.10a-3.10c, as follows:

$$x_2 = ua + x_1 = (-1)a + 0a = -a$$

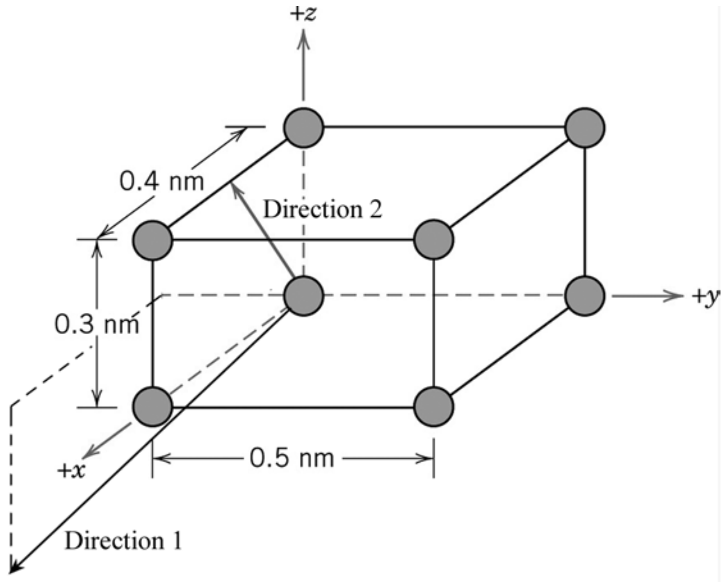
$$y_2 = vb + y_1 = (0)b + 0b = -0b$$

$$z_2 = wc + z_1 = (1)c + 0c = c$$

Therefore, coordinates for the vector head are $-a$, $0b$, and c. To locate the vector head, we start at the origin, point *O*, and move from the origin along the minus *x*-axis *a* units (from point *O* to point *P*). There is no projection along the *y*-axis since the next index is zero. Since the final coordinate is *c*, we move from point *P* parallel to the *z*-axis, *c* units (to point *Q*). Thus, the $[\bar{1}01]$ direction corresponds to the vector passing from the origin to point *Q*, as indicated in the figure.



3.33 *What are the indices for the directions indicated by the two vectors in the following sketch?*



Solution

We are asked for the indices of the two directions sketched in the figure. Unit cell edge lengths are $a = 0.4$ nm, $b = 0.5$ nm, and $c = 0.3$ nm. In solving this problem we will use the symbols a, b, and c rather than the magnitudes of these parameters

The tail of the Direction 1 vector passes through the origin, therefore, its tail coordinates are

$x_1 = 0a$

$y_1 = 0b$

$z_1 = 0c$

And the vector head coordinates are as follows:

$x_2 = a$

$y_2 = -b/2$

$z_2 = -c$

To determine the directional indices we employ Equations 3.10a, 3.10b, and 3.10c. Because there is a 2 in the denominator for y_2 we will assume $n = 2$. Hence

$$\boldsymbol{u} = \boldsymbol{n}\left(\frac{\boldsymbol{x}_2 - \boldsymbol{x}_1}{\boldsymbol{a}}\right) = (2)\left(\frac{\boldsymbol{a} - 0\boldsymbol{a}}{\boldsymbol{a}}\right) = 2$$

$$v = n\left(\frac{y_2 - y_1}{b}\right) = (2)\left(\frac{-b/2 - 0b}{b}\right) = -1$$

$$w = n\left(\frac{z_2 - z_1}{c}\right) = (2)\left(\frac{-c \ - \ 0c}{c}\right) = -2$$

Therefore, Direction 1 is a $[2\bar{1}\bar{2}]$ direction.

We use the same procedure to determine the indices for Direction 2. Again, because the vector tail passes through the origin of the coordinate system, the values of x_1, y_1, and z_1 are the same as for Direction 1. Furthermore, vector head coordinates are as follows:

$x_2 = a/2$

$y_2 = 0b$

$z_2 = c$

We again choose a value of 2 for *n* because of the 2 in the denominator of the x_2 coordinate. Therefore,

$$u = n\left(\frac{x_2 - x_1}{a}\right) = (2)\left(\frac{a/2 - 0a}{a}\right) = 1$$

$$v = n\left(\frac{y_2 - y_1}{b}\right) = (2)\left(\frac{0b \ - \ 0b}{b}\right) = 0$$

$$w = n\left(\frac{z_2 - z_1}{c}\right) = (2)\left(\frac{c \ - \ 0c}{c}\right) = 2$$

Therefore, Direction 2 is a [102] direction.

3.34 *Within a cubic unit cell, sketch the following directions:*

(a)	*[101]*	*(e)*	$[\bar{1}1\bar{1}]$
(b)	*[211]*	*(f)*	$[\bar{2}12]$
(c)	$[10\bar{2}]$	*(g)*	$[3\bar{1}2]$
(d)	$[3\bar{1}3]$	*(h)*	*[301]*

Solution

(a) For the [101] direction, it is the case that

$u = 1$ $v = 0$ $w = 1$

lf we select the origin of the coordinate system as the position of the vector tail, then

$x_1 = 0a$ $y_1 = 0b$ $z_1 = 0c$

It is now possible to determine values of x_2, y_2, and z_2 using rearranged forms of Equations 3.10a through 3.10c as follows:

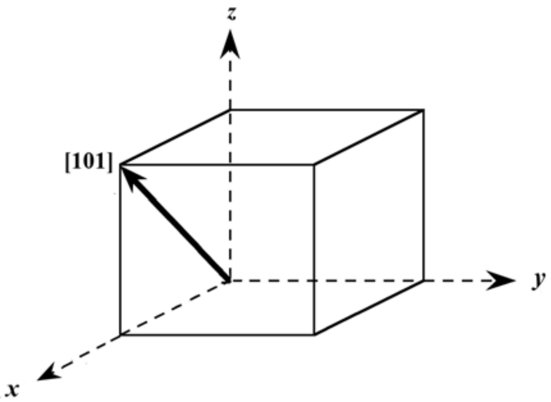
$$x_2 = ua + x_1 = (1)a + 0a = a$$

$$y_2 = vb + y_1 = (0)b + 0b = 0b$$

$$z_2 = wc + z_1 = (1)c + 0c = c$$

Thus, the vector head is located at *a*, 0*b*, and *c*, and the direction vector having these head coordinates is plotted below.

[Note: even though the unit cell is cubic, which means that the unit cell edge lengths are the same (i.e., *a*), in order to clarify construction of the direction vector, we have chosen to use *b* and *c* to designate edge lengths along *y* and *z* axes, respectively.]



(b) For a [211] direction, it is the case that

$u = 2$ $v = 1$ $w = 1$

lf we select the origin of the coordinate system as the position of the vector tail, then

$x_1 = 0a$ $y_1 = 0b$ $z_1 = 0c$

It is now possible to determine values of x_2, y_2, and z_2 using rearranged forms of Equations 3.10a through 3.10c as follows:

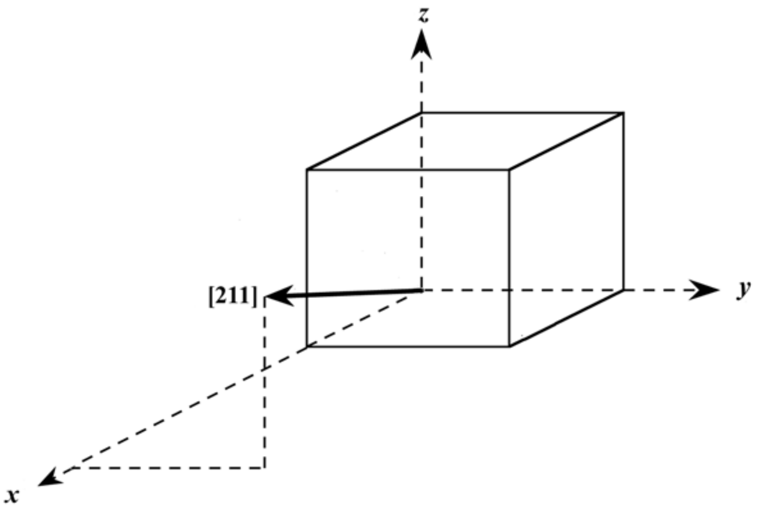
$$x_2 = ua + x_1 = (2)a + 0a = 2a$$

$$y_2 = vb + y_1 = (1)b + 0b = b$$

$$z_2 = wc + z_1 = (1)c + 0c = c$$

Thus, the vector head is located at 2*a*, *b*, and *c*, and the direction vector having these head coordinates is plotted below.

[Note: even though the unit cell is cubic, which means that the unit cell edge lengths are the same (i.e., *a*), in order to clarify construction of the direction vector, we have chosen to use *b* and *c* to designate edge lengths along *y* and *z* axes, respectively.]



(c) For the $[10\bar{2}]$ direction, it is the case that

$u = 1$ $v = 0$ $w = -2$

lf we select the origin of the coordinate system as the position of the vector tail, then

$x_1 = 0a$ $y_1 = 0b$ $z_1 = 0c$

It is now possible to determine values of x_2, y_2, and z_2 using rearranged forms of Equations 3.10a through 3.10c as follows:

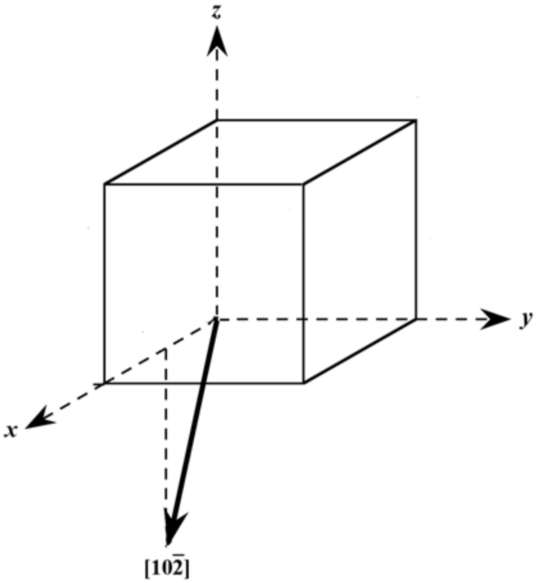
$$x_2 = ua + x_1 = (1)a + 0a = a$$

$$y_2 = vb + y_1 = (0)b + 0b = 0b$$

$$z_2 = wc + z_1 = (-2)c + 0c = -2c$$

Thus, the vector head is located at *a*, 0*b*, and *c*. However, in order to reduce the vector length, we have divided these coordinates by ½, which gives the new set of head coordinates as *a/*2, 0*b*, and –*c*; the direction vector having these head coordinates is plotted below.

[Note: even though the unit cell is cubic, which means that the unit cell edge lengths are the same (i.e., *a*), in order to clarify construction of the direction vector, we have chosen to use *b* and *c* to designate edge lengths along *y* and *z* axes, respectively.]



(d) For the $[3\bar{1}3]$ direction, it is the case that

$u = 3$ $v = -1$ $w = 3$

lf we select the origin of the coordinate system as the position of the vector tail, then

$x_1 = 0a$ $y_1 = 0b$ $z_1 = 0c$

It is now possible to determine values of x_2, y_2, and z_2 using rearranged forms of Equations 3.10a through 3.10c as follows:

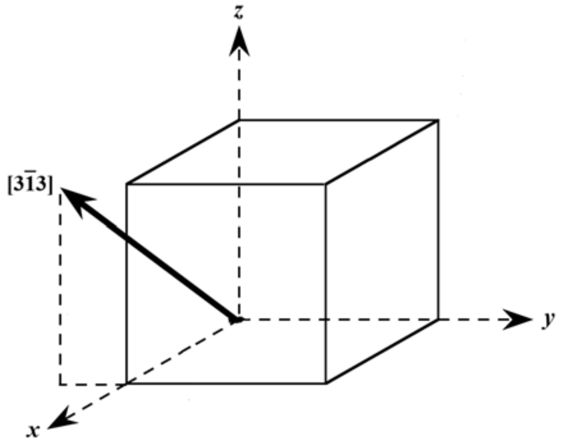
$$x_2 = ua + x_1 = (3)a + 0a = 3a$$

$$y_2 = vb + y_1 = (-1)b + 0b = -b$$

$$z_2 = wc + z_1 = (3)c + 0c = 3c$$

Thus, the vector head is located at 3*a*, –*b*, and 3*c*. However, in order to reduce the vector length, we have divided these coordinates by 1/3, which gives the new set of head coordinates as *a*, –*b/*3, and *c*; the direction vector having these head coordinates is plotted below.

[Note: even though the unit cell is cubic, which means that the unit cell edge lengths are the same (i.e., *a*), in order to clarify construction of the direction vector, we have chosen to use *b* and *c* to designate edge lengths along *y* and *z* axes, respectively.]



(e) For the $[\bar{1}1\bar{1}]$ direction, it is the case that

$u = -1 \qquad v = 1 \qquad w = -1$

lf we select the origin of the coordinate system as the position of the vector tail, then

$x_1 = 0a \qquad y_1 = 0b \qquad z_1 = 0c$

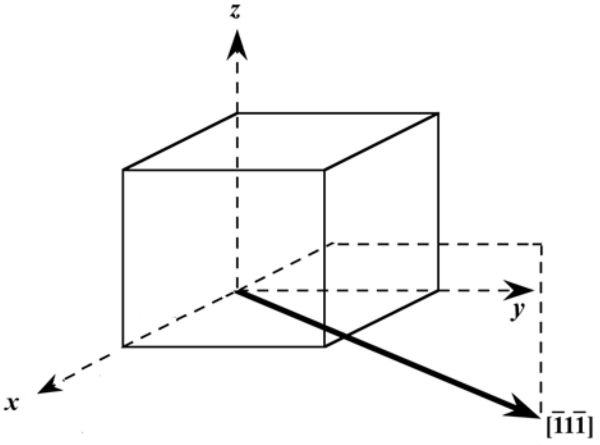
It is now possible to determine values of x_2, y_2, and z_2 using rearranged forms of Equations 3.10a through 3.10c as follows:

$$x_2 = ua + x_1 = (-1)a + 0a = -a$$

$$y_2 = vb + y_1 = (1)b + 0b = b$$

$$z_2 = wc + z_1 = (-1)c + 0c = -c$$

Thus, the vector head is located at $-a$, b, and $-c$, and the direction vector having these head coordinates is plotted below.



[Note: even though the unit cell is cubic, which means that the unit cell edge lengths are the same (i.e., *a*), in order to clarify construction of the direction vector, we have chosen to use *b* and *c* to designate edge lengths along *y* and *z* axes, respectively.]

(f) For the $[\bar{2}12]$ direction, it is the case that

$u = -2 \qquad v = 1 \qquad w = 2$

If we select the origin of the coordinate system as the position of the vector tail, then

$x_1 = 0a \qquad y_1 = 0b \qquad z_1 = 0c$

It is now possible to determine values of x_2, y_2, and z_2 using rearranged forms of Equations 3.10a through 3.10c as follows:

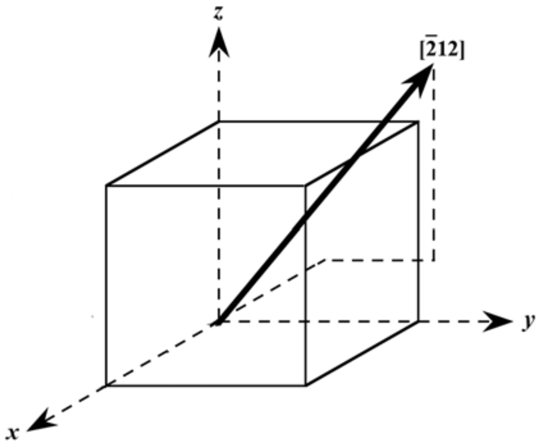
$$x_2 = ua + x_1 = (-2)a + 0a = -2a$$

$$y_2 = vb + y_1 = (1)b + 0b = b$$

$$z_2 = wc + z_1 = (2)c + 0c = 2c$$

Thus, the vector head is located at –2*a*, *b*, and 2*c*. However, in order to reduce the vector length, we have divided these coordinates by 1/2, which gives the new set of head coordinates as –*a*, *b/*2, and *c*; the direction vector having these head coordinates is plotted below.

[Note: even though the unit cell is cubic, which means that the unit cell edge lengths are the same (i.e., *a*), in order to clarify construction of the direction vector, we have chosen to use *b* and *c* to designate edge lengths along *y* and *z* axes, respectively.]



(g) For the $[3\bar{1}2]$ direction, it is the case that

$u = 3 \qquad v = -1 \qquad w = 2$

If we select the origin of the coordinate system as the position of the vector tail, then

$x_1 = 0a \qquad y_1 = 0b \qquad z_1 = 0c$

It is now possible to determine values of x_2, y_2, and z_2 using rearranged forms of Equations 3.10a through 3.10c as follows:

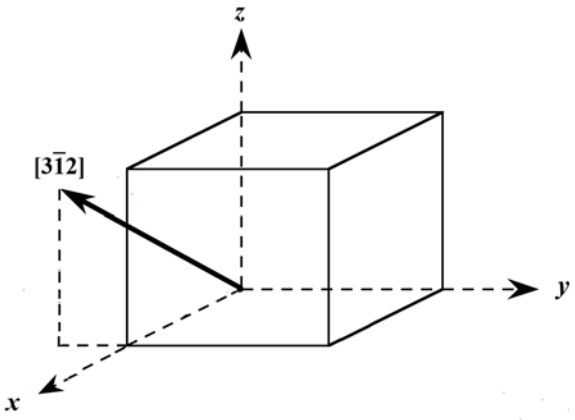
$$x_2 = ua + x_1 = (3)a + 0a = 3a$$

$$y_2 = vb + y_1 = (-1)b + 0b = -b$$

$$z_2 = wc + z_1 = (2)c + 0c = 2c$$

Thus, the vector head is located at 3*a*, –*b*, and 2*c*. However, in order to reduce the vector length, we have divided these coordinates by 1/3, which gives the new set of head coordinates as *a*, –*b/*3, and 2*c/*3; the direction vector having these head coordinates is plotted below.

[Note: even though the unit cell is cubic, which means that the unit cell edge lengths are the same (i.e., *a*), in order to clarify construction of the direction vector, we have chosen to use *b* and *c* to designate edge lengths along *y* and *z* axes, respectively.]



(g) For the [301] direction, it is the case that

$u = 3 \qquad v = 0 \qquad w = 1$

lf we select the origin of the coordinate system as the position of the vector tail, then

$x_1 = 0a \qquad y_1 = 0b \qquad z_1 = 0c$

It is now possible to determine values of x_2, y_2, and z_2 using rearranged forms of Equations 3.10a through 3.10c as follows:

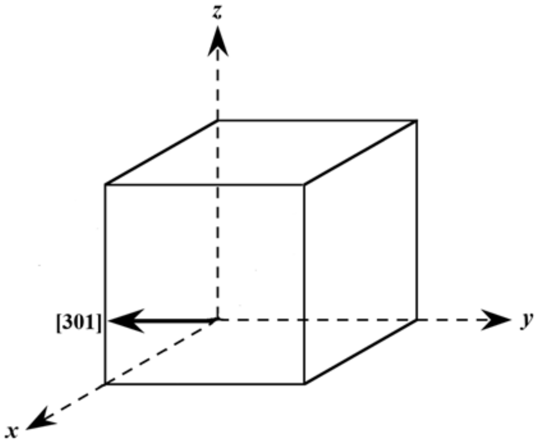
$$x_2 = ua + x_1 = (3)a + 0a = 3a$$

$$y_2 = vb + y_1 = (0)b + 0b = 0b$$

$$z_2 = wc + z_1 = (1)c + 0c = c$$

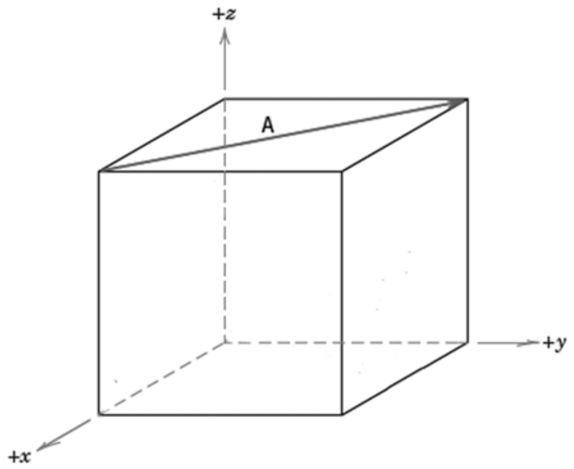
Thus, the vector head is located at 3*a*, 0*b*, and *c*. However, in order to reduce the vector length, we have divided these coordinates by 1/3, which gives the new set of head coordinates as *a*, 0*b*, and *c/*3; the direction vector having these head coordinates is plotted below.

[Note: even though the unit cell is cubic, which means that the unit cell edge lengths are the same (i.e., *a*), in order to clarify construction of the direction vector, we have chosen to use *b* and *c* to designate edge lengths along *y* and *z* axes, respectively.]



3.35 *Determine the indices for the directions shown in the following cubic unit cell:*

For Direction A



We determine the indices of this direction vector using Equations 3.10a-3.10c—that is, by subtracting vector tail coordinates from head coordinates. Tail coordinates are as follows:

$x_1 = a$ $y_1 = 0b$ $z_1 = c$

Whereas head coordinates are as follows:

$x_2 = 0a$ $y_2 = b$ $z_2 = c$

From Equations 3.10a, 3.10b, and 3.10c assuming a value of 1 for the parameter *n*

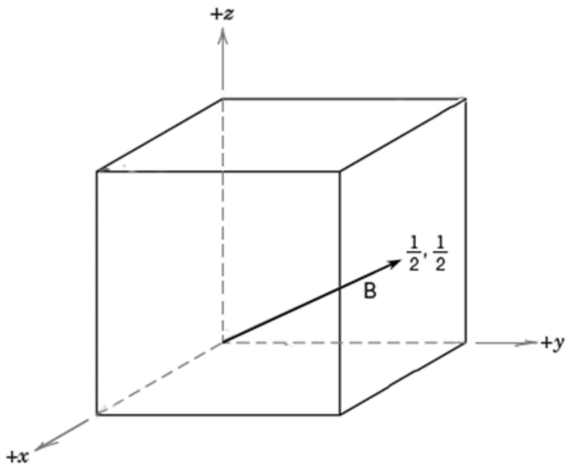
$$u = n\left(\frac{x_2 - x_1}{a}\right) = (1)\left(\frac{0a - a}{a}\right) = -1$$

$$v = n\left(\frac{y_2 - y_1}{b}\right) = (1)\left(\frac{b - 0b}{b}\right) = 1$$

$$w = n\left(\frac{z_2 - z_1}{c}\right) = (1)\left(\frac{c - c}{c}\right) = 0$$

Therefore, Direction A is $[\bar{1}10]$.

For Direction B



We determine the indices of this direction vector using Equations 3.10a-3.10c—that is, by subtracting vector tail coordinates from head coordinates. Because the tail passes through the origin of the unit cell, its coordinates are as follows:

$x_1 = 0a$ $y_1 = 0b$ $z_1 = 0c$

Whereas head coordinates are as follows:

$x_2 = a/2$ $y_2 = b$ $z_2 = c/2$

From Equations 3.10a, 3.10b, and 3.10c assuming a value of 2 for the parameter *n*

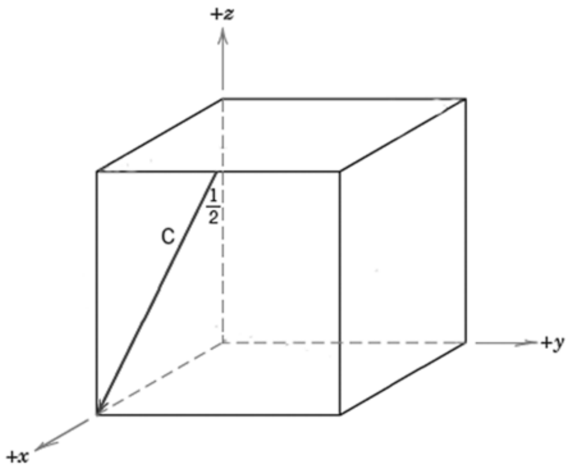
$$u = n\left(\frac{x_2 - x_1}{a}\right) = (2)\left(\frac{a/2 - 0a}{a}\right) = 1$$

$$v = n\left(\frac{y_2 - y_1}{b}\right) = (2)\left(\frac{b - 0b}{b}\right) = 2$$

$$w = n\left(\frac{z_2 - z_1}{c}\right) = (2)\left(\frac{c/2 - 0c}{c}\right) = 1$$

Therefore, Direction B is [121].

For direction C



We determine the indices of this direction vector using Equations 3.10a-3.10c—that is, by subtracting vector tail coordinates from head coordinates. The tail coordinates are as follows:

$x_1 = a$ $\qquad y_1 = b/2$ $\qquad z_1 = c$

Whereas head coordinates are as follows:

$x_2 = a$ $\qquad y_2 = 0b$ $\qquad z_2 = 0c$

From Equations 3.10a, 3.10b, and 3.10c assuming a value of 2 for the parameter n

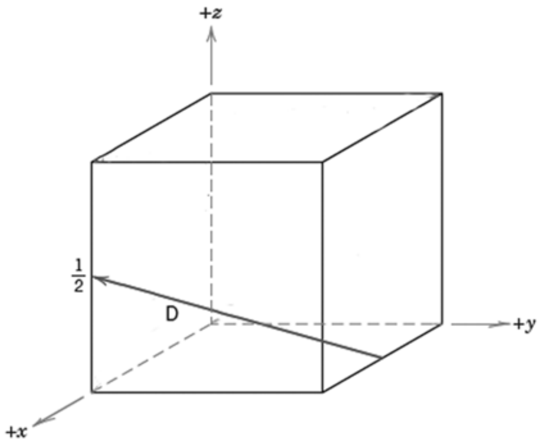
$$u = n\left(\frac{x_2 - x_1}{a}\right) = (2)\left(\frac{a - a}{a}\right) = 0$$

$$v = n\left(\frac{y_2 - y_1}{b}\right) = (2)\left(\frac{0b - b/2}{b}\right) = -1$$

$$w = n\left(\frac{z_2 - z_1}{c}\right) = (2)\left(\frac{0c - c}{c}\right) = -2$$

Therefore, Direction C is $[0\bar{1}\bar{2}]$.

For direction D



We determine the indices of this direction vector using Equations 3.10a-3.10c—that is, by subtracting vector tail coordinates from head coordinates. Tail coordinates are as follows:

$x_1 = a/2$ $y_1 = b$ $z_1 = 0c$

Whereas head coordinates are as follows:

$x_2 = a$ $y_2 = 0b$ $z_2 = c/2$

From Equations 3.10a, 3.10b, and 3.10c assuming a value of 2 for the parameter *n*

$$u = n\left(\frac{x_2 - x_1}{a}\right) = (2)\left(\frac{a - a/2}{a}\right) = 1$$

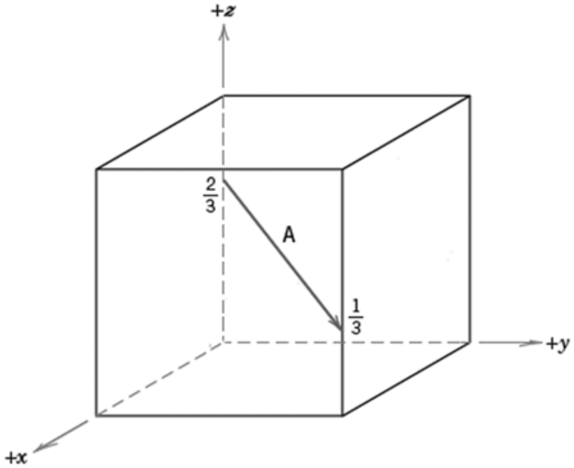
$$v = n\left(\frac{y_2 - y_1}{b}\right) = (2)\left(\frac{0b - b}{b}\right) = -2$$

$$w = n\left(\frac{z_2 - z_1}{c}\right) = (2)\left(\frac{c/2 - 0c}{c}\right) = 1$$

Therefore, Direction D is $[1\bar{2}1]$.

3.36 *Determine the indices for the directions shown in the following cubic unit cell:*

Direction A



We determine the indices of this direction vector using Equations 3.10a-3.10c—that is, by subtracting vector tail coordinates from head coordinates. Tail coordinates are as follows:

$x_1 = 0a$ $y_1 = 0b$ $z_1 = 2c/3$

Whereas head coordinates are as follows:

$x_2 = a$ $y_2 = b$ $z_2 = c/3$

From Equations 3.10a, 3.10b, and 3.10c assuming a value of 3 for the parameter *n*

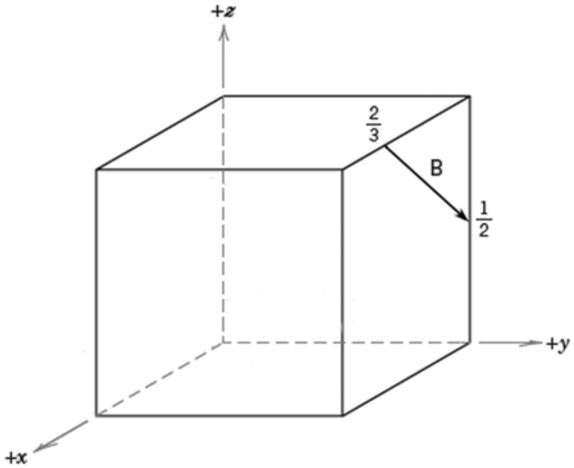
$$u = n\left(\frac{x_2 - x_1}{a}\right) = (3)\left(\frac{a - 0a}{a}\right) = 3$$

$$v = n\left(\frac{y_2 - y_1}{b}\right) = (3)\left(\frac{b - 0b}{b}\right) = 3$$

$$w = n\left(\frac{z_2 - z_1}{c}\right) = (3)\left(\frac{c/3 - 2c/3}{c}\right) = -1$$

Therefore, Direction A is $[33\bar{1}]$.

Direction B:



We determine the indices of this direction vector using Equations 3.10a-3.10c—that is, by subtracting vector tail coordinates from head coordinates. Tail coordinates are as follows:

$x_1 = 2a/3$ $\quad y_1 = b$ $\quad z_1 = c$

Whereas head coordinates are as follows:

$x_2 = 0a$ $\quad y_2 = b$ $\quad z_2 = c/2$

From Equations 3.10a, 3.10b, and 3.10c assuming a value of 3 for the parameter n

$$u = n\left(\frac{x_2 - x_1}{a}\right) = (3)\left(\frac{0a - 2a/3}{a}\right) = -2$$

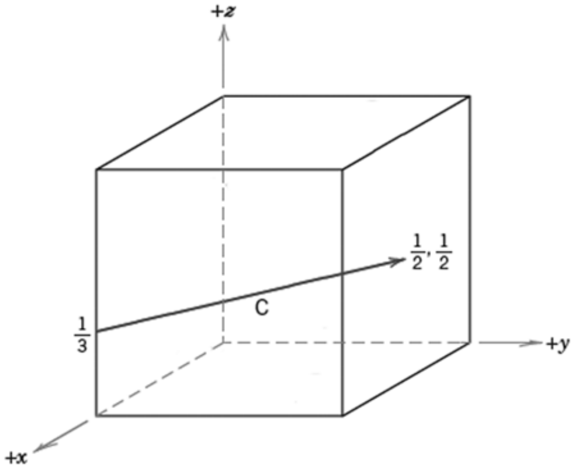
$$v = n\left(\frac{y_2 - y_1}{b}\right) = (3)\left(\frac{b - b}{b}\right) = 0$$

$$w = n\left(\frac{z_2 - z_1}{c}\right) = (3)\left(\frac{c/2 - c}{c}\right) = -\frac{3}{2}$$

In order to reduce these values to the lowest set of integers, we multiply each by the factor 2.

Therefore, Direction B is $[\bar{4}0\bar{3}]$.

Direction C:



We determine the indices of this direction vector using Equations 3.10a-3.10c—that is, by subtracting vector tail coordinates from head coordinates. Tail coordinates are as follows:

$x_1 = a$ $y_1 = 0b$ $z_1 = c/3$

Whereas head coordinates are as follows:

$x_2 = a/2$ $y_2 = b$ $z_2 = c/2$

From Equations 3.10a, 3.10b, and 3.10c assuming a value of 3 for the parameter n

$$u = n\left(\frac{x_2 - x_1}{a}\right) = (3)\left(\frac{a/2 - a}{a}\right) = -\frac{3}{2}$$

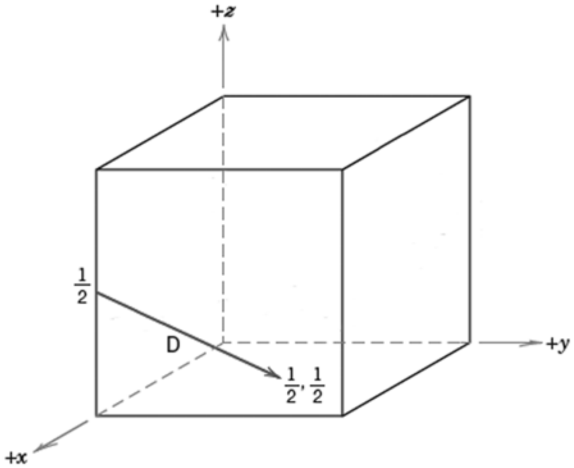
$$v = n\left(\frac{y_2 - y_1}{b}\right) = (3)\left(\frac{b - 0b}{b}\right) = 3$$

$$w = n\left(\frac{z_2 - z_1}{c}\right) = (3)\left(\frac{c/2 - c/3}{c}\right) = \frac{1}{2}$$

In order to reduce these values to the lowest set of integers, we multiply each by the factor 2.

Therefore, Direction C is $[\bar{3}61]$.

Direction D:



We determine the indices of this direction vector using Equations 3.10a-3.10c—that is, by subtracting vector tail coordinates from head coordinates. Tail coordinates are as follows:

$x_1 = a$ $y_1 = 0b$ $z_1 = c/2$

Whereas head coordinates are as follows:

$x_2 = a/2$ $y_2 = b/2$ $z_2 = 0c$

From Equations 3.10a, 3.10b, and 3.10c assuming a value of 2 for the parameter *n*

$$u = n\left(\frac{x_2 - x_1}{a}\right) = (2)\left(\frac{a/2 - a}{a}\right) = -1$$

$$v = n\left(\frac{y_2 - y_1}{b}\right) = (2)\left(\frac{b/2 - 0b}{b}\right) = 1$$

$$w = n\left(\frac{z_2 - z_1}{c}\right) = (2)\left(\frac{0c - c/2}{c}\right) = -1$$

Therefore, Direction D is $[\bar{1}1\bar{1}]$.

3.37 (a) *What are the direction indices for a vector that passes from point* $\frac{1}{4}0\frac{1}{2}$ *to point* $\frac{3}{4}\frac{1}{2}\frac{1}{2}$ *in a cubic unit cell?*

(b) *Repeat part (a) for a monoclinic unit cell.*

Solution

(a) Point coordinate indices for the vector tail, $\frac{1}{4}0\frac{1}{2}$, means that

$$q = \frac{1}{4} \qquad r = 0 \qquad s = \frac{1}{2}$$

or that. using Equations 3.9a-3.9c, lattice positions references to the three axis are determine as follows:

$$\text{lattice position referenced to the } x \text{ axis} = qa = \left(\frac{1}{4}\right)a = \frac{a}{4} = x_1$$

$$\text{lattice position referenced to the } y \text{ axis} = rb = (0)b = 0b = y_1$$

$$\text{lattice position referenced to the } z \text{ axis} = sc = \left(\frac{1}{2}\right)c = \frac{c}{2} = z_1$$

Similarly for the vector head:

$$q = \frac{3}{4} \qquad r = \frac{1}{2} \qquad s = \frac{1}{2}$$

And we determine lattice positions for using Equations 3.9a-3.9c, in a similar manner:

$$\text{lattice position referenced to the } x \text{ axis} = qa = \left(\frac{3}{4}\right)a = \frac{3a}{4} = x_2$$

$$\text{lattice position referenced to the } y \text{ axis} = rb = \left(\frac{1}{2}\right)b = \frac{b}{2} = y_2$$

$$\text{lattice position referenced to the } z \text{ axis} = sc = \left(\frac{1}{2}\right)c = \frac{c}{2} = z_2$$

And, finally, determination of the *u*, *v*, and *w* direction indices is possible using Equations 3.10a-3.10c; because there is a 4 in the denominators of two of the lattice positions, let us assume a value of 4 for the parameter *n* in these equations. Therefore,

$$u = n\left(\frac{x_2 - x_1}{a}\right) = (4)\left(\frac{\frac{3a}{4} - \frac{a}{4}}{a}\right) = 2$$

$$v = n\left(\frac{y_2 - y_1}{b}\right) = (4)\left(\frac{\frac{b}{2} - 0b}{b}\right) = 2$$

$$w = n\left(\frac{z_2 - z_1}{c}\right) = (4)\left(\frac{\frac{c}{2} - \frac{c}{2}}{c}\right) = 0$$

Because it is possible to reduce these indices to the smallest set of integers by dividing each by the factor 2, this vector points in a $[110]$ direction.

(b) For a monoclinic unit cell, the direction indices will also be [110]. Lattice position coordinates for both vector head and tail will be the same as for cubic. Likewise, incorporating these lattice position coordinates into Equations 3.10a-3.10c also yield

$u = 1$

$v = 1$

$w = 0$

3.38 *(a) What are the direction indices for a vector that passes from point* $\frac{1}{3}\frac{1}{2}0$ *to point* $\frac{2}{3}\frac{3}{4}\frac{1}{2}$ *in a tetragonal unit cell?*

(b) Repeat part (a) for a rhombohedral unit cell.

Solution

(a) Point coordinate indices for the vector tail, $\frac{1}{3}\frac{1}{2}\mathbf{0}$, means that

$$q = \frac{1}{3} \qquad r = \frac{1}{2} \qquad s = 0$$

or that. using Equations 3.9a-3.9c, lattice positions references to the three axis are determine as follows:

lattice position referenced to the x axis = $qa = \left(\frac{1}{3}\right)a = \frac{a}{3} = x_1$

lattice position referenced to the y axis $= rb = \left(\frac{1}{2}\right)b = \frac{b}{2} = y_1$

lattice position referenced to the z axis = $sc = (0)c = 0c = z_1$

Similarly for the vector head:

$$q = \frac{2}{3} \qquad r = \frac{3}{4} \qquad s = \frac{1}{2}$$

And we determine lattice positions for using Equations 3.9a-3.9c, in a similar manner:

lattice position referenced to the x axis = $qa = \left(\frac{2}{3}\right)a = \frac{2a}{3} = x_2$

lattice position referenced to the y axis = $rb = \left(\frac{3}{4}\right)b = \frac{3b}{4} = y_2$

lattice position referenced to the z axis = $sc = \left(\frac{1}{2}\right)c = \frac{c}{2} = z_2$

And, finally, determination of the u, v, and w direction indices is possible using Equations 3.10a-3.10c; because there is a 4 in one lattice position denominator, and 3 in two others, let us assume a value of 12 for the parameter n in these equations. Therefore,

$$u = n\left(\frac{x_2 - x_1}{a}\right) = (12)\left(\frac{\frac{2a}{3} - \frac{a}{3}}{a}\right) = 4$$

$$v = n\left(\frac{y_2 - y_1}{b}\right) = (12)\left(\frac{\dfrac{3b}{4} - \dfrac{b}{2}}{b}\right) = 3$$

$$w = n\left(\frac{z_2 - z_1}{c}\right) = (12)\left(\frac{\dfrac{c}{2} - 0c}{c}\right) = 6$$

Therefore, the direction of the vector passing between these two points is a [436].

(b) For a rhombohedral unit cell, the direction indices will also be [436]. Lattice position coordinates for both vector head and tail will be the same as for tetragonal. Likewise, incorporating these lattice position coordinates into Equations 3.10a-3.10c also yield

u = 4

v = 3

w = 6

3.39 *For tetragonal crystals, cite the indices of directions that are equivalent to each of the following directions:*

(a) [011]

(b) [100]

Solution

(a) For tetragonal crystals, lattice parameter relationships are as follows: $a = b \neq c$ and $\alpha = \beta = \gamma = 90°$. One way to determine indices of directions that are equivalent to [011] is to find indices for all direction vectors that have the same length as the vector for the [011] direction. Let us assign vector tail coordinates to the origin of the coordinate system, then $x_1 = y_1 = z_1 = 0$. Under these circumstances, vector length $\bar{\mathbf{V}}$ is equal to

$$\bar{\mathbf{V}} = \sqrt{x_2^2 + y_2^2 + z_2^2}$$

For the [011] direction

$x_2 = 0a$

$y_2 = b = a$ (since, for tetragonal $a = b$)

$z_2 = c$

Therefore, the vector length for the [011] direction $(\bar{\mathbf{V}}_{011})$ is equal to

$$\bar{\mathbf{V}}_{011} = \sqrt{x_2^2 + y_2^2 + z_2^2}$$

$$= \sqrt{(0a)^2 + a^2 + c^2}$$

$$= \sqrt{a^2 + c^2}$$

It is now necessary to find all combinations of x_2, y_2, and z_2 that yield the above expression for $(\bar{\mathbf{V}}_{011})$. First of all, only values of $+c$ and $-c$, when squared yield c^2. This means that for the index w (of [uvw]) only values of +1 and −1 are possible.

With regard to values of the u and v indices, the sum of x_2^2 and y_2^2 must equal a^2. Therefore one of either u or v must be zero, whereas the other may be either +1 or −1. Therefore, in addition to [011] there are seven combinations u, v, and w indices that meet these criteria, which are listed as follows: [101], $[\bar{1}0\bar{1}]$, $[\bar{1}01]$, $[10\bar{1}]$, $[01\bar{1}]$, $[0\bar{1}1]$, and $[0\bar{1}\bar{1}]$.

(b) As with part (a), if we assign the vector tail coordinates to the origin of the coordinate system, then for the [100] direction vector head coordinates are as follows:

$x_2 = a$

$y_2 = 0b = 0a$ (since, for tetragonal $a = b$)

$z_2 = 0c$

Therefore, the vector length for the [100] direction $(\bar{V}_{100})$ is equal to

$$\bar{V}_{100} = \sqrt{x_2^2 + y_2^2 + z_2^2}$$

$$= \sqrt{(a)^2 + (0a)^2 + (0c)^2}$$

$$= \sqrt{a^2} = a$$

It is now necessary to find all combinations of x_2, y_2, and z_2 that yield the above expression for $(\bar{V}_{100})$. First of all, for all directions $c = 0$ because c is not included in the expression for $\bar{V}_{100}$. This means that for the index w (of $[uvw]$) for all directions must be zero.

With regard to values of the u and v indices, the sum of x_2^2 and y_2^2 must equal a^2. Therefore one of either u or v must be zero, whereas the other may be either +1 or –1. Therefore, in addition to [100] there are three combinations u, v, and w indices that meet these criteria, which are listed as follows: $[\bar{1}00]$, [010], and $[0\bar{1}0]$.

3.40 *Convert the [110] and $[00\bar{1}]$ directions into the four-index Miller–Bravais scheme for hexagonal unit cells.*

Solution

We are asked to convert [110] and $[00\bar{1}]$ directions into the four-index Miller-Bravais scheme for hexagonal unit cells. For [110]

$$U = 1$$

$$V = 1$$

$$W = 0$$

From Equations 3.11a-3.11d

$$u = \frac{1}{3}(2U - V) = \frac{1}{3}[(2)(1) - 1] = \frac{1}{3}$$

$$v = \frac{1}{3}(2V - U) = \frac{1}{3}[(2)(1) - 1] = \frac{1}{3}$$

$$t = -(U + V) = -\left(\frac{1}{3} + \frac{1}{3}\right) = -\frac{2}{3}$$

$$w = W = 0$$

It is necessary to multiply these numbers by 3 in order to reduce them to the lowest set of integers. Thus, the direction is represented as [*uvtw*] = $[11\bar{2}0]$.

For the $[00\bar{1}]$ direction

$$U = 0$$

$$V = 0$$

$$W = -1$$

Therefore, conversion to the four-index scheme is accomplished as follows:

$$U = \frac{1}{3}[(2)(0) - 0] = 0$$

$$V = \frac{1}{3}[(2)(0) - 0] = 0$$

$$t = -(0 + 0) = 0$$

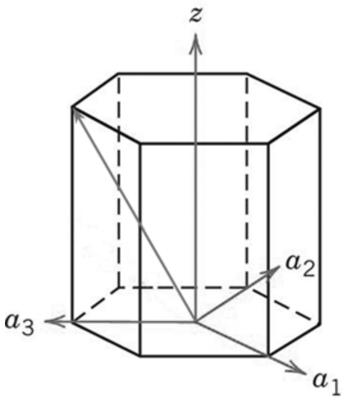
$$w = -1$$

Thus, the direction is represented as $[uvtw] = [000\bar{1}]$.

3.41 *Determine the indices for the directions shown in the following hexagonal unit cells:*

Solutions

(a)



One way solve this problem is to begin by determining the *U*, *V*, and *W* indices for the vector referenced to the three-axis scheme; this is possible using Equations 3.13a through 3.13c. Because the tail of the vector passes through the origin, $a_1'' = a_2'' = 0a$, and $z'' = 0c$ Furthermore, coordinates for the vector head are as follows:

$$a_1' = -a \qquad a_2' = -a \qquad z' = c$$

Now, solving for *U*, *V*, and *W* using Equations 3.13a, 3.13b, and 3.13c assuming a value of 1 for the parameter *n*

$$U = n\left(\frac{a_1' - a_1''}{a}\right) = (1)\left(\frac{-a - 0a}{a}\right) = -1$$

$$V = n\left(\frac{a_2' - a_2''}{a}\right) = (1)\left(\frac{-a - 0a}{a}\right) = -1$$

$$W = n\left(\frac{z' - z''}{c}\right) = (1)\left(\frac{c - 0c}{c}\right) = 1$$

Now, it becomes necessary to convert these indices into an index set referenced to the four-axis scheme. This requires the use of Equations 3.11a through 3.11d, as follows:

$$u = \frac{1}{3}(2U - V) = \frac{1}{3}\left[(2)(-1) - (-1)\right] = -\frac{1}{3}$$

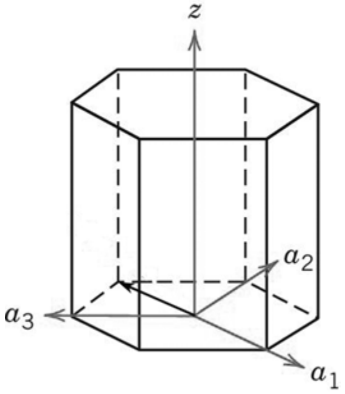
$$v = \frac{1}{3}(2V - U) = \frac{1}{3}\left[(2)(-1) - (-1)\right] = -\frac{1}{3}$$

$$t = -(u + v) = -\left(-\frac{1}{3} - \frac{1}{3}\right) = \frac{2}{3}$$

$$w = W = 1$$

Multiplication of these three indices by the factor 3 reduces them to the lowest set, which equals values for *u*, *v*, *t*, and *w* of –1, –1, 2, and 3. Therefore the vector represents the $[\bar{1}\bar{1}23]$ direction.

(b)



This problem is to begin by determining the *U*, *V*, and *W* indices for the vector referenced to the three-axis scheme; this is possible using Equations 3.13a through 3.13c. Because the tail of the vector passes through the origin, $a_1'' = a_2'' = 0a$, and $z'' = 0c$ Furthermore, coordinates for the vector head are as follows:

$$a_1' = -a \qquad a_2' = 0a \qquad z' = 0c$$

Now, solving for *U*, *V*, and *W* using Equations 3.13a, 3.13b, and 3.13c assuming a value of 1 for the parameter *n*

$$U = n\left(\frac{a_1' - a_1''}{a}\right) = (1)\left(\frac{-a - 0a}{a}\right) = -1$$

$$V = n\left(\frac{a_2' - a_2''}{a}\right) = (1)\left(\frac{0a - 0a}{a}\right) = 0$$

$$w = n\left(\frac{z' - z''}{c}\right) = (1)\left(\frac{0c - 0c}{c}\right) = 0$$

Now, it becomes necessary to convert these indices into an index set referenced to the four-axis scheme. This requires the use of Equations 3.11a through 3.11d, as follows:

$$u = \frac{1}{3}(2U - V) = \frac{1}{3}\left[(2)(-1) - (0)\right] = -\frac{2}{3}$$

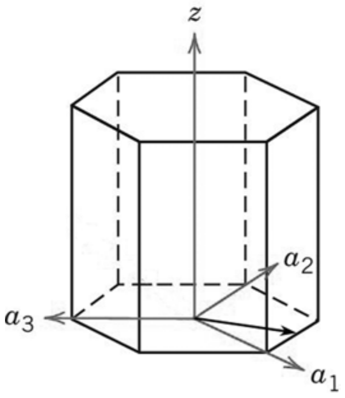
$$v = \frac{1}{3}(2V - U) = \frac{1}{3}\left[(2)(0) - (-1)\right] = \frac{1}{3}$$

$$t = -(u + v) = -\left(-\frac{2}{3} + \frac{1}{3}\right) = \frac{1}{3}$$

$$w = W = 0$$

Multiplication of these three indices by the factor 3 reduces them to the lowest set, which equals values for *u*, *v*, *t*, and *w* of –2, 1, 1, and 0. Therefore the vector represents the $[\bar{2}110]$ direction.

(c)



This problem is to begin by determining the *U*, *V*, and *W* indices for the vector referenced to the three-axis scheme; this is possible using Equations 3.13a through 3.13c. Because the tail of the vector passes through the origin, $a_1'' = a_2'' = 0a$, and $z'' = 0c$ Furthermore, coordinates for the vector head are as follows:

$a_1' = a$ $a_2' = a/2$ $z' = 0c$

Now, solving for *U*, *V*, and *W* using Equations 3.13a, 3.13b, and 3.13c assuming a value of 1 for the parameter *n*

$$U = n\left(\frac{a_1' - a_1''}{a}\right) = (1)\left(\frac{a - 0a}{a}\right) = 1$$

$$V = n\left(\frac{a_2' - a_2''}{a}\right) = (1)\left(\frac{a/2 - 0a}{a}\right) = \frac{1}{2}$$

$$W = n\left(\frac{z' - z''}{c}\right) = (1)\left(\frac{0c - 0c}{c}\right) = 0$$

Multiplying these integers by the factor 2, reduces them to the following indices:

$U = 2$ $V = 1$ $W = 0$

Now, it becomes necessary to convert these indices into an index set referenced to the four-axis scheme. This requires the use of Equations 3.11a through 3.11d, as follows:

$$u = \frac{1}{3}(2U - V) = \frac{1}{3}\left[(2)(2) - (1)\right] = \frac{3}{3} = 1$$

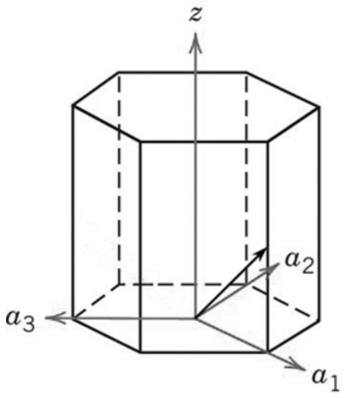
$$v = \frac{1}{3}(2V - U) = \frac{1}{3}\left[(2)(1) - 2\right] = 0$$

$$t = -(u + v) = -\left(1 + 0\right) = -1$$

$$w = W = 0$$

Therefore, the values for *u*, *v*, *t*, and *w* are 1, 0, −1, and 0, and the vector represents the $[10\bar{1}0]$ direction.

(d)



We begin by determining the *U*, *V*, and *W* indices for the vector referenced to the three-axis scheme; this is possible using Equations 3.13a through 3.13c. Because the tail of the vector passes through the origin, $a_1'' = a_2'' = 0a$, and $z'' = 0c$ Furthermore, coordinates for the vector head are as follows:

$$a_1' = a \qquad a_2' = 0a \qquad z' = c/2$$

Now, solving for *U*, *V*, and *W* using Equations 3.13a, 3.13b, and 3.13c assuming a value of 1 for the parameter *n*

$$U = n\left(\frac{a_1' - a_1''}{a}\right) = (1)\left(\frac{a - 0a}{a}\right) = 1$$

$$V = n\left(\frac{a_2' - a_2''}{a}\right) = (1)\left(\frac{0a - 0a}{a}\right) = 0$$

$$W = n\left(\frac{z' - z''}{c}\right) = (1)\left(\frac{c/2 - 0c}{c}\right) = \frac{1}{2}$$

Multiplying these integers by the factor 2, reduces them to the following indices:

$$U = 2 \qquad V = 0 \qquad W = 1$$

Now, it becomes necessary to convert these indices into an index set referenced to the four-axis scheme. This requires the use of Equations 3.11a through 3.11d, as follows:

$$u = \frac{1}{3}(2U - V) = \frac{1}{3}\left[(2)(2) - (0)\right] = \frac{4}{3}$$

$$v = \frac{1}{3}(2V - U) = \frac{1}{3}\left[(2)(0) - (2)\right] = -\frac{2}{3}$$

$$t = -(u + v) = -\left(\frac{4}{3} - \frac{2}{3}\right) = -\frac{2}{3}$$

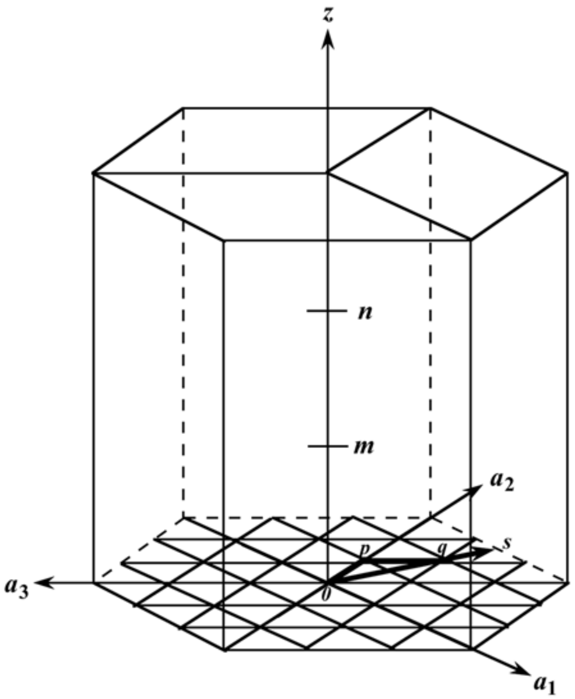
$$w = W = 1$$

Multiplication of these three indices by the factor 3 reduces them to the lowest set, which equals values for *u*, *v*, *t*, and *w* of 4, –2, –2, and 3. Therefore, this vector represents the $[4\bar{2}\bar{2}3]$ direction.

3.42 *Sketch the* $[01\overline{1}0]$ *and* $[\overline{22}43]$ *directions in a hexagonal unit cell.*

Solution

The first portion of this problem asks that we plot the $[01\overline{1}0]$ within a hexagonal unit cell. Below is shown this direction plotted within a hexagonal unit cell having a ruled-net coordinate scheme.



For the sake of convenience we will position the vector tail at the origin of the coordinate system. This means that $a_1'' = a_2'' = a_3'' = \mathbf{0}a$ and $z'' = \mathbf{0}c$. Coordinates for the vector head $(a_1', a_2', a_3' \text{ and } z')$ may be determined using rearranged forms of Equations 3.12a through 3.12d, taking the value of *n* to be unity, and since, for this $[01\overline{1}0]$ direction

$u = 0$ $v = 1$ $t = -1$ $w = 0$

Thus, vector head coordinates are determined as follows:

$$a_1' = \frac{ua}{3n} + a_1'' = \frac{0a}{3(1)} + 0a = 0a$$

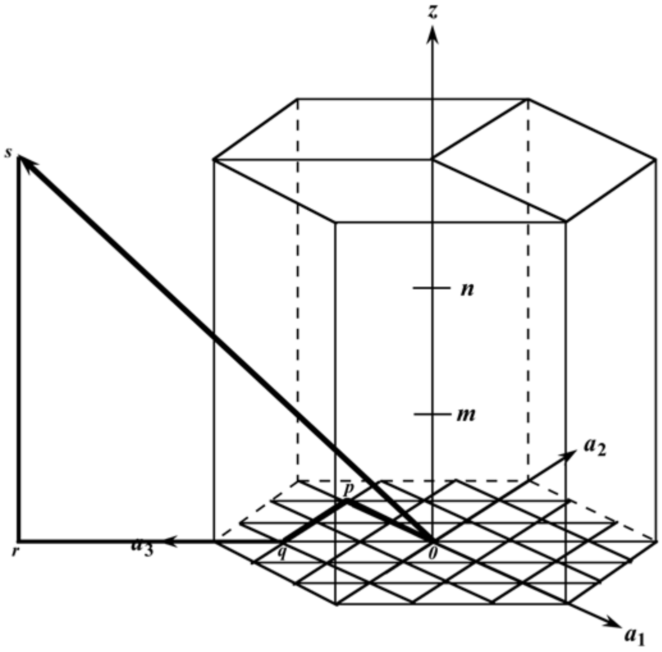
$$a_2' = \frac{va}{3n} + a_2'' = \frac{a}{3(1)} + 0a = \frac{a}{3}$$

$$a_3' = \frac{ta}{3n} + a_3'' = \frac{-a}{3(1)} + 0a = -\frac{a}{3}$$

$$z' = \frac{wc}{3n} + z'' = \frac{0c}{3(1)} + 0c = 0c$$

In constructing this vector, we begin at the origin of the coordinate system, point *o*. Because $a_1' = 0a$, we do not move in the direction of the a_1 axis. However, because $a_2' = \frac{a}{3}$, we proceed from point *o*, $\frac{a}{3}$ units distance along the a_2, from point *o* to point *p*, and from here $-\frac{a}{3}$ units parallel to the a_3 axis, from point *p* to point *q*. Since the z' is zero, it is not necessary to proceed from point *q* parallel to the *z* axis. Thus, the $[01\bar{1}0]$ direction corresponds to the vector that extends from point *o* to point *s* as shown.

For the second portion of the problem, we are asked to plot the $[\bar{2}\bar{2}43]$ direction, which is shown below.



For the sake of convenience we will position the vector tail at the origin of the coordinate system. This means that $a_1'' = a_2'' = a_3'' = 0a$ and $z'' = 0c$. Coordinates for the vector head $(a_1', a_2', a_3' \text{ and } z')$ may be determined using rearranged forms of Equations 3.12a through 3.12d, taking the value of *n* to be unity, and since, for this $[\bar{2}\bar{2}43]$ direction

$u = -2 \qquad v = -2 \qquad t = 4 \qquad w = 3$

Thus, vector head coordinates are determined as follows:

$$a_1' = \frac{ua}{3n} + a_1'' = \frac{-2a}{3(1)} + 0a = -\frac{2a}{3}$$

$$a_2' = \frac{va}{3n} + a_2'' = \frac{-2a}{3(1)} + 0a = -\frac{2a}{3}$$

$$a_3' = \frac{ta}{3n} + a_3'' = \frac{4a}{3(1)} + 0a = \frac{4a}{3}$$

$$z' = \frac{wc}{3n} + z'' = \frac{3c}{3(1)} + 0c = c$$

In constructing this vector, we begin at the origin of the coordinate system, point *o*. Because $a_1' = -\frac{2a}{3}$, we move $-\frac{2a}{3}$ along the a_1 axis, from point *o* to point *p*. From here we proceed $-\frac{2a}{3}$ units parallel to the a_2 axis $(a_2' = -\frac{2a}{3})$, from point *p* to point *q*. Next we proceed $\frac{4a}{3}$ units parallel to the a_3 axis, from point *q* to point *r*, and, finally, from point *r*, *c* units parallel to the *z* axis to point *s*. Hence, this $[\bar{2}\bar{2}43]$ direction corresponds to the vector that extends from point *o* to point *s*, as shown in the above diagram.

3.43 *Using Equations 3.11a, 3.11b, 3.11c, and 3.11d, derive expressions for each of the three U, V, and W indices in terms of the four u, v, t, and w indices.*

Solution

It is first necessary to do an expansion of Equation 3.11a as

$$u = \frac{1}{3}(2U - V) = \frac{2U}{3} - \frac{V}{3}$$

And solving this expression for *V* yields

$$V = 2U - 3u$$

Now, substitution of this expression into Equation 3.11b gives

$$v = \frac{1}{3}(2V - U) = \frac{1}{3}\Big[(2)(2U - 3u) - U\Big] = U - 2u$$

Or

$$U = v + 2u$$

And, solving for *v* from Equation 3.11c leads to

$$v = -(u + t)$$

which, when substituted into the above expression for *U*, yields

$$U = v + 2u = -u - t + 2u = u - t$$

In solving for an expression for *V*, we begin with the one of the above expressions for this parameter—i.e.,

$$V = 2U - 3u$$

Now, substitution of the above expression for *U* into this equation leads to

$$V = 2U - 3u = (2)(u - t) - 3u = -u - 2t$$

And solving for *u* from Equation 3.11c gives

$$\boldsymbol{u} = -\boldsymbol{v} - \boldsymbol{t}$$

which, when substituted in the previous equation results in the following expression for *V*

$$\boldsymbol{V} = -\boldsymbol{u} - 2\boldsymbol{t} = -(-\boldsymbol{v} - \boldsymbol{t}) - 2\boldsymbol{t} = \boldsymbol{v} - \boldsymbol{t}$$

And, from Equation 3.11d

$$W = w$$

Crystallographic Planes

3.44 *(a) Draw an orthorhombic unit cell, and within that cell a* $(02\bar{1})$ *plane.*

(b) Draw a monoclinic unit cell, and within that cell a (200) plane.

Solution

(a) We are asked to draw a $(02\bar{1})$ plane within an orthorhombic unit cell. For the orthorhombic crystal system, relationships among the lattice parameters are as follows:

$a \neq b \neq c$

$\alpha = \beta = \gamma = 90°$

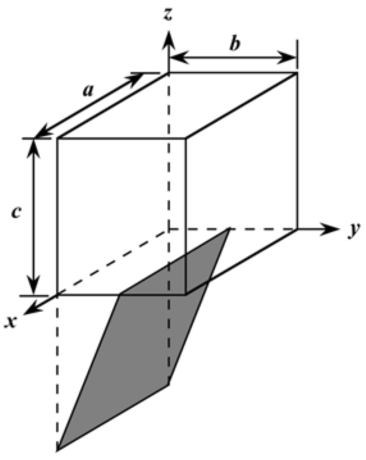
Thus, the three coordinate axes are parallel to one another. In order to construct the $(02\bar{1})$ plane it is necessary to determine intersections with the coordinate axes. The *A*, *B*, and *C* intercepts are computed using rearranged forms of Equations 3.14a, 3.14b, and 3.14c with $h = 0$, $k = 2$, and $l = -1$. Thus, intercept values are as follows (assuming $n = 1$):

$$A = \frac{na}{h} = \frac{(1)a}{0} = \infty a$$

$$B = \frac{nb}{k} = \frac{(1)b}{2} = \frac{b}{2}$$

$$C = \frac{nc}{l} = \frac{(1)c}{-1} = -c$$

Thus, intercepts with the *x*, *y*, and *z* axes are respectively, ∞a, $b/2$, and $-c$; this plane parallels the *x* axis inasmuch as its intercept is infinity. The plane that satisfies these requirements has been drawn within the orthorhombic unit cell below.



(b) In this part of the problem we are asked to draw a (200) plane within a monoclinic unit cell. For the monoclinic crystal system, relationships among the lattice parameters are as follows:

$a \neq b \neq c$

$\alpha = \gamma = 90° \neq \beta$

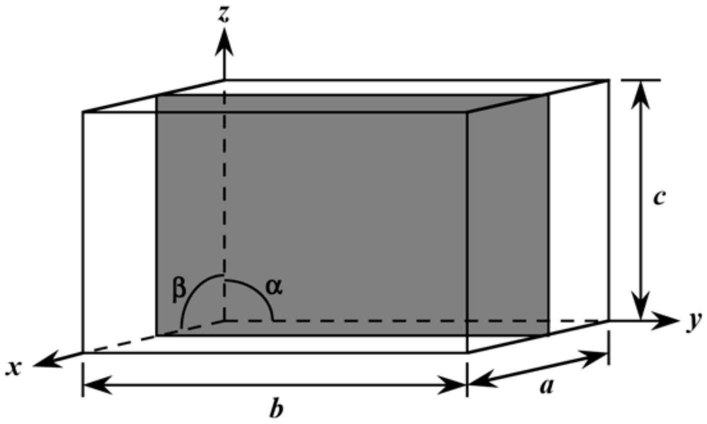
In order to construct the (200) plane it is necessary to determine intersections with the coordinate axes. The *A*, *B*, and *C* intercepts are computed using rearranged forms of Equations 3.14a, 3.14b, and 3.14c with $h = 2$, $k = 0$, and $l = 0$. Thus, intercept values are as follows (assuming $n = 1$):

$$A = \frac{na}{h} = \frac{(1)a}{2} = \frac{a}{2}$$

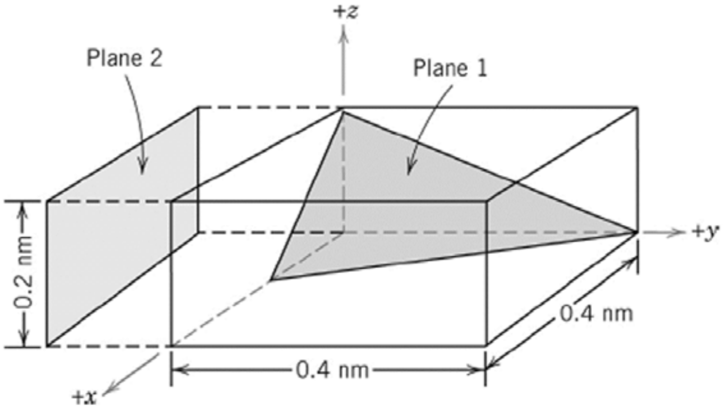
$$B = \frac{nb}{k} = \frac{(1)b}{0} = \infty b$$

$$C = \frac{nc}{l} = \frac{(1)c}{0} = \infty c$$

Thus, intercepts with the *x, y,* and *z* axes are respectively, *a/*2, ∞*b*, and ∞*c;* this plane parallels both the *y* and *z* axes inasmuch their intercepts are infinity. The plane that satisfies these requirements has been drawn within the monoclinic unit cell below.



3.45 *What are the indices for the two planes drawn in the following sketch?*



Solution

In order to solve for the *h*, *k*, and *l* indices for these two crystallographic planes it is necessary to use Equations 3.14a, 3.14b, and 3.14c.

For Plane 1, the intercepts with the *x*, *y*, and *z* axes are *a*/2 (0.2 nm), *b* (0.4 nm), and *c* (0.2 nm)—that is

$A = a/2 \qquad B = b \qquad C = c$

Thus, from Equations 3.14a-3.14c (assuming $n = 1$) we have the following:

$$h = \frac{na}{A} = \frac{(1)a}{a/2} = 2$$

$$k = \frac{nb}{B} = \frac{(1)b}{b} = 1$$

$$l = \frac{nc}{C} = \frac{(1)c}{c} = 1$$

Therefore, Plane 1 is a (211) plane.

Plane 2 is parallel to both the *x* and *z* axes, which means that the respective intercepts are ∞a and ∞c. The intercept with the *y* axis is at $-b/2$ (0.2 nm). Thus, values of the intercepts are as follows:

$A = \infty a \qquad B = -b/2 \qquad C = \infty c$

And when we incorporate these values into Equations 3.14a, 3.14b, and 3.14c, computations of the *h*, *k*, and *l* indices are as follows (assuming that $n = 1$):

$$h = \frac{na}{A} = \frac{(1)a}{\infty a} = 0$$

$$k = \frac{nb}{B} = \frac{(1)b}{-b/2} = -2$$

$$l = \frac{nc}{C} = \frac{(1)c}{\infty c} = 0$$

Therefore, Plane 2 is a $(0\bar{2}0)$plane, which is also parallel to a $(0\,\bar{1}0)$plane.

3.46 *Sketch within a cubic unit cell the following planes:*

(a) $(10\bar{1})$

(b) $(2\bar{1}1)$

(c) (012)

(d) $(3\bar{1}3)$

(e) $(\bar{1}1\bar{1})$

(f) $(\bar{2}12)$

(g) $(3\bar{1}2)$

(h) (301)

Solutions

In order to plot each of these planes it is necessary to determine the axial intercepts using rearranged forms of Equations 3.14a, 3.14b, and 3.14c.

The indices for plane (a) are as follows:

$h = 1 \qquad k = 0 \qquad l = -1$

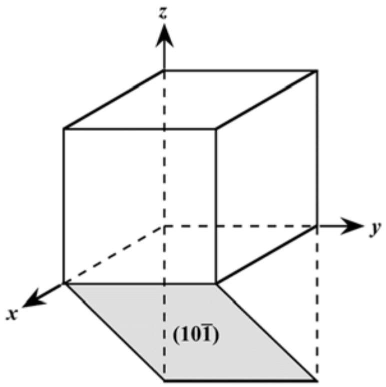
Thus, we solve for the *A*, *B*, and *C* intercepts using rearranged Equations 3.14 as follows (assuming that *n* = 1):

$$A = \frac{na}{h} = \frac{(1)a}{1} = a$$

$$B = \frac{nb}{k} = \frac{(1)b}{0} = \infty b$$

$$C = \frac{nc}{l} = \frac{(1)c}{-1} = -c$$

Thus, this plane intersects the *x* and *z* axes at *a* and –*c*, respectively, and parallels the *y* axis. This plane has been drawn in the following sketch.



The indices for plane (b) are as follows:

$h = 2 \qquad k = -1 \qquad l = 1$

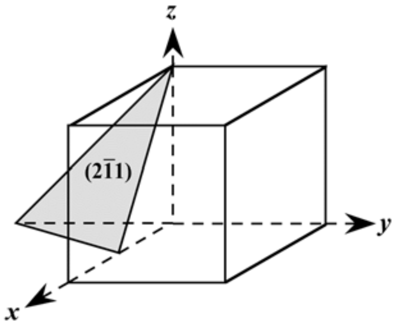
Thus, we solve for the *A*, *B*, and *C* intercepts using rearranged Equations 3.14 as follows (assuming that *n* = 1):

$$A = \frac{na}{h} = \frac{(1)a}{2} = \frac{a}{2}$$

$$B = \frac{nb}{k} = \frac{(1)b}{-1} = -b$$

$$C = \frac{nc}{l} = \frac{(1)c}{1} = c$$

Thus, this plane intersects the *x*, *y*, and *z* axes at *a*/2, –*b*, and *c*, respectively. This plane has been drawn in the following sketch.



The indices for plane (c) are as follows:

$h = 0$ $k = 1$ $l = 2$

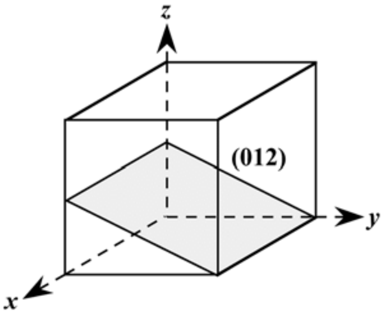
Thus, we solve for the *A*, *B*, and *C* intercepts using rearranged Equations 3.14 as follows (assuming that *n* = 1):

$$A = \frac{na}{h} = \frac{(1)a}{0} = \infty a$$

$$B = \frac{nb}{k} = \frac{(1)b}{1} = b$$

$$C = \frac{nc}{l} = \frac{(1)c}{2} = \frac{c}{2}$$

Thus, this plane intersects the *y*, and *z* axes at *b* and *c*/2, respectively, and parallels the *x* axis. This plane has been drawn in the following sketch.



The indices for plane (d) are as follows:

$h = 3$ $k = -1$ $l = 3$

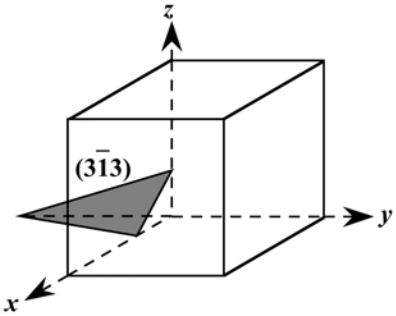
Thus, we solve for the *A*, *B*, and *C* intercepts using rearranged Equations 3.14 as follows (assuming that *n* = 1):

$$A = \frac{na}{h} = \frac{(1)a}{3} = \frac{a}{3}$$

$$B = \frac{nb}{k} = \frac{(1)b}{-1} = -b$$

$$C = \frac{nc}{l} = \frac{(1)c}{3} = \frac{c}{3}$$

Thus, this plane intersects the *x*, *y*, and *z* axes at *a/*3, –*b* and *c/*3, respectively. This plane has been drawn in the following sketch.



The indices for plane (e) are as follows:

$h = -1$ $k = 1$ $l = -1$

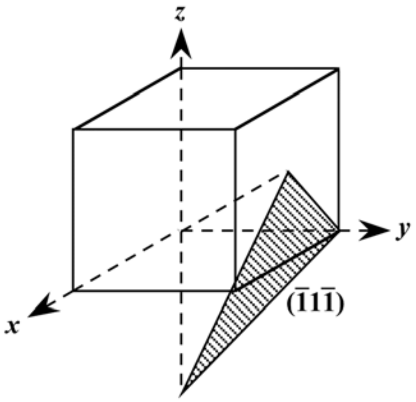
Thus, we solve for the *A*, *B*, and *C* intercepts using rearranged Equations 3.14 as follows (assuming that *n* = 1):

$$A = \frac{na}{h} = \frac{(1)a}{-1} = -a$$

$$B = \frac{nb}{k} = \frac{(1)b}{1} = b$$

$$C = \frac{nc}{l} = \frac{(1)c}{-1} = -c$$

Thus, this plane intersects the *x*, *y*, and *z* axes at –*a*, *b* and –*c*, respectively. This plane has been drawn in the following sketch.



The indices for plane (f) are as follows:

$h = -2$ $k = 1$ $l = 2$

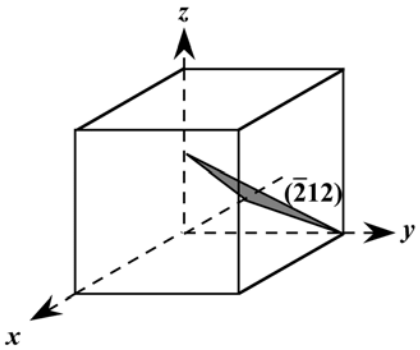
Thus, we solve for the *A*, *B*, and *C* intercepts using rearranged Equations 3.14 as follows (assuming that *n* = 1):

$$A = \frac{na}{h} = \frac{(1)a}{-2} = -\frac{a}{2}$$

$$B = \frac{nb}{k} = \frac{(1)b}{1} = b$$

$$C = \frac{nc}{l} = \frac{(1)c}{2} = \frac{c}{2}$$

Thus, this plane intersects the *x*, *y*, and *z* axes at –*a*/2, *b* and *c*/2, respectively. This plane has been drawn in the following sketch.



The indices for plane (g) are as follows:

$h = 3$ $k = -1$ $l = 2$

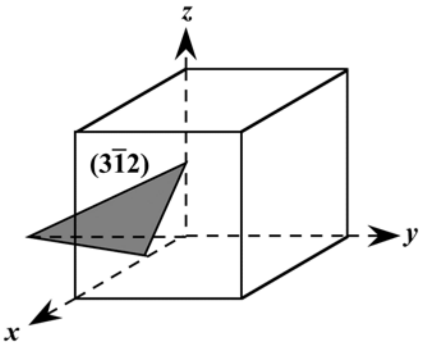
Thus, we solve for the *A*, *B*, and *C* intercepts using rearranged Equations 3.14 as follows (assuming that *n* = 1):

$$A = \frac{na}{h} = \frac{(1)a}{3} = \frac{a}{3}$$

$$B = \frac{nb}{k} = \frac{(1)b}{-1} = -b$$

$$C = \frac{nc}{l} = \frac{(1)c}{2} = \frac{c}{2}$$

Thus, this plane intersects the *x*, *y*, and *z* axes at *a/*3, –*b* and *c/*2, respectively. This plane has been drawn in the following sketch.



The indices for plane (h) are as follows:

$h = 3$ $k = 0$ $l = 1$

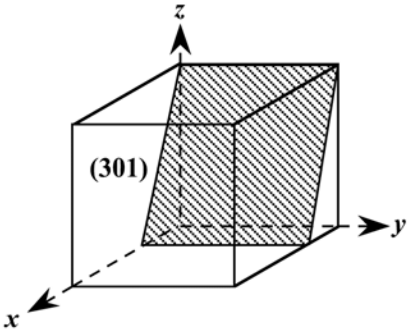
Thus, we solve for the *A*, *B*, and *C* intercepts using rearranged Equations 3.14 as follows (assuming that *n* = 1):

$$A = \frac{na}{h} = \frac{(1)a}{3} = \frac{a}{3}$$

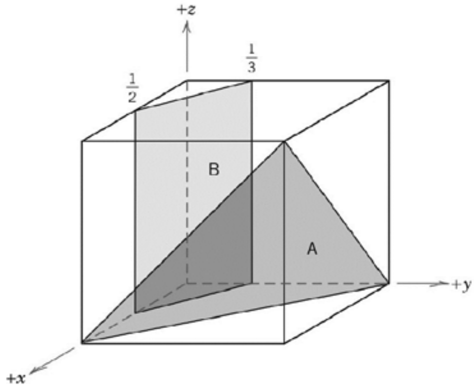
$$B = \frac{nb}{k} = \frac{(1)b}{0} = \infty b$$

$$C = \frac{nc}{l} = \frac{(1)c}{1} = c$$

Thus, this plane intersects the *x* and *z* axes at *a/*3 and *c*, respectively, and parallels the *y* axis. This plane has been drawn in the following sketch.



3.47 *Determine the Miller indices for the planes shown in the following unit cell:*



Solution

For plane A, the first thing we need to do is determine the intercepts of this plane with the *x, y,* and *z* axes. If we extend the plane back into the plane of the page, it will intersect the *z* axis at –*c*. Furthermore, intersections with the *x* and *y* axes are, respectively, *a* and *b*. The is, values of the intercepts *A*, *B*, and *C*, are *a, b,* and –*c*. If we assume that the value of *n* is 1, the values of *h, k,* and *l* are determined using Equations 3.14a, 3.14b, and 3.14c as follows:

$$h = \frac{na}{A} = \frac{(1)a}{a} = 1$$

$$k = \frac{nb}{B} = \frac{(1)b}{b} = 1$$

$$l = \frac{nc}{C} = \frac{(1)c}{-c} = -1$$

Therefore, the A plane is a $(11\bar{1})$plane.

For plane B, its intersections with with the *x, y,* and *z* axes are *a*/2, *b*/3, and ∞*c* (because this plane parallels the *z* axis)—these three values are equal to *A*, *B,* and *C*, respectively. If we assume that the value of *n* is 1, the values of *h, k,* and *l* are determined using Equations 3.14a, 3.14b, and 3.14c as follows:

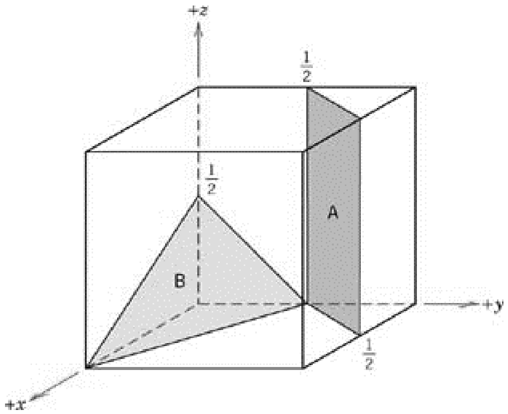
$$h = \frac{na}{A} = \frac{(1)a}{a/2} = 2$$

$$k = \frac{nb}{B} = \frac{(1)b}{b/3} = 3$$

$$l = \frac{nc}{C} = \frac{(1)c}{\infty c} = 0$$

Therefore, the B plane is a (230) plane.

3.48 *Determine the Miller indices for the planes shown in the following unit cell:*



For plane A, we will move the origin of the coordinate system one unit cell distance to the right along the *y* axis. Referenced to this new origin, the plane's intersections with with the *x* and *y* axes are *a*/2, –*b*/2; since it is parallel to the *z* axis, the intersections is taken as and ∞*c*—these three values are equal to *A*, *B*, and *C*, respectively. If we assume that the value of *n* is 1/2 (because of the *a*/2 and –*b*/2 intercepts), the values of *h*, *k*, and *l* are determined using Equations 3.14a, 3.14b, and 3.14c as follows:

$$h = \frac{na}{A} = \frac{(1/2)a}{a/2} = 1$$

$$k = \frac{nb}{B} = \frac{(1/2)b}{-b/2} = -1$$

$$l = \frac{nc}{C} = \frac{(1/2)c}{\infty c} = 0$$

Therefore, plane A is a $(1\bar{1}0)$ plane.

For plane B, its intersections with with the *x, y,* and *z* axes are *a*, *b*/2, and *c/*2; therefore, these three values are equal to *A*, *B*, and *C*, respectively. If we assume that the value of *n* is 1, the values of *h*, *k*, and *l* are determined using Equations 3.14a, 3.14b, and 3.14c as follows:

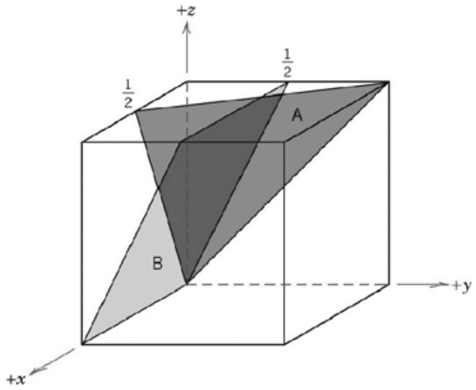
$$h = \frac{na}{A} = \frac{(1)a}{a} = 1$$

$$k = \frac{nb}{B} = \frac{(1)b}{b/2} = 2$$

$$l = \frac{nc}{C} = \frac{(1)c}{c/2} = 2$$

Therefore, the B plane is a (122) plane.

3.49 *Determine the Miller indices for the planes shown in the following unit cell:*



<u>Solution</u>

Since Plane A passes through the origin of the coordinate system as shown, we will move the origin of the coordinate system one unit cell distance vertically along the *z* axis. Referenced to this new origin, intercepts with the *x*, *y*, and *z* axes are, respectively, *a*/2, *b*, and –*c*. If we assume that the value of *n* is 1, the values of *h, k,* and *l* are determined using Equations 3.14a, 3.14b, and 3.14c as follows:

$$h = \frac{na}{A} = \frac{(1)a}{a/2} = 2$$

$$k = \frac{nb}{B} = \frac{(1)b}{b} = 1$$

$$l = \frac{nc}{C} = \frac{(1)c}{-c} = -1$$

Therefore, the A plane is a $(21\bar{1})$plane.

For plane B, since the plane passes through the origin of the coordinate system as shown, we will move the origin one unit cell distance up vertically along the *z* axis. Referenced to this new origin, intercepts with the *y* and *z* axes are, respectively, *b*/2 and –*c*. Because the plane is parallel to the *x* axis, its intersections is taken as and ∞*a*. Thus, values of *A*, *B*, and *C*, respectively, correspond to ∞*a*, *b/*2, and –*c*. If we assume that the value of *n* is 1, the values of *h*, *k*, and *l* are determined using Equations 3.14a, 3.14b, and 3.14c as follows:

$$h = \frac{na}{A} = \frac{(1)a}{\infty a} = 0$$

$$k = \frac{nb}{B} = \frac{(1)b}{b/2} = 2$$

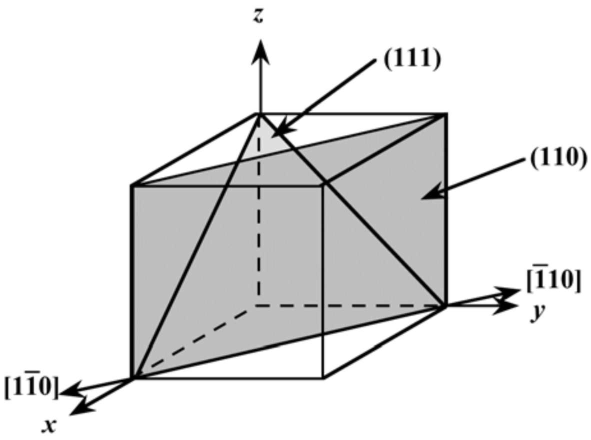
$$l = \frac{nc}{C} = \frac{(1)c}{-c} = -1$$

Therefore, the B plane is a $(02\bar{1})$ plane.

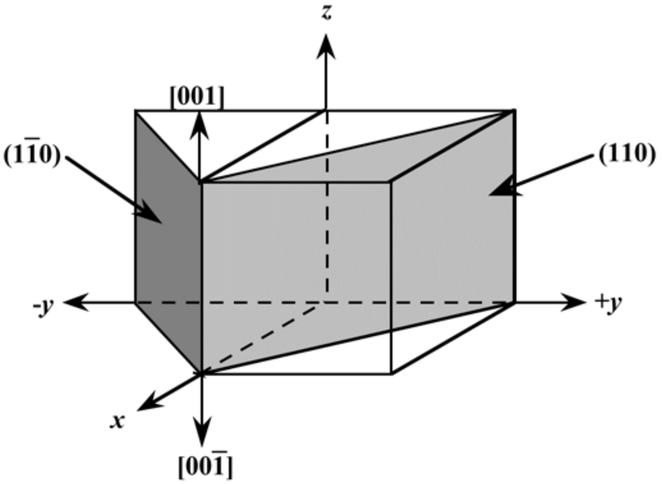
3.50 *Cite the indices of the direction that results from the intersection of each of the following pairs of planes within a cubic crystal: (a) the (110) and (111) planes, (b) the (110) and* $(1\bar{1}0)$ *planes, and (c) the* $(11\bar{1})$ *and (001) planes.*

Solution

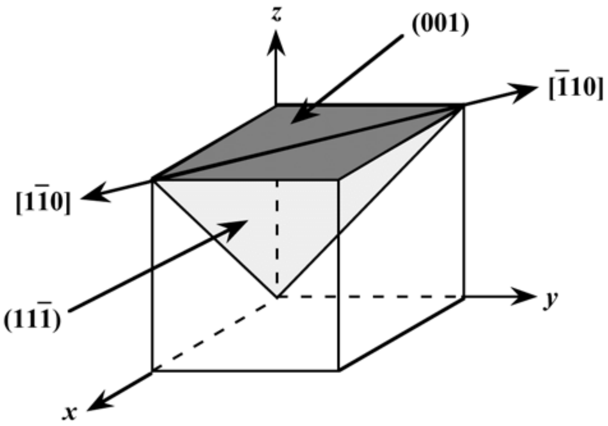
(a) In the figure below is shown (110) and (111) planes, and, as indicated, their intersection results in a $[\bar{1}10]$, or equivalently, a $[1\bar{1}0]$ direction.



(b) In the figure below is shown (110) and $(1\bar{1}0)$ planes, and, as indicated, their intersection results in a [001], or equivalently, a $[00\bar{1}]$ direction.



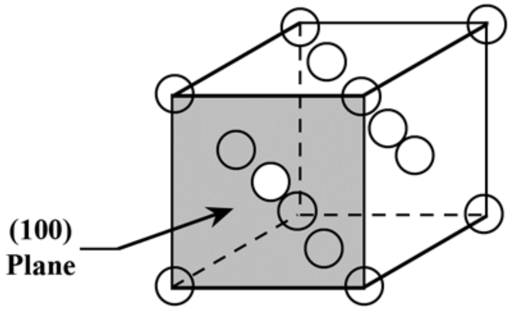
(c) In the figure below is shown $(11\bar{1})$ and (001) planes, and, as indicated, their intersection results in a $[\bar{1}10]$, or equivalently, a $[1\bar{1}0]$ direction.

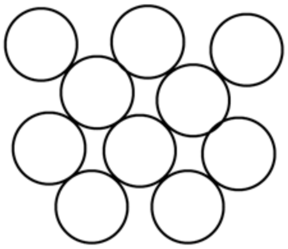


3.51 *Sketch the atomic packing of (a) the (100) plane for the FCC crystal structure, and (b) the (111) plane for the BCC crystal structure (similar to Figures 3.12b and 3.13b).*

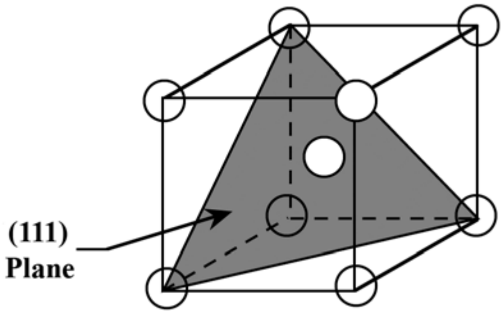
Solution

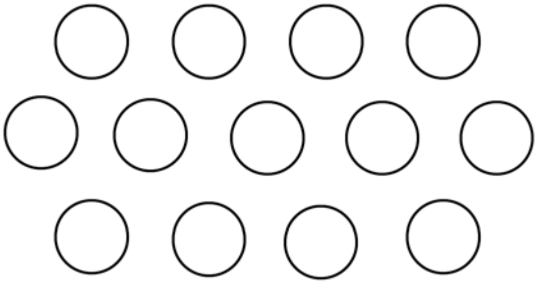
(a) An FCC unit cell, its (100) plane, and the atomic packing of this plane are indicated below.





(b) A BCC unit cell, its (111) plane, and the atomic packing of this plane are indicated below.





3.*52 Consider the reduced-sphere unit cell shown in Problem 3.23, having an origin of the coordinate system positioned at the atom labeled O. For the following sets of planes, determine which are equivalent:*

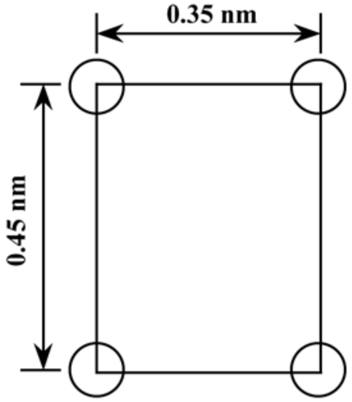
(a) (100), $(0\bar{1}0)$*, and (001)*

(b) (110), (101), (011), and $(\bar{1}01)$

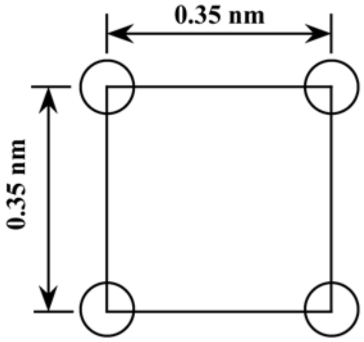
(c) (111), $(1\bar{1}1)$*,* $(11\bar{1})$*), and* $(\bar{1}1\bar{1})$

Solution

(a) The unit cell in Problem 3.20 is body-centered tetragonal. Of the three planes given in the problem statement the (100) and $(0\bar{1}0)$ are equivalent—that is, have the same atomic packing. The atomic packing for these two planes as well as the (001) are shown in the figure below.

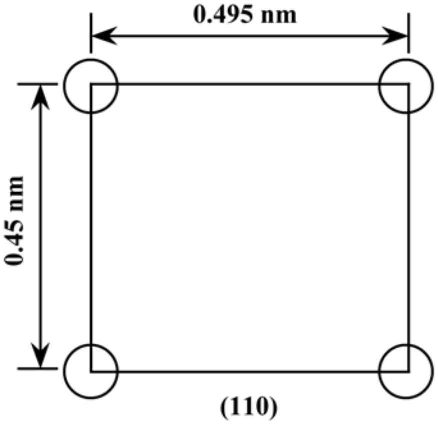


(100), $(0\bar{1}0)$

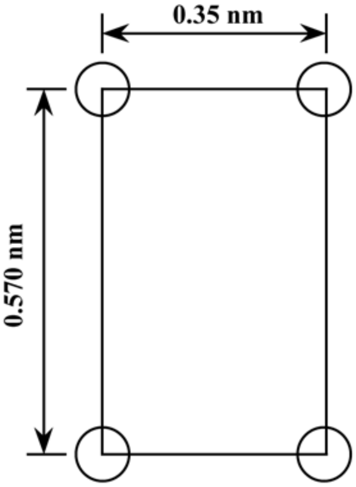


(001)

(b) Of the four planes cited in the problem statement, only (101), (011), and $(\bar{1}01)$ are equivalent—have the same atomic packing. The atomic arrangement of these planes as well as the (110) are presented in the figure below. *Note:* the 0.495 nm dimension for the (110) plane comes from the relationship $\left[(0.35\text{ nm})^2 + (0.35\text{ nm})^2\right]^{1/2}$. Likewise, the 0.570 nm dimension for the (101), (011), and $(\bar{1}01)$ planes comes from $\left[(0.35\text{ nm})^2 + (0.45\text{ nm})^2\right]^{1/2}$.

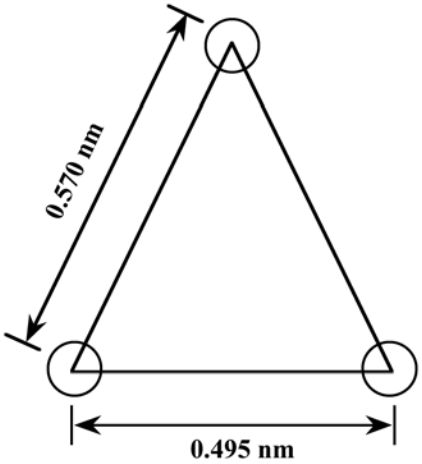


(110)

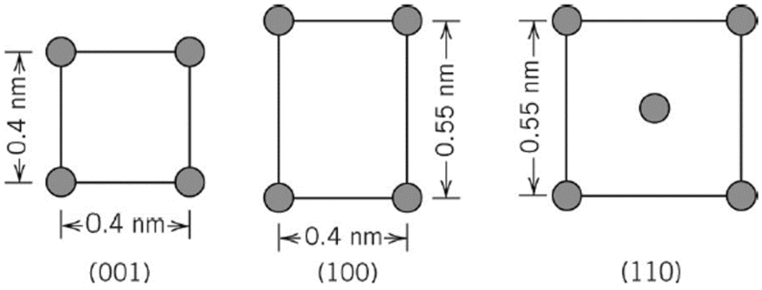


(101), (011), $(\bar{1}01)$

(c) All of the (111), $(1\bar{1}1)$, $(11\bar{1})$, and $(\bar{1}1\bar{1})$ planes are equivalent, that is, have the same atomic packing as illustrated in the following figure:



3.53 *The accompanying figure shows three different crystallographic planes for a unit cell of a hypothetical metal. The circles represent atoms:*

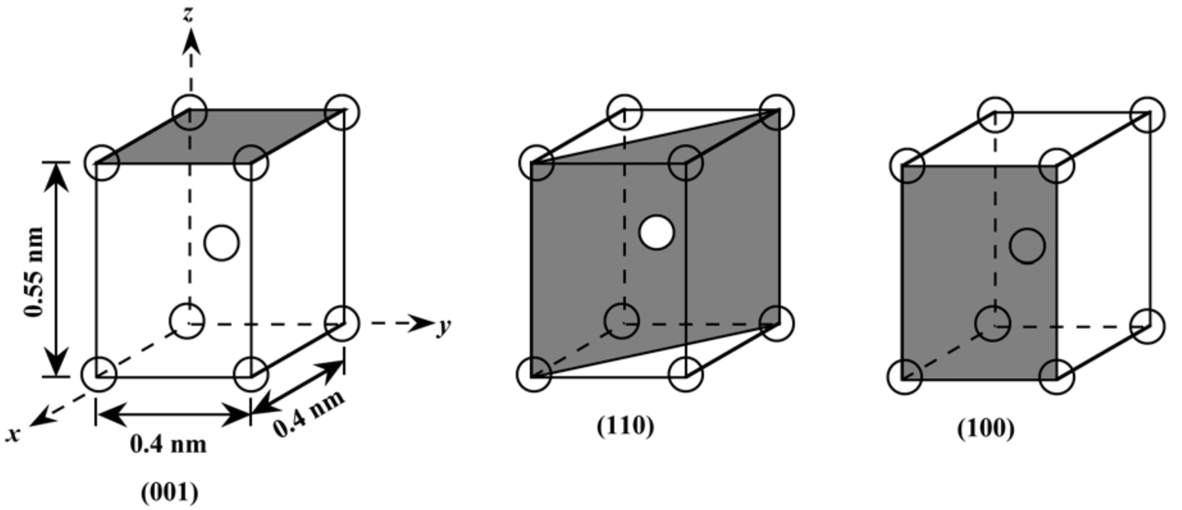


(a) To what crystal system does the unit cell belong?

(b) What would this crystal structure be called?

Solution

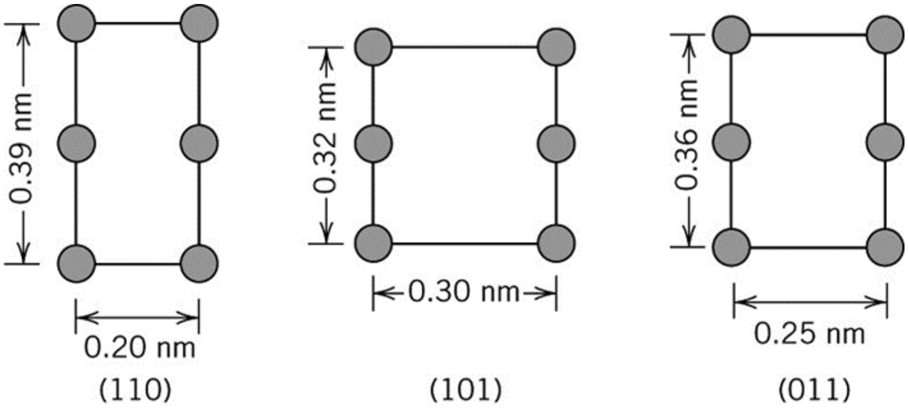
Unit cells are constructed below from the three crystallographic planes provided in the problem statement.



(a) This unit cell belongs to the *tetragonal system* since $a = b = 0.40$ nm, $c = 0.55$ nm, and $\alpha = \beta = \gamma = 90°$.

(b) This crystal structure would be called *body-centered tetragonal* since the unit cell has tetragonal symmetry, and an atom is located at each of the corners, as well as the cell center.

3.54 *The accompanying figure shows three different crystallographic planes for a unit cell of some hypothetical metal. The circles represent atoms:*



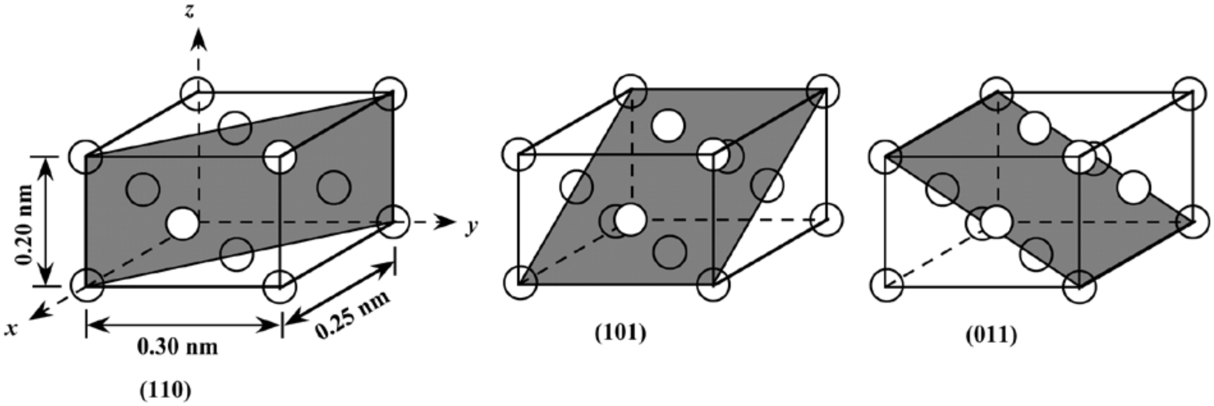
(a) To what crystal system does the unit cell belong?

(b) What would this crystal structure be called?

(c) If the density of this metal is 18.91 g/cm^3, determine its atomic weight.

Solution

The unit cells constructed below show the three crystallographic planes that were provided in the problem statement.



(a) This unit cell belongs to *the orthorhombic crystal system* since a = 0.25 nm, b = 0.30 nm, c = 0.20 nm, and $\alpha = \beta = \gamma = 90°$.

(b) This crystal structure would be called *face-centered orthorhombic* since the unit cell has orthorhombic symmetry, and an atom is located at each of the corners, as well as at each of the face centers.

(c) In order to compute its atomic weight, we employ a rearranged form of Equation 3.8, with $n = 4$; thus

$$A = \frac{\rho V_C N_{\mathrm{A}}}{n}$$

$$= \frac{\left(18.91\ \mathrm{g/cm^3}\right)(2.0)(2.5)(3.0)\left(\times\ 10^{-24}\ \mathrm{cm^3/unit\ cell}\right)\left(6.022\ \times\ 10^{23}\ \mathrm{atoms/mol}\right)}{4\ \mathrm{atoms/unit\ cell}}$$

= 42.7 g/mol

3.55 *Convert the (111) and* $(0\bar{1}2)$ *planes into the four-index Miller–Bravais scheme for hexagonal unit cells.*

Solution

This problem asks that we convert (111) and $(0\bar{1}2)$ planes into the four-index Miller-Bravais scheme, (*hkil*), for hexagonal cells. For (111), $h = 1$, $k = 1$, and $l = 1$, and, from Equation 3.15, the value of i is equal to

$$i = -(h + k) = -(1 + 1) = -2$$

Therefore, the (111) plane becomes $(11\bar{2}1)$.

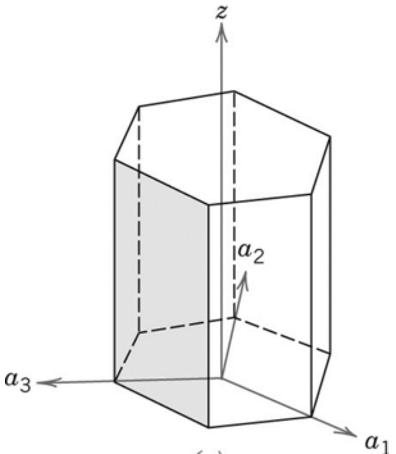
Now for the $(0\bar{1}2)$ plane, $h = 0$, $k = -1$, and $l = 2$, and computation of i using Equation 3.15 leads to

$$i = -(h + k) = -[0 + (-1)] = 1$$

such that $(0\bar{1}2)$ becomes $(0\bar{1}12)$.

3.56 *Determine the indices for the planes shown in the following hexagonal unit cells:*

Solutions



(a)

For this plane, intersections with a_1, a_2, and z axes are ∞a, $-a$, and ∞c (the plane parallels both a_1 and z axes). Therefore, these three values are equal to A, B, and C, respectively. If we assume that the value of n is 1, the values of h, k, and l are determined using Equations 3.14a, 3.14b, and 3.14c as follows:

$$h = \frac{na}{A} = \frac{(1)a}{\infty a} = 0$$

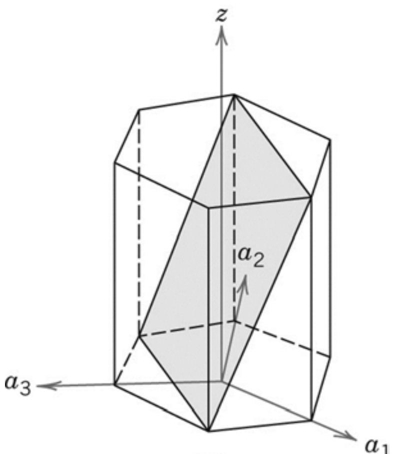
$$k = \frac{na}{B} = \frac{(1)a}{-a} = -1$$

$$l = \frac{nc}{C} = \frac{(1)c}{\infty c} = 0$$

Now, from Equation 3.15, the value of i is

$$i = -(h + k) = -[0 + (-1)] = 1$$

Hence, this is a $(0\bar{1}10)$ plane.



(b)

For this plane, intersections with a_1, a_2, and z axes are $-a$, $-a$, and $c/2$. Therefore, these three values are equal to A, B, and C, respectively. If we assume that the value of n is 1, the values of h, k, and l are determined using Equations 3.14a, 3.14b, and 3.14c as follows:

$$h = \frac{na}{A} = \frac{(1)a}{-a} = -1$$

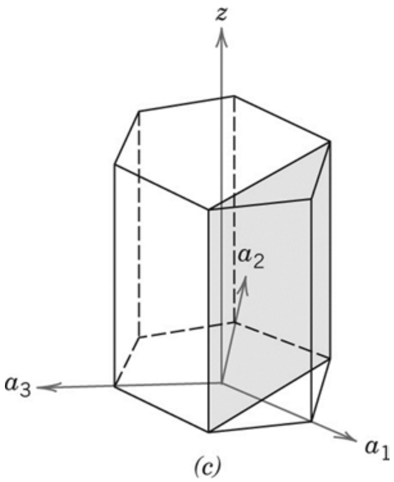
$$k = \frac{na}{B} = \frac{(1)a}{-a} = -1$$

$$l = \frac{nc}{C} = \frac{(1)c}{c/2} = 2$$

Now, from Equation 3.15, the value of i is

$$i = -(h + k) = -[-1 \;\; -1)] = 2$$

Hence, this is a $(\bar{1}\bar{1}22)$ plane.



(c)

For this plane, intersections with a_1, a_2, and z axes are $a/2$, $–a$, and ∞c (the plane parallels the z axis). Therefore, these three values are equal to A, B, and C, respectively. If we assume that the value of n is 1, the values of h, k, and l are determined using Equations 3.14a, 3.14b, and 3.14c as follows:

$$h = \frac{na}{A} = \frac{(1)a}{a/2} = 2$$

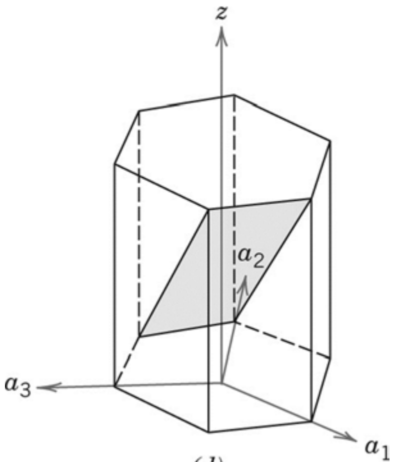
$$k = \frac{na}{B} = \frac{(1)a}{-a} = -1$$

$$l = \frac{nc}{C} = \frac{(1)c}{\infty c} = 0$$

Now, from Equation 3.15, the value of i is

$$i = -(h + k) = -(2 \; -1) \; = -1$$

Hence, this is a $(2\bar{1}\bar{1}0)$ plane.



(d)

For this plane, intersections with a_1, a_2, and z axes are $–a$, a, and $c/2$. Therefore, these three values are equal to A, B, and C, respectively. If we assume that the value of n is 1, the values of h, k, and l are determined using Equations 3.14a, 3.14b, and 3.14c as follows:

$$h = \frac{na}{A} = \frac{(1)a}{-a} = -1$$

$$k = \frac{na}{B} = \frac{(1)a}{a} = 1$$

$$l = \frac{nc}{C} = \frac{(1)c}{c/2} = 2$$

Now, from Equation 3.15, the value of i is

$$i = -(h + k) = -(-1 + 1) = 0$$

Hence, this is a $(\bar{1}102)$ plane.

3.57 *Sketch the* $(01\bar{1}1)$ *and* $(2\bar{1}\bar{1}0)$ *planes in a hexagonal unit cell.*

Solution

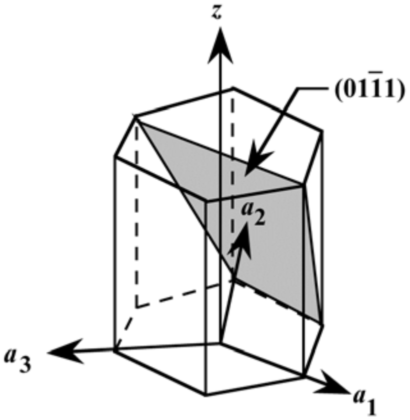
For $(01\bar{1}1)$ the values of *h*, *k*, *i*, and *l* are, respectively, 0, 1, –1, and 1. Now, for *h*, *k,* and *l*, we solve for values of intersections with the a_1, a_2, and *z* axes (i.e., *A*, *B*, and *C*) using rearranged forms of Equations 3.14a, 3.14b, and 3.14c (assuming a value of 1 for the parameter *n*) as follows:

$$A = \frac{na}{h} = \frac{(1)a}{0} = \infty a$$

$$B = \frac{na}{k} = \frac{(1)a}{1} = a$$

$$C = \frac{nc}{l} = \frac{(1)c}{1} = c$$

Hence, this plane is parallel to the a_1 axis, and intersects the a_2 axis at *a*, the a_3 axis at –*a*, and the *z*-axis at *c*. The plane having these intersections is shown in the figure below.



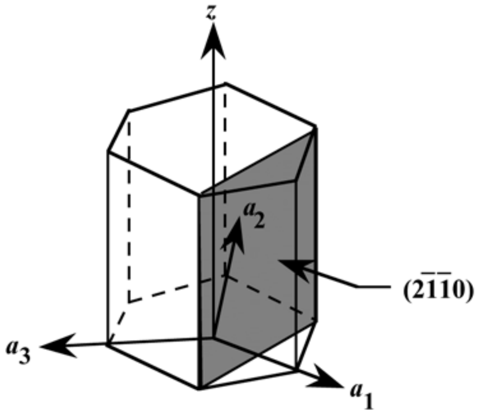
For the $(2\bar{1}\bar{1}0)$ plane, the values of *h*, *k*, *i*, and *l* are, respectively, 2, –1, –1, and 0. Now, for *h*, *k*, and *l*, we solve for values of intersections with the a_1, a_2, and *z* axes (i.e., *A*, *B*, and *C*) using rearranged forms of Equations 3.14a, 3.14b, and 3.14c (assuming a value of 1 for the parameter *n*) as follows:

$$A = \frac{na}{h} = \frac{(1)a}{2} = \frac{a}{2}$$

$$B = \frac{na}{k} = \frac{(1)a}{-1} = -a$$

$$C = \frac{nc}{l} = \frac{(1)c}{0} = \infty c$$

Thus, this plane is parallel to the c axis, and intersects the a_1 axis at $a/2$ and the a_2 axis at $-a$. The plane having these intersections is shown in the figure below.



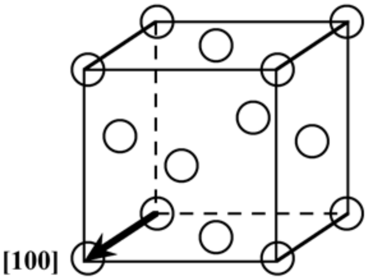
Linear and Planar Densities

3.58 *(a) Derive linear density expressions for FCC [100] and [111] directions in terms of the atomic radius R.*

(b) Compute and compare linear density values for these same two directions for copper (Cu).

Solution

(a) In the figure below is shown a [100] direction within an FCC unit cell.

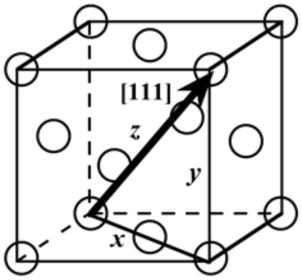


For this [100] direction there is one atom at each of the two unit cell corners, and, thus, there is the equivalent of 1 atom that is centered on the direction vector. The length of this direction vector is just the unit cell edge length, $2R\sqrt{2}$ (Equation 3.1). Therefore, the expression for the linear density of this plane is

$$\mathrm{LD}_{100} = \frac{\text{number of atoms centered on [100] direction vector}}{\text{length of [100] direction vector}}$$

$$= \frac{1 \text{ atom}}{2R\sqrt{2}} = \frac{1}{2R\sqrt{2}}$$

An FCC unit cell within which is drawn a [111] direction is shown below.



For this [111] direction, the vector shown passes through only the centers of the single atom at each of its ends, and, thus, there is the equivalence of 1 atom that is centered on the direction vector. The length of this direction vector is denoted by z in this figure, which is equal to

$$z = \sqrt{x^2 + y^2}$$

where x is the length of the bottom face diagonal, which is equal to $4R$. Furthermore, y is the unit cell edge length, which is equal to $2R\sqrt{2}$ (Equation 3.1). Thus, using the above equation, the length z may be calculated as follows:

$$z = \sqrt{(4R)^2 + (2R\sqrt{2})^2} = \sqrt{24R^2} = 2R\sqrt{6}$$

Therefore, the expression for the linear density of this direction is

$$\mathrm{LD}_{111} = \frac{\text{number of atoms centered on [111] direction vector}}{\text{length of [111] direction vector}}$$

$$= \frac{1\text{ atom}}{2R\sqrt{6}} = \frac{1}{2R\sqrt{6}}$$

(b) From the table inside the front cover, the atomic radius for copper is 0.128 nm. Therefore, the linear density for the [100] direction is

$$\mathrm{LD}_{100}(\mathrm{Cu}) = \frac{1}{2R\sqrt{2}} = \frac{1}{(2)(0.128\text{ nm})\sqrt{2}} = 2.76\text{ nm}^{-1} = 2.76 \times 10^9\text{ m}^{-1}$$

While for the [111] direction

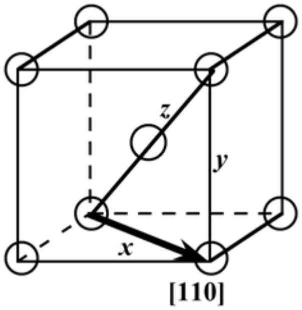
$$\mathrm{LD}_{111}(\mathrm{Cu}) = \frac{1}{2R\sqrt{6}} = \frac{1}{(2)(0.128\text{ nm})\sqrt{6}} = 1.59\text{ nm}^{-1} = 1.59 \times 10^9\text{ m}^{-1}$$

3.59 *(a) Derive linear density expressions for BCC [110] and [111] directions in terms of the atomic radius R.*

(b) Compute and compare linear density values for these same two directions for iron (Fe).

Solution

(a) In the figure below is shown a [110] direction within a BCC unit cell.



For this [110] direction there is one atom at each of the two unit cell corners, and, thus, there is the equivalence of 1 atom that is centered on the direction vector. The length of this direction vector is denoted by x in this figure, which is equal to

$$x = \sqrt{z^2 - y^2}$$

where y is the unit cell edge length, which, from Equation 3.4 is equal to $\frac{4R}{\sqrt{3}}$. Furthermore, z is the length of the unit cell diagonal, which is equal to $4R$ Thus, using the above equation, the length x may be calculated as follows:

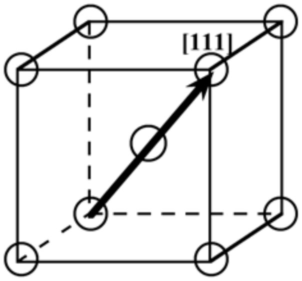
$$x = \sqrt{(4R)^2 - \left(\frac{4R}{\sqrt{3}}\right)^2} = \sqrt{\frac{32R^2}{3}} = 4R\sqrt{\frac{2}{3}}$$

Therefore, the expression for the linear density of this direction is

$$\mathrm{LD}_{110} = \frac{\text{number of atoms centered on [110] direction vector}}{\text{length of [110] direction vector}}$$

$$= \frac{1 \text{ atom}}{4R\sqrt{\frac{2}{3}}} = \frac{\sqrt{3}}{4R\sqrt{2}}$$

A BCC unit cell within which is drawn a [111] direction is shown below.



For although the [111] direction vector shown passes through the centers of three atoms, there is an equivalence of only two atoms associated with this unit cell—one-half of each of the two atoms at the end of the vector, in addition to the center atom belongs entirely to the unit cell. Furthermore, the length of the vector shown is equal to 4*R*, since all of the atoms whose centers the vector passes through touch one another. Therefore, the linear density is equal to

$$\mathrm{LD}_{111} = \frac{\text{number of atoms centered on [111] direction vector}}{\text{length of [111] direction vector}}$$

$$= \frac{2\text{ atoms}}{4R} = \frac{1}{2R}$$

(b) From the table inside the front cover, the atomic radius for iron is 0.124 nm. Therefore, the linear density for the [110] direction is

$$\mathrm{LD}_{110}(\mathrm{Fe}) = \frac{\sqrt{3}}{4R\sqrt{2}} = \frac{\sqrt{3}}{(4)(0.124\text{ nm})\sqrt{2}} = 2.47\text{ nm}^{-1} = 2.47 \times 10^9\text{ m}^{-1}$$

While for the [111] direction

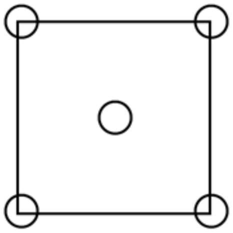
$$\mathrm{LD}_{111}(\mathrm{Fe}) = \frac{1}{2R} = \frac{1}{(2)(0.124\text{ nm})} = 4.03\text{ nm}^{-1} = 4.03 \times 10^9\text{ m}^{-1}$$

3.60 *(a) Derive planar density expressions for FCC (100) and (111) planes in terms of the atomic radius R.*

(b) Compute and compare planar density values for these same two planes for aluminum (Al).

Solution

(a) In the figure below is shown a (100) plane for an FCC unit cell.

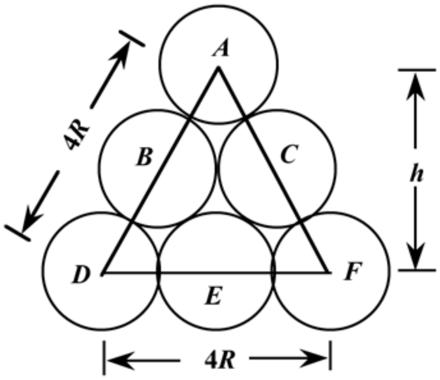


For this (100) plane there is one atom at each of the four cube corners, each of which is shared with four adjacent unit cells, while the center atom lies entirely within the unit cell. Thus, there is the equivalence of 2 atoms associated with this FCC (100) plane. The planar section represented in the above figure is a square, wherein the side lengths are equal to the unit cell edge length, $2R\sqrt{2}$ (Equation 3.1); and, thus, the area of this square is just $(2R\sqrt{2})^2$ = $8R^2$. Hence, the planar density for this (100) plane is just

$$\mathrm{PD}_{100} = \frac{\text{number of atoms centered on (100) plane}}{\text{area of (100) plane}}$$

$$= \frac{2 \text{ atoms}}{8R^2} = \frac{1}{4R^2}$$

That portion of an FCC (111) plane contained within a unit cell is shown below.



There are six atoms whose centers lie on this plane, which are labeled *A* through *F*. One-sixth of each of atoms *A*, *D*, and *F* are associated with this plane (yielding an equivalence of one-half atom), with one-half of each of atoms *B*, *C*, and *E* (or an equivalence of one and one-half atoms) for a total equivalence of two atoms. Now, the area of the triangle shown in the above figure is equal to one-half of the product of the base length and the height, *h*. If we consider half of the triangle, then

$$(2R)^2 + h^2 = (4R)^2$$

which leads to $h = 2R\sqrt{3}$. Thus, the area is equal to

$$\text{Area} = \frac{4R(h)}{2} = \frac{(4R)\left(2R\sqrt{3}\right)}{2} = 4R^2\sqrt{3}$$

And, thus, the planar density is

$$\text{PD}_{111} = \frac{\text{number of atoms centered on (111) plane}}{\text{area of (111) plane}}$$

$$= \frac{2 \text{ atoms}}{4R^2\sqrt{3}} = \frac{1}{2R^2\sqrt{3}}$$

(b) From the table inside the front cover, the atomic radius for aluminum is 0.143 nm. Therefore, the planar density for the (100) plane is

$$\text{PD}_{100}(\text{Al}) = \frac{1}{4R^2} = \frac{1}{4(0.143 \text{ nm})^2} = 12.23 \text{ nm}^{-2} = 1.223 \times 10^{19} \text{ m}^{-2}$$

While for the (111) plane

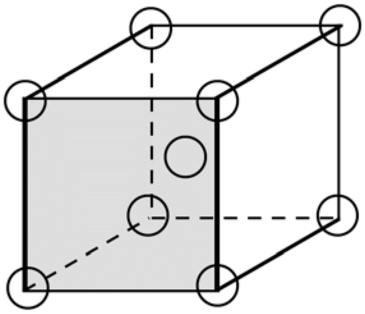
$$\text{PD}_{111}(\text{Al}) = \frac{1}{2R^2\sqrt{3}} = \frac{1}{2\sqrt{3}(0.143 \text{ nm})^2} = 14.12 \text{ nm}^{-2} = 1.412 \times 10^{19} \text{ m}^{-2}$$

3.61 *(a) Derive planar density expressions for BCC (100) and (110) planes in terms of the atomic radius R.*

(b) Compute and compare planar density values for these same two planes for molybdenum (Mo).

Solution

(a) A BCC unit cell within which is drawn a (100) plane is shown below.

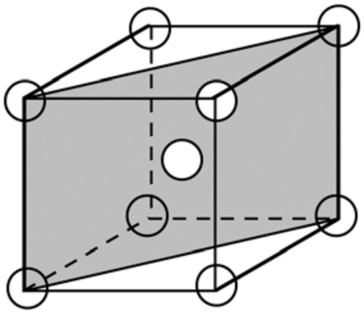


For this (100) plane there is one atom at each of the four cube corners, each of which is shared with four adjacent unit cells. Thus, there is the equivalence of 1 atom associated with this BCC (100) plane. The planar section represented in the above figure is a square, wherein the side lengths are equal to the unit cell edge length, $\frac{4R}{\sqrt{3}}$ (Equation 3.4); thus, the area of this square is just $\left(\frac{4R}{\sqrt{3}}\right)^2 = \frac{16R^2}{3}$. Hence, the planar density for this (100) plane is just

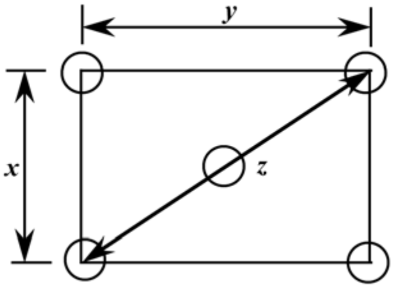
$$\text{PD}_{100} = \frac{\text{number of atoms centered on (100) plane}}{\text{area of (100) plane}}$$

$$= \frac{1 \text{ atom}}{\frac{16\,R^2}{3}} = \frac{3}{16\,R^2}$$

A BCC unit cell within which is drawn a (110) plane is shown below.



For this (110) plane there is one atom at each of the four cube corners through which it passes, each of which is shared with four adjacent unit cells, while the center atom lies entirely within the unit cell. Thus, there is the equivalence of 2 atoms associated with this BCC (110) plane. The planar section represented in the above figure is a rectangle, as noted in the figure below.



From this figure, the area of the rectangle is the product of x and y. The length x is just the unit cell edge length, which for BCC (Equation 3.4) is $\frac{4R}{\sqrt{3}}$. Now, the diagonal length z is equal to 4R. For the triangle bounded by the lengths x, y, and z

$$y = \sqrt{z^2 - x^2}$$

Or

$$y = \sqrt{(4R)^2 - \left(\frac{4R}{\sqrt{3}}\right)^2} = \frac{4R\sqrt{2}}{\sqrt{3}}$$

Thus, in terms of R, the area of this (110) plane is just

$$\textbf{Area(110)} = xy = \left(\frac{4R}{\sqrt{3}}\right)\left(\frac{4R\sqrt{2}}{\sqrt{3}}\right) = \frac{16R^2\sqrt{2}}{3}$$

And, finally, the planar density for this (110) plane is just

$$\text{PD}_{110} = \frac{\text{number of atoms centered on (110) plane}}{\text{area of (110) plane}}$$

$$= \frac{2 \text{ atoms}}{\frac{16R^2\sqrt{2}}{3}} = \frac{3}{8R^2\sqrt{2}}$$

(b) From the table inside the front cover, the atomic radius for molybdenum is 0.136 nm. Therefore, the planar density for the (100) plane is

$$\mathrm{PD}_{100}(\mathrm{Mo}) = \frac{3}{16R^2} = \frac{3}{16(0.136\ \mathrm{nm})^2} = 10.14\ \mathrm{nm}^{-2} = 1.014 \times 10^{19}\ \mathrm{m}^{-2}$$

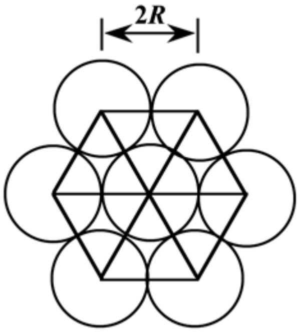
While for the (110) plane

$$\mathrm{PD}_{110}(\mathrm{Mo}) = \frac{3}{8R^2\sqrt{2}} = \frac{3}{8(0.136\ \mathrm{nm})^2\sqrt{2}} = 14.34\ \mathrm{nm}^{-2} = 1.434 \times 10^{19}\ \mathrm{m}^{-2}$$

3.62 *(a) Derive the planar density expression for the HCP (0001) plane in terms of the atomic radius R. (b) Compute the planar density value for this same plane for titanium (Ti).*

Solution

(a) A (0001) plane for an HCP unit cell is show below.



Each of the 6 perimeter atoms in this plane is shared with three other unit cells, whereas the center atom is shared with no other unit cells; this gives rise to three equivalent atoms belonging to this plane.

In terms of the atomic radius *R*, the area of each of the 6 equilateral triangles that have been drawn is $R^2\sqrt{3}$, or the total area of the plane shown is $6R^2\sqrt{3}$. And the planar density for this (0001) plane is equal to

$$\text{PD}_{0001} = \frac{\text{number of atoms centered on (0001) plane}}{\text{area of (0001) plane}}$$

$$= \frac{3 \text{ atoms}}{6R^2\sqrt{3}} = \frac{1}{2R^2\sqrt{3}}$$

(b) From the table inside the front cover, the atomic radius for titanium is 0.145 nm. Therefore, the planar density for the (0001) plane is

$$\text{PD}_{0001}(\text{Ti}) = \frac{1}{2R^2\sqrt{3}} = \frac{1}{2\sqrt{3}(0.145 \text{ nm})^2} = 13.73 \text{ nm}^{-2} = 1.373 \times 10^{19} \text{ m}^{-2}$$

Polycrystalline Materials

3.63 *Explain why the properties of polycrystalline materials are most often isotropic.*

Solution

Although each individual grain in a polycrystalline material may be anisotropic, if the grains have random orientations, then the solid aggregate of the many anisotropic grains will behave isotropically.

X-Ray Diffraction: Determination of Crystal Structures

3.64 *The interplanar spacing d_{hkl} for planes in a unit cell having orthorhombic geometry is given by*

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

where a, b, and c are the lattice parameters.

(a) To what equation does this expression reduce for crystals having cubic symmetry?

(b) For crystals having tetragonal symmetry?

Solution

(a) For the crystals having cubic symmetry, $a = b = c$. Making this substitution into the above equation leads to

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{a^2} + \frac{l^2}{a^2}$$

$$= \frac{h^2 + k^2 + l^2}{a^2}$$

(b) For crystals having tetragonal symmetry, $a = b \neq c$. Replacing b with a in the equation found in the problem statement leads to

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{a^2} + \frac{l^2}{c^2}$$

$$= \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

3.65 *Using the data for aluminum in Table 3.1, compute the interplanar spacing for the (110) set of planes.*

Solution

From the Table 3.1, aluminum has an FCC crystal structure and an atomic radius of 0.1431 nm. Using Equation 3.1, the lattice parameter *a* may be computed as

$$\boldsymbol{a} = 2R\sqrt{2} = \mathbf{(2)(0.1431\ nm)}\sqrt{2} = \mathbf{0.4045\ nm}$$

Now, the interplanar spacing d_{110} is determined using Equation 3.22 as

$$d_{110} = \frac{a}{\sqrt{(1)^2 + (1)^2 + (0)^2}} = \frac{0.4045\ \text{nm}}{\sqrt{2}} = \mathbf{0.2860\ nm}$$

3.66 *Using the data for α-iron in Table 3.1, compute the interplanar spacings for the (111) and (211) sets of planes.*

Solution

From the table, α-iron has a BCC crystal structure and an atomic radius of 0.1241 nm. Using Equation 3.4 the lattice parameter, *a*, may be computed as follows:

$$a = \frac{4R}{\sqrt{3}} = \frac{(4)(0.1241\ \text{nm})}{\sqrt{3}} = 0.2866\ \text{nm}$$

Now, the d_{111} interplanar spacing may be determined using Equation 3.22 as

$$d_{111} = \frac{a}{\sqrt{(1)^2 + (1)^2 + (1)^2}} = \frac{0.2866\ \text{nm}}{\sqrt{3}} = 0.1655\ \text{nm}$$

And, similarly for d_{211}

$$d_{211} = \frac{a}{\sqrt{(2)^2 + (1)^2 + (1)^2}} = \frac{0.2866\ \text{nm}}{\sqrt{6}} = 0.1170\ \text{nm}$$

3.67 *Determine the expected diffraction angle for the first-order reflection from the (310) set of planes for BCC chromium (Cr) when monochromatic radiation of wavelength 0.0711 nm is used.*

Solution

We first calculate the lattice parameter using Equation 3.4 and the value of *R* (0.1249 nm) cited in Table 3.1, as follows:

$$a = \frac{4R}{\sqrt{3}} = \frac{(4)(0.1249\ \text{nm})}{\sqrt{3}} = 0.2884\ \ \text{nm}$$

Next, the interplanar spacing for the (310) set of planes may be determined using Equation 3.22 according to

$$d_{310} = \frac{a}{\sqrt{(3)^2 + (1)^2 + (0)^2}} = \frac{0.2884\ \text{nm}}{\sqrt{10}} = 0.0912\ \ \text{nm}$$

And finally, employment of Equation 3.21 yields the diffraction angle as

$$\sin\theta = \frac{n\lambda}{2d_{310}} = \frac{(1)(0.0711\ \text{nm})}{(2)(0.0912\ \text{nm})} = 0.390$$

Which leads to

$$\theta = \sin^{-1}(0.390) = 22.94°$$

And, finally

$$2\theta = (2)(22.94°) = 45.88°$$

3.68 *Determine the expected diffraction angle for the first-order reflection from the (111) set of planes for FCC nickel (Ni) when monochromatic radiation of wavelength 0.1937 nm is used.*

Solution

We first calculate the lattice parameter using Equation 3.1 and the value of *R* (0.1246 nm) cited in Table 3.1, as follows:

$$a = 2R\sqrt{2} = (2)(0.1246 \text{ nm})\sqrt{2} = 0.3524 \text{ nm}$$

Next, the interplanar spacing for the (111) set of planes may be determined using Equation 3.22 according to

$$d_{111} = \frac{a}{\sqrt{(1)^2 + (1)^2 + (1)^2}} = \frac{0.3524 \text{ nm}}{\sqrt{3}} = 0.2035 \text{ nm}$$

And finally, employment of Equation 3.21 yields the diffraction angle as

$$\sin\theta = \frac{n\lambda}{2d_{111}} = \frac{(1)(0.1937 \text{ nm})}{(2)(0.2035 \text{ nm})} = 0.476$$

Which leads to

$$\theta = \sin^{-1}(0.476) = 28.42°$$

And, finally

$$2\theta = (2)(28.42°) = 56.84°$$

3.69 *The metal rhodium (Rh) has an FCC crystal structure. If the angle of diffraction for the (311) set of planes occurs at 36.12° (first-order reflection) when monochromatic x-radiation having a wavelength of 0.0711 nm is used, compute the following: (a) the interplanar spacing for this set of planes and (b) the atomic radius for a Rh atom.*

<u>Solution</u>

(a) From the data given in the problem, and realizing that 36.12° = 2θ, the interplanar spacing for the (311) set of planes for rhodium may be computed using Equation 3.21 as

$$d_{311} = \frac{n\lambda}{2\sin\theta} = \frac{(1)(0.0711\ \text{nm})}{(2)\left(\sin\dfrac{36.12^\circ}{2}\right)} = 0.1147\ \text{nm}$$

(b) In order to compute the atomic radius we must first determine the lattice parameter, *a*, using Equation 3.22, and then *R* from Equation 3.1 since Rh has an FCC crystal structure. Therefore,

$$a = d_{311}\sqrt{(3)^2 + (1)^2 + (1)^2} = (0.1147\ \text{nm})\left(\sqrt{11}\right) = 0.3804\ \text{nm}$$

And, from Equation 3.1

$$R = \frac{a}{2\sqrt{2}} = \frac{0.3804\ \text{nm}}{2\sqrt{2}} = 0.1345\ \text{nm}$$

3.70 *The metal niobium (Nb) has a BCC crystal structure. If the angle of diffraction for the (211) set of planes occurs at 75.99° (first-order reflection) when monochromatic x-radiation having a wavelength of 0.1659 nm is used, compute the following: (a) the interplanar spacing for this set of planes and (b) the atomic radius for the Nb atom.*

Solution

(a) From the data given in the problem statement, and realizing that 75.99° = 2θ, the interplanar spacing for the (211) set of planes for Nb may be computed using Equation 3.21 as follows:

$$d_{211} = \frac{n\lambda}{2\sin\theta} = \frac{(1)(0.1659\ \text{nm})}{(2)\left(\sin\dfrac{75.99^\circ}{2}\right)} = 0.1348\ \text{nm}$$

(b) In order to compute the atomic radius we must first determine the lattice parameter, *a*, using Equation 3.22, and then *R* from Equation 3.4 since Nb has a BCC crystal structure. Therefore,

$$a = d_{211}\sqrt{(2)^2 + (1)^2 + (1)^2} = (0.1347\ \text{nm})\left(\sqrt{6}\right) = 0.3300\ \text{nm}$$

And, from a rearranged form Equation 3.4

$$R = \frac{a\sqrt{3}}{4} = \frac{(0.3300\ \text{nm})\sqrt{3}}{4} = 0.1429\ \text{nm}$$

3.71 *For which set of crystallographic planes will a first-order diffraction peak occur at a diffraction angle of 44.53° for FCC nickel (Ni) when monochromatic radiation having a wavelength of 0.1542 nm is used?*

Solution

The first step to solve this problem is to compute the value of θ in Equation 3.21. Because the diffraction angle, 2θ, is equal to 44.53°, $\theta = 44.53°/2 = 22.27°$. We can now determine the interplanar spacing using Equation 3.21; thus

$$d_{hkl} = \frac{n\lambda}{2 \sin \theta} = \frac{(1)(0.1542 \text{ nm})}{(2)(\sin 22.27°)} = 0.2035 \text{ nm}$$

Now, employment of both Equations 3.22 and 3.1 (since Ni's crystal structure is FCC), and the value of *R* for nickel from Table 3.1 (0.1246 nm) leads to

$$\sqrt{h^2 + k^2 + l^2} = \frac{a}{d_{hkl}} = \frac{2R\sqrt{2}}{d_{hkl}}$$

$$= \frac{(2)(0.1246 \text{ nm})\sqrt{2}}{(0.2035 \text{ nm})} = 1.732$$

This means that

$$h^2 + k^2 + l^2 = (1.732)^2 = 3.0$$

From Table 3.5 and for the FCC crystal structure, the only three integers the sum of the squares of which equals 3.0 are 1, 1, and 1. Therefore, the set of planes responsible for this diffraction peak is the (111) set.

3.72 *For which set of crystallographic planes will a first-order diffraction peak occur at a diffraction angle of 136.15° for BCC tantalum (Ta) when monochromatic radiation having a wavelength of 0.1937 nm is used?*

Solution

The first step to solve this problem is to compute the value of θ in Equation 3.21. Because the diffraction angle, 2θ, is equal to 136.15°, θ = 136.15°/2 = 68.08°. We can now determine the interplanar spacing using Equation 3.21; thus

$$d_{hkl} = \frac{n\lambda}{2\sin\theta} = \frac{(1)(0.1937\ \text{nm})}{(2)\left(\sin 68.08°\right)} = \mathbf{0.1044\ nm}$$

Now, employment of both Equations 3.22 and 3.4 (since Ta's crystal structure is BCC), and the value of R for Ta from Table 3.1 (0.1430 nm) leads to

$$\sqrt{h^2 + k^2 + l^2} = \frac{a}{d_{hkl}} = \frac{\frac{4R}{\sqrt{3}}}{d_{hkl}} = \frac{4R}{d_{hkl}\sqrt{3}}$$

$$= \frac{(4)(0.1430\ \text{nm})}{(0.1044\ \text{nm})\sqrt{3}} = 3.163$$

This means that

$$h^2 + k^2 + l^2 = (3.163)^2 = \mathbf{10.0}$$

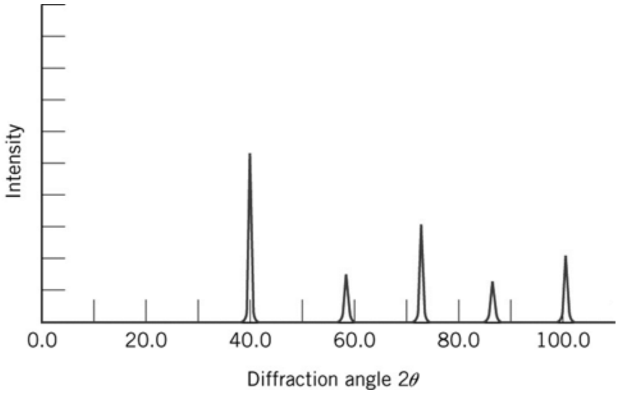
From Table 3.5 and for the BCC crystal structure, the only three integers the sum of the squares of which equals 10.0 are 3, 1, and 0. Therefore, the set of planes responsible for this diffraction peak is the (310) set.

3.73 *Figure 3.26 shows the first five peaks of the x-ray diffraction pattern for tungsten (W), which has a BCC crystal structure; monochromatic x-radiation having a wavelength of 0.1542 nm was used.*

(a) Index (i.e., give h, k, and l indices) for each of these peaks.

(b) Determine the interplanar spacing for each of the peaks.

(c) For each peak, determine the atomic radius for W, and compare these with the value presented in Table 3.1.



Solution

(a) Since W has a BCC crystal structure, and using information in Table 3.5, indices for the first five peaks are (110), (200), (211), (220), and (310).

(b) For each peak, in order to calculate the interplanar spacing we must employ Equation 3.21. For the first peak, which occurs at 40.2°= 2θ, then θ = 40.2°/2 =20.1°.

$$d_{110} = \frac{n\lambda}{2\sin\theta} = \frac{(1)(0.1542\text{ nm})}{(2)(\sin 20.1°)} = 0.2244\text{ nm}$$

(c) Employment of Equations 3.22 and 3.4 is necessary for the computation of *R* for W as

$$R = \frac{a\sqrt{3}}{4} = \frac{(d_{hkl})(\sqrt{3})\sqrt{(h)^2 + (k)^2 + (l)^2}}{4}$$

$$= \frac{(0.2244\text{ nm})(\sqrt{3})\sqrt{(1)^2 + (1)^2 + (0)^2}}{4}$$

$$= 0.1374\text{ nm}$$

Similar computations are made for the other peaks which results are tabulated below:

Peak Index	2θ	d_{hkl}(nm)	R (nm)
200	58.4	0.1580	0.1369
211	73.3	0.1292	0.1370
220	87.0	0.1120	0.1371
310	100.7	0.1001	0.1371

The atomic radius for tungsten cited in Table 3.1 is 0.1371 nm.

3.74 *The following table lists diffraction angles for the first four peaks (first-order) of the x-ray diffraction pattern for platinum (Pt), which has an FCC crystal structure; monochromatic x-radiation having a wavelength of 0.0711 nm was used.*

Plane Indices	*Diffraction Angle (2θ)*
(111)	*18.06°*
(200)	*20.88°*
(220)	*26.66°*
(311)	*31.37°*

(a) Determine the interplanar spacing for each of the peaks.

(b) For each peak, determine the atomic radius for Pt, and compare these with the value presented in Table 3.1.

Solution

(a) For each peak, in order to calculate the interplanar spacing we must employ Equation 3.21. For the first peak [which occurs by diffraction from the (111) set of planes] and occurs at 18.06°––that is, $2\theta = 18.06°$, which means that $\theta = 18.06°/2 = 9.03°$. Using Equation 3.21, the interplanar spacing is computed as follows:

$$d_{111} = \frac{n\lambda}{2 \sin \theta} = \frac{(1)(0.0711 \text{ nm})}{(2)\left(\sin 9.03°\right)} = 0.2265 \text{ nm}$$

(b) Employment of Equations 3.22 and 3.1 is necessary for the computation of R for Pt as

$$R = \frac{a}{2\sqrt{2}} = \frac{(d_{hkl})\sqrt{(h)^2 + (k)^2 + (l)^2}}{2\sqrt{2}}$$

$$= \frac{(d_{111})\sqrt{(1)^2 + (1)^2 + (1)^2}}{2\sqrt{2}}$$

$$= \frac{(0.2265 \text{ nm})\sqrt{(1)^2 + (1)^2 + (1)^2}}{2\sqrt{2}}$$

$$= 0.1387 \text{ nm}$$

Similar computations are made for the other peaks which results are tabulated below:

Peak Index	2θ	d_{hkl}(nm)	R (nm)
200	20.88	0.1962	0.1387
220	29.72	0.1386	0.1386
311	34.93	0.1185	0.1390

The atomic radius for platinum cited in Table 3.1 is 0.1387 nm.

3.75 *The following table lists diffraction angles for the first three peaks (first-order) of the x-ray diffraction pattern for some metal. Monochromatic x-radiation having a wavelength of 0.1397 nm was used.*

(a) Determine whether this metal's crystal structure is FCC, BCC or neither FCC or BCC, and explain the reason for your choice.

(b) If the crystal structure is either BCC or FCC, identify which of the metals in Table 3.1 gives this diffraction pattern. Justify your decision.

Peak Number	Diffraction Angle (2θ)
1	34.51°
2	40.06°
3	57.95°

Solution

(a) The steps in solving this part of the problem are as follows:

1. For each of these peaks compute the value of d_{hkl} using Equation 3.21 in the form

$$d_{hkl} = \frac{n\lambda}{2\sin\theta} \qquad \text{(P.1)}$$

taking $n = 1$ since this is a first-order reflection, and $\lambda = 0.1397$ nm (as given in the problem statement).

2. Using the value of d_{hkl} for each peak, determine the value of a from Equation 3.22 for both BCC and FCC crystal structures—that is

$$a = d_{hkl}\sqrt{h^2 + k^2 + l^2} \qquad \text{(P.2)}$$

For BCC the planar indices for the first three peaks are (110), (200), and (211), which yield the respective $h^2 + k^2 + l^2$ values of 2, 4, and 6. On the other hand, for FCC planar indices for the first three peaks are (111), (200), and (220), which yield the respective $h^2 + k^2 + l^2$ values of 3, 4, and 8.

3. If the three values of a are the same (or nearly the same) for either BCC or FCC then the crystal structure is which of BCC or FCC has the same a value.

4. If none of the set of a values for both FCC and BCC are the same (or nearly the same) then the crystal structure is neither BCC or FCC.

Step 1

Using Equation P.1, the three values of d_{hkl} are computed as follows:

$$d_1 = \frac{n\lambda}{2\sin\theta_1} = \frac{(1)(0.1397\text{ nm})}{(2)\sin\left(\frac{34.51°}{2}\right)} = 0.2355\text{ nm}$$

$$d_2 = \frac{n\lambda}{2\sin\theta_2} = \frac{(1)(0.1397\text{ nm})}{(2)\sin\left(\frac{40.06°}{2}\right)} = 0.2039\text{ nm}$$

$$d_3 = \frac{n\lambda}{2\sin\theta_3} = \frac{(1)(0.1397\text{ nm})}{(2)\sin\left(\frac{57.95°}{2}\right)} = 0.1442\text{ nm}$$

Step 2

Using Equation P.2 let us first compute values of *a* for BCC.

For the (110) set of planes

$$a_1(\text{BCC}) = d_1\sqrt{h^2+k^2+l^2} = (0.2355\text{ nm})\sqrt{1^2+1^2+0^2} = 0.3330\text{ nm}$$

For the (200) set of planes:

$$a_2(\text{BCC}) = d_2\sqrt{h^2+k^2+l^2} = (0.2039\text{ nm})\sqrt{2^2+0^2+0^2} = 0.4078\text{ nm}$$

And for the (211) set of planes:

$$a_3(\text{BCC}) = d_3\sqrt{h^2+k^2+l^2} = (0.1442\text{ nm})\sqrt{2^2+1^2+1^2} = 0.3532\text{ nm}$$

Inasmuch as these three values of *a* are not nearly the same, the crystal structure is not BCC.

We now repeat this procedure for the FCC crystal structure.

For the (111) set of planes:

$$a_1(\text{FCC}) = d_1\sqrt{h^2+k^2+l^2} = (0.2355\text{ nm})\sqrt{1^2+1^2+1^2} = 0.4079\text{ nm}$$

Whereas for the (200) set of planes:

$$a_2(\text{FCC}) = d_2\sqrt{h^2+k^2+l^2} = (0.2039\text{ nm})\sqrt{2^2+0^2+0^2} = 0.4078\text{ nm}$$

And, finally, for the (220) set of planes:

$$a_3(\text{FCC}) = d_3\sqrt{h^2 + k^2 + l^2} = (0.1442 \text{ nm})\sqrt{2^2 + 2^2 + 0^2} = 0.4079 \text{ nm}$$

Inasmuch as $a_1 = a_2 = a_3$ the crystal structure is FCC.

(b) Since we know the value of *a* for this FCC crystal structure, it is possible to calculate the value of the atomic radius *R* using a rearranged form of Equation 3.1; and once we know the value of *R*, we just find that metal in Table 3.1 that has this atomic radius. Thus, we calculate the value of *R* as follows (using a value of 0.4079 for *a*):

$$R = \frac{a}{2\sqrt{2}} = \frac{0.4079 \text{ nm}}{2\sqrt{2}} = 0.1442 \text{ nm}$$

From Table 3.1 the only FCC metal that has this atomic radius is *gold* (although both aluminum, and silver have an FCC crystal structure and *R* values close to this value).

3.76 *The following table lists diffraction angles for the first three peaks (first-order) of the x-ray diffraction pattern for some metal. Monochromatic x-radiation having a wavelength of 0.0711 nm was used.*

(a) Determine whether this metal's crystal structure is FCC, BCC or neither FCC or BCC and explain the reason for your choice.

(b) If the crystal structure is either BCC or FCC, identify which of the metals in Table 3.1 gives this diffraction pattern. Justify your decision.

Peak Number	*Diffraction Angle* *(2θ)*
1	*18.27°*
2	*25.96°*
3	*31.92°*

Solution

(a) The steps in solving this part of the problem are as follows:

1. For each of these peaks compute the value of d_{hkl} using Equation 3.21 in the form

$$d_{hkl} = \frac{n\lambda}{2\sin\theta} \qquad \text{(P.1)}$$

taking $n = 1$ since this is a first-order reflection, and $\lambda = 0.0711$ nm (as given in the problem statement).

2. Using the value of d_{hkl} for each peak, determine the value of a from Equation 3.22 for both BCC and FCC crystal structures—that is

$$a = d_{hkl}\sqrt{h^2 + k^2 + l^2} \qquad \text{(P.2)}$$

For BCC the planar indices for the first three peaks are (110), (200), and (211), which yield the respective $h^2 + k^2 + l^2$ values of 2, 4, and 6. On the other hand, for FCC planar indices for the first three peaks are (111), (200), and (220), which yield the respective $h^2 + k^2 + l^2$ values of 3, 4, and 8.

3. If the three values of a are the same (or nearly the same) for either BCC or FCC then the crystal structure is which of BCC or FCC has the same a value.

4. If none of the set of a values for both FCC and BCC are the same (or nearly the same) then the crystal structure is neither BCC or FCC.

Step 1

Using Equation P.1, the three values of d_{hkl} are computed as follows:

$$d_1 = \frac{n\lambda}{2\sin\theta_1} = \frac{(1)(0.0711\text{ nm})}{(2)\sin\left(\frac{18.27°}{2}\right)} = 0.2239\text{ nm}$$

$$d_2 = \frac{n\lambda}{2\sin\theta_2} = \frac{(1)(0.0711\text{ nm})}{(2)\sin\left(\frac{25.96°}{2}\right)} = 0.1583\text{ nm}$$

$$d_3 = \frac{n\lambda}{2\sin\theta_3} = \frac{(1)(0.0711\text{ nm})}{(2)\sin\left(\frac{31.92°}{2}\right)} = 0.1293\text{ nm}$$

Step 2

Using Equation P.2 let us first compute values of *a* for BCC.

For the (110) set of planes

$$a_1(\text{BCC}) = d_1\sqrt{h^2+k^2+l^2} = (0.2239\text{ nm})\sqrt{1^2+1^2+0^2} = 0.3166\text{ nm}$$

For the (200) set of planes:

$$a_2(\text{BCC}) = d_2\sqrt{h^2+k^2+l^2} = (0.1583\text{ nm})\sqrt{2^2+0^2+0^2} = 0.3166\text{ nm}$$

And for the (211) set of planes:

$$a_3(\text{BCC}) = d_3\sqrt{h^2+k^2+l^2} = (0.1293\text{ nm})\sqrt{2^2+1^2+1^2} = 0.3167\text{ nm}$$

Inasmuch as $a_1 = a_2 \cong a_3$ the crystal structure is BCC, and it is not necessary to pursue the possibility of FCC.

(b) Since we know the value of *a* for this BCC crystal structure, it is possible to calculate the value of the atomic radius *R* using a rearranged form of Equation 3.4; and once we know the value of *R*, we just find that metal in Table 3.1 that has this atomic radius. Thus, we calculate the value of *R* as follows (using a value of 0.3166 for *a*):

$$R = \frac{a\sqrt{3}}{4} = \frac{(0.3166\text{ nm})\sqrt{3}}{4} = 0.1371\text{ nm}$$

From Table 3.1 the BCC metal that has this atomic radius is *tungsten* (although molybdenum has a BCC crystal structure and an *R* close to this value).

Noncrystalline Solids

3.77 *Would you expect a material in which the atomic bonding is predominantly ionic in nature to be more or less likely to form a noncrystalline solid upon solidification than a covalent material? Why? (See Section 2.6.)*

<u>Solution</u>

A material in which atomic bonding is predominantly ionic in nature is less likely to form a noncrystalline solid upon solidification than a covalent material because covalent bonds are directional whereas ionic bonds are nondirectional; it is more difficult for the atoms in a covalent material to assume positions giving rise to an ordered structure.

FUNDAMENTALS OF ENGINEERING QUESTIONS AND PROBLEMS

3.1FE *A hypothetical metal has the BCC crystal structure, a density of 7.24 g/cm*^{3}*, and an atomic weight of 48.9 g/mol. The atomic radius of this metal is:*

(A) 0.122 nm *(C) 0.0997 nm*

(B) 1.22 nm *(D) 0.154 nm*

Solution

The volume of a BCC unit cell is calculated using Equation 3.4 as follows

$$V_C = a^3 = \left(\frac{4R}{\sqrt{3}}\right)^3 = \frac{64R^3}{3\sqrt{3}}$$

Now, using Equation 3.8, we may determine the density as follows:

$$\rho = \frac{nA}{V_C N_\mathrm{A}}$$

$$= \frac{nA}{\left(\dfrac{64R^3}{3\sqrt{3}}\right)N_\mathrm{A}} = \frac{\left(3\sqrt{3}\right)nA}{64R^3 N_\mathrm{A}}$$

And, from this expression, solving for *R*, leads to

$$R = \left[\frac{\left(3\sqrt{3}\right)nA}{64\rho N_\mathrm{A}}\right]^{1/3}$$

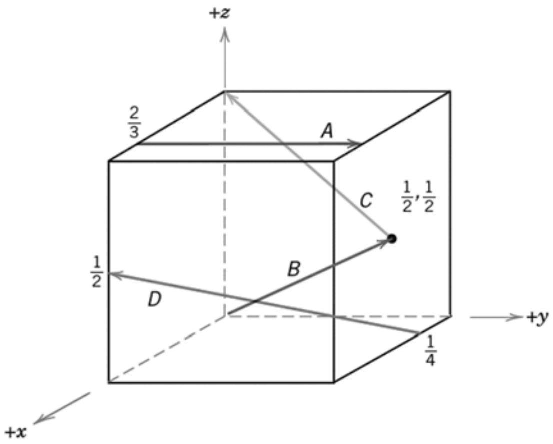
Since there are two atoms per unit cell (n = 2) and incorporating values for the density (ρ) and atomic weight (A) provided in the problem statement, we calculate the value of *R* as follows:

$$= \left[\frac{(3\sqrt{3})(2\ \text{atoms/unit cell})(48.9\ \text{g/mol})}{(64)(7.24\ \text{g/cm}^3)(6.022\times 10^{23}\ \text{atoms/mol})}\right]^{1/3}$$

$$= 1.22 \times 10^{-8}\ \text{cm} = 0.122\ \text{nm}$$

which is answer A.

3.2FE *In the following unit cell, which vector represents the [121] direction?*



Solution

In order to solve this problem, let us take the position of the [121] direction vector as the origin of the coordinate system, and then, using Equations 3.10a, 3.10b, and 3.10c, determine the head coordinates of the vector. The vector in the illustration that coincides with this vector or is parallel to it corresponds to the [121] direction.

Using this scheme, vector tail coordinates are as follows:

$x_1 = 0a$ $\qquad$ $y_1 = 0b$ $\qquad$ $z_1 = 0c$

For this direction, values of the *u*, *v*, and *w* indices are as follows:

$u = 1$ $\qquad$ $v = 2$ $\qquad$ $w = 1$

Now, assuming a value of 1 for the parameter *n*, values of the head coordinates (x_2, y_2 , and z_2) are determined (using Equations 3.10) as follows:

$$x_2 = ua + x_1 = (1)a + 0a = a$$

$$y_2 = vb + y_1 = (2)b + 0b = 2b$$

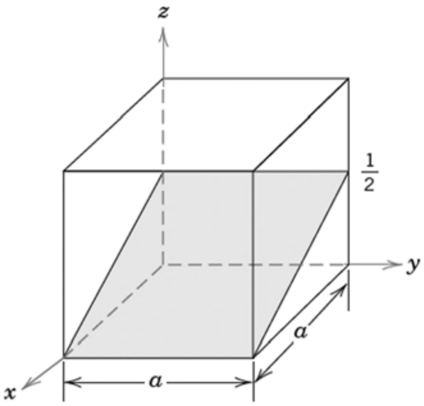
$$z_2 = wc + z_1 = (1)c + 0c = c$$

If we now divide these three head coordinates by a factor of 2, it is possible, in a stepwise manner, locate the location of the vector head as follows: move *a*/2 units along the *x* axis, then *b* units parallel to the *y* axis, and from here *c*/2 units parallel to the *z* axis. The vector from the origin to this point corresponds to B.

3.3FE *What are the Miller indices for the plane shown in the following cubic unit cell?*

(A) (201) (C) $(10\frac{1}{2})$

(B) $\left(1\infty\frac{1}{2}\right)$ (D) (102)



Solution

The Miller indices for this direction may be determined using Equations 3.14a, 3.14b, and 3.14c. However, it is first necessary to note intersections of this plane with the *x, y,* and *z* coordinate axes. These respective intercepts are *a*, ∞*a* (since the plane is parallel to the *y* axis), and *a*/2; that is

$A = a$ $B = \infty a$ $C = a/2$

Thus, using Equations 3.14, values of the *h, k,* and *l* indices (assuming that *n* = 1)are as follows:

$$h = \frac{na}{A} = \frac{(1)a}{a} = 1$$

$$k = \frac{na}{B} = \frac{(1)a}{\infty a} = 0$$

$$l = \frac{nc}{C} = \frac{(1)c}{c/2} = 2$$

Therefore this is a (102) plane, which means that D is the correct answer.

CHAPTER 4

IMPERFECTIONS IN SOLIDS

PROBLEM SOLUTIONS

Vacancies and Self-Interstitials

4.1 *The equilibrium fraction of lattice sites that are vacant in silver (Ag) at 700°C is 2 × 10*$^{-6}$*. Calculate the number of vacancies (per meter cubed) at 700°C. Assume a density of 10.35 g/cm*^{3} *for Ag.*

Solution

This problem is solved using two steps: (1) calculate the total number of lattice sites in silver, N_{Ag}, using Equation 4.2; and (2) multiply this number by fraction of lattice that are vacant, 2 × 10^{-6}. The parameter N_{Ag} is related to the density, (ρ), Avogadro's number (N_{A}), and the atomic weight (A_{Ag}=107.87 g/mol, from inside the front cover) according to Equation 4.2 as

$$N_{\text{Ag}} = \frac{N_{\text{A}}\rho_{\text{Ag}}}{A_{\text{Ag}}}$$

$$= \frac{(6.022 \times 10^{23} \text{ atoms/mol})(10.35 \text{ g/cm}^3)(10^6 \text{ cm}^3/\text{m}^3)}{107.87 \text{ g/mol}}$$

$$= 5.78 \times 10^{28} \text{ atoms/m}^3$$

The number of vacancies per meter cubed in silver at 700°C, N_v, is determined as follows:

$$N_v = (2 \times 10^{-6})N_{\text{Ag}}$$

$$= (2 \times 10^{-6})(5.78 \times 10^{28} \text{ atoms/m}^3) = 1.156 \times 10^{23} \text{ vacancies/m}^3$$

4.2 *For some hypothetical metal, the equilibrium number of vacancies at 900°C is 2.3 × 10^{25} m^{-3}. If the density and atomic weight of this metal are 7.40 g/cm^3 and 85.5 g/mol, respectively, calculate the fraction of vacancies for this metal at 900°C.*

Solution

This problem is solved using two steps: (1) calculate the total number of lattice sites in silver, N, using Equation 4.2, and (2) take the ratio of the equilibrium number of vacancies given in the problem statement (N_v = 2.3 × 10^{25} m^{-3}) and this value of N. From Equation 4.2

$$N = \frac{N_A \rho}{A}$$

$$= \frac{(6.022 \times 10^{23} \text{ atoms/mol})(7.40 \text{ g/cm}^3)(10^6 \text{cm}^3/\text{m}^3)}{85.5 \text{ g/mol}}$$

$$= 5.21 \times 10^{28} \text{ atoms/m}^3$$

The fraction of vacancies is equal to the N_v/N ratio, which is computed as follows:

$$\frac{N_v}{N} = \frac{2.3 \times 10^{25} \text{ m}^{-3}}{5.21 \times 10^{28} \text{ atoms/m}^3}$$

$$= 4.41 \times 10^{-4}$$

4.3 *(a) Calculate the fraction of atom sites that are vacant for copper (Cu) at its melting temperature of 1084°C (1357 K). Assume an energy for vacancy formation of 0.90 eV/atom.*

(b) Repeat this calculation at room temperature (298 K).

(c) What is ratio of N_V */N(1357 K) and* N_V */N(298 K)?*

Solution

(a) In order to compute the fraction of atom sites that are vacant in copper at 1357 K, we must employ Equation 4.1. As stated in the problem, Q_V = 0.90 eV/atom. Thus,

$$\frac{N_v}{N} = \exp\left(-\frac{Q_v}{kT}\right) = \exp\left[-\frac{0.90\text{ eV/atom}}{(8.62 \times 10^{-5}\text{ eV/atom-K})(1357\text{ K})}\right]$$

$$= 4.56 \times 10^{-4} = N_v/N(1357\text{ K})$$

(b) We repeat this computation at room temperature (298 K), as follows:

$$\frac{N_v}{N} = \exp\left(-\frac{Q_v}{kT}\right) = \exp\left[-\frac{0.90\text{ eV/atom}}{(8.62 \times 10^{-5}\text{ eV/atom-K})(298\text{ K})}\right]$$

$$= 6.08 \times 10^{-16} = N_v/N(298\text{ K})$$

(c) And, finally the ratio of N_V /N(1357 K) and N_V /N(298 K) is equal to the following:

$$\frac{N_v/N(1357\text{ K})}{N_v/N(298\text{ K})} = \frac{4.56 \times 10^{-4}}{6.08 \times 10^{-16}} = 7.5 \times 10^{11}$$

4.4 *Calculate the number of vacancies per cubic meter in gold (Au) at 900°C. The energy for vacancy formation is 0.98 eV/atom. Furthermore, the density and atomic weight for Au are 18.63 g/cm*^{3} *(at 900°C) and 196.9 g/mol, respectively.*

Solution

Determination of the number of vacancies per cubic meter in gold at 900°C (1173 K) requires the utilization of Equations 4.1 and 4.2 as follows:

$$N_v = N \exp\left(-\frac{Q_v}{kT}\right) = \frac{N_{\mathrm{A}}\,\rho_{\mathrm{Au}}}{A_{\mathrm{Au}}} \exp\left(-\frac{Q_v}{kT}\right)$$

Inserting into this expression he density and atomic weight values for gold leads to the following:

$$N_v = \frac{(6.022 \times 10^{23}\ \text{atoms/mol})(18.63\ \text{g/cm}^3)}{196.9\ \text{g/mol}} \exp\left[-\frac{0.98\ \text{eV/atom}}{(8.62 \times 10^{-5}\ \text{eV/atom-K})(1173\ \text{K})}\right]$$

$$= 3.52 \times 10^{18}\ \text{cm}^{-3} = 3.52 \times 10^{24}\ \text{m}^{-3}$$

4.5 *Calculate the energy for vacancy formation in nickel (Ni), given that the equilibrium number of vacancies at 850°C (1123 K) is 4.7 ×* 10^{22} m^{-3}*. The atomic weight and density (at 850°C) for Ni are, respectively, 58.69 g/mol and 8.80 g/*cm^3*.*

Solution

This problem calls for the computation of the activation energy for vacancy formation in nickel. Upon examination of Equation 4.1, all parameters besides Q_v are given except N, the total number of atomic sites. However, N is related to the density, (ρ), Avogadro's number (N_A), and the atomic weight (A) according to Equation 4.2 as

$$N = \frac{N_A \rho_{Ni}}{A_{Ni}}$$

$$= \frac{(6.022 \times 10^{23} \text{ atoms/mol})(8.80 \text{ g/cm}^3)}{58.69 \text{ g/mol}}$$

$$= 9.03 \times 10^{22} \text{ atoms/cm}^3 = 9.03 \times 10^{28} \text{ atoms/m}^3$$

Now, taking natural logarithms of both sides of Equation 4.1, yields he following

$$\ln N_v = \ln N - \frac{Q_v}{kT}$$

We make Q_v the dependent variable after some algebraic manipulation as

$$Q_v = -kT \ln\left(\frac{N_v}{N}\right)$$

Incorporation into this expression, values for N_v (determined above as 9.03 × 10^{28} atoms/m^3), N (provided in the problem statement, 4.7 × 10^{22} m^{-3}). T (850°C = 1123 K) and k, leads to the following:

$$Q_v = -\left(8.62 \times 10^{-5} \text{ eV/atom-K}\right)(1123 \text{ K}) \ln\left[\frac{4.7 \times 10^{22} \text{ m}^{-3}}{9.03 \times 10^{28} \text{ m}^{-3}}\right]$$

$$= 1.40 \text{ eV/atom}$$

Impurities in Solids

4.6 *Atomic radius, crystal structure, electronegativity, and the most common valence are given in the following table for several elements; for those that are nonmetals, only atomic radii are indicated.*

Element	***Atomic Radius (nm)***	***Crystal Structure***	***Electronegativity***	***Valence***
Ni	*0.1246*	*FCC*	*1.8*	*+2*
C	*0.071*			
H	*0.046*			
O	*0.060*			
Ag	*0.1445*	*FCC*	*1.4*	*+1*
Al	*0.1431*	*FCC*	*1.5*	*+3*
Co	*0.1253*	*HCP*	*1.7*	*+2*
Cr	*0.1249*	*BCC*	*1.6*	*+3*
Fe	*0.1241*	*BCC*	*1.7*	*+2*
Pt	*0.1387*	*FCC*	*1.5*	*+2*
Zn	*0.1332*	*HCP*	*1.7*	*+2*

Which of these elements would you expect to form the following with nickel:

(a) A substitutional solid solution having complete solubility

(b) A substitutional solid solution of incomplete solubility

(c) An interstitial solid solution

Solution

For complete substitutional solubility the four Hume-Rothery rules must be satisfied: (1) the difference in atomic radii between Ni and the other element (ΔR%) must be less than ±15%; (2) the crystal structures must be the same; (3) the electronegativities must be similar; and (4) the valences should be the same.

Element	ΔR%	Crystal Structure	ΔElectro-negativity	Valence
Ni		**FCC**		**2+**
C	–43			
H	–63			
O	–52			
Ag	+16	FCC	-0.4	1+
Al	+15	FCC	-0.3	3+
Co	+0.6	HCP	-0.1	2+
Cr	+0.2	BCC	-0.2	3+
Fe	-0.4	BCC	-0.1	2+
Pt	+11	FCC	-0.3	2+
Zn	+7	HCP	-0.1	2+

(a) Pt is the only element that meets all of the criteria and thus forms a substitutional solid solution having complete solubility. At elevated temperatures Co and Fe experience allotropic transformations to the FCC crystal structure, and thus display complete solid solubility at these temperatures.

(b) Ag, Al, Co, Cr, Fe, and Zn form substitutional solid solutions of incomplete solubility. All these metals have either BCC or HCP crystal structures, and/or the difference between their atomic radii and that for Ni are greater than ±15%, and/or have a valence different than 2+.

(c) C, H, and O form interstitial solid solutions. These elements have atomic radii that are significantly smaller than the atomic radius of Ni.

4.7 *Which of the following systems (i.e., pair of metals) would you expect to exhibit complete solid solubility? Explain your answers.*

(a) Cr-V

(b) Mg-Zn

(c) Al-Zr

(d) Ag-Au

(e) Pb-Pt

Solution

In order for there to be complete solubility (substitutional) for each pair of metals, the four Hume-Rothery rules must be satisfied: (1) the difference in atomic radii between Ni and the other element ($\Delta R\%$) must be less than ±15%; (2) the crystal structures must be the same; (3) the electronegativities must be similar; and (4) the valences should be the same.

(a) A comparison of these four criteria for the Cr-V system is given below:

Metal	***Atomic Radius (nm)***	***Crystal Structure***	***Electronegativity***	***Valence***
Cr	0.125	BCC	1.6	+3
V	0.132	BCC	1.5	+5 (+3)

For chromium and vanadium, the percent difference in atomic radii is approximately 6%, the crystal structures are the same (BCC), and there is very little difference in their electronegativities. The most common valence for Cr is +3; although the most common valence of V is +5, it can also exist as +3. Therefore, chromium and vanadium are completely soluble in one another.

(b) A comparison of these four criteria for the Mg-Zn system is given below:

Metal	***Atomic Radius (nm)***	***Crystal Structure***	***Electronegativity***	***Valence***
Mg	0.160	HCP	1.3	+2
Zn	0.133	HCP	1.7	+2

For magnesium and zinc, the percent difference in atomic radii is approximately 17%, the crystal structures are the same (HCP), and there is some difference in their electronegativities (1.3 vs. 1.7). The most common valence for both Mg and Zn is +2. Magnesium and zinc are not completely soluble in one another, primarily because of the difference in atomic radii.

(c) A comparison of these four criteria for the Al-Zr system is given below:

Metal	***Atomic Radius (nm)***	***Crystal Structure***	***Electronegativity***	***Valence***
Al	0.143	FCC	1.5	+3
Zr	0.159	HCP	1.2	+4

For aluminum and zirconium, the percent difference in atomic radii is approximately 11%, the crystal structures are different (FCC and HCP), there is some difference in their electronegativities (1.5 vs. 1.2). The most common valences for Al and Zr are +3 and +4, respectively. Aluminum and zirconium are not completely soluble in one another, primarily because of the difference in crystal structures.

(d) A comparison of these four criteria for the Ag-Au system is given below:

Metal	***Atomic Radius (nm)***	***Crystal Structure***	***Electronegativity***	***Valence***
Ag	0.144	FCC	1.4	+1
Au	0.144	FCC	1.4	+1

For silver and gold, the atomic radii are the same, the crystal structures are the same (FCC), their electronegativities are the same (1.4), and their common valences are +1. Silver and gold are completely soluble in one another because all four criteria are satisfied.

(d) A comparison of these four criteria for the Pb-Pt system is given below:

Metal	***Atomic Radius (nm)***	***Crystal Structure***	***Electronegativity***	***Valence***
Pb	0.175	FCC	1.6	+2
Pt	0.139	FCC	1.5	+2

For lead and platinum, the percent difference in atomic radii is approximately 20%, the crystal structures are the same (FCC), their electronegativities are nearly the same (1.6 vs. 1.5), and the most common valence for both of them is +2. Lead and platinum are not completely soluble in one another, primarily because of the difference in atomic radii.

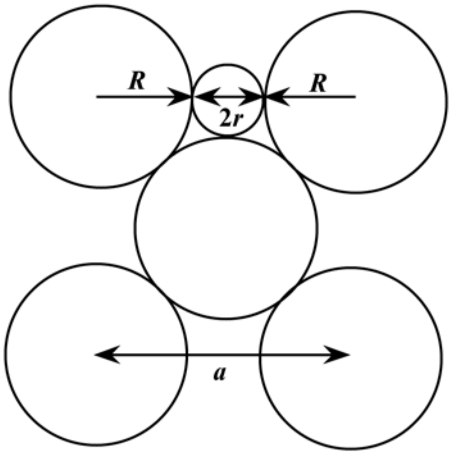
4.8 *(a) Compute the radius r of an impurity atom that will just fit into an FCC octahedral site in terms of the atomic radius R of the host atom (without introducing lattice strains).*

(b) Repeat part (a) for the FCC tetrahedral site.

(Note: You may want to consult Figure 4.3a.)

Solution

(a) In the drawing below is shown the atoms on the (100) face of an FCC unit cell; the small circle represents an impurity atom that just fits within the octahedral interstitial site that is located at the center of the unit cell edge.



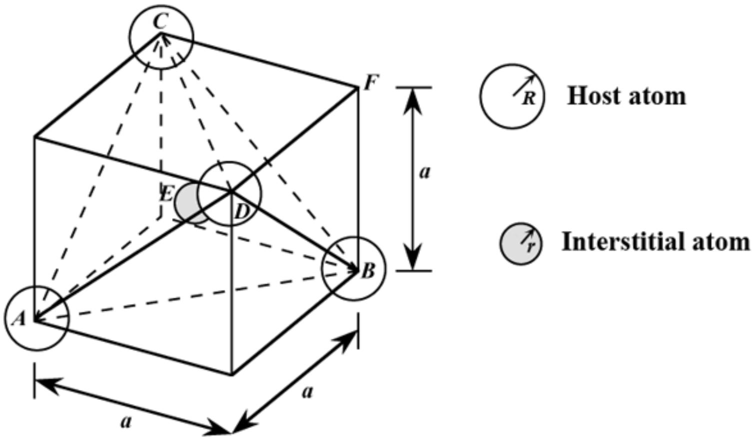
The diameter of an atom that will just fit into this site (2*r*) is just the difference between that unit cell edge length (*a*) and the radii of the two host atoms that are located on either side of the site (*R*); that is

$$2r = a - 2R$$

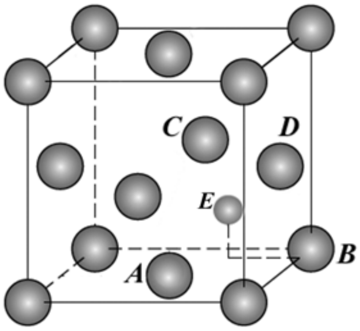
However, for FCC *a* is related to *R* according to Equation 3.1 as $a = 2R\sqrt{2}$; therefore, solving for *r* from the above equation gives

$$r = \frac{a - 2R}{2} = \frac{2R\sqrt{2} - 2R}{2} = 0.414R$$

(b) Drawing (*a*) below shows one quadrant of an FCC unit cell, which is a cube; corners of the tetrahedron correspond to atoms that are labeled *A*, *B*, *C*, and *D*. These corresponding atom positions are noted in the FCC unit cell in drawing (*b*). In both of these drawings, atoms have been reduced from their normal sizes for clarity. The interstitial atom resides at the center of the tetrahedron, which is designated as point *E*, in both (*a*) and (*b*).



(*a*)



(*b*)

Let us now express the host and interstitial atom radii in terms of the cube edge length, designated as *a*. From Figure (*a*), the spheres located at positions *A* and *B* touch each other along the bottom face diagonal. Thus,

$$\overline{AB} = 2R$$

But

$$(\overline{AB})^2 = a^2 + a^2 = 2a^2$$

or

$$\overline{AB} = a\sqrt{2} = 2R$$

And

$$a = \frac{2R}{\sqrt{2}}$$

There will also be an anion located at the corner, point *F* (not drawn), and the cube diagonal $\overline{AEF}$ will be related to the atomic radii as

$$\overline{AEF} = 2(r + R)$$

(The line *AEF* has not been drawn to avoid confusion.) From the triangle *ABF*

$$(\overline{AB})^2 + (\overline{FB})^2 = (\overline{AEF})^2 \qquad \text{(P4.8a)}$$

But,

$$\overline{FB} = a = \frac{2R}{\sqrt{2}}$$

and

$$\overline{AB} = 2R$$

from above. Substitution of the parameters involving *r* and *R* noted above into Equation P4.8a leads to the following:

$$(2R)^2 + \left(\frac{2R}{\sqrt{2}}\right)^2 = \left[2(r + R)\right]^2$$

Solving for *r* leads to

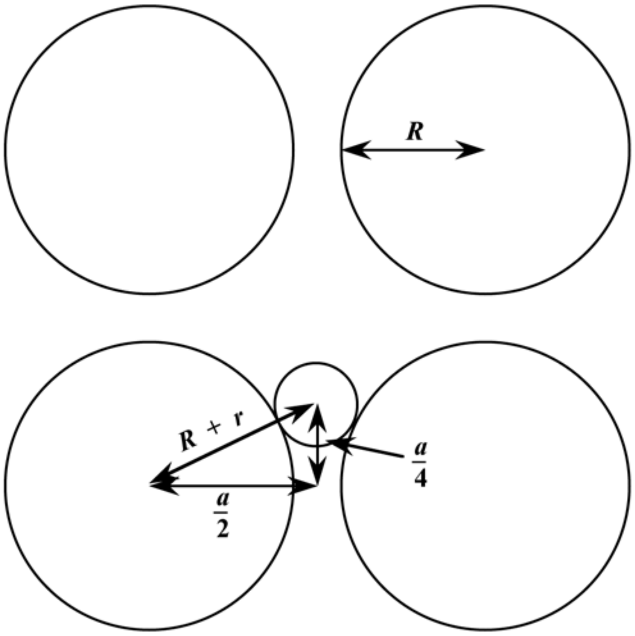
$$r = R\left(\frac{\sqrt{6} - 2}{2}\right) = 0.225R$$

4.9 *Compute the radius r of an impurity atom that will just fit into a BCC tetrahedral site in terms of the atomic radius R of the host atom (without introducing lattice strains).*

(Note: You may want to consult Figure 4.3b.)

Solution

A (100) face of a BCC unit cell is shown below.



The interstitial atom that just fits into this interstitial site is shown by the small circle. It is situated in the plane of this (100) face, midway between the two vertical unit cell edges, and one quarter of the distance between the bottom and top cell edges. From the right triangle` defined by the three arrows we may write

$$\left(\frac{a}{2}\right)^2 + \left(\frac{a}{4}\right)^2 = (R + r)^2$$

However, from Equation 3.4, $a = \frac{4R}{\sqrt{3}}$, and, therefore, making this substitution, the above equation takes the form

$$\left(\frac{4R}{2\sqrt{3}}\right)^2 + \left(\frac{4R}{4\sqrt{3}}\right)^2 = R^2 + 2Rr + r^2$$

After rearrangement the following quadratic equation results in:

$$r^2 + 2Rr - 0.667R^2 = 0$$

And upon solving for *r:*

$$r = \frac{-(2R) \pm \sqrt{(2R)^2 - (4)(1)(-0.667R^2)}}{2}$$

$$= \frac{-2R \pm 2.582R}{2}$$

And, finally

$$r(+) = \frac{-2R + 2.582R}{2} = 0.291R$$
$$r(-) = \frac{-2R - 2.582R}{2} = -2.291R$$

Of course, only the *r*(+) root is possible, and, therefore, *r* = 0.291*R*.

4.10 *(a) Using the result of Problem 4.8(a), compute the radius of an octahedral interstitial site in FCC iron.*

(b) On the basis of this result and the answer to Problem 4.9, explain why a higher concentration of carbon will dissolve in FCC iron than in iron that has a BCC crystal structure.

Solution

(a) From Problem 4.8(a), the radius of an octahedral interstitial site, r, is related to the atomic radius of the host material according to $r = 0.414R$. The atomic radius of an iron atom is 0.124 nm; therefore, the radius of this octahedral site in iron is

$$r_{\mathrm{Fe(Oct)}} = 0.414R_{\mathrm{Fe}} = (0.414)(0.124\ \mathrm{nm}) = 0.051\ \mathrm{nm}$$

(b) Carbon atoms are situated in octahedral sites in FCC iron, and, for BCC iron, in tetrahedral sites. The relationship between r and R for BCC iron, as determined in problem 4.9 is $r = 0.291R$. Therefore, in BCC iron, the radius of the tetrahedral site is

$$r_{\mathrm{Fe(Tet)}} = 0.291R_{\mathrm{Fe}} = (0.291)(0.124\ \mathrm{nm}) = 0.036\ \mathrm{nm}$$

Because the radius of the octahedral site in FCC iron (0.051 nm) is greater the radius of the tetrahedral site in BCC iron (0.036 nm), a higher concentration of carbon will dissolve in FCC.

4.11 *(a) For BCC iron, compute the radius of a tetrahedral interstitial site. (See the result of Problem 4.9.)*

(b) Lattice strains are imposed on iron atoms surrounding this site when carbon atoms occupy it. Compute the approximate magnitude of this strain by taking the difference between the carbon atom radius and the site radius and then dividing this difference by the site radius.

Solution

(a) The relationship between r and R for BCC iron, as determined in problem 4.9 is $r = 0.291R$. Therefore, in BCC iron, the radius of the tetrahedral site is

$$r_{\mathrm{Fe(Tet)}} = 0.291R_{\mathrm{Fe}} = (0.291)(0.124 \text{ nm}) = 0.036 \text{ nm}$$

(b) The radius of a carbon atom (r_C) is 0.071 nm (as taken from the inside cover of the book). The lattice strain introduced by a carbon atom the is situated on a BCC tetrahedral site is determined as follows:

$$\text{Lattice strain} = \frac{r_\mathrm{C} - r_{\mathrm{Fe(Tet)}}}{r_{\mathrm{Fe(Tet)}}} = \frac{0.071 \text{ nm} - 0.036 \text{ nm}}{0.036 \text{ nm}} = 0.97$$

Specification of Composition

4.12 *Derive the following equations:*

(a) Equation 4.7a

(b) Equation 4.9a

(c) Equation 4.10a

(d) Equation 4.11b

Solution

(a) This problem asks that we derive Equation 4.7a. To begin, C_1 is defined according to Equation 4.3a as

$$C_1 = \frac{m_1}{m_1 + m_2} \times 100$$

or, equivalently

$$C_1 = \frac{m'_1}{m'_1 + m'_2} \times 100$$

where the primed *m*'s indicate masses in grams. From Equation 4.4 we may write

$$m'_1 = n_{m1} A_1$$

$$m'_2 = n_{m2} A_2$$

And, substitution into the C_1 expression above

$$C_1 = \frac{n_{m1} A_1}{n_{m1} A_1 + n_{m2} A_2} \times 100$$

From Equation 4.5a it is the case that

$$n_{m1} = \frac{C'_1 (n_{m1} + n_{m2})}{100}$$

$$n_{m2} = \frac{C'_2 (n_{m1} + n_{m2})}{100}$$

And substitution of these expressions into the above equation (for C_1) leads to

$$C_1 = \frac{C_1' A_1}{C_1' A_1 + C_2' A_2} \times 100$$

which is just Equation 4.7a.

(b) This part of the problem asks that we derive Equation 4.9a. To begin, C_1'' is defined as the mass of component 1 per unit volume of alloy, or

$$C_1'' = \frac{m_1}{V}$$

If we assume that the total alloy volume V is equal to the sum of the volumes of the two constituents--i.e., $V = V_1 + V_2$—then

$$C_1'' = \frac{m_1}{V_1 + V_2}$$

Furthermore, the volume of each constituent is related to its density and mass as

$$V_1 = \frac{m_1}{\rho_1}$$

$$V_2 = \frac{m_2}{\rho_2}$$

This leads to

$$C_1'' = \frac{m_1}{\dfrac{m_1}{\rho_1} + \dfrac{m_2}{\rho_2}}$$

From Equation 4.3a, m_1 and m_2 may be expressed as follows:

$$m_1 = \frac{C_1 (m_1 + m_2)}{100}$$

$$m_2 = \frac{C_2 (m_1 + m_2)}{100}$$

Substitution of these equations into the preceding expression (for C_1'') yields

$$C_1'' = \frac{\dfrac{C_1(m_1+m_2)}{100}}{\dfrac{\dfrac{C_1(m_1+m_2)}{100}}{\rho_1} + \dfrac{\dfrac{C_2(m_1+m_2)}{100}}{\rho_2}}$$

$$= \frac{C_1}{\dfrac{C_1}{\rho_1} + \dfrac{C_2}{\rho_2}}$$

If the densities ρ_1 and ρ_2 are given in units of g/cm^3, then conversion to units of kg/m^3 requires that we multiply this equation by 10^3, inasmuch as

$$1 \text{ g/cm}^3 = 10^3 \text{ kg/m}^3$$

Therefore, the previous equation takes the form

$$C_1'' = \frac{C_1}{\dfrac{C_1}{\rho_1} + \dfrac{C_2}{\rho_2}} \times 10^3$$

the desired expression.

(c) Now we are asked to derive Equation 4.10a. The density of an alloy ρ_{ave} is just the total alloy mass M divided by its volume V

$$\rho_{\text{ave}} = \frac{M}{V}$$

Or, in terms of the component elements 1 and 2

$$\rho_{\text{ave}} = \frac{m_1 + m_2}{V_1 + V_2}$$

[*Note:* Here it is assumed that the total alloy volume is equal to the separate volumes of the individual components, which is only an approximation; normally V will not be exactly equal to $(V_1 + V_2)$].

Each of V_1 and V_2 may be expressed in terms of its mass and density as,

$$V_1 = \frac{m_1}{\rho_1}$$

$$V_2 = \frac{m_2}{\rho_2}$$

When these expressions are substituted into the above equation (for ρ_{ave}), we get

$$\rho_{\text{ave}} = \frac{m_1 + m_2}{\dfrac{m_1}{\rho_1} + \dfrac{m_2}{\rho_2}}$$

Furthermore, from Equation 4.3a

$$m_1 = \frac{C_1(m_1 + m_2)}{100}$$

$$m_2 = \frac{C_2(m_1 + m_2)}{100}$$

Which, when substituted into the above ρ_{ave} expression yields

$$\rho_{\text{ave}} = \frac{m_1 + m_2}{\dfrac{\dfrac{C_1(m_1 + m_2)}{100}}{\rho_1} + \dfrac{\dfrac{C_2(m_1 + m_2)}{100}}{\rho_2}}$$

And, finally, this equation reduces to

$$\rho_{\text{ave}} = \frac{100}{\dfrac{C_1}{\rho_1} + \dfrac{C_2}{\rho_2}}$$

(d) And, finally, the derivation of Equation 4.11b for A_{ave} is requested. The alloy average molecular weight is just the ratio of total alloy mass in grams M' and the total number of moles in the alloy N_m. That is

$$A_{\text{ave}} = \frac{M'}{N_m} = \frac{m_1' + m_2'}{n_{m1} + n_{m2}}$$

But using Equation 4.4 we may write

$$m_1' = n_{m1} A_1$$

$$m_2' = n_{m2} A_2$$

Which, when substituted into the above A_{ave} expression yields

$$A_{\text{ave}} = \frac{M'}{N_m} = \frac{n_{m1} A_1 + n_{m2} A_2}{n_{m1} + n_{m2}}$$

Furthermore, from Equation 4.5a

$$n_{m1} = \frac{C_1' (n_{m1} + n_{m2})}{100}$$

$$n_{m2} = \frac{C_2' (n_{m1} + n_{m2})}{100}$$

Thus, substitution of these expressions into the above equation for A_{ave} yields

$$A_{\text{ave}} = \frac{\dfrac{C_1' A_1 (n_{m1} + n_{m2})}{100} + \dfrac{C_2' A_2 (n_{m1} + n_{m2})}{100}}{n_{m1} + n_{m2}}$$

$$= \frac{C_1' A_1 + C_2' A_2}{100}$$

which is the desired result.

4.13 *What is the composition, in atom percent, of an alloy that consists of 92.5 wt% Ag and 7.5 wt% Cu?*

Solution

In order to compute composition, in atom percent, of a 92.5 wt% Ag-7.5 wt% Cu alloy, we employ Equation 4.6 given the atomic weights of silver and copper (found on the inside of the book's cover):

A_{Ag} = 107.87 g/mol

A_{Cu} = 63.55 g/mol

These compositions in atom percent are determined as follows:

$$C'_{\mathrm{Ag}} = \frac{C_{\mathrm{Ag}} A_{\mathrm{Cu}}}{C_{\mathrm{Ag}} A_{\mathrm{Cu}} + C_{\mathrm{Cu}} A_{\mathrm{Ag}}} \times 100$$

$$= \frac{(92.5)(63.55 \text{ g/mol})}{(92.5)(63.55 \text{ g/mol}) + (7.5)(107.87 \text{ g/mol})} \times 100$$

= 87.9 at%

$$C'_{\mathrm{Cu}} = \frac{C_{\mathrm{Cu}} A_{\mathrm{Ag}}}{C_{\mathrm{Ag}} A_{\mathrm{Cu}} + C_{\mathrm{Cu}} A_{\mathrm{Ag}}} \times 100$$

$$= \frac{(7.5)(107.87 \text{ g/mol})}{(92.5)(63.55 \text{ g/mol}) + (7.5)(107.87 \text{ g/mol})} \times 100$$

= 12.1 at%

4.14 *What is the composition, in atom percent, of an alloy that consists of 5.5 wt% Pb and 94.5 wt% Sn?*

Solution

In order to compute composition, in atom percent, of a 5.5 wt% Pb-94.5 wt% Sn alloy, we employ Equation 4.6 given the atomic weights of lead and tin (found on the inside of the book's cover):

A_{Pb} = 207.2 g/mol

A_{Sn} = 118.71 g/mol

These compositions in atom percent are determined as follows:

$$C'_{\mathrm{Pb}} = \frac{C_{\mathrm{Pb}}A_{\mathrm{Sn}}}{C_{\mathrm{Pb}}A_{\mathrm{Sn}} + C_{\mathrm{Sn}}A_{\mathrm{Pb}}} \times 100$$

$$= \frac{(5.5)(118.71\ \mathrm{g/mol})}{(5.5)(118.71\ \mathrm{g/mol}) + (94.5)(207.2\ \mathrm{g/mol})} \times 100$$

= 3.23 at%

$$C'_{\mathrm{Sn}} = \frac{C_{\mathrm{Sn}}A_{\mathrm{Pb}}}{C_{\mathrm{Pb}}A_{\mathrm{Sn}} + C_{\mathrm{Sn}}A_{\mathrm{Pb}}} \times 100$$

$$= \frac{(94.5)(207.2\ \mathrm{g/mol})}{(5.5)(118.71\ \mathrm{g/mol}) + (94.5)(207.2\ \mathrm{g/mol})} \times 100$$

= 96.77 at%

4.15 *What is the composition, in weight percent, of an alloy that consists of 5 at% Cu and 95 at% Pt?*

Solution

In order to compute composition, in weight percent, of a 5 at% Cu-95 at% Pt alloy, we employ Equation 4.7 given the atomic weights of copper and platinum (found on the inside of the book's cover):

A_{Cu} = 63.55 g/mol

A_{Pt} = 195.08 g/mol

These compositions in weight percent are determined as follows:

$$C_{\text{Cu}} = \frac{C'_{\text{Cu}} A_{\text{Cu}}}{C'_{\text{Cu}} A_{\text{Cu}} + C'_{\text{Pt}} A_{\text{Pt}}} \times 100$$

$$= \frac{(5)(63.55 \text{ g/mol})}{(5)(63.55 \text{ g/mol}) + (95)(195.08 \text{ g/mol})} \times 100$$

$$= 1.68 \text{ wt\%}$$

$$C_{\text{Pt}} = \frac{C'_{\text{Pt}} A_{\text{Pt}}}{C'_{\text{Cu}} A_{\text{Cu}} + C'_{\text{Pt}} A_{\text{Pt}}} \times 100$$

$$= \frac{(95)(195.08 \text{ g/mol})}{(5)(63.55 \text{ g/mol}) + (95)(195.08 \text{ g/mol})} \times 100$$

$$= 98.32 \text{ wt\%}$$

4.16 *Calculate the composition, in weight percent, of an alloy that contains 105 kg of iron, 0.2 kg of carbon, and 1.0 kg of chromium.*

Solution

The concentration, in weight percent, of an element in an alloy may be computed using Equation 4.3b. For this alloy, the concentration of iron (C_{Fe}) is just

$$C_{\mathrm{Fe}} = \frac{m_{\mathrm{Fe}}}{m_{\mathrm{Fe}} + m_{\mathrm{C}} + m_{\mathrm{Cr}}} \times 100$$

$$= \frac{105\ \mathrm{kg}}{105\ \mathrm{kg} + 0.2\ \mathrm{kg} + 1.0\ \mathrm{kg}} \times 100 = 98.87\ \mathrm{wt\%}$$

Similarly, for carbon

$$C_{\mathrm{C}} = \frac{0.2\ \mathrm{kg}}{105\ \mathrm{kg} + 0.2\ \mathrm{kg} + 1.0\ \mathrm{kg}} \times 100 = 0.19\ \mathrm{wt\%}$$

And for chromium

$$C_{\mathrm{Cr}} = \frac{1.0\ \mathrm{kg}}{105\ \mathrm{kg} + 0.2\ \mathrm{kg} + 1.0\ \mathrm{kg}} \times 100 = 0.94\ \mathrm{wt\%}$$

4.17 *What is the composition, in atom percent, of an alloy that contains 33 g of copper and 47 g of zinc?*

Solution

The concentration of an element in an alloy, in atom percent, may be computed using Equation 4.5a. However, it first becomes necessary to compute the number of moles of both Cu and Zn, using Equation 4.4. Atomic weights of copper and zinc (found on the inside of the book's cover) are as follows:

A_{Cu} = 63.55 g/mol

A_{Zn} = 65.41 g/mol

Thus, the number of moles of Cu is just

$$n_{m_{\text{Cu}}} = \frac{m'_{\text{Cu}}}{A_{\text{Cu}}} = \frac{33\text{ g}}{63.55\text{ g/mol}} = 0.519\text{ mol}$$

Likewise, for Zn

$$n_{m_{\text{Zn}}} = \frac{47\text{ g}}{65.41\text{ g/mol}} = 0.719\text{ mol}$$

Now, use of Equation 4.5a yields

$$C'_{\text{Cu}} = \frac{n_{m_{\text{Cu}}}}{n_{m_{\text{Cu}}} + n_{m_{\text{Zn}}}} \times 100$$

$$= \frac{0.519\text{ mol}}{0.519\text{ mol} + 0.719\text{ mol}} \times 100 = 41.9\text{ at\%}$$

Also,

$$C'_{\text{Zn}} = \frac{0.719\text{ mol}}{0.519\text{ mol} + 0.719\text{ mol}} \times 100 = 58.1\text{ at\%}$$

4.18 *What is the composition, in atom percent, of an alloy that contains 44.5 lb$_m$ of Ag, 83.7 lb$_m$ of Au, and 5.3 lb$_m$ of Cu?*

Solution

In this problem we are asked to determine the concentrations, in atom percent, of the Ag-Au-Cu alloy. It is first necessary to convert the amounts of Ag, Au, and Cu into grams.

$$m'_{\mathrm{Ag}} = (44.5\ \mathrm{lb_m})(453.6\ \mathrm{g/lb_m}) = 20{,}185\ \mathrm{g}$$

$$m'_{\mathrm{Au}} = (83.7\ \mathrm{lb_m})(453.6\ \mathrm{g/lb_m}) = 37{,}966\ \mathrm{g}$$

$$m'_{\mathrm{Cu}} = (5.3\ \mathrm{lb_m})(453.6\ \mathrm{g/lb_m}) = 2{,}404\ \mathrm{g}$$

These masses must next be converted into moles (Equation 4.4), as

$$n_{m_{\mathrm{Ag}}} = \frac{m'_{\mathrm{Ag}}}{A_{\mathrm{Ag}}} = \frac{20{,}185\ \mathrm{g}}{107.87\ \mathrm{g/mol}} = 187.1\ \mathrm{mol}$$

$$n_{m_{\mathrm{Au}}} = \frac{37{,}966\ \mathrm{g}}{196.97\ \mathrm{g/mol}} = 192.8\ \mathrm{mol}$$

$$n_{m_{\mathrm{Cu}}} = \frac{2{,}404\ \mathrm{g}}{63.55\ \mathrm{g/mol}} = 37.8\ \mathrm{mol}$$

Now, employment of Equation 4.5b, gives

$$C'_{\mathrm{Ag}} = \frac{n_{m_{\mathrm{Ag}}}}{n_{m_{\mathrm{Ag}}} + n_{m_{\mathrm{Au}}} + n_{m_{\mathrm{Cu}}}} \times 100$$

$$= \frac{187.1\ \mathrm{mol}}{187.1\ \mathrm{mol} + 192.8\ \mathrm{mol} + 37.8\ \mathrm{mol}} \times 100 = 44.8\ \mathrm{at\%}$$

$$C'_{\mathrm{Au}} = \frac{192.8\ \mathrm{mol}}{187.1\ \mathrm{mol} + 192.8\ \mathrm{mol} + 37.8\ \mathrm{mol}} \times 100 = 46.2\ \mathrm{at\%}$$

$$C'_{\mathrm{Cu}} = \frac{37.8\ \mathrm{mol}}{187.1\ \mathrm{mol} + 192.8\ \mathrm{mol} + 37.8\ \mathrm{mol}} \times 100 = 9.0\ \mathrm{at\%}$$

4.19 *Convert the atom percent composition in Problem 4.18 to weight percent.*

Solution

This problem calls for a conversion of composition in atom percent to composition in weight percent. The composition in atom percent for Problem 4.18 is 44.8 at% Ag, 46.2 at% Au, and 9.0 at% Cu. Modification of Equation 4.7 to take into account a three-component alloy leads to the following

$$C_{\text{Ag}} = \frac{C'_{\text{Ag}} A_{\text{Ag}}}{C'_{\text{Ag}} A_{\text{Ag}} + C'_{\text{Au}} A_{\text{Au}} + C'_{\text{Cu}} A_{\text{Cu}}} \times 100$$

$$= \frac{(44.8)(107.87 \text{ g/mol})}{(44.8)(107.87 \text{ g/mol}) + (46.2)(196.97 \text{ g/mol}) + (9.0)(63.55 \text{ g/mol})} \times 100$$

= 33.3 wt%

$$C_{\text{Au}} = \frac{C'_{\text{Au}} A_{\text{Au}}}{C'_{\text{Ag}} A_{\text{Ag}} + C'_{\text{Au}} A_{\text{Au}} + C'_{\text{Cu}} A_{\text{Cu}}} \times 100$$

$$= \frac{(46.2)(196.97 \text{ g/mol})}{(44.8)(107.87 \text{ g/mol}) + (46.2)(196.97 \text{ g/mol}) + (9.0)(63.55 \text{ g/mol})} \times 100$$

= 62.7 wt%

$$C_{\text{Cu}} = \frac{C'_{\text{Cu}} A_{\text{Cu}}}{C'_{\text{Ag}} A_{\text{Ag}} + C'_{\text{Au}} A_{\text{Au}} + C'_{\text{Cu}} A_{\text{Cu}}} \times 100$$

$$= \frac{(9.0)(63.55 \text{ g/mol})}{(44.8)(107.87 \text{ g/mol}) + (46.2)(196.97 \text{ g/mol}) + (9.0)(63.55 \text{ g/mol})} \times 100$$

= 4.0 wt%

4.20 *Calculate the number of atoms per cubic meter in Pb.*

Solution

This problem calls for a determination of the number of atoms per cubic meter for lead. In order to solve this problem, one must employ Equation 4.2,

$$N = \frac{N_A \rho_{Pb}}{A_{Pb}}$$

The density of Pb (from the table inside of the front cover) is 11.35 g/cm^3, while its atomic weight is 207.2 g/mol. Thus,

$$N = \frac{(6.022 \times 10^{23} \text{ atoms/mol})(11.35 \text{ g/cm}^3)}{207.2 \text{ g/mol}}$$

$$= 3.30 \times 10^{22} \text{ atoms/cm}^3 = 3.30 \times 10^{28} \text{ atoms/m}^3$$

4.21 *Calculate the number of atoms per cubic meter in Cr.*

Solution

This problem calls for a determination of the number of atoms per cubic meter for chromium. In order to solve this problem, one must employ Equation 4.2,

$$N = \frac{N_A \rho_{Cr}}{A_{Cr}}$$

The density of Cr (from the table inside of the front cover) is 7.19 g/cm^3, while its atomic weight is 52.00 g/mol. Thus,

$$N = \frac{(6.022 \times 10^{23} \text{ atoms/mol})(7.19 \text{ g/cm}^3)}{52.00 \text{ g/mol}}$$

$$= 8.33 \times 10^{22} \text{ atoms/cm}^3 = 8.33 \times 10^{28} \text{ atoms/m}^3$$

4.22 *The concentration of Si in an Fe-Si alloy is 0.25 wt%. What is the concentration in kilograms of Si per cubic meter of alloy?*

Solution

In order to compute the concentration in kg/m^3 of Si in a 0.25 wt% Si-99.75 wt% Fe alloy we must employ Equation 4.9 as

$$C''_{\mathrm{Si}} = \frac{C_{\mathrm{Si}}}{\dfrac{C_{\mathrm{Si}}}{\rho_{\mathrm{Si}}} + \dfrac{C_{\mathrm{Fe}}}{\rho_{\mathrm{Fe}}}} \times 10^3$$

From inside the front cover, densities for silicon and iron are 2.33 and 7.87 g/cm^3, respectively; therefore

$$C''_{\mathrm{Si}} = \frac{0.25}{\dfrac{0.25}{2.33\ \mathrm{g/cm^3}} + \dfrac{99.75}{7.87\ \mathrm{g/cm^3}}} \times 10^3$$

$$= 19.6\ \mathrm{kg/m^3}$$

4.23 *The concentration of phosphorus in silicon is* 1.0×10^{-7} *at%. What is the concentration in kilograms of phosphorus per cubic meter?*

Solution

Strategy for solving:

Step 1: Convert the concentration of P from at% to wt% using Equation 4.7a

Step 2: Compute the concentration of kilograms per cubic meter using Equation 4.9a

Step 1: From Equation 4.7a, the concentration of P in weight percent is determined as follows:

$$C_P = \frac{C'_P A_P}{C'_P A_P + C'_{Si} A_{Si}} \times 100$$

where

$C'_{Fe} = 1.0 \times 10^{-7}$ at%

$C'_{Si} = 100.00$ at% – 1.0×10^{-7} at% = 99.9999999 at%

$A_P = 30.97$ g/mol (from inside front cover)

$A_{Si} = 28.09$ g/mol (from inside front cover)

Now, solve for C_P using the above equation

$$C_P = \frac{(1.0 \times 10^{-7} \text{ at\%})(30.97 \text{ g/mol})}{(1.0 \times 10^{-7} \text{ at\%})(30.97 \text{ g/mol}) + (99.9999999 \text{ at\%})(28.09 \text{ g.mol})} \times 100$$

$$= 1.103 \times 10^{-7} \text{ wt\%}$$

Step 2

We now compute the number of kilograms per meter cubed (Equation 4.9a) with

$\rho_{Si} = 2.33$ g/cm^3 (from inside front cover)

$\rho_P = 1.82$ g/cm^3 (from inside front cover)

$C_{Si} = 100.00$ wt% – 1.103×10^{-7} wt% = 99.999999890

Therefore

$$C''_P = \left(\frac{C_P}{\dfrac{C_P}{\rho_P} + \dfrac{C_{Si}}{\rho_{Si}}} \right) \times 10^3$$

$$= \left(\frac{1.103 \times 10^{-7}\ \text{wt\%}}{\dfrac{1.103 \times 10^{-7}\ \text{wt\%}}{1.82\ \text{g/cm}^3} + \dfrac{99.999999890\ \text{wt\%}}{2.33\ \text{g/cm}^3}} \right) \times 10^3$$

$$2.57 \times 10^{-6}\ \text{kg/m}^3$$

4.24 *Determine the approximate density of a Ti-6Al-4V titanium (Ti) alloy that has a composition of 90 wt% Ti, 6 wt% Al, and 4 wt% V.*

Solution

In order to solve this problem, Equation 4.10a is modified to take the following form:

$$\rho_{\text{ave}} = \frac{100}{\dfrac{C_{\text{Ti}}}{\rho_{\text{Ti}}} + \dfrac{C_{\text{Al}}}{\rho_{\text{Al}}} + \dfrac{C_{\text{V}}}{\rho_{\text{V}}}}$$

And, using the density values for Ti, Al, and V—i.e., 4.51 g/cm^3, 2.71 g/cm^3, and 6.10 g/cm^3—(as taken from inside the front cover of the text), the density is computed as follows:

$$\rho_{\text{ave}} = \frac{100}{\dfrac{90 \text{ wt\%}}{4.51 \text{ g/cm}^3} + \dfrac{6 \text{ wt\%}}{2.71 \text{ g/cm}^3} + \dfrac{4 \text{ wt\%}}{6.10 \text{ g/cm}^3}}$$

$$= 4.38 \text{ g/cm}^3$$

4.25 *Calculate the unit cell edge length for an 80 wt% Ag–20 wt% Pd alloy. All of the palladium is in solid solution, the crystal structure for this alloy is FCC, and the room-temperature density of Pd is 12.02 g/cm^3.*

Solution

In order to solve this problem it is necessary to employ Equation 3.8; in this expression density and atomic weight will be averages for the alloy—that is

$$\rho_{\text{ave}} = \frac{nA_{\text{ave}}}{V_C N_{\text{A}}}$$

Inasmuch as the unit cell is cubic, then $V_C = a^3$, then

$$\rho_{\text{ave}} = \frac{nA_{\text{ave}}}{a^3 N_{\text{A}}}$$

And solving this equation for the unit cell edge length, leads to

$$a = \left(\frac{nA_{\text{ave}}}{\rho_{\text{ave}} N_{\text{A}}}\right)^{1/3}$$

Expressions for A_{ave} and ρ_{ave} are found in Equations 4.11a and 4.10a, respectively, which, when incorporated into the above expression yields

$$a = \left[\frac{n\left(\dfrac{100}{\dfrac{C_{\text{Ag}}}{A_{\text{Ag}}} + \dfrac{C_{\text{Pd}}}{A_{\text{Pd}}}}\right)}{\left(\dfrac{100}{\dfrac{C_{\text{Ag}}}{\rho_{\text{Ag}}} + \dfrac{C_{\text{Pd}}}{\rho_{\text{Pd}}}}\right) N_{\text{A}}}\right]^{1/3}$$

Since the crystal structure is FCC, the value of n in the above expression is 4 atoms per unit cell. The atomic weights for Ag and Pd are 107.87 and 106.4 g/mol, respectively (Figure 2.8), whereas the densities for the Ag and Pd are 10.49 g/cm^3 (inside front cover) and 12.02 g/cm^3. Substitution of these, as well as the concentration values stipulated in the problem statement, into the above equation gives

$$a = \left[\frac{(4 \text{ atoms/unit cell}) \left(\dfrac{100}{\dfrac{80 \text{ wt\%}}{107.87 \text{ g/mol}} + \dfrac{20 \text{ wt\%}}{106.4 \text{ g/mol}}} \right)}{\left(\dfrac{100}{\dfrac{80 \text{ wt\%}}{10.49 \text{ g/cm}^3} + \dfrac{20 \text{ wt\%}}{12.02 \text{ g/cm}^3}} \right) \left(6.022 \times 10^{23} \text{ atoms/mol} \right)} \right]^{1/3}$$

$$= 4.050 \times 10^{-8} \text{ cm} = 0.4050 \text{ nm}$$

4.26 *Some hypothetical alloy is composed of 25 wt% of metal A and 75 wt% of metal B. If the densities of metals A and B are 6.17 and 8.00 g/cm*^{3}*, respectively, and their respective atomic weights are 171.3 and 162.0 g/mol, determine whether the crystal structure for this alloy is simple cubic, face-centered cubic, or body-centered cubic. Assume a unit cell edge length of 0.332 nm.*

Solution

In order to solve this problem it is necessary to employ Equation 3.8; in this expression density and atomic weight will be averages for the alloy—that is

$$\rho_{\text{ave}} = \frac{nA_{\text{ave}}}{V_C N_{\text{A}}}$$

Inasmuch as for each of the possible crystal structures, the unit cell is cubic, then $V_C = a^3$, or

$$\rho_{\text{ave}} = \frac{nA_{\text{ave}}}{a^3 N_{\text{A}}}$$

Now, in order to determine the crystal structure it is necessary to solve for n, the number of atoms per unit cell. For $n = 1$, the crystal structure is simple cubic, whereas for n values of 2 and 4, the crystal structure will be either BCC or FCC, respectively. When we solve the above expression for n the result is as follows:

$$n = \frac{\rho_{\text{ave}} a^3 N_{\text{A}}}{A_{\text{ave}}}$$

Expressions for A_{ave} and ρ_{ave} are found in Equations 4.11a and 4.10a, respectively, which, when incorporated into the above expression yields

$$n = \frac{\left(\dfrac{100}{\dfrac{C_{\text{A}}}{\rho_{\text{A}}} + \dfrac{C_{\text{B}}}{\rho_{\text{B}}}}\right) a^3 N_{\text{A}}}{\left(\dfrac{100}{\dfrac{C_{\text{A}}}{A_{\text{A}}} + \dfrac{C_{\text{B}}}{A_{\text{B}}}}\right)}$$

Substitution of the concentration values (i.e., C_{A} = 25 wt% and C_{B} = 75 wt%) as well as values for the other parameters given in the problem statement, into the above equation gives

$$n = \frac{\left(\dfrac{100}{\dfrac{25\text{ wt\%}}{6.17\text{ g/cm}^3} + \dfrac{75\text{ wt\%}}{8.00\text{ g/cm}^3}}\right)(3.32 \times 10^{-8}\text{ nm})^3(6.022 \times 10^{23}\text{ atoms/mol})}{\left(\dfrac{100}{\dfrac{25\text{ wt\%}}{171.3\text{ g/mol}} + \dfrac{75\text{ wt\%}}{162.0\text{ g/mol}}}\right)}$$

$$= 1.00\text{ atom/unit cell}$$

Therefore, on the basis of this value, the crystal structure is *simple cubic*.

4.27 *For a solid solution consisting of two elements (designated as 1 and 2), sometimes it is desirable to determine the number of atoms per cubic centimeter of one element in a solid solution,* N_1*, given the concentration of that element specified in weight percent,* C_1*. This computation is possible using the following expression:*

$$N_1 = \frac{N_A C_1}{\dfrac{C_1 A_1}{\rho_1} + \dfrac{A_1}{\rho_2}(100 - C_1)} \tag{4.21}$$

where N_A *is Avogadro's number,* ρ_1 *and* ρ_2 *are the densities of the two elements, and* A_1 *is the atomic weight of element 1.*

Derive Equation 4.21 using Equation 4.2 and expressions contained in Section 4.4.

Solution

This problem asks that we derive Equation 4.21, using other equations given in the chapter. The concentration of component 1 in atom percent (C_1') is just 100 c_1' where c_1' is the atom fraction of component 1. Furthermore, c_1' is defined as $c_1' = N_1/N$ where N_1 and N are, respectively, the number of atoms of component 1 and total number of atoms per cubic centimeter. Thus, from the above discussion the following holds:

$$N_1 = \frac{C_1' N}{100}$$

Substitution into this expression of the appropriate form of N from Equation 4.2 yields

$$N_1 = \frac{C_1' N_A \rho_{\text{ave}}}{100 A_{\text{ave}}}$$

And, finally, substitution into this equation expressions for C_1' (Equation 4.6a), ρ_{ave} (Equation 4.10a), A_{ave} (Equation 4.11a), and realizing that $C_2 = (C_1 - 100)$, and after some algebraic manipulation we obtain the desired expression:

$$N_1 = \frac{N_A C_1}{\dfrac{C_1 A_1}{\rho_1} + \dfrac{A_1}{\rho_2}(100 - C_1)}$$

4.28 *Molybdenum (Mo) forms a substitutional solid solution with tungsten (W). Compute the number of molybdenum atoms per cubic centimeter for a molybdenum-tungsten alloy that contains 16.4 wt% Mo and 83.6 wt% W. The densities of pure molybdenum and tungsten are 10.22 and 19.30 g/cm^3, respectively.*

Solution

This problem asks us to determine the number of molybdenum atoms per cubic centimeter for a 16.4 wt% Mo-83.6 wt% W solid solution. To solve this problem, employment of Equation 4.21 is necessary, using the following values:

$C_1 = C_{\text{Mo}} = 16.4$ wt%
$\rho_1 = \rho_{\text{Mo}} = 10.22$ g/cm^3
$\rho_2 = \rho_{\text{W}} = 19.30$ g/cm^3
$A_1 = A_{\text{Mo}} = 95.94$ g/mol

Thus

$$N_{\text{Mo}} = \frac{N_A C_{\text{Mo}}}{\dfrac{C_{\text{Mo}} A_{\text{Mo}}}{\rho_{\text{Mo}}} + \dfrac{A_{\text{Mo}}}{\rho_{\text{W}}}\left(100 - C_{\text{Mo}}\right)}$$

$$= \frac{(6.022 \times 10^{23} \text{ atoms/mol})(16.4 \text{ wt\%})}{\dfrac{(16.4 \text{ wt\%})(95.94 \text{ g/mol})}{10.22 \text{ g/cm}^3} + \dfrac{95.94 \text{ g/mol}}{19.3 \text{ g/cm}^3}\left(100 - 16.4 \text{ wt\%}\right)}$$

$$= 1.73 \times 10^{22} \text{ atoms/cm}^3$$

4.29 *Niobium forms a substitutional solid solution with vanadium. Compute the number of niobium atoms per cubic centimeter for a niobium-vanadium alloy that contains 24 wt% Nb and 76 wt% V. The densities of pure niobium and vanadium are 8.57 and 6.10 g/cm^3, respectively.*

Solution

This problem asks us to determine the number of niobium atoms per cubic centimeter for a 24 wt% Nb-76 wt% V solid solution. To solve this problem, employment of Equation 4.21 is necessary, using the following values:

$C_1 = C_{\mathrm{Nb}}$ = 24 wt%
$\rho_1 = \rho_{\mathrm{Nb}}$ = 8.57 g/cm^3
$\rho_2 = \rho_{\mathrm{V}}$ = 6.10 g/cm^3
$A_1 = A_{\mathrm{Nb}}$ = 92.91 g/mol

Thus

$$N_{\mathrm{Nb}} = \frac{N_{\mathrm{A}} C_{\mathrm{Nb}}}{\dfrac{C_{\mathrm{Nb}} A_{\mathrm{Nb}}}{\rho_{\mathrm{Nb}}} + \dfrac{A_{\mathrm{Nb}}}{\rho_{\mathrm{V}}}\left(100 - C_{\mathrm{Nb}}\right)}$$

$$= \frac{(6.022 \times 10^{23}\ \text{atoms/mol})(24\ \text{wt\%})}{\dfrac{(24\ \text{wt\%})(92.91\ \text{g/mol})}{8.57\ \text{g/cm}^3} + \dfrac{92.91\ \text{g/mol}}{6.10\ \text{g/cm}^3}(100 - 24\ \text{wt\%})}$$

$$= 1.02 \times 10^{22}\ \text{atoms/cm}^3$$

4.30 *Consider an iron-carbon alloy that contains 0.2 wt% C, in which all the carbon atoms reside in tetrahedral interstitial sites. Compute the fraction of these sites that are occupied by carbon atoms.*

Solution

The following strategy will be used to solve this problem:

Step 1: compute the number of Fe atoms per centimeter cubed using Equation 4.21

Step 2: compute the number of C atoms per centimeter cubed also using Equation 4.21

Step 3: compute the number of unit cells per centimeter cubed by dividing the number of Fe atoms per centimeter cubed (Step 1) by two since there are two Fe atoms per BCC unit cell

Step 4: compute the number of total interstitial sites per centimeter cubed by multiplying the number of tetrahedral interstitial sites by the number of unit cells per cubic centimeter (from Step 3)

Step 5: The fraction of tetrahedral sites occupied by carbon atoms is computed by dividing the number of carbon atoms per centimeter cubed (Step 3) by the total number of interstitial sites per cubic centimeter

The solution to this problem involves using the following values:

C_C = 0.2 wt%

C_{Fe} = 99.8 wt%

ρ_C = 2.25 g/cm^3

ρ_{Fe} = 7.87 g/cm^3

A_C = 12.01 g/mol

A_{Fe} = 55.85 g/mol

Step 1: We compute the number of Fe atoms per cubic centimeter using Equation 4.21 as:

$$N_{Fe} = \frac{N_A C_{Fe}}{\dfrac{C_{Fe} A_{Fe}}{\rho_{Fe}} + \dfrac{A_{Fe}}{\rho_C}(100 - C_{Fe})}$$

$$= \frac{(6.022 \times 10^{23} \text{ atoms/mol})(99.8 \text{ wt\% Fe})}{\dfrac{(99.8 \text{ wt\% Fe})(55.85 \text{ g/mol})}{7.87 \text{ g/cm}^3} + \dfrac{(55.85 \text{ g/mol})}{2.25 \text{ g/cm}^3}(100 \text{ wt\%} - 99.8 \text{ wt\%})}$$

$$8.43 \times 10^{22} \text{ Fe atoms/cm}^3$$

Step 2: We can compute the number of C atoms per cubic centimeter also using Equation 4.21 as follows:

$$N_{\mathrm{C}} = \frac{N_{\mathrm{A}} C_{\mathrm{C}}}{\dfrac{C_{\mathrm{C}} A_{\mathrm{C}}}{\rho_{\mathrm{C}}} + \dfrac{A_{\mathrm{C}}}{\rho_{\mathrm{Fe}}}(100 - C_{\mathrm{C}})}$$

$$= \frac{(6.022 \times 10^{23} \text{ atoms/cm}^3)(0.2 \text{ wt\%})}{\dfrac{(0.2 \text{ wt\%})(12.01 \text{ g/mol})}{2.25 \text{ g/cm}^3} + \dfrac{12.01 \text{ g/mol}}{7.87 \text{ g/cm}^3}(100 \text{ wt\%} - 0.2 \text{ wt\%})}$$

$$= 7.85 \times 10^{20} \text{ C atoms/cm}^3$$

Step 3: the number of unit cells per centimeter cubed is determined by dividing the number of Fe atoms per centimeter cubed (Step 1) by two since there are two Fe atoms per BCC unit cell—that is

$$\text{no. unit cells/cm}^3 = \frac{N_{\mathrm{Fe}}}{2}$$

$$= \frac{8.43 \times 10^{22} \text{ Fe atoms/cm}^3}{2} = 4.22 \times 10^{22}$$

Step 4: We compute the number of total interstitial sites per centimeter cubed by multiplying the number of tetrahedral interstitial sites per unit cell by the number of unit cells per cubic centimeter (from Step 3). From Figure 4.3*b*, there are 4 tetrahedral sites located on the front face plane of the unit cell—one site for each of the unit cell edges in this plane. Inasmuch as there are 6 faces on this unit cell there are 6 × 4 = 24 interstitial sites for this unit cell. However, each of these sites is shared by 2 unit cells, which means that only 12 sites belong to each unit cell. Therefore the number of tetrahedral sites per centimeter cubed corresponds to 12 times the number of unit cells per cubic centimeter (n_s)—that is

$$n_s = (12 \text{ sites/unit cell})(4.22 \times 10^{22} \text{ unit cells/cm}^3)$$

$$= 5.06 \times 10^{23} \text{ sites/cm}^3$$

Step 5: The fraction of tetrahedral sites occupied by carbon atoms is computed by dividing the number of carbon atoms per centimeter cubed (Step 3) by the total number of interstitial sites per cubic centimeter, that is

$$\text{fraction sites occupied} = \frac{N_{\mathrm{C}}}{n_s}$$

$$= \frac{7.85 \times 10^{20} \text{ C atoms/cm}^3}{5.06 \times 10^{23} \text{ sites/cm}^3} = 1.55 \times 10^{-3}$$

4.31 *For a BCC iron-carbon alloy that contains 0.1 wt% C, calculate the fraction of unit cells that contain carbon atoms.*

Solution

It is first necessary to compute the number of carbon atoms per cubic centimeter of alloy using Equation 4.21. For this problem

$A_1 = A_C$ = 12.011 g/mol (from inside the front cover)

$C_1 = C_C$ = 0.1 wt%

$\rho_1 = \rho_C$ = 2.25 g/cm^3 (from inside front cover)

$\rho_2 = \rho_{Fe}$ = 7.87 g/cm^3 (from inside front cover)

Now using from Equation 4.21

$$N_C = \frac{N_A C_C}{\dfrac{C_C A_C}{\rho_C} + \dfrac{A_C}{\rho_{Fe}}(100 - C_C)}$$

$$= \frac{(6.022 \times 10^{23} \text{ atoms/mol})(0.1 \text{ wt\%})}{\dfrac{(0.1 \text{ wt\%})(12.011 \text{ g/mol})}{2.25 \text{ g/cm}^3} + \dfrac{(12.011 \text{ g/mol})}{7.87 \text{ g/cm}^3}(100 - 0.1 \text{ wt\%})}$$

$$= 3.94 \times 10^{20} \text{ C atoms/cm}^3$$

We now perform the same calculation for iron atoms, where

$A_1 = A_{Fe}$ = 55.85 g/mol (from inside the front cover)

$C_1 = C_{Fe}$ = 100% – 0.1 wt% = 99.9 wt%

$\rho_1 = \rho_{Fe}$ = 7.87 g/cm^3 (from inside front cover)

$\rho_2 = \rho_C$ = 2.25 g/cm^3 (from inside front cover)

Therefore,

$$= \frac{(6.022 \times 10^{23} \text{ atoms/mol})(99.9 \text{ wt\%})}{\dfrac{(99.9 \text{ wt\%})(55.85 \text{ g/mol})}{7.87 \text{ g/cm}^3} + \dfrac{(55.85 \text{ g/mol})}{2.25 \text{ g/cm}^3}(100 - 99.9 \text{ wt\%})}$$

$$= 8.46 \times 10^{22} \text{ Fe atoms/cm}^3$$

From Section 3.4 there are two Fe atoms associated with each unit cell; hence, the number of unit cells in a centimeter cubed, n_i, is equal to

$$n_i = \frac{\text{No. Fe atoms/cm}^3}{\text{No. atoms/unit cell}}$$

$$= \frac{8.46 \times 10^{22}\ \text{atoms/cm}^3}{2\ \text{atoms/unit cell}} = 4.23 \times 10^{22}\ \text{unit cells/cm}^3$$

Now, the fraction of unit cells that contain carbon atoms, n_f , is just the number of carbon atoms per centimeter cubed (3.94×10^{20}) divided by the number of unit cells per centimeter cubed (4.23×10^{22}), or

$$n_f = \frac{3.94 \times 10^{20}\ \text{C atoms/cm}^3}{4.23 \times 10^{22}\ \text{unit cells/cm}^3}$$

$$= 9.31 \times 10^{-3}\ \text{atoms/unit cell}$$

The reciprocal of n_f is the number of unit cells per atom—viz.

$$\frac{1}{n_f} = \frac{1}{9.31 \times 10^{-3}\ \text{atoms/unit cell}}$$

$$= 107.5\ \text{unit cells/atom}$$

That is, there is one carbon atom per 107.5 unit cells.

4.32 *For Si to which has had added 1.0 × 10^{-5} at% of aluminum (Al), calculate the number of Al atoms per cubic meter.*

Solution

To make this computation we need to use Equation 4.21. However, because the concentration of Al is given in atom percent, it is necessary to convert 1.0 × 10^{-5} at% to weight percent using Equation 4.7a. For this computation

$C_1 = C_{\text{Al}}$ = concentration of Al in wt%

$C'_1 = C'_{\text{Al}}$ atom percent of Al = 1.0 × 10^{-5} at%

$C'_2 = C'_{\text{Si}}$ atom percent of Si = 100 at% – 1.0 × 10^{-5} at% = 99.99999 at%

$A_1 = A_{\text{Al}}$ = atomic weight of Al = 26.98 g/mol (from inside front cover)

$A_2 = A_{\text{Si}}$ = atomic weight of Si = 28.09 g/mol (from inside front cover)

Now using Equation 4.7a we compute the value of C_1 (or C_{Al}) as follows:

$$C_1 = \frac{C'_1 A_1}{C'_1 A_1 + C'_2 A_2} \times 100$$

$$= \frac{(1.0 \times 10^{-5} \text{ wt\%})(26.98 \text{ g/mol})}{(1.0 \times 10^{-5} \text{ wt\%})(26.98 \text{ g/mol}) + (99.99999 \text{ wt\%})(28.09 \text{ g/mol})} \times 100$$

9.60 × 10^{-6} wt%

Now employment of Equation 4.21 with

N_1= number of Al atoms per meter cubed

C_1 = concentration of Al in weight percent = 9.60 × 10^{-6} wt%

A_1 = atomic weight of Al = 26.98 g/mol (inside front cover)

ρ_1 = density of Al = 2.71 g/cm^3 (inside front cover)

ρ_2 = density of silicon = 2.33 g/cm^3 (inside front cover)

leads to

$$N_1 = \frac{N_A C_1}{\dfrac{C_1 A_1}{\rho_1} + \dfrac{A_1}{\rho_2}(100 - C_1)}$$

$$= \frac{(6.022 \times 10^{23} \text{ atoms/mol})(9.60 \times 10^{-6} \text{ wt\%})}{\dfrac{(9.60 \times 10^{-6} \text{ wt\%})(26.98 \text{ g/mol})}{2.71 \text{ g/cm}^3} + \dfrac{(26.98 \text{ g/mol})}{2.33 \text{ g/cm}^3}(100 - 9.60 \times 10^{-6} \text{ wt\%})}$$

$$= 4.99 \times 10^{15} \text{ Al atoms/cm}^3$$

4.33 *Sometimes it is desirable to determine the weight percent of one element,* C_1*, that will produce a specified concentration in terms of the number of atoms per cubic centimeter,* N_1*, for an alloy composed of two types of atoms. This computation is possible using the following expression:*

$$C_1 = \frac{100}{1 + \frac{N_A \rho_2}{N_1 A_1} - \frac{\rho_2}{\rho_1}} \qquad (4.22)$$

where N_A *is Avogadro's number,* ρ_1 *and* ρ_2 *are the densities of the two elements, and* A_1 *is the atomic weight of element 1.*

Derive Equation 4.22 using Equation 4.2 and expressions contained in Section 4.4.

Solution

This problem asks that we derive Equation 4.22, using other equations given in the chapter. The number of atoms of component 1 per cubic centimeter is just equal to the atom fraction of component 1 (c_1') times the total number of atoms per cubic centimeter in the alloy (*N*). Thus, using the equivalent of Equation 4.2 for *N*, we may write

$$N_1 = c_1' N = \frac{c' N_A \rho_{ave}}{A_{ave}}$$

Realizing that

$$c_1' = \frac{C_1'}{100}$$

and

$$C_2' = 100 - C_1'$$

and substitution of the expressions for ρ_{ave} and A_{ave}, Equations 4.10b and 4.11b, respectively, leads to

$$N_1 = \frac{c_1' N_A \rho_{ave}}{A_{ave}}$$

$$= \frac{(c_1' N_A)\left(\dfrac{C_1' A_1 + C_2' A_2}{\dfrac{C_1' A_1}{\rho_1} + \dfrac{C_2' A_2}{\rho_2}}\right)}{\dfrac{C' A_1 + C_2' A_2}{100}}$$

$$= \frac{N_A C_1' \rho_1 \rho_2}{C_1' \rho_2 A_1 + (100 - C_1') \rho_1 A_2}$$

And, solving for C_1' leads to

$$C_1' = \frac{100 \, N_1 \rho_1 A_2}{N_A \rho_1 \rho_2 - N_1 \rho_2 A_1 + N_1 \rho_1 A_2}$$

Substitution of this expression for C_1' into Equation 4.7a, which may be written in the following form

$$C_1 = \frac{\left(\dfrac{100 \, N_1 \rho_1 A_2}{N_A \rho_1 \rho_2 - N_1 \rho_2 A_1 + N_1 \rho_1 A_2}\right) A_1}{\left(\dfrac{100 \, N_1 \rho_1 A_2}{N_A \rho_1 \rho_2 - N_1 \rho_2 A_1 + N_1 \rho_1 A_2}\right) A_1 + \left[100 - \left(\dfrac{100 \, N_1 \rho_1 A_2}{N_A \rho_1 \rho_2 - N_1 \rho_2 A_1 + N_1 \rho_1 A_2}\right)\right] A_2} \times 100$$

which simplifies to

$$C_1 = \frac{100}{1 + \dfrac{N_A \rho_2}{N_1 A_1} - \dfrac{\rho_2}{\rho_1}}$$

the desired expression.

4.34 *Gold (Au) forms a substitutional solid solution with silver (Ag). Compute the weight percent of gold that must be added to silver to yield an alloy that contains 5.5 × 10^{21} Au atoms per cubic centimeter. The densities of pure Au and Ag are 19.32 and 10.49 g/cm^3, respectively.*

Solution

To solve this problem, employment of Equation 4.22 is necessary, using the following values:

$N_1 = N_{\text{Au}} = 5.5 \times 10^{21}$ atoms/cm^3
$\rho_1 = \rho_{\text{Au}} = 19.32$ g/cm^3
$\rho_2 = \rho_{\text{Ag}} = 10.49$ g/cm^3
$A_1 = A_{\text{Au}} = 196.97$ g/mol (found inside front cover)
$A_2 = A_{\text{Ag}} = 107.87$ g/mol (found inside from cover)

Thus

$$C_{\text{Au}} = \frac{100}{1 + \dfrac{N_{\text{A}}\rho_{\text{Ag}}}{N_{\text{Au}}A_{\text{Au}}} - \dfrac{\rho_{\text{Ag}}}{\rho_{\text{Au}}}}$$

$$= \frac{100}{1 + \dfrac{(6.022 \times 10^{23}\ \text{atoms/mol})(10.49\ \text{g/cm}^3)}{(5.5 \times 10^{21}\ \text{atoms/cm}^3)(196.97\ \text{g/mol})} - \left(\dfrac{10.49\ \text{g/cm}^3}{19.32\ \text{g/cm}^3}\right)}$$

= 15.9 wt%

4.35 *Germanium (Ge) forms a substitutional solid solution with silicon (Si). Compute the weight percent of germanium that must be added to silicon to yield an alloy that contains 2.43 × 10^{21} Ge atoms per cubic centimeter. The densities of pure Ge and Si are 5.32 and 2.33 g/cm^3, respectively.*

Solution

To solve this problem, employment of Equation 4.22 is necessary, using the following values:

$N_1 = N_{\mathrm{Ge}} = 2.43 \times 10^{21}$ atoms/cm^3
$\rho_1 = \rho_{\mathrm{Ge}} = 5.32$ g/cm^3
$\rho_2 = \rho_{\mathrm{Si}} = 2.33$ g/cm^3
$A_1 = A_{\mathrm{Ge}} = 72.64$ g/mol (found inside front cover)
$A_2 = A_{\mathrm{Si}} = 28.09$ g/mol (found inside front cover)

Thus

$$C_{\mathrm{Ge}} = \frac{100}{1 + \dfrac{N_{\mathrm{A}}\rho_{\mathrm{Si}}}{N_{\mathrm{Ge}}A_{\mathrm{Ge}}} - \dfrac{\rho_{\mathrm{Si}}}{\rho_{\mathrm{Ge}}}}$$

$$= \frac{100}{1 + \dfrac{(6.022 \times 10^{23}\ \text{atoms/mol})(2.33\ \text{g/cm}^3)}{(2.43 \times 10^{21}\ \text{atoms/cm}^3)(72.64\ \text{g/mol})} - \left(\dfrac{2.33\ \text{g/cm}^3}{5.32\ \text{g/cm}^3}\right)}$$

$$= 11.7\ \text{wt\%}$$

4.36 *Electronic devices found in integrated circuits are composed of very high purity silicon to which has been added small and very controlled concentrations of elements found in Groups IIIA and VA of the periodic table. For Si to which has had added 6.5 × 10^{21} atoms per cubic meter of phosphorus, compute (a) the weight percent and (b) the atom percent of P present.*

Solution

(a) This part of the problem is solved using Equation 4.22, in which

C_1 = concentration of P in wt%

N_1 = number of P atoms per cubic centimeter = $(6.5 \times 10^{21}\ \text{atoms/m}^3)(1\ \text{m}^3/10^6\ \text{cm}^3)$

$= 6.5 \times 10^{15}\ \text{atoms/cm}^3$

A_1 = atomic weight of P = 30.97 g/mol (inside front cover)

ρ_1 = density of P = 1.82 g/cm^3 (inside front cover)

ρ_2 = density of silicon = 2.33 g/cm^3 (inside front cover)

And, from Equation 4.22

$$C_1 = \frac{100}{1 + \dfrac{N_A \rho_2}{N_1 A_1} - \dfrac{\rho_2}{\rho_1}}$$

$$= \frac{100}{1 + \dfrac{(6.022 \times 10^{23}\ \text{atoms/mol})(2.33\ \text{g/cm}^3)}{(6.5 \times 10^{15}\ \text{atoms/cm}^3)(30.97\ \text{g/mol})} - \dfrac{2.33\ \text{g/cm}^3}{1.82\ \text{g/cm}^3}}$$

$$= 1.43 \times 10^{-5}\ \text{wt\%}$$

(b) To convert from weight percent to atom percent we use Equation 4.6a where

C_1' = atom percent of P

C_1 = weight percent of P = 1.43×10^{-5} wt%

C_2 = weight percent of Si = 100 wt% – 1.43×10^{-5} wt% = 99.9999857

A_1 = atomic weight of P = 30.97 g/mol

A_2 = atomic weight of Si = 28.09 g/mol

And from Equation 4.6a we obtain the following:

$$C_1' = \frac{C_1A_2}{C_1A_2 + C_2A_1} \times 100$$

$$= \frac{(1.43 \times 10^{-5} \text{ wt\%})(28.09 \text{ g/mol})}{(1.43 \times 10^{-5} \text{ wt\%})(28.09 \text{ g/mol}) + (99.9999857 \text{ wt\%})(30.97 \text{ g/mol})} \times 100$$

$$= 1.30 \times 10^{-5} \text{ at\%}$$

4.37 *Iron and vanadium both have the BCC crystal structure, and V forms a substitutional solid solution for concentrations up to approximately 20 wt% V at room temperature. Compute the unit cell edge length for a 90 wt% Fe–10 wt% V alloy.*

Solution

This problems asks that we compute the unit cell edge length for a 90 wt% Fe-10 wt% V alloy. First of all, the atomic radii for Fe and V (using the table inside the front cover) are 0.124 and 0.132 nm, respectively. Also, using Equation 3.8 it is possible to compute the unit cell volume, and inasmuch as the unit cell is cubic, the unit cell edge length is just the cube root of the volume. However, it is first necessary to calculate the density and average atomic weight of this alloy using Equations 4.10a and 4.11a. Inasmuch as the densities of iron and vanadium are 7.87g/cm^3 and 6.10 g/cm^3, respectively, (as taken from inside the front cover), the average density is just

$$\rho_{\text{ave}} = \frac{100}{\dfrac{C_{\text{V}}}{\rho_{\text{V}}} + \dfrac{C_{\text{Fe}}}{\rho_{\text{Fe}}}}$$

$$= \frac{100}{\dfrac{10\text{ wt\%}}{6.10\text{ g/cm}^3} + \dfrac{90\text{ wt\%}}{7.87\text{ g/cm}^3}}$$

$$= 7.65\text{ g/cm}^3$$

And for the average atomic weight

$$A_{\text{ave}} = \frac{100}{\dfrac{C_{\text{V}}}{A_{\text{V}}} + \dfrac{C_{\text{Fe}}}{A_{\text{Fe}}}}$$

$$= \frac{100}{\dfrac{10\text{ wt\%}}{50.94\text{ g/mol}} + \dfrac{90\text{ wt\%}}{55.85\text{ g/mol}}}$$

$$= 55.32\text{ g/mol}$$

Now, V_C is determined from Equation 3.8 as (taking the number of atoms per unit cell, n = 2, since the crystal structure of the alloy is BCC)

$$V_C = \frac{nA_{\text{ave}}}{\rho_{\text{ave}} N_{\text{A}}}$$

$$= \frac{(2 \text{ atoms/unit cell})(55.32 \text{ g/mol})}{(7.65 \text{ g/cm}^3)(6.022 \times 10^{23} \text{ atoms/mol})}$$

$$= 2.40 \times 10^{-23} \text{ cm}^3\text{/unit cell}$$

And, finally, because the unit cell is of cubic symmetry

$$a = (V_C)^{1/3}$$

$$= (2.40 \times 10^{-23} \text{ cm}^3\text{/unit cell})^{1/3}$$

$$= 2.89 \times 10^{-8} \text{ cm} = 0.289 \text{ nm}$$

Dislocations—Linear Defects

4.38 *Cite the relative Burgers vector–dislocation line orientations for edge, screw, and mixed dislocations.*

Answer

The Burgers vector and dislocation line are perpendicular for edge dislocations, parallel for screw dislocations, and neither perpendicular nor parallel for mixed dislocations

Interfacial Defects

4.39 *For an FCC single crystal, would you expect the surface energy for a (100) plane to be greater or less than that for a (111) plane? Why? (Note: You may want to consult the solution to Problem 3.60 at the end of Chapter 3.)*

Answer

The surface energy for a crystallographic plane will depend on its packing density [i.e., the planar density (Section 3.11)]—that is, the higher the packing density, the greater the number of nearest-neighbor atoms, and the more atomic bonds in that plane that are satisfied, and, consequently, the lower the surface energy. From the solution to Problem 3.60, planar densities for FCC (100) and (111) planes are $\frac{1}{4R^2}$ and $\frac{1}{2R^2\sqrt{3}}$, respectively—that is $\frac{0.25}{R^2}$ and $\frac{0.29}{R^2}$ (where *R* is the atomic radius). Thus, since the planar density for (111) is greater, it will have the lower surface energy.

4.40 *For a BCC single crystal, would you expect the surface energy for a (100) plane to be greater or less than that for a (110) plane? Why? (Note: You may want to consult the solution to Problem 3.61 at the end of Chapter 3.)*

Answer

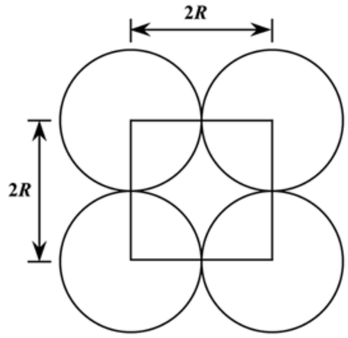
The surface energy for a crystallographic plane will depend on its packing density [i.e., the planar density (Section 3.11)]—that is, the higher the packing density, the greater the number of nearest-neighbor atoms, and the more atomic bonds in that plane that are satisfied, and, consequently, the lower the surface energy. From the solution to Problem 3.61, the planar densities for BCC (100) and (110) are $\frac{3}{16R^2}$ and $\frac{3}{8R^2\sqrt{2}}$, respectively—that is $\frac{0.19}{R^2}$ and $\frac{0.27}{R^2}$. Thus, since the planar density for (110) is greater, it will have the lower surface energy.

4.41 *For a single crystal of some hypothetical metal that has the simple cubic crystal structure (Figure 3.3), would you expect the surface energy for a (100) plane to be greater, equal to, or less than a (110) plane. Why?*

Answer

The surface energy for a crystallographic plane will depend on its packing density [i.e., the planar density (Section 3.11)]—that is, the higher the packing density, the greater the number of nearest-neighbor atoms, and the more atomic bonds in that plane that are satisfied, and, consequently, the lower the surface energy.

It becomes necessary to determine the packing densities of the (100) and (110) planes for the simple cubic crystal structure. Below is shown a (100) plane for simple cubic.



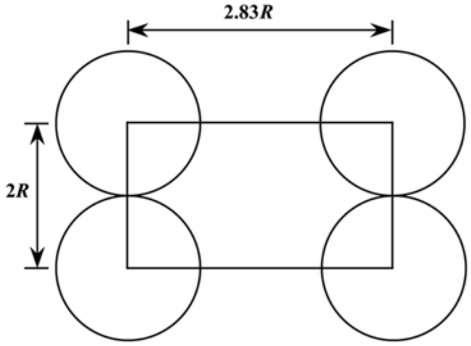
(100)

For this plane there is one atom at each of the four corners, which is shared with four adjacent unit cells. Thus there is the equivalence of one atom associated with this (100) plane. The planar section is a square, where in the side lengths are equal to the unit cell edge length, 2*R*. Thus the area of this square is $4R^2$, which yields a planar density of

$$\mathrm{PD}_{100} = \frac{\text{number of atoms centered on the (100) plane}}{\text{area of (100) plane}}$$

$$= \frac{1 \text{ atom}}{4R^2} = \frac{0.25}{R^2}$$

We now repeat this procedure for a (110) plane, which is shown below.



(110)

Because each of these atoms is shared with four other unit cells, there is the equivalence of 1 atom associated with the plane. This planar section is a rectangle with dimensions of $2R \times 2R\sqrt{2}$ (Note: $2\sqrt{2} = 2.83$). Thus the area of this rectangle is $4R^2\sqrt{2} = 5.66R^2$. The planar density for the (110) plane is, therefore,

$$\mathrm{PD}_{110} = \frac{1 \text{ atom}}{5.66R^2} = \frac{0.18}{R^2}$$

Thus, because the planar density for (100) is greater, it will have the lower surface energy.

4.42 *(a) For a given material, would you expect the surface energy to be greater than, the same as, or less than the grain boundary energy? Why?*

(b) The grain boundary energy of a small-angle grain boundary is less than for a high-angle one. Why is this so?

<u>Answer</u>

(a) The surface energy will be greater than the grain boundary energy. For grain boundaries, some atoms on one side of a boundary will bond to atoms on the other side; such is not the case for surface atoms. Therefore, there will be fewer unsatisfied bonds along a grain boundary.

(b) The small-angle grain boundary energy is lower than for a high-angle one because more atoms bond across the boundary for the small-angle, and, thus, there are fewer unsatisfied bonds.

4.43 *(a) Briefly describe a twin and a twin boundary.*

(b) Cite the difference between mechanical and annealing twins.

Answer

(a) A twin boundary is an interface such that atoms on one side are located at mirror image positions of those atoms situated on the other boundary side. The region on one side of this boundary is called a twin.

(b) Mechanical twins are produced as a result of mechanical deformation and generally occur in BCC and HCP metals. Annealing twins form during annealing heat treatments, most often in FCC metals.

4.44 *For each of the following stacking sequences found in FCC metals, cite the type of planar defect that exists:*

(a) . . . A B C A B C B A C B A . . .

(b) . . . A B C A B C B C A B C . . .

Copy the stacking sequences, and indicate the position(s) of planar defect(s) with a vertical dashed line.

<u>Answer</u>

(a) The interfacial defect that exists for this stacking sequence is a twin boundary, which occurs at the indicated position.

The stacking sequence on one side of this position is mirrored on the other side.

(b) The interfacial defect that exists within this FCC stacking sequence is a stacking fault, which occurs between the two lines.

Within this region, the stacking sequence is HCP.

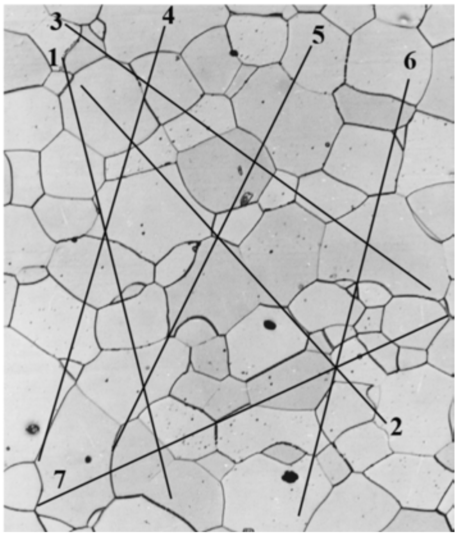
Grain Size Determination

4.45 *(a) Using the intercept method determine the mean intercept length, in millimeters, of the specimen whose microstructure is shown in Figure 4.15b; use at least seven straight-line segments.*

(b) Estimate the ASTM grain size number for this material.

Solution

(a) Below is shown the photomicrograph of Figure 4.15*b*, on which seven straight line segments, each of which is 60 mm long has been constructed; these lines are labeled "1" through "7".



Since the length of each line is 60 mm and there are 7 lines, the total line length (L_T in Equation 4.16) is 420 mm. Tabulated below is the number of grain-boundary intersections for each line:

Line Number	No. Grains Intersected
1	11
2	10
3	9
4	8.5
5	7
6	10
7	8
Total	63.5

Because L_T = 420 mm, P = 63.5 grain-boundary intersections, and the magnification M = 100×, the mean intercept length $\bar{\ell}$ is computed using Equation 4.16 as follows:

$$\bar{\ell} = \frac{L_T}{PM} = \frac{420 \text{ mm}}{(63.5 \text{ intersections})(100\times)}$$

$$= 0.066 \text{ mm}$$

(b) The ASTM grain size number G is computed by substitution of this value for $\bar{\ell}$ into Equation 4.19a as follows:

$$G = -6.6457 \log \bar{\ell} - 3.298$$

$$= (-6.6457)[\log(0.066 \text{ mm})] - 3.298$$

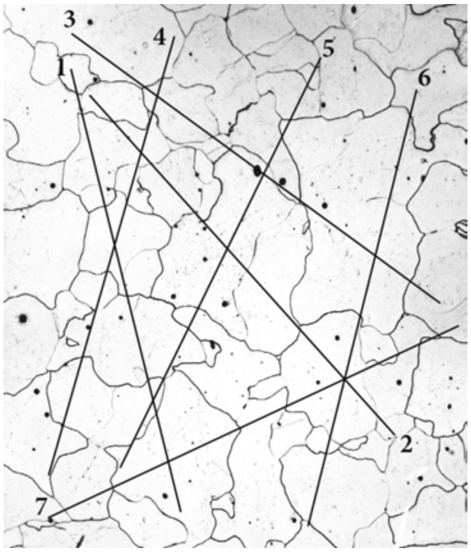
$$= 4.55$$

4.46 *(a) Employing the intercept technique, determine the mean intercept length for the steel specimen whose microstructure is shown in Figure 9.25a; use at least seven straight-line segments.*

(b) Estimate the ASTM grain size number for this material.

Solution

(a) Below is shown the photomicrograph of Figure 9.25*a*, on which seven straight line segments, each of which is 60 mm long has been constructed; these lines are labeled "1" through "7".



Since the length of each line is 60 mm and there are 7 lines, the total line length (L_T in Equation 4.16) is 420 mm. Tabulated below is the number of grain-boundary intersections for each line:

Line Number	No. Grains Intersected
1	7
2	7
3	7
4	8
5	10
6	6
7	8
Total	53

Because L_T = 420 mm, P = 56 grain-boundary intersections, and the magnification M = 90×, the mean intercept length $\bar{\ell}$ is computed using Equation 4.16 as follows:

$$\bar{\ell} = \frac{L_T}{PM} = \frac{420\ \text{mm}}{(53\ \text{intersections})(90\times)}$$

$$= 0.088\ \text{mm}$$

(b) The ASTM grain size number G is computed by substitution of this value for $\bar{\ell}$ into Equation 4.19a as follows:

$$G = -6.6457 \log \bar{\ell} - 3.298$$

$$= (-6.6457)[\log(0.088\ \text{mm})] - 3.298$$

$$= 3.72$$

4.47 *For an ASTM grain size of 6, approximately how many grains would there be per square inch under each of the following conditions?*

(a) At a magnification of 100×

(b) Without any magnification?

Solution

(a) This part of problem asks that we compute the number of grains per square inch for an ASTM grain size of 6 at a magnification of 100×. All we need do is solve for the parameter *n* in Equation 4.17, inasmuch as *G* = 6. Thus

$$n = 2^{G-1}$$

$$= 2^{6-1} = 32 \text{ grains/in.}^2$$

(b) Now it is necessary to compute the value of *n* for no magnification. In order to solve this problem it is necessary to use Equation 4.18:

$$n_M \left(\frac{M}{100}\right)^2 = 2^{G-1}$$

where n_M = the number of grains per square inch at magnification *M*, and *G* is the ASTM grain size number. Without any magnification, *M* in the above equation is 1, and therefore,

$$n_1 \left(\frac{1}{100}\right)^2 = 2^{6-1} = 32$$

And, solving for n_1, n_1 = 320,000 grains/in.^{2}.

4.48 *Determine the ASTM grain size number if 30 grains per square inch are measured at a magnification of 250×.*

Solution

In order to solve this problem we make use of Equation 4.18:

$$n_M \left(\frac{M}{100}\right)^2 = 2^{G-1}$$

where n_M = the number of grains per square inch at magnification M, and G is the ASTM grain size number. Solving the above equation for G, and realizing that n_M = 30, while M = 250. Some algebraic manipulation of Equation 4.18 is necessary. Taking logarithms of both sides of this equation leads to

$$\log\left[n_M \left(\frac{M}{100}\right)^2\right] = \log\left(2^{G-1}\right)$$

Or

$$\log n_M + 2\log\left(\frac{M}{100}\right) = (G-1)\log 2$$

And solving this equation for G

$$\frac{\log n_M + 2\log\left(\frac{M}{100}\right)}{\log 2} = G - 1$$

or

$$G = \frac{\log\, n_M \; + \; 2\, \log\left(\frac{M}{100}\right)}{\log\, 2} + 1$$

From the problem statement:

n_M =30

M = 250

And, therefore

$$G = \frac{\log\, 30 \; + \; 2\, \log\left(\frac{250}{100}\right)}{\log\, 2} \; + \; 1 = 8.6$$

4.49 *Determine the ASTM grain size number if 25 grains per square inch are measured at a magnification of 75×.*

Solution

In order to solve this problem we make use of Equation 4.18—viz.

$$n_M \left(\frac{M}{100}\right)^2 = 2^{G-1}$$

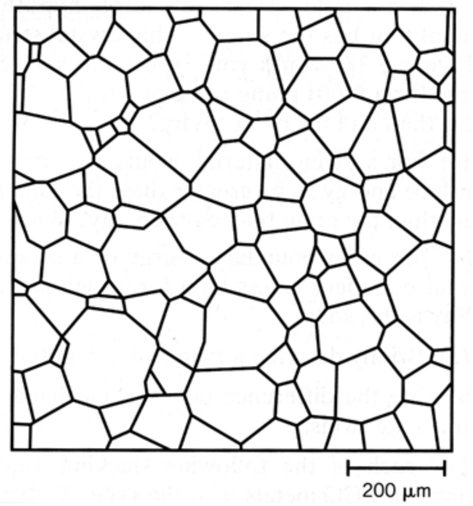
where n_M = the number of grains per square inch at magnification M, and G is the ASTM grain size number. By algebraic manipulation of Equation 4.18 (as outlined in Problem 4.48) we make G the dependent variable, which leads to the following expression:

$$G = \frac{\log n_M + 2 \log \left(\frac{M}{100}\right)}{\log 2} + 1$$

For n_M = 25 and M = 75, the value of G is

$$G = \frac{\log 25 + 2 \log \left(\frac{75}{100}\right)}{\log 2} + 1 = 4.8$$

4.50 *The following is a schematic micrograph that represents the microstructure of some hypothetical metal.*



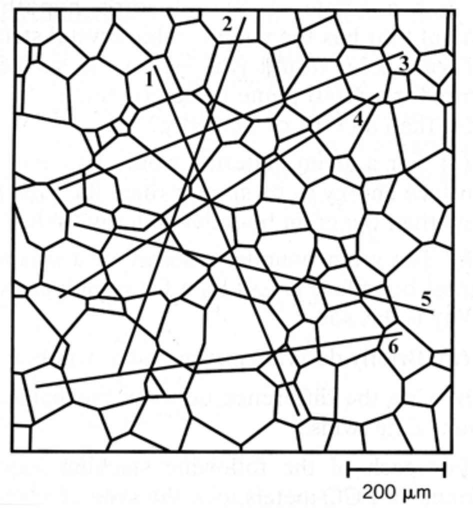
Determine the following:

(a) Mean intercept length

(b) ASTM grain size number, G

Solution

(a) Below is shown this photomicrograph on which six straight line segments, each of which is 50 mm long has been constructed; these lines are labeled "1" through "6".



Since the length of each line is 50 mm and there are 6 lines, the total line length (L_T in Equation 4.16) is 300 mm. Tabulated below is the number of grain-boundary intersections for each line:

Line Number	No. Grains Intersected
1	7
2	8
3	8
4	8
5	8
6	8
Total	47

Because L_T = 300 mm, P = 47 grain-boundary intersections, and the magnification M = 200×, the mean intercept length $\bar{\ell}$ is computed using Equation 4.16 as follows:

$$\bar{\ell} = \frac{L_T}{PM} = \frac{300 \text{ mm}}{(47 \text{ intersections})(200\times)}$$

$$= 0.032 \text{ mm}$$

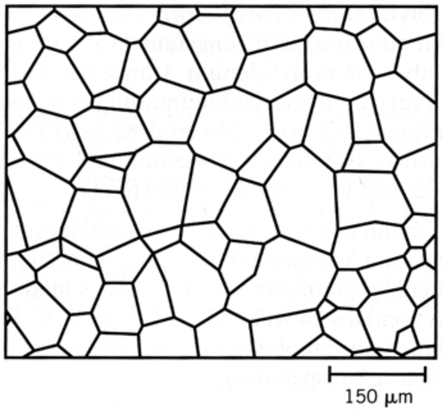
(b) The ASTM grain size number G is computed by substitution of this value for $\bar{\ell}$ into Equation 4.19a as follows:

$$G = -6.6457 \log \bar{\ell} - 3.298$$

$$= (-6.6457)[\log(0.032 \text{ mm})] - 3.298$$

$$= 6.64$$

4.51 *The following is a schematic micrograph that represents the microstructure of some hypothetical metal.*



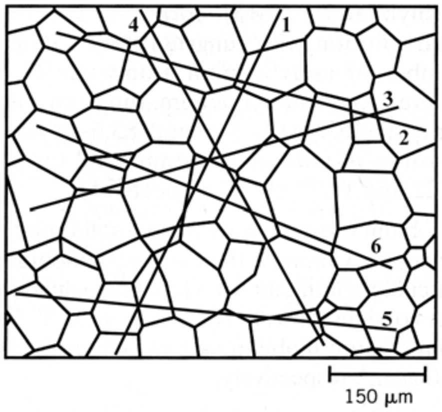
Determine the following:

(a) Mean intercept length

(b) ASTM grain size number, G

Solution

(a) Below is shown this photomicrograph on which six straight line segments, each of which is 50 mm long has been constructed; these lines are labeled “1” through “6”.



Since the length of each line is 50 mm and there are 6 lines, the total line length (L_T in Equation 4.16) is 300 mm. Tabulated below is the number of grain-boundary intersections for each line:

Line Number	No. Grains Intersected
1	8
2	9
3	10
4	8
5	9
6	8
Total	52

Because L_T = 300 mm, P = 52 grain-boundary intersections, and the magnification M = 150×, the mean intercept length $\bar{\ell}$ is computed using Equation 4.16 as follows:

$$\bar{\ell} = \frac{L_T}{PM} = \frac{300\text{ mm}}{(52\text{ intersections})(150\times)}$$

$$= 0.038\text{ mm}$$

(b) The ASTM grain size number G is computed by substitution of this value for $\bar{\ell}$ into Equation 4.19a as follows:

$$G = -6.6457\log\bar{\ell} - 3.298$$

$$= (-6.6457)[\log(0.038\text{ mm})] - 3.298$$

DESIGN PROBLEMS

Specification of Composition

4.D1 *Aluminum–lithium (Al-Li) alloys have been developed by the aircraft industry to reduce the weight and improve the performance of its aircraft. A commercial aircraft skin material having a density of 2.47 g/cm^3 is desired. Compute the concentration of Li (in wt%) that is required.*

Solution

Solution of this problem requires the use of Equation 4.10a, which takes the form

$$\rho_{\text{ave}} = \frac{100}{\dfrac{C_{\text{Li}}}{\rho_{\text{Li}}} + \dfrac{C_{\text{Al}}}{\rho_{\text{Al}}}} = \frac{100}{\dfrac{C_{\text{Li}}}{\rho_{\text{Li}}} + \dfrac{100 - C_{\text{Li}}}{\rho_{\text{Al}}}}$$

inasmuch as $C_{\text{Li}} + C_{\text{Al}} = 100$. According to the table inside the front cover, the respective densities of Li and Al are 0.534 and 2.71 g/cm^3. Upon algebraic manipulation of the above equation and solving for C_{Li} leads to

$$C_{\text{Li}} = \frac{100\,\rho_{\text{Li}}(\rho_{\text{Al}} - \rho_{\text{ave}})}{\rho_{\text{ave}}(\rho_{\text{Al}} - \rho_{\text{Li}})}$$

Incorporation of values for ρ_{ave}, ρ_{Al}, and ρ_{Li} yields the following value for C_{Li}:

$$C_{\text{Li}} = \frac{(100)(0.534\ \text{g/cm}^3)(2.71\ \text{g/cm}^3 - 2.47\ \text{g/cm}^3)}{(2.47\ \text{g/cm}^3)(2.71\ \text{g/cm}^3 - 0.534\ \text{g/cm}^3)}$$

$$= 2.38\ \text{wt\%}$$

4.D2 *Copper (Cu) and platinum (Pt) both have the FCC crystal structure, and Cu forms a substitutional solid solution for concentrations up to approximately 6 wt% Cu at room temperature. Determine the concentration in weight percent of Cu that must be added to Pt to yield a unit cell edge length of 0.390 nm.*

Solution

To begin, it is necessary to employ Equation 3.8, and solve for the unit cell volume, V_C, as

$$V_C = \frac{nA_{\text{ave}}}{\rho_{\text{ave}} N_{\text{A}}}$$

where A_{ave} and ρ_{ave} are the atomic weight and density, respectively, of the Pt-Cu alloy. Inasmuch as both of these materials have the FCC crystal structure, which has cubic symmetry, V_C is just the cube of the unit cell length, a. That is

$$V_C = a^3 = (0.390 \text{ nm})^3$$

$$= (3.90 \times 10^{-8} \text{ cm})^3 = 5.932 \times 10^{-23} \text{ cm}^3$$

It is now necessary to construct expressions for A_{ave} and ρ_{ave} in terms of the concentration of copper, C_{Cu}, using Equations 4.11a and 4.10a. For A_{ave} we have

$$A_{\text{ave}} = \frac{100}{\dfrac{C_{\text{Cu}}}{A_{\text{Cu}}} + \dfrac{(100 - C_{\text{Cu}})}{A_{\text{Pt}}}}$$

$$= \frac{100}{\dfrac{C_{\text{Cu}}}{63.55 \text{ g/mol}} + \dfrac{(100 - C_{\text{Cu}})}{195.08 \text{ g/mol}}}$$

since the atomic weights for Cu and Pt are, respectively, 63.55 and 195.08 g/mol (as noted inside the front cover). Now, the expression for ρ_{ave} is as follows:

$$\rho_{\text{ave}} = \frac{100}{\dfrac{C_{\text{Cu}}}{\rho_{\text{Cu}}} + \dfrac{(100 - C_{\text{Cu}})}{\rho_{\text{Pt}}}}$$

$$= \frac{100}{\dfrac{C_{\text{Cu}}}{8.94\ \text{g/cm}^3} + \dfrac{(100 - C_{\text{Cu}})}{21.45\ \text{g/cm}^3}}$$

given the densities of 8.94 and 21.45 g/cm^3 for the respective metals. Within the FCC unit cell there are 4 equivalent atoms, and thus, the value of n in Equation 3.8 is 4; hence, the expression for V_C may be written in terms of the concentration of Cu in weight percent as follows:

$$V_C = 5.932 \times 10^{-23}\ \text{cm}^3$$

$$= \frac{nA_{\text{ave}}}{\rho_{\text{ave}} N_{\text{A}}}$$

$$= \frac{(4\ \text{atoms/unit cell})\left[\dfrac{100}{\dfrac{C_{\text{Cu}}}{63.55\ \text{g/mol}} + \dfrac{(100 - C_{\text{Cu}})}{195.08\ \text{g/mol}}}\right]}{\left[\dfrac{100}{\dfrac{C_{\text{Cu}}}{8.94\ \text{g/cm}^3} + \dfrac{(100 - C_{\text{Cu}})}{21.45\ \text{g/cm}^3}}\right](6.022 \times 10^{23}\ \text{atoms/mol})}$$

And solving this expression for C_{Cu} leads to C_{Cu} = 2.825 wt%.

FUNDAMENTALS OF ENGINEERING QUESTIONS AND PROBLEMS

4.1FE *Calculate the number of vacancies per cubic meter at 1000°C for a metal that has an energy for vacancy formation of 1.22 eV/atom, a density of 6.25 g/cm*^{3}*, and an atomic weight of 37.4 g/mol.*

(A) $1.49 \times 10^{18}\ m^{-3}$

(B) $7.18 \times 10^{22}\ m^{-3}$

(C) $1.49 \times 10^{24}\ m^{-3}$

(D) $2.57 \times 10^{24}\ m^{-3}$

Solution

Determination of the number of vacancies per cubic meter at 1000°C (1273 K) requires the utilization of Equations 4.1 and 4.2 as follows:

$$N_v = N\ \exp\left(-\frac{Q_v}{kT}\right) = \frac{N_A \rho}{A} \exp\left(-\frac{Q_v}{kT}\right)$$

Incorporation into this expression values for Q_v, ρ, and A provided in the problem statement yields the following for N_v:

$$N_v = \frac{(6.022 \times 10^{23}\ \text{atoms/mol})(6.25\ \text{g/cm}^3)}{37.4\ \text{g/mol}} \exp\left[-\frac{1.22\ \text{eV/atom}}{(8.62 \times 10^{-5}\ \text{eV/atom-K})(1273\ \text{K})}\right]$$

$$= 1.49 \times 10^{18}\ \text{cm}^{-3} = 1.49 \times 10^{24}\ \text{m}^{-3}$$

which is answer C.

4.2FE *What is the composition, in atom percent, of an alloy that consists of 4.5 wt% Pb and 95.5 wt% Sn? The atomic weights for Pb and Sn are 207.19 g/mol and 118.71 g/mol, respectively.*

(A) 2.6 at% Pb and 97.4 at% Sn

(B) 7.6 at% Pb and 92.4 at% Sn

(C) 97.4 at% Pb and 2.6 at% Sn

(D) 92.4 at% Pb and 7.6 at% Sn

Solution

We are asked to compute the composition of an alloy in atom percent. Employment of Equation 4.6a leads to

$$C'_{\mathrm{Pb}} = \frac{C_{\mathrm{Pb}} A_{\mathrm{Sn}}}{C_{\mathrm{Pb}} A_{\mathrm{Sn}} + C_{\mathrm{Sn}} A_{\mathrm{Pb}}} \times 100$$

$$= \frac{(4.5)(118.71\ \mathrm{g/mol})}{(4.5)(118.71\ \mathrm{g/mol}) + (95.5)(207.19\ \mathrm{g/mol})} \times 100$$

$$= 2.6\ \text{at\%}$$

$$C'_{\mathrm{Sn}} = \frac{C_{\mathrm{Sn}} A_{\mathrm{Pb}}}{C_{\mathrm{Sn}} A_{\mathrm{Pb}} + C_{\mathrm{Pb}} A_{\mathrm{Sn}}} \times 100$$

$$= \frac{(95.5)(207.19\ \mathrm{g/mol})}{(95.5)(207.19\ \mathrm{g/mol}) + (4.5)(118.71\ \mathrm{g/mol})} \times 100$$

$$= 97.4\ \text{at\%}$$

which is answer A (2.6 at% Pb and 97.4 at% Sn).

4.3FE *What is the composition, in weight percent, of an alloy that consists of 94.1 at% Ag and 5.9 at% Cu? The atomic weights for Ag and Cu are 107.87 g/mol and 63.55 g/mol, respectively.*

(A) 9.6 wt% Ag and 90.4 wt% Cu

(B) 3.6 wt% Ag and 96.4 wt% Cu

(C) 90.4 wt% Ag and 9.6 wt% Cu

(D) 96.4 wt% Ag and 3.6 wt% Cu

Solution

To compute composition, in weight percent, of a 94.1 at% Ag-5.9 at% Cu alloy, we employ Equation 4.7 as follows:

$$C_{\mathrm{Ag}} = \frac{C'_{\mathrm{Ag}}A_{\mathrm{Ag}}}{C'_{\mathrm{Ag}}A_{\mathrm{Ag}} + C'_{\mathrm{Cu}}A_{\mathrm{Cu}}} \times 100$$

$$= \frac{(94.1)(107.87\ \mathrm{g/mol})}{(94.1)(107.87\ \mathrm{g/mol}) + (5.9)(63.55\ \mathrm{g/mol})} \times 100$$

= 96.4 wt%

$$C_{\mathrm{Cu}} = \frac{C'_{\mathrm{Cu}}A_{\mathrm{Cu}}}{C'_{\mathrm{Ag}}A_{\mathrm{Ag}} + C'_{\mathrm{Cu}}A_{\mathrm{Cu}}} \times 100$$

$$= \frac{(5.9)(63.55\ \mathrm{g/mol})}{(94.1)(107.87\ \mathrm{g/mol}) + (5.9)(63.55\ \mathrm{g/mol})} \times 100$$

= 3.6 wt%

which is answer D (96.4 wt% Ag and 3.6 wt% Cu).

seCHAPTER 5

DIFFUSION

PROBLEM SOLUTIONS

Introduction

5.1 *Briefly explain the difference between self-diffusion and interdiffusion.*

Answer

Self-diffusion is atomic migration in pure metals--i.e., when all atoms exchanging positions are of the same type. Interdiffusion is diffusion of atoms of one metal into another metal.

5.2 *Self-diffusion involves the motion of atoms that are all of the same type; therefore, it is not subject to observation by compositional changes, as with interdiffusion. Suggest one way in which self-diffusion may be monitored.*

<u>Answer</u>

Self-diffusion may be monitored by using radioactive isotopes of the metal being studied. The motion of these isotopic atoms may be detected by measurement of radioactivity level.

Diffusion Mechanisms

5.3 *(a) Compare interstitial and vacancy atomic mechanisms for diffusion.*

(b) Cite two reasons why interstitial diffusion is normally more rapid than vacancy diffusion.

Answer

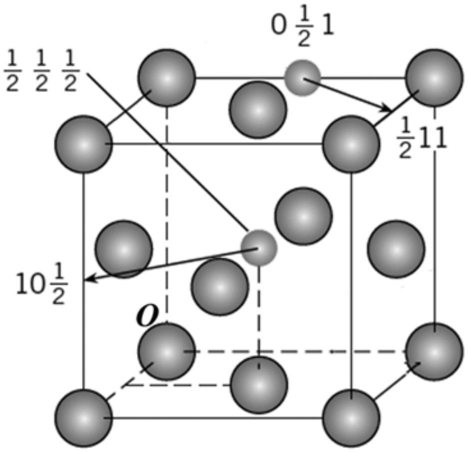
(a) With vacancy diffusion, atomic motion is from one lattice site to an adjacent vacancy. Self-diffusion and the diffusion of substitutional impurities proceed via this mechanism. On the other hand, atomic motion is from interstitial site to adjacent interstitial site for the interstitial diffusion mechanism.

(b) Interstitial diffusion is normally more rapid than vacancy diffusion because: (1) interstitial atoms, being smaller, are more mobile; and (2) the probability of an empty adjacent interstitial site is greater than for a vacancy adjacent to a host (or substitutional impurity) atom.

5.4 *Carbon diffuses in iron via an interstitial mechanism—for FCC iron from one octahedral site to an adjacent one. In Section 4.3 (Figure 4.3a), we note that two general sets of point coordinates for this site are* $0\frac{1}{2}1$ *and* $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. *Specify the family of crystallographic directions in which this diffusion of carbon in FCC iron takes place.*

Solution

Below is shown a schematic FCC unit cell, and in addition representations of interstitial atoms located in both $\mathbf{0\frac{1}{2}1}$ and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ octahedral sites. In addition, arrows have been drawn from each of these atoms to a nearest octahedral site: from $\mathbf{0\frac{1}{2}1}$ to $\frac{1}{2}\mathbf{11}$, and from $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ to $\mathbf{10}\frac{1}{2}$. (*Note*: These point coordinates are referenced to the coordinate system having its origin located at the center of the bottom, rear atom, the one labeled with an *O*.)



Using the procedure detailed in Section 3.9 for determining the crystallographic direction of a vector (i.e., subtraction of vector tail coordinates from head coordinates) coordinates for the $\mathbf{0\frac{1}{2}1}$ **to** $\frac{1}{2}\mathbf{11}$ vector are as follows:

x coordinate: $\frac{1}{2} - 0 = \frac{1}{2}$

y coordinate: $1 - \frac{1}{2} = \frac{1}{2}$

z coordinate: 1 – 1 = 0

In order to reduce these coordinates to integers it is necessary to multiply each by the factor "2". Therefore, this vector points in a [110] direction.

Applying this same procedure to the $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ to $10\frac{1}{2}$ vector we obtain the following:

x coordinate: $1 - \frac{1}{2} = \frac{1}{2}$

y coordinate: $0 - \frac{1}{2} = -\frac{1}{2}$

z coordinate: $\frac{1}{2} - \frac{1}{2} = 0$

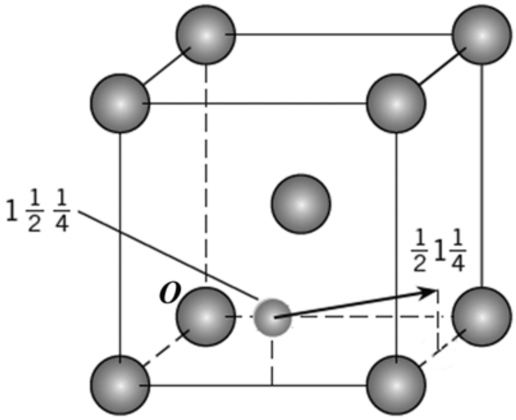
Again, multiplying these indices by 2 leads to the $[1\bar{1}0]$ direction.

Therefore, the family of crystallographic directions for the diffusion of interstitial atoms in FCC metals is $\langle 110 \rangle$.

5.5 *Carbon diffuses in iron via an interstitial mechanism—for BCC iron from one tetrahedral site to an adjacent one. In Section 4.3 (Figure 4.3b) we note that a general set of point coordinates for this site are* $1\frac{1}{2}\frac{1}{4}$. *Specify the family of crystallographic directions in which this diffusion of carbon in BCC iron takes place.*

Solution

Below is shown a schematic BCC unit cell, and in addition the representation of an interstitial atom located in a $1\frac{1}{2}\frac{1}{4}$ tetrahedral site. In addition, an arrow has been drawn from this atom to a nearest tetrahedral site: from $1\frac{1}{2}\frac{1}{4}$ to $\frac{1}{2}1\frac{1}{4}$. (*Note*: These point coordinates are referenced to the coordinate system having its origin located at the center of the bottom, rear atom, the one labeled with an *O*.)



Using the procedure detailed in Section 3.9 for determining the crystallographic direction of a vector (i.e., subtraction of vector tail coordinates from head coordinates) coordinates for this $1\frac{1}{2}\frac{1}{4}$ to $\frac{1}{2}1\frac{1}{4}$ vector are as follows:

x coordinate: $\frac{1}{2} - 1 = -\frac{1}{2}$

y coordinate: $1 - \frac{1}{2} = \frac{1}{2}$

z coordinate: $\frac{1}{4} - \frac{1}{4} = 0$

In order to reduce these coordinates to integers it is necessary to multiply each by the factor "2". Therefore, this vector points in a $[\bar{1}10]$ direction.

Thus, the family of crystallographic directions for the diffusion of interstitial atoms in BCC metals is $\langle 110 \rangle$.

Fick's First Law

5.6 *Briefly explain the concept of steady state as it applies to diffusion.*

Answer

Steady-state diffusion is the situation wherein the rate of diffusion into a given system is just equal to the rate of diffusion out, such that there is no net accumulation or depletion of diffusing species--i.e., the diffusion flux is independent of time.

5.7 *(a) Briefly explain the concept of a driving force.*

(b) What is the driving force for steady-state diffusion?

Answer

(a) The driving force is that which compels a reaction to occur.

(b) The driving force for steady-state diffusion is the concentration gradient.

5.8 *The purification of hydrogen gas by diffusion through a palladium sheet was discussed in Section 5.3. Compute the number of kilograms of hydrogen that pass per hour through a 6-mm thick sheet of palladium having an area of 0.25* m^2 *at 600°C. Assume a diffusion coefficient of 1.7 ×* 10^{-8} m^2/s*, that the respective concentrations at the high- and low-pressure sides of the plate are 2.0 and 0.4 kg of hydrogen per cubic meter of palladium, and that steady-state conditions have been attained.*

Solution

This problem calls for the mass of hydrogen, per hour, that diffuses through a Pd sheet. It first becomes necessary to employ both Equations 5.1 and 5.2. Combining these expressions and solving for the mass yields

$$M = JAt = -DAt\frac{\Delta C}{\Delta x}$$

$$= -(1.7 \times 10^{-8}\ \mathrm{m^2/s})(0.25\ \mathrm{m^2})(3600\ \mathrm{s/h})\left[\frac{0.4 - 2.0\ \mathrm{kg/m^3}}{6 \times 10^{-3}\ \mathrm{m}}\right]$$

$$= 4.1 \times 10^{-3}\ \mathrm{kg/h}$$

5.9 *A sheet of steel 2.5-mm thick has nitrogen atmospheres on both sides at 900°C and is permitted to achieve a steady-state diffusion condition. The diffusion coefficient for nitrogen in steel at this temperature is 1.85 × 10^{-10} m^2/s, and the diffusion flux is found to be 1.0 × 10^{-7} $kg/m^2 \cdot s$. Also, it is known that the concentration of nitrogen in the steel at the high-pressure surface is 2 kg/m^3. How far into the sheet from this high-pressure side will the concentration be 0.5 kg/m^3? Assume a linear concentration profile.*

Solution

This problem is solved by using Equation 5.2 in the form

$$J = -\ D\frac{C_A - C_B}{x_A - x_B}$$

If we take C_A to be the point at which the concentration of nitrogen is 2 kg/m^3, then it becomes necessary to solve the above equation for x_B, as

$$x_B = x_A + D\left[\frac{C_A - C_B}{J}\right]$$

Assume x_A is zero at the surface, in which case

$$x_B = 0 + (1.85 \times 10^{-10}\ \mathrm{m^2/s})\left[\frac{2\ \mathrm{kg/m^3} - 0.5\ \mathrm{kg/m^3}}{1.0 \times 10^{-7}\ \mathrm{kg/m^2\text{-}s}}\right]$$

$$= 2.78 \times 10^{-3}\ \mathrm{m} = 2.78\ \mathrm{mm}$$

5.10 *A sheet of BCC iron 2-mm thick was exposed to a carburizing gas atmosphere on one side and a decarburizing atmosphere on the other side at 675°C. After reaching steady state, the iron was quickly cooled to room temperature. The carbon concentrations at the two surfaces of the sheet were determined to be 0.015 and 0.0068 wt%, respectively. Compute the diffusion coefficient if the diffusion flux is 7.36 × 10^{-9} kg/m^2·s. Hint: Use Equation 4.9 to convert the concentrations from weight percent to kilograms of carbon per cubic meter of iron.*

Solution

Let us first convert the carbon concentrations from weight percent to kilograms carbon per meter cubed using Equation 4.9a; the densities of carbon and iron are 2.25 g/cm^3 and 7.87 g/cm^3. For 0.015 wt% C

$$C''_{\mathrm{C}} = \frac{C_{\mathrm{C}}}{\dfrac{C_{\mathrm{C}}}{\rho_{\mathrm{C}}} + \dfrac{C_{\mathrm{Fe}}}{\rho_{\mathrm{Fe}}}} \times 10^3$$

$$= \frac{0.015}{\dfrac{0.015}{2.25\ \mathrm{g/cm^3}} + \dfrac{99.985}{7.87\ \mathrm{g/cm^3}}} \times 10^3$$

1.18 kg C/m^3

Similarly, for 0.0068 wt% C

$$C''_{\mathrm{C}} = \frac{0.0068}{\dfrac{0.0068}{2.25\ \mathrm{g/cm^3}} + \dfrac{99.9932}{7.87\ \mathrm{g/cm^3}}} \times 10^3$$

= 0.535 kg C/m^3

Now, using a rearranged form of Equation 5.2

$$D = -J\frac{\Delta x}{\Delta C} = -J\left[\frac{x_{\mathrm{A}} - x_{\mathrm{B}}}{C_{\mathrm{A}} - C_{\mathrm{B}}}\right]$$

and incorporating values of plate thickness and diffusion flux, provided in the problem statement, as well as the two concentrations of carbon determined above, the diffusion coefficient is computed as follows:

$$D = -\left(7.36 \times 10^{-9}\ \mathrm{kg/m^2\text{-}s}\right)\left[\frac{2 \times 10^{-3}\ \mathrm{m}}{0.535\ \mathrm{kg/m^3} - 1.18\ \mathrm{kg/m^3}}\right]$$

$$= 2.3 \times 10^{-11}\ \mathrm{m^2/s}$$

5.11 *When α-iron is subjected to an atmosphere of nitrogen gas, the concentration of nitrogen in the iron, C_N (in weight percent), is a function of hydrogen pressure, p_{N_2}(in MPa), and absolute temperature (T) according to*

$$C_{\mathrm{N}} = 4.90 \times 10^{-3}\sqrt{p_{\mathrm{N}_2}}\,\exp\left(-\frac{37{,}600\ \mathrm{J/mol}}{RT}\right) \qquad (5.14)$$

Furthermore, the values of D_0 and Q_d for this diffusion system are 5.0×10^{-7} m²/s and 77,000 J/mol, respectively. Consider a thin iron membrane 1.5-mm thick that is at 300°C. Compute the diffusion flux through this membrane if the nitrogen pressure on one side of the membrane is 0.10 MPa (0.99 atm) and that on the other side is 5.0 MPa (49.3 atm).

Solution

This problems asks for us to compute the diffusion flux of nitrogen gas through a 1.5-mm thick plate of iron at 300°C when the pressures on the two sides are 0.10 and 5.0 MPa. Ultimately we will employ Equation 5.2 to solve this problem. However, it first becomes necessary to determine the concentration of hydrogen at each face using Equation 5.14. At the low pressure (or B) side

$$C_{\mathrm{N(B)}} = \left(4.90 \times 10^{-3}\right)\sqrt{0.10\ \mathrm{MPa}}\,\exp\left[-\frac{37{,}600\ \mathrm{J/mol}}{(8.31\ \mathrm{J/mol\text{-}K})(300 + 273\ \mathrm{K})}\right]$$

$$5.77 \times 10^{-7}\ \mathrm{wt\%}$$

Whereas, for the high pressure (or A) side

$$C_{\mathrm{N(A)}} = \left(4.90 \times 10^{-3}\right)\sqrt{5.0\ \mathrm{MPa}}\,\exp\left[-\frac{37{,}600\ \mathrm{J/mol}}{(8.31\ \mathrm{J/mol\text{-}K})(300 + 273\ \mathrm{K})}\right]$$

$$4.08 \times 10^{-6}\ \mathrm{wt\%}$$

We now convert concentrations in weight percent to mass of nitrogen per unit volume of solid. At face B there are 5.77×10^{-7} g (or 5.77×10^{-10} kg) of hydrogen in 100 g of Fe, which is virtually pure iron. From the density of iron (7.87 g/cm³), the volume iron in 100 g (V_B) is just

$$V_{\mathrm{B}} = \frac{100\ \mathrm{g}}{7.87\ \mathrm{g/cm^3}} = 12.7\ \mathrm{cm^3} = 1.27 \times 10^{-5}\ \mathrm{m^3}$$

Therefore, the concentration of hydrogen at the B face in kilograms of N per cubic meter of alloy [$C''_{\mathrm{N(B)}}$] is just

$$C''_{\mathrm{N(B)}} = \frac{C_{\mathrm{N(B)}}}{V_{\mathrm{B}}}$$

$$= \frac{5.77 \times 10^{-10}\ \mathrm{kg}}{1.27 \times 10^{-5}\ \mathrm{m}^3} = 4.54 \times 10^{-5}\ \mathrm{kg/m}^3$$

At the A face the volume of iron in 100 g (V_A) will also be 1.27 × 10^{-5} m^3, and

$$C''_{\mathrm{N(A)}} = \frac{C_{\mathrm{N(A)}}}{V_{\mathrm{A}}}$$

$$= \frac{4.08 \times 10^{-9}\ \mathrm{kg}}{1.27 \times 10^{-5}\ \mathrm{m}^3} = 3.21 \times 10^{-4}\ \mathrm{kg/m}^3$$

Thus, the concentration gradient is just the difference between these concentrations of nitrogen divided by the thickness of the iron membrane; that is

$$\frac{\Delta C}{\Delta x} = \frac{C''_{\mathrm{N(B)}} - C''_{\mathrm{N(A)}}}{x_{\mathrm{B}} - x_{\mathrm{A}}}$$

$$= \frac{4.54 \times 10^{-5}\ \mathrm{kg/m}^3 - 3.21 \times 10^{-4}\ \mathrm{kg/m}^3}{1.5 \times 10^{-3}\ \mathrm{m}} = -\ 0.184\ \mathrm{kg/m}^4$$

At this time it becomes necessary to calculate the value of the diffusion coefficient at 300°C using Equation 5.8. Thus,

$$D = D_0 \exp\left(-\frac{Q_d}{RT}\right)$$

$$= (5.0 \times 10^{-7}\ \mathrm{m}^2/\mathrm{s}) \exp\left[-\frac{77{,}000\ \mathrm{J/mol}}{(8.31\ \mathrm{J/mol\text{-}K})(300 + 273\ \mathrm{K})}\right]$$

$$= 4.74 \times 10^{-14}\ \mathrm{m}^2/\mathrm{s}$$

And, finally, the diffusion flux is computed using Equation 5.2 by taking the negative product of this diffusion coefficient and the concentration gradient, as

$$J = -D\frac{\Delta C}{\Delta x}$$

$$= -\left(4.74 \times 10^{-14}\ \text{m}^2/\text{s}\right)\left(-\ 0.184\ \text{kg/m}^4\right) = 8.72 \times 10^{-15}\ \text{kg/m}^2\text{-s}$$

Fick's Second Law—Nonsteady-State Diffusion

5.12 *Show that*

$$C_x = \frac{B}{\sqrt{Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$

is also a solution to Equation 5.4b. The parameter B is a constant, being independent of both x and t. Hint: from Equation 5.4b, demonstrate that

$$\frac{\partial\left[\frac{B}{\sqrt{Dt}} \exp\left(-\frac{x^2}{4Dt}\right)\right]}{\partial t}$$

is equal to

$$D\left\{\frac{\partial^2\left[\frac{B}{\sqrt{Dt}} \exp\left(-\frac{x^2}{4Dt}\right)\right]}{\partial x^2}\right\}$$

Solution

When these differentiations are carried out, both are equal to the following expression:

$$\frac{B}{2D^{1/2}t^{3/2}}\left(\frac{x^2}{2Dt} - 1\right)\exp\left(-\frac{x^2}{4Dt}\right)$$

5.13 *Determine the carburizing time necessary to achieve a carbon concentration of 0.30 wt% at a position 4 mm into an iron–carbon alloy that initially contains 0.10 wt% C. The surface concentration is to be maintained at 0.90 wt% C, and the treatment is to be conducted at 1100°C. Use the diffusion data for γ-Fe in Table 5.2.*

Solution

We are asked to compute the carburizing (i.e., diffusion) time required for a specific nonsteady-state diffusion situation. It is first necessary to use Equation 5.5:

$$\frac{C_x - C_0}{C_s - C_0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

wherein, $C_x = 0.30$, $C_0 = 0.10$, $C_s = 0.90$, and $x = 4\text{ mm} = 4 \times 10^{-3}$ m. Thus,

$$\frac{C_x - C_0}{C_s - C_0} = \frac{0.30 - 0.10}{0.90 - 0.10} = 0.2500 = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

or

$$\operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = 1 - 0.2500 = 0.7500$$

By linear interpolation using data from Table 5.1

z	erf(z)
0.80	0.7421
z	0.7500
0.85	0.7707

which leads to the following:

$$\frac{z - 0.800}{0.850 - 0.800} = \frac{0.7500 - 0.7421}{0.7707 - 0.7421}$$

From which

$$z = 0.814 = \frac{x}{2\sqrt{Dt}}$$

Now, from Table 5.2, data for the diffusion of carbon into γ-iron are as follows:

$D_0 = 2.3 \times 10^{-5}$ m^2/s

Q_d = 148,000 J/mol

Therefore at 1100°C (1373 K)

$$D = (2.3 \times 10^{-5}\ \mathrm{m^2/s})\exp\left[-\frac{148{,}000\ \mathrm{J/mol}}{(8.31\ \mathrm{J/mol\text{-}K})(1373\ \mathrm{K})}\right]$$

$$= 5.35 \times 10^{-11}\ \mathrm{m^2/s}$$

Thus,

$$0.814 = \frac{4 \times 10^{-3}\ \mathrm{m}}{(2)\sqrt{(5.35 \times 10^{-11}\ \mathrm{m^2/s})(t)}}$$

Solving for *t* yields

$$t = \frac{(4 \times 10^{-3}\ \mathrm{m})^2}{(2)^2(0.814)^2(5.35 \times 10^{-11}\ \mathrm{m^2/s})}$$

$$t = 1.13 \times 10^5\ \mathrm{s} = 31.3\ \mathrm{h}$$

5.14 *An FCC iron–carbon alloy initially containing 0.55 wt% C is exposed to an oxygen-rich and virtually carbon-free atmosphere at 1325 K (1052°C). Under these circumstances the carbon diffuses from the alloy and reacts at the surface with the oxygen in the atmosphere—that is, the carbon concentration at the surface position is maintained essentially at 0 wt% C. (This process of carbon depletion is termed decarburization.) At what position will the carbon concentration be 0.25 wt% after a 10-h treatment? The value of D at 1325 K is* 3.3×10^{-11} m^2/s.

Solution

This problem asks that we determine the position at which the carbon concentration is 0.25 wt% after a 10-h heat treatment at 1325 K when C_0 = 0.55 wt% C. From Equation 5.5

$$\frac{C_x - C_0}{C_s - C_0} = \frac{0.25 - 0.55}{0 - 0.55} = 0.5455 = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Thus,

$$\operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = 0.4545$$

Using data in Table 5.1 and linear interpolation

z	erf (z)
0.40	0.4284
z	0.4545
0.45	0.4755

$$\frac{z - 0.40}{0.45 - 0.40} = \frac{0.4545 - 0.4284}{0.4755 - 0.4284}$$

which leads to,

$$z = 0.4277$$

This means that

$$\frac{x}{2\sqrt{Dt}} = 0.4277$$

And, finally

$$x = 2(0.4277)\sqrt{Dt} = (0.8554)\sqrt{(3.3 \times 10^{-11}\ \mathrm{m^2/s})(3.6 \times 10^4\ \mathrm{s})}$$

$$= 9.32 \times 10^{-4}\ \text{m} = 0.932\ \text{mm}$$

Note: This problem may also be solved using the "Diffusion" module in the *VMSE* software. Open the "Diffusion" module, click on the "Diffusion Design" submodule, and then do the following:

1. Enter the given data in left-hand window that appears. In the window below the label "D Value" enter the value of the diffusion coefficient—viz. "3.3e-11".

2. In the window just below the label "Initial, C0" enter the initial concentration—viz. "0.55".

3. In the window the lies below "Surface, Cs" enter the surface concentration—viz. "0".

4. Then in the "Diffusion Time t" window enter the time in seconds; in 10 h there are (60 s/min)(60 min/h)(10 h) = 36,000 s—so enter the value "3.6e4".

5. Next, at the bottom of this window click on the button labeled "Add curve".

6. On the right portion of the screen will appear a concentration profile for this particular diffusion situation. A diamond-shaped cursor will appear at the upper left-hand corner of the resulting curve. Click and drag this cursor down the curve to the point at which the number below "Concentration:" reads "0.25 wt%". Then read the value under the "Distance:". For this problem, this value (the solution to the problem) is 0.91 mm.

5.15 *Nitrogen from a gaseous phase is to be diffused into pure iron at 675°C. If the surface concentration is maintained at 0.2 wt% N, what will be the concentration 2 mm from the surface after 25 h? The diffusion coefficient for nitrogen in iron at 675°C is 2.8 × 10^{-11} m^2/s.*

Solution

This problem asks us to compute the nitrogen concentration (C_x) at the 2 mm position after a 25 h diffusion time, when diffusion is nonsteady-state. From Equation 5.5

$$\frac{C_x - C_0}{C_s - C_0} = \frac{C_x - 0}{0.2 - 0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$= 1 - \operatorname{erf}\left[\frac{2 \times 10^{-3}\ \text{m}}{(2)\sqrt{(2.8 \times 10^{-11}\ \text{m}^2/\text{s})(25\ \text{h})(3600\ \text{s/h})}}\right]$$

$$= 1 - \operatorname{erf}(0.630)$$

Using data in Table 5.1 and linear interpolation

z	erf (z)
0.600	0.6039
0.630	*y*
0.650	0.6420

$$\frac{0.630 - 0.600}{0.650 - 0.600} = \frac{y - 0.6039}{0.6420 - 0.6039}$$

from which

$$y = \operatorname{erf}(0.630) = 0.6268$$

Thus,

$$\frac{C_x - 0}{0.2 - 0} = 1.0 - 0.6268$$

And solving for C_x gives

$$C_x = 0.075\ \text{wt\% N}$$

Note: This problem may also be solved using the "Diffusion" module in the *VMSE* software. Open the "Diffusion" module, click on the "Diffusion Design" submodule, and then do the following:

1. Enter the given data in left-hand window that appears. In the window below the label "D Value" enter the value of the diffusion coefficient—viz. "2.8e-11".

2. In the window just below the label "Initial, C0" enter the initial concentration—viz. "0".

3. In the window the lies below "Surface, Cs" enter the surface concentration—viz. "0.2".

4. Then in the "Diffusion Time t" window enter the time in seconds; in 25 h there are (60 s/min)(60 min/h)(25 h) = 90,000 s—so enter the value "9e4".

5. Next, at the bottom of this window click on the button labeled "Add curve".

6. On the right portion of the screen will appear a concentration profile for this particular diffusion situation. A diamond-shaped cursor will appear at the upper left-hand corner of the resulting curve. Click and drag this cursor down the curve to the point at which the number below "Distance:" reads "2.00 mm". Then read the value under the "Concentration:". For this problem, this value (the solution to the problem) is 0.07 wt%.

5.16 *Consider a diffusion couple composed of two semi-infinite solids of the same metal and that each side of the diffusion couple has a different concentration of the same elemental impurity; furthermore, assume each impurity level is constant throughout its side of the diffusion couple. For this situation, the solution to Fick's second law (assuming that the diffusion coefficient for the impurity is independent of concentration) is as follows:*

$$C_x = C_2 + \left(\frac{C_1 - C_2}{2}\right)\left[1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right] \tag{5.15}$$

The schematic diffusion profile in Figure 5.13 shows these concentration parameters as well as concentration profiles at times t = 0 and t > 0. Please note that at t = 0, the x = 0 position is taken as the initial diffusion couple interface, whereas C_1 is the impurity concentration for x < 0, and C_2 is the impurity content for x > 0.

Consider a diffusion couple composed of pure nickel and a 55 wt% Ni-45 wt% Cu alloy (similar to the couple shown in Figure 5.1). Determine the time this diffusion couple must be heated at 1000°C (1273 K) in order to achieve a composition of 56.5 wt% Ni a distance of 15 μm into the Ni-Cu alloy referenced to the original interface. Values for the preexponential and activation energy for this diffusion system are 2.3 × 10^{-4} m^2/s and 252,000 J/mol.

Solution

This problem calls for us to determine the value of time *t* in Equation 5.15 given the following values:

C_1 = 100 wt% Ni

C_2 = 55 wt% Ni

C_x = 56.5 wt% Ni

T = 1273 K

x = 15 μm = 15 × 10^{-6} m

D_0 = 2.3 × 10^{-4} m^2/s

Q_d = 252,000 J/mol

Let us first of all compute the value of the diffusion coefficient *D* using Equation 5.8:

$$D = D_0 \exp\left(-\frac{Q_d}{RT}\right)$$

$$= (2.3 \times 10^{-4}\ \text{m}^2/\text{s}) \exp\left[-\frac{252{,}000\ \text{J/mol}}{(8.31\ \text{J/mol}{\cdot}\text{K})(1273\ \text{K})}\right]$$

$$= 1.04 \times 10^{-14}\ \mathrm{m^2/s}$$

Now incorporating values for all of the parameters except *t* into Equation 5.12 leads to

$$56.5\ \text{wt\% Ni} = 55\ \text{wt\% Ni} + \left(\frac{100\ \text{wt\% Ni} - 55\ \text{wt\% Cu}}{2}\right)\left[1 - \mathrm{erf}\left(\frac{15 \times 10^{-6}\ \mathrm{m}}{2\sqrt{(1.04 \times 10^{-14}\ \mathrm{m^2/s})(t)}}\right)\right]$$

This expression reduces to the following:

$$0.9333 = \mathrm{erf}\left(\frac{73.54\ \mathrm{s}^{1/2}}{\sqrt{t}}\right)$$

From Table 5.1 to determine the value of *z* when erf(*z*) = 0.9333 an interpolation procedure is necessary as follows:

z	erf(*z*)
1.2	0.9103
z	0.9333
1.3	0.9340

$$\frac{z - 1.2}{1.3 - 1.2} = \frac{0.9333 - 0.9103}{0.9340 - 0.9103}$$

And solving for *z* we have

$$z = 1.297$$

Which means that

$$\frac{73.54\ \mathrm{s}^{1/2}}{\sqrt{t}} = 1.297$$

Or that

$$t = \left(\frac{73.54}{1.297}\ \mathrm{s}^{1/2}\right)^2$$

$$= 3215\ \text{s} = 53.6\ \text{min} = 0.89\ \text{h}$$

5.17 *Consider a diffusion couple composed of two cobalt-iron alloys; one has a composition of 75 wt% Co-25 wt% Fe; the other alloy composition is 50 wt% Co-50 wt% Fe. If this couple is heated to a temperature of 800°C (1073 K) for 20,000 s, determine how far from the original interface into the 50 wt% Co-50 wt% Fe alloy the composition has increased to 52 wt%Co-48 wt% Fe. For the diffusion coefficient, assume values of 6.6 × 10*$^{-6}$ *m*^{2}*/s and 247,000 J/mol, respectively, for the preexponential and activation energy.*

Solution

This problem calls for us to determine the value of the distance, *x*, in Equation 5.15 given the following values:

C_1 = 75 wt% Co

C_2 = 50 wt% Co

C_x = 52 wt% Co

T = 1073 K

t = 20,000 s

$D_0 = 6.6 \times 10^{-6}$ m^2/s

Q_d = 247,000 J/mol

Let us first of all compute the value of the diffusion coefficient *D* using Equation 5.8:

$$D = D_0 \exp\left(-\frac{Q_d}{RT}\right)$$

$$= (6.6 \times 10^{-6}\ \mathrm{m^2/s})\exp\left[-\frac{247{,}000\ \mathrm{J/mol}}{(8.31\ \mathrm{J/mol\text{i}K})(1073\ \mathrm{K})}\right]$$

$$= 6.15 \times 10^{-18}\ \mathrm{m^2/s}$$

Now incorporating values for all of the parameters except *x* into Equation 5.15 leads to

$$52\ \mathrm{wt\%\ Co} = 50\ \mathrm{wt\%\ Co} + \left(\frac{75\ \mathrm{wt\%\ Co} - 50\ \mathrm{wt\%\ Co}}{2}\right)\left[1 - \mathrm{erf}\left(\frac{x}{2\sqrt{(6.15 \times 10^{-18}\ \mathrm{m^2/s})(20{,}000\ \mathrm{s})}}\right)\right]$$

This expression reduces to the following:

$$0.8400 = \mathrm{erf}\left(\frac{x}{7.01 \times 10^{-7}\ \mathrm{m}}\right)$$

From Table 5.1 to determine the value of *z* when erf(*z*) = 0.8400 an interpolation procedure is necessary as follows:

z	erf(*z*)
0.95	0.8209
z	0.8400
1.0	0.8427

$$\frac{z - 0.95}{1.0 - 0.95} = \frac{0.8400 - 0.8209}{0.8427 - 0.8209}$$

And solving for *z* we have

$$z = 0.994$$

Which means that

$$\frac{x}{7.01 \times 10^{-7}\ \mathrm{m}} = 0.994$$

Or that

$$x = (7.01 \times 10^{-7}\ \mathrm{m})(0.994)$$

$$= 6.97 \times 10^{-7}\ \mathrm{m} = 0.697\ \mu\mathrm{m}$$

5.18 *Consider a diffusion couple between silver and a gold alloy that contains 10 wt% silver. This couple is heat treated at an elevated temperature and it was found that after 850 s the concentration of silver had increased to 12 wt% at 10 μm from the interface into the Ag-Au alloy. Assuming preexponential and activation energy values of 7.2 × 10^{-6} m^2/s and 168,000 J/mol, compute the temperature of this heat treatment. (Note: you may find Figure 5.13 and Equation 5.15 helpful.)*

Solution

This problem calls for us to determine the value of time *t* in Equation 5.15 given the following values:

C_1 = 100 wt% Ag

C_2 = 10 wt Ag

C_x = 12 wt% Ag

t = 850 s

x = 10 μm = 10 × 10^{-6} m

D_0 = 7.2 × 10^{-6} m^2/s

Q_d = 168,000 J/mol

We first of all substitute values for all of the above parameters—except for D_0 and Q_d. This leads to the following expressions:

$$C_x = C_2 + \left(\frac{C_1 - C_2}{2}\right)\left[1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right]$$

$$12\ \text{wt\%} = 10\ \text{wt\%} + \left(\frac{100\ \text{wt\%} - 10\ \text{wt\%}}{2}\right)\left[1 - \operatorname{erf}\left(\frac{10 \times 10^{-6}\ \text{m}}{2\sqrt{D(850\ \text{s})}}\right)\right]$$

This equation reduces to the following:

$$0.9556 = \operatorname{erf}\left(\frac{1.715 \times 10^{-7}}{\sqrt{D}}\right)$$

Or

$$0.9556 = \operatorname{erf}(z)$$

It is now necessary to determine using the data in Table 5.1 the value of *z* for which the error function has a value of 0.9556. This requires an interpolation using the following data:

z	erf(z)
1.4	0.9523
z	0.9556
1.5	0.9661

The interpolation equation is

$$\frac{1.5 - z}{1.5 - 1.4} = \frac{0.9661 - 0.9556}{0.9661 - 0.9523}$$

Solving for z from this equation gives

$$z = 1.424$$

Incorporating this value into the above equation yields

$$1.424 = \frac{1.715 \times 10^{-7}}{\sqrt{D}}$$

from which D is equal to

$$D = 1.45 \times 10^{-14} \text{ m}^2/\text{s}$$

We may now compute the temperature at which the diffusion coefficient has this value using Equation 5.8. Taking natural logarithms of both sides of Equation 5.8 leads to

$$\ln D - \ln D_0 - \frac{Q_d}{RT}$$

And, solving for T

$$T = -\frac{Q_d}{R(\ln D - \ln D_0)}$$

Into which we insert values of D, D_0, and Q_d as follows:

$$T = -\frac{168{,}000 \text{ J/m}}{(8.31 \text{ J/mol}\cdot\text{K})\left[\ln(1.45 \times 10^{-14} \text{ m}^2/\text{s}) - \ln(7.2 \times 10^{-6} \text{ m}^2/\text{s})\right]}$$

$$= 1010 \text{ K } (737°\text{C})$$

5.19 *For a steel alloy it has been determined that a carburizing heat treatment of 15 h duration will raise the carbon concentration to 0.35 wt% at a point 2.0 mm from the surface. Estimate the time necessary to achieve the same concentration at a 6.0-mm position for an identical steel and at the same carburizing temperature.*

Solution

This problem calls for an estimate of the time necessary to achieve a carbon concentration of 0.35 wt% at a point 6.0 mm from the surface. From Equation 5.6b,

$$\frac{x^2}{Dt} = \text{constant}$$

But since the temperature is constant, so also is *D* constant, which means that

$$\frac{x^2}{t} = \text{constant}$$

or

$$\frac{x_1^2}{t_1} = \frac{x_2^2}{t_2}$$

Thus, if we assign x_1 = 0.2 mm, x_2 = 0.6 mm, and t_1 15 h, then

$$\frac{(2.0\ \text{mm})^2}{15\ \text{h}} = \frac{(6.0\ \text{mm})^2}{t_2}$$

from which

$$t_2 = 135\ \text{h}$$

Factors That Influence Diffusion

5.20 *Cite the values of the diffusion coefficients for the interdiffusion of carbon in both α-iron (BCC) and γ-iron (FCC) at 900°C. Which is larger? Explain why this is the case.*

Solution

We are asked to compute the diffusion coefficients of C in both α and γ iron at 900°C. Using the data in Table 5.2,

$$D_\alpha = (1.1 \times 10^{-6} \text{ m}^2/\text{s}) \exp\left[-\frac{87{,}400 \text{ J/mol}}{(8.31 \text{ J/mol-K})(1173 \text{ K})}\right]$$

$$= 1.40 \times 10^{-10} \text{ m}^2/\text{s}$$

$$D_\gamma = (2.3 \times 10^{-5} \text{ m}^2/\text{s}) \exp\left[-\frac{148{,}000 \text{ J/mol}}{(8.31 \text{ J/mol-K})(1173 \text{ K})}\right]$$

$$= 5.86 \times 10^{-12} \text{ m}^2/\text{s}$$

The *D* for diffusion of C in BCC α iron is larger, the reason being that the atomic packing factor is smaller than for FCC γ iron (0.68 versus 0.74—Section 3.4); this means that there is slightly more interstitial void space in the BCC Fe, and, therefore, the motion of the interstitial carbon atoms occurs more easily.

5.21 *Using the data in Table 5.2, compute the value of D for the diffusion of magnesium in aluminum at 400°C.*

Solution

This problem asks us to compute the magnitude of *D* for the diffusion of Mg in Al at 400°C (673 K). Incorporating the appropriate data from Table 5.2—i.e.,

$D_0 = 1.2 \times 10^{-4}$ m^2/s

Q_d = 130,000 J/mol

into Equation 5.8 leads to

$$D = D_0 \exp\left(-\frac{Q_d}{RT}\right)$$

$$= \left(1.2 \times 10^{-4} \text{ m}^2/\text{s}\right) \exp\left[-\frac{130{,}000 \text{ J/mol}}{(8.31 \text{ J/mol-K})(673 \text{ K})}\right]$$

$$= 9.64 \times 10^{-15} \text{ m}^2/\text{s}$$

Note: This problem may also be solved using the "Diffusion" module in the *VMSE* software. Open the "Diffusion" module, click on the "D vs 1/T Plot" submodule, and then do the following:

1. In the left-hand window that appears, click on the "Mg-Al" pair under the "Diffusing Species"-"Host Metal" headings.

2. Next, at the bottom of this window, click the "Add Curve" button.

3. A log D versus 1/T plot then appears, with a line for the temperature dependence of the diffusion coefficient for Mg in Al. At the top of this curve is a diamond-shaped cursor. Click-and-drag this cursor down the line to the point at which the entry under the "Temperature (T):" label reads 673 K (inasmuch as this is the Kelvin equivalent of 400ºC). Finally, the diffusion coefficient value at this temperature is given under the label "Diff Coeff (D):". For this problem, the value is 8.0×10^{-15} m^2/s.

5.22 *Using the data in Table 5.2 compute the value of D for the diffusion of nitrogen in FCC iron at 950°C.*

Solution

This problem asks us to compute the magnitude of *D* for the diffusion of N in FCC Fe at 950°C. Incorporating the appropriate data from Table 5.2—i.e.,

$D_0 = 9.1 \times 10^{-5}$ m^2/s

Q_d = 168,000 J/mol

into Equation 5.8 leads to

$$D = D_0 \exp\left(-\frac{Q_d}{RT}\right)$$

$$= (9.1 \times 10^{-5} \text{ m}^2/\text{s}) \exp\left[-\frac{168{,}000 \text{ J/mol}}{(8.31 \text{ J/mol-K})(950°\text{C} + 273)}\right]$$

$$= 6.0 \times 10^{-12} \text{ m}^2/\text{s}$$

Note: this problem may also be solved using the "Diffusion" module in the *VMSE* software. Open the "Diffusion" module, click on the "D vs 1/T Plot" submodule, and then do the following:

1. In the left-hand window that appears, click on the "Custom 1 under the "Diffusing Species" heading (since none of the preset systems is for the diffusion of nitrogen in FCC iron).

2. Under "D_0" within the "Diffusion Coefficients" box enter "9.1e-5"; and under "Q_d" enter "168".

3. It is necessary to enter maximum and minimum temperatures within the "Temperature Range" box. Because our temperature of interest is 950°C, enter "900" in the "T Min" "C" box, and "1000" in the T Max "C" box.

3. Upon clicking on the "Add Curve" box, a log D versus 1/T plot then appears, with a line for the temperature dependence of the diffusion coefficient for N in FCC iron. At the top of this curve is a diamond-shaped cursor. Click-and-drag this cursor down the line to the point at which the entry under the "Temperature (T):" label reads 1223 K (inasmuch as this is the Kelvin equivalent of 950ºC). Finally, the diffusion coefficient value at this temperature is given under the label "Diff Coeff (D):". For this problem, the value is 6.0×10^{-12} m^2/s.

5.23 *At what temperature will the diffusion coefficient for the diffusion of zinc in copper have a value of* 2.6×10^{-16} m^2/s*? Use the diffusion data in Table 5.2.*

Solution

We are asked to calculate the temperature at which the diffusion coefficient for the diffusion of Zn in Cu has a value of 2.6×10^{-16} m^2/s. Solving for T from Equation 5.9a

$$T = -\frac{Q_d}{R(\ln D - \ln D_0)}$$

and using the data from Table 5.2 for the diffusion of Zn in Cu (i.e., $D_0 = 2.4 \times 10^{-5}$ m^2/s and Q_d = 189,000 J/mol) , we get

$$T = -\frac{189{,}000 \text{ J/mol}}{(8.31 \text{ J/mol-K})\left[\ln\left(2.6 \times 10^{-16} \text{ m}^2/\text{s}\right) - \ln\left(2.4 \times 10^{-5} \text{ m}^2/\text{s}\right)\right]}$$

$$= 901 \text{ K} = 628°\text{C}$$

Note: This problem may also be solved using the “Diffusion” module in the *VMSE* software. Open the “Diffusion” module, click on the “D vs 1/T Plot” submodule, and then do the following:

1. In the left-hand window that appears, there is a preset set of data for the diffusion of Zn in Cu system. Therefore, click on the "Cu-Ni" box.

2. In the column on the right-hand side of this window the activation energy-preexponential data for this problem. In the window under “D0” the preexponential value, “2.4e-5”, is displayed. Next just below the “Qd” the activation energy value (in KJ/mol), “189” is displayed. In the "Temperature Range" window minimum ("T Min") and maximum ("T Max") temperatures are displayed, in both °C and K. The default values for minimum and maximum temperatures are 800ºC and 1140ºC, respectively.

3. Next, at the bottom of this window, click the "Add Curve" button.

4. A log D versus 1/T plot then appears, with a line for the temperature dependence of the diffusion coefficient for Zn in Cu. At the top of this curve is a diamond-shaped cursor. We want to click-and-drag this cursor down the line (to the right) to the point at which the entry under the “Diff Coeff (D):” label reads 2.6×10^{-16} m^2/s. As we drag the cursor to the right, the value of the diffusion coefficient continues to decrease, but only to about 1.5

× 10^{-14} m^2/s. This means that the temperature at which the diffusion coefficient is 2.6 × 10^{-16} m^2/s is lower than 800ºC. Therefore, let us change the T Min value to 600ºC. After this change is made click again on the "Add Curve", and a new curve appears. Now click and drag the cursor to the right until "2.6 × 10^{-16} m^2/s " is displayed under "Diff Coeff (D)". At this time under the "Temperature (T)" label is displayed the temperature—in this case "902 K".

5.24 *At what temperature will the diffusion coefficient for the diffusion of nickel in copper have a value of* 4.0×10^{-17} *m*^{2}*/s? Use the diffusion data in Table 5.2.*

Solution

We are asked to calculate the temperature at which the diffusion coefficient for the diffusion of Ni in Cu has a value of 4.0×10^{-17} m^2/s. Solving for T from Equation 5.9a

$$T = -\frac{Q_d}{R(\ln D - \ln D_0)}$$

and using the data from Table 5.2 for the diffusion of Ni in Cu (i.e., $D_0 = 1.9 \times 10^{-4}$ m^2/s and Q_d = 230,000 J/mol) , we get

$$T = -\frac{230{,}000 \text{ J/mol}}{(8.31 \text{ J/mol-K})\left[\ln\left(4.0 \times 10^{-17} \text{ m}^2/\text{s}\right) - \ln\left(1.9 \times 10^{-4} \text{ m}^2/\text{s}\right)\right]}$$

$$= 948 \text{ K} = 675°\text{C}$$

Note: This problem may also be solved using the “Diffusion” module in the *VMSE* software. Open the “Diffusion” module, click on the “D vs 1/T Plot” submodule, and then do the following:

1. In the left-hand window that appears, there is a preset set of data, but none for the diffusion of Ni in Cu. This requires us specify our settings by clicking on the “Custom1” box.

2. In the column on the right-hand side of this window enter the data for this problem, which are taken from Table 5.2. In the window under “D0” the preexponential value, enter “1.9e-4”. Next just below in the “Qd” window enter the activation energy value (in KJ/mol), in this case "230". It is now necessary to specify a temperature range over which the data is to be plotted—let us arbitrarily pick 500°C to be the miminum, which is entered in the "T Min" under "Temperature Range" window; we will also select 1000°C to be the maximum temperature, which is entered in the "T Max" window.

3. Next, at the bottom of this window, click the "Add Curve" button.

4. A log D versus 1/T plot then appears, with a line for the temperature dependence of the diffusion coefficient for Ni in Cu. At the top of this curve is a diamond-shaped cursor. We next click-and-drag this cursor

down the line to the point at which the entry under the “Diff Coeff (D):” label reads 4.0×10^{-17} m^2/s. The temperature that appears under the "Temperature (T)" label is 949 K, which is the solution.

5.25 *The preexponential and activation energy for the diffusion of chromium in nickel are 1.1 × 10^{-4} m^2/s and 272,000 J/mol, respectively. At what temperature will the diffusion coefficient have a value of 1.2 × 10^{-14} m^2/s?*

Solution

We are asked to calculate the temperature at which the diffusion coefficient for the diffusion of Cr in Ni has a value of 1.2 × 10^{-14} m^2/s. Solving for T from Equation 5.9a

$$T = -\frac{Q_d}{R(\ln D - \ln D_0)}$$

and using the data the problem statement (i.e., $D_0 = 1.1 \times 10^{-4}\ m^2/s$ and Q_d = 272,000 J/mol) , we get

$$T = -\frac{272{,}000 \text{ J/mol}}{(8.31 \text{ J/mol-K})\left[\ln\left(1.2 \times 10^{-14} \text{ m}^2/\text{s}\right) - \ln\left(1.1 \times 10^{-4} \text{ m}^2/\text{s}\right)\right]}$$

$$= 1427 \text{ K} = 1154°\text{C}$$

Note: This problem may also be solved using the “Diffusion” module in the *VMSE* software. Open the “Diffusion” module, click on the “D vs 1/T Plot” submodule, and then do the following:

1. In the left-hand window that appears, there is a preset set of data, but none for the diffusion of Cr in Ni. This requires us specify our settings by clicking on the “Custom1” box.

2. In the column on the right-hand side of this window enter the data for this problem, which are given in the problem statement. In the window under “D0” enter “1.1e-4”. Next just below in the “Qd” window enter the activation energy value (in KJ/mol), in this case "272". It is now necessary to specify a temperature range over which the data is to be plotted—let us arbitrarily pick 1000°C to be the miminum, which is entered in the "T Min" under "Temperature Range" window; we will also select 1500°C to be the maximum temperature, which is entered in the "T Max" window.

3. Next, at the bottom of this window, click the "Add Curve" button.

4. A log D versus 1/T plot then appears, with a line for the temperature dependence of the diffusion coefficient for Cr in Ni. At the top of this curve is a diamond-shaped cursor. We next click-and-drag this cursor

down the line to the point at which the entry under the “Diff Coeff (D):” label reads 1.2 × 10^{-14} m^2/s. The temperature that appears under the "Temperature (T)" label is 1430 K.

5.26 *The activation energy for the diffusion of copper in silver is 193,000 J/mol. Calculate the diffusion coefficient at 1200 K (927°C), given that D at 1000 K (727°C) is 1.0 × 10^{-14} m^2/s.*

Solution

To solve this problem it first becomes necessary to solve for D_0 from a rearranged form of Equation 5.8 and using 1000 K diffusion data:

$$D_0 = D \exp\left(\frac{Q_d}{RT}\right)$$

$$= (1.0 \times 10^{-14}\ \text{m}^2/\text{s}) \exp\left[\frac{193{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(1000\ \text{K})}\right]$$

$$1.22 \times 10^{-4}\text{m}^2/\text{s}$$

Now, solving for D at 1200 K (again using Equation 5.8) gives

$$D = (1.22 \times 10^{-4}\ \text{m}^2/\text{s}) \exp\left[-\frac{193{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(1200\ \text{K})}\right]$$

$$4.8 \times 10^{-13}\ \text{m}^2/\text{s}$$

5.27 *The diffusion coefficients for nickel in iron are given at two temperatures, as follows:*

T (K)	*D (m^2/s)*
1473	*2.2×10^{-15}*
1673	*4.8×10^{-14}*

(a) Determine the values of D_0 and the activation energy Q_d.

(b) What is the magnitude of D at 1300°C (1573 K)?

Solution

(a) Using Equation 5.9a, we set up two simultaneous equations with Q_d and D_0 as unknowns as follows:

$$\ln D_1 = \ln D_0 - \frac{Q_d}{R}\left(\frac{1}{T_1}\right)$$

$$\ln D_2 = \ln D_0 - \frac{Q_d}{R}\left(\frac{1}{T_2}\right)$$

Now, solving for Q_d in terms of temperatures T_1 and T_2 (1473 K and 1673 K) and D_1 and D_2 (2.2×10^{-15} and 4.8×10^{-14} m^2/s), we get

$$Q_d = -R\,\frac{\ln D_1 - \ln D_2}{\dfrac{1}{T_1} - \dfrac{1}{T_2}}$$

$$= -\,(8.31\ \text{J/mol-K})\,\frac{\left[\ln\left(2.2 \times 10^{-15}\right) - \ln\left(4.8 \times 10^{-14}\right)\right]}{\dfrac{1}{1473\ \text{K}} - \dfrac{1}{1673\ \text{K}}}$$

= 315,700 J/mol

Now, solving for D_0 from a rearranged form of Equation 5.8 (and using the 1473 K value of D)

$$D_0 = D_1 \exp\left(\frac{Q_d}{RT_1}\right)$$

$$= \left(2.2 \times 10^{-15}\ \text{m}^2/\text{s}\right)\exp\left[\frac{315{,}700\ \text{J/mol}}{(8.31\ \text{J/mol-K})(1473\ \text{K})}\right]$$

$$= 3.5 \times 10^{-4} \text{ m}^2/\text{s}$$

(b) Using these values of D_0 and Q_d, D at 1573 K is just

$$D = (3.5 \times 10^{-4} \text{ m}^2/\text{s}) \exp\left[-\frac{315{,}700 \text{ J/mol}}{(8.31 \text{ J/mol-K})(1573 \text{ K})}\right]$$

$$= 1.1 \times 10^{-14} \text{ m}^2/\text{s}$$

Note: This problem may also be solved using the “Diffusion” module in the *VMSE* software. Open the “Diffusion” module, click on the “D0 and Qd from Experimental Data” submodule, and then do the following:

1. In the left-hand window that appears, enter the two temperatures from the table in the book (viz. “1473” and “1673”, in the first two boxes under the column labeled “T (K)”. Next, enter the corresponding diffusion coefficient values (viz. “2.2e-15” and “4.8e-14”).

3. Next, at the bottom of this window, click the “Plot data” button.

4. A log D versus 1/T plot then appears, with a line for the temperature dependence for this diffusion system. At the top of this window are give values for D_0 and Q_d; for this specific problem these values are 3.49 × 10^{-4} m^2/s ("Do=3.49E-04") and 315 kJ/mol ("Qd=315"), respectively

5. To solve the (b) part of the problem we utilize the diamond-shaped cursor that is located at the top of the line on this plot. Click-and-drag this cursor down the line to the point at which the entry under the “Temperature (T):” label reads “1573”. The value of the diffusion coefficient at this temperature is given under the label “Diff Coeff (D):”. For our problem, this value is 1.2 × 10^{-14} m^2/s ("1.2E-14 m^2/s").

5.28 *The diffusion coefficients for carbon in nickel are given at two temperatures are as follows:*

T (°C)	*D (m^2/s)*
600	*5.5×10^{-14}*
700	*3.9×10^{-13}*

(a) Determine the values of D_0 and Q_d.

(b) What is the magnitude of D at 850°C?

Solution

(a) Using Equation 5.9a, we set up two simultaneous equations with Q_d and D_0 as unknowns as follows:

$$\ln D_1 = \ln D_0 - \frac{Q_d}{R}\left(\frac{1}{T_1}\right)$$

$$\ln D_2 = \ln D_0 - \frac{Q_d}{R}\left(\frac{1}{T_2}\right)$$

Solving for Q_d in terms of temperatures T_1 and T_2 (873 K [600°C] and 973 K [700°C]) and D_1 and D_2 (5.5×10^{-14} and 3.9×10^{-13} m^2/s), we get

$$Q_d = -R\,\frac{\ln D_1 - \ln D_2}{\frac{1}{T_1} - \frac{1}{T_2}}$$

$$= -\frac{(8.31 \text{ J/mol-K})\left[\ln\left(5.5 \times 10^{-14}\right) - \ln\left(3.9 \times 10^{-13}\right)\right]}{\frac{1}{873 \text{ K}} - \frac{1}{973 \text{ K}}}$$

$$= 138{,}300 \text{ J/mol}$$

Now, solving for D_0 from a rearranged form of Equation 5.8 (and using the 600°C value of *D*)

$$D_0 = D_1 \exp\left(\frac{Q_d}{RT_1}\right)$$

$$= \left(5.5 \times 10^{-14} \text{ m}^2/\text{s}\right)\exp\left[\frac{138{,}300 \text{ J/mol}}{(8.31 \text{ J/mol-K})(873 \text{ K})}\right]$$

$$= 1.05 \times 10^{-5}\ \mathrm{m^2/s}$$

(b) Using these values of D_0 and Q_d, D at 1123 K (850°C) is just

$$D = (1.05 \times 10^{-5}\ \mathrm{m^2/s})\exp\left[-\frac{138{,}300\ \mathrm{J/mol}}{(8.31\ \mathrm{J/mol\text{-}K})(1123\ \mathrm{K})}\right]$$

$$= 3.8 \times 10^{-12}\ \mathrm{m^2/s}$$

Note: this problem may also be solved using the “Diffusion” module in the *VMSE* software. Open the “Diffusion” module, click on the “D0 and Qd from Experimental Data” submodule, and then do the following:

1. In the left-hand window that appears, enter the two temperatures from the table in the book (converted from degrees Celsius to Kelvins) (viz. “873” (600ºC) and “973” (700ºC), in the first two boxes under the column labeled “T (K)”. Next, enter the corresponding diffusion coefficient values (viz. “5.5e-14” and “3.9e-13”).

3. Next, at the bottom of this window, click the “Plot data” button.

4. A log D versus 1/T plot then appears, with a line for the temperature dependence for this diffusion system. At the top of this window are give values for D_0 and Q_d; for this specific problem these values are 1.04×10^{-5} $\mathrm{m^2/s}$ ("Do=1.04E-05") and 138 kJ/mol ("Qd=138"), respectively

5. It is not possible to solve part (b) of this problem using this submodule—data plotted do not extend to 850ºC. Therefore, it necessary to utilize the "D vs 1/T Plot" submodule.

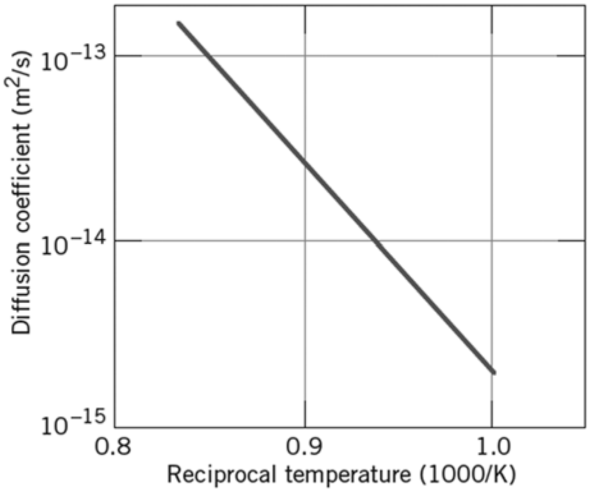
6. Open this submoduile, and in the left-hand window that appears, there is a preset set of data, but none for the diffusion of C in Ni. This requires us specify our settings by clicking on the “Custom1” box.

7. In the column on the right-hand side of this window enter the data for this problem, which have already been determined. In the window under “D0” the preexponential value, enter “1.04e-5”. Next just below in the “Qd” window enter the activation energy value (in KJ/mol), in this case "138". It is now necessary to specify a temperature range over which the data is to be plotted—since we are interested in the value of *D* at 850ºC let us arbitrarily pick 600°C to be the miminum, which is entered in the "T Min" under "Temperature Range" window; let us also select 900°C to be the maximum temperature, which is entered in the "T Max" window.

8. Next, at the bottom of this window, click the "Add Curve" button.

9. A log D versus 1/T plot then appears, with a line for the temperature dependence of the diffusion coefficient for C in Ni. At the top of this curve is a diamond-shaped cursor. We next click-and-drag this cursor down the line to the point at which the entry under the "Temperature (T)" label reads 1123 K. The value of the diffusion coefficient at this temperature is displayed below the “Diff Coeff (D)” label, which is 3.9×10^{-12} m^2/s.

5.29 *The accompanying figure shows a plot of the logarithm (to the base 10) of the diffusion coefficient versus reciprocal of the absolute temperature for the diffusion of gold in silver. Determine values for the activation energy and preexponential.*



Solution

This problem asks us to determine the values of Q_d and D_0 for the diffusion of Au in Ag from the plot of log *D* versus 1/*T*. According to Equation 5.9b the slope of this plot is equal to $-\frac{Q_d}{2.3R}$ (rather than $-\frac{Q_d}{R}$ since we are using log *D* rather than ln *D*); furthermore, the intercept at 1/*T* = 0 gives the value of log D_0. The slope is equal to

$$\text{slope} = \frac{\Delta(\log D)}{\Delta\left(\frac{1}{T}\right)} = \frac{\log D_1 - \log D_2}{\frac{1}{T_1} - \frac{1}{T_2}}$$

Taking $1/T_1$ and $1/T_2$ as 1.0×10^{-3} and $0.90 \times 10^{-3}\ \text{K}^{-1}$, respectively, then the corresponding values of log D_1 and log D_2 are –14.68 and –13.57. Therefore,

$$Q_d = -2.3\ R\ (\text{slope})$$

$$Q_d = -2.3\ R\ \frac{\log D_1 - \log D_2}{\frac{1}{T_1} - \frac{1}{T_2}}$$

$$= -(2.3)(8.31\ \text{J/mol-K})\left[\frac{-14.68 - (-13.57)}{\left(1.0 \times 10^{-3} - 0.90 \times 10^{-3}\right)\text{K}^{-1}}\right]$$

$$= 212{,}200 \text{ J/mol}$$

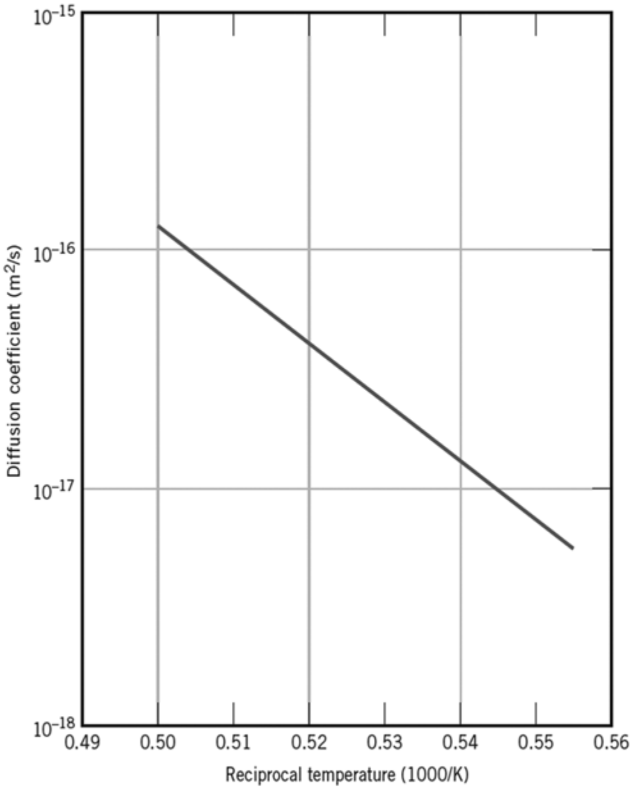
Rather than trying to make a graphical extrapolation to determine D_0, a more accurate value is obtained analytically using a rearranged form of Equation 5.9b taking a specific value of both D and T (from $1/T$) from the plot given in the problem; for example, $D = 1.0 \times 10^{-14}$ m^2/s at $T = 1064$ K ($1/T = 0.94 \times 10^{-3}$ K^{-1}). Therefore

$$D_0 = D \exp\left(\frac{Q_d}{RT}\right)$$

$$= (1.0 \times 10^{-14} \text{ m}^2/\text{s}) \exp\left[\frac{212{,}200 \text{ J/mol}}{(8.31 \text{ J/mol-K})(1064 \text{ K})}\right]$$

$$= 2.65 \times 10^{-4} \text{ m}^2/\text{s}$$

5.30 The accompanying figure shows a plot of the logarithm (to the base 10) of the diffusion coefficient versus reciprocal of the absolute temperature for the diffusion of vanadium in molybdenum. Determine values for the activation energy and preexponential.



Solution

This problem asks us to determine the values of Q_d and D_0 for the diffusion of V in Mo from the plot of log D versus $1/T$. According to Equation 5.9b the slope of this plot is equal to $-\frac{Q_d}{2.3R}$ (rather than $-\frac{Q_d}{R}$ since we are using log D rather than ln D); furthermore, the intercept at $1/T = 0$ gives the value of log D_0. The slope is equal to

$$\text{slope} = \frac{\Delta(\log D)}{\Delta\left(\frac{1}{T}\right)} = \frac{\log D_1 - \log D_2}{\frac{1}{T_1} - \frac{1}{T_2}}$$

Taking $1/T_1$ and $1/T_2$ as 0.50×10^{-3} and 0.55×10^{-3} K^{-1}, respectively, then the corresponding values of log D_1 and log D_2 are –15.90 and –17.13. Therefore,

$$Q_d = -2.3\, R\, (\text{slope})$$

$$Q_d = -2.3\,R\,\frac{\log D_1 - \log D_2}{\dfrac{1}{T_1} - \dfrac{1}{T_2}}$$

$$= -(2.3)(8.31\ \text{J/mol-K})\left[\frac{-15.90 - (-17.13)}{\left(0.50 \times 10^{-3} - 0.55 \times 10^{-3}\right)\,\text{K}^{-1}}\right]$$

$$= 470{,}200\ \text{J/mol}$$

Rather than trying to make a graphical extrapolation to determine D_0, a more accurate value is obtained analytically using Equation 5.9b taking a specific value of both D and T (from $1/T$) from the plot given in the problem; for example, $D = 1.26 \times 10^{-16}$ m^2/s at $T = 2000$ K ($1/T = 0.50 \times 10^{-3}$ K^{-1}). Therefore

$$D_0 = D\,\exp\left(\frac{Q_d}{RT}\right)$$

$$= \left(1.26 \times 10^{-16}\ \text{m}^2/\text{s}\right)\exp\left[\frac{470{,}200\ \text{J/mol}}{(8.31\ \text{J/mol-K})(2000\ \text{K})}\right]$$

$$= 2.44 \times 10^{-4}\ \text{m}^2/\text{s}$$

5.31 *From Figure 5.12 calculate activation energy for the diffusion of*

(a) copper in silicon, and

(b) aluminum in silicon

(c) How do these values compare?

Solution

(a) In order to determine the activation energy for the diffusion of copper in silicon, it is necessary to take the slope of its log *D* versus 1/*T* curve. The activation energy Q_d is equal to the equation cited in Example Problem 5.5—viz.

$$Q_d = -2.3R\left[\frac{\log D_1 - \log D_2}{\dfrac{1}{T_1} - \dfrac{1}{T_1}}\right]$$

On the plot of Figure 5.12, for copper, let us arbitrarily take

$1/T_1 = 1.5 \times 10^{-3}\ (\text{K}^{-1})$

$1/T_2 = 0.6 \times 10^{-3}\ (\text{K}^{-1})$

Their corresponding log *D* values are

$\log D_1 = -9.6$

$\log D_2 = -7.7$

Thus,

$$Q_d = -(2.3)(8.31\ \text{J/mol}\cdot\text{K})\left[\frac{-9.6 - (-7.7)}{1.5 \times 10^{-3}\ \text{K}^{-1} - 0.6 \times 10^{-3}\ \text{K}^{-1}}\right]$$

$$= \mathbf{40{,}350\ J/mol}$$

(b) For aluminum in silicon, let us use the following two log *D* versus 1/*T* values:

$1/T_1 = 1.5 \times 10^{-3}\ (\text{K}^{-1})$

$1/T_2 = 0.6 \times 10^{-3}\ (\text{K}^{-1})$

Their corresponding log *D* values are

$\log D_1 = -29.0$

$\log D_2 = -13.5$

Therefore, the activation energy is equal to

$$Q_d = -(2.3)(8.31\ \text{J/mol}\cdot\text{K})\left[\frac{-29.0 - (-13.5)}{1.5 \times 10^{-3}\ \text{K}^{-1} - 0.6 \times 10^{-3}\ \text{K}^{-1}}\right]$$

$$= \mathbf{330{,}000\ J/mol}$$

(c) The activation energy for the diffusion of Al in Si (330,000 J/mol) is approximately eight times the value for the diffusion of Cu in Si (40,350 J/mol).

5.32 *Carbon is allowed to diffuse through a steel plate 10 mm thick. The concentrations of carbon at the two faces are 0.85 and 0.40 kg C/cm^3 Fe, which are maintained constant. If the preexponential and activation energy are 5.0 × 10^{-7} m^2/s and 77,000 J/mol, respectively, compute the temperature at which the diffusion flux is 6.3 × 10^{-10} kg/m^2·s.*

Solution

This problem asks that we compute the temperature at which the diffusion flux is 6.3 × 10^{-10} kg/m^2-s. Combining Equations 5.2 and 5.8 yields

$$J = -D\frac{\Delta C}{\Delta x}$$

$$= -D_0\frac{\Delta C}{\Delta x}\exp\left(-\frac{Q_d}{RT}\right)$$

Taking natural logarithms of both sides of this equation yields the following expression:

$$\ln J = \ln\left(-D_0\frac{\Delta C}{\Delta x}\right) - \frac{Q_d}{RT}$$

Or

$$\frac{Q_d}{RT} = \ln\left(-D_0\frac{\Delta C}{\Delta x}\right) - \ln J = \ln\left(-\frac{D_0\Delta C}{J\Delta x}\right)$$

And solving for T from this expression leads to

$$T = \left(\frac{Q_d}{R}\right)\frac{1}{\ln\left(-\frac{D_0\Delta C}{J\,\Delta x}\right)}$$

Now, incorporating values of the parameters in this equation provided in the problem statement leads to the following:

$$T = \left(\frac{77{,}000\text{ J/mol}}{8.31\text{ J/mol-K}}\right)\frac{1}{\ln\left[-\frac{(5.0\times10^{-7}\text{ m}^2\text{/s})(0.40\text{ kg/m}^3 - 0.85\text{ kg/m}^3)}{(6.3\times10^{-10}\text{ kg/m}^2\text{-s})(10\ \times\ 10^{-3}\text{ m})}\right]}$$

$$= 884\text{ K} = 611°\text{C}$$

5.33 *The steady-state diffusion flux through a metal plate is 7.8 × 10^{-8} kg/m^2·s at a temperature of 1200°C (1473 K) and when the concentration gradient is –500 kg/m^4. Calculate the diffusion flux at 1000°C (1273 K) for the same concentration gradient and assuming an activation energy for diffusion of 145,000 J/mol.*

Solution

In order to solve this problem, we must first compute the value of D_0 from the data given at 1200°C (1473 K); this requires the combining of both Equations 5.2 and 5.8 as

$$J = -D\frac{\Delta C}{\Delta x}$$

$$= -D_0\frac{\Delta C}{\Delta x}\exp\left(-\frac{Q_d}{RT}\right)$$

Solving for D_0 from the above expression gives

$$D_0 = -\frac{J}{\dfrac{\Delta C}{\Delta x}}\exp\left(\frac{Q_d}{RT}\right)$$

And incorporating values of the parameters in this expressions provided in the problem statement yields the following:

$$D_0 = -\left(\frac{7.8\times10^{-8}\ \text{kg/m}^2\text{-s}}{-500\ \text{kg/m}^4}\right)\exp\left[\frac{145{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(1200+273\ \text{K})}\right]$$

$$= 2.18 \times 10^{-5}\ \text{m}^2/\text{s}$$

The value of the diffusion flux at 1273 K may be computed using these same two equations as follows:

$$J = -D_0\left(\frac{\Delta C}{\Delta x}\right)\exp\left(-\frac{Q_d}{RT}\right)$$

$$= -(2.18\times10^{-5}\ \text{m}^2/\text{s})(-500\ \text{kg/m}^4)\exp\left[-\frac{145{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(1273\ \text{K})}\right]$$

$$= 1.21 \times 10^{-8}\ \text{kg/m}^2\text{-s}$$

5.34 *At approximately what temperature would a specimen of γ-iron have to be carburized for 4 h to produce the same diffusion result as carburization at 1000°C for 12 h?*

Solution

To solve this problem it is necessary to employ Equation 5.7

$$Dt = \text{constant}$$

which, for this problem, takes the form

$$D_{1000}t_{1000} = D_T t_T$$

At 1000°C, and using the data from Table 5.2, for the diffusion of carbon in γ-iron—i.e.,

$D_0 = 2.3 \times 10^{-5}$ m^2/s

$Q_d = 148{,}000$ J/mol

the diffusion coefficient is equal to

$$D_{1000} = (2.3 \times 10^{-5}\ \text{m}^2/\text{s})\exp\left[-\frac{148{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(1000 + 273\ \text{K})}\right]$$

$$= 1.93 \times 10^{-11}\ \text{m}^2/\text{s}$$

Thus, from the above for of Equation 5.7

$$(1.93 \times 10^{-11}\ \text{m}^2/\text{s})(12\ \text{h}) = D_T(4\ \text{h})$$

And, solving for D_T

$$D_T = \frac{(1.93 \times 10^{-11}\ \text{m}^2/\text{s})(12\ \text{h})}{4\ \text{h}} = 5.79 \times 10^{-11}\ \text{m}^2/\text{s}$$

Now, solving for T from Equation 5.9a gives

$$T = -\frac{Q_d}{R(\ln D_T - \ln D_0)}$$

$$= -\frac{148{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})\left[\ln(5.79 \times 10^{-11}\ \text{m}^2/\text{s}) - \ln(2.3 \times 10^{-5}\ \text{m}^2/s)\right]}$$

= 1381 K = 1108°C

5.35 *(a) Calculate the diffusion coefficient for magnesium in aluminum at 450°C.*

(b) What time will be required at 550°C to produce the same diffusion result (in terms of concentration at a specific point) as for 15 h at 450°C?

Solution

(a) We are asked to calculate the diffusion coefficient for Mg in Al at 450°C. From Table 5.2, for this diffusion system

$D_0 = 1.2 \times 10^{-4}$ m^2/s

Q_d =130,000 J/mol

Thus, from Equation 5.8

$$D = D_0 \exp\left(-\frac{Q_d}{RT}\right)$$

$$= (1.2 \times 10^{-4} \text{ m}^2/\text{s}) \exp\left[-\frac{130{,}000 \text{ J/mol}}{(8.31 \text{ J/mol-K})(450 + 273 \text{ K})}\right]$$

$$= 4.81 \times 10^{-14} \text{ m}^2/\text{s}$$

(b) This portion of the problem calls for the time required at 550°C to produce the same diffusion result as for 15 h at 450°C. Equation 5.7 is employed as

$$D_{450} t_{450} = D_{550} t_{550}$$

Now, from Equation 5.8 the value of the diffusion coefficient at 550°C is calculated as

$$D_{550} = (1.2 \times 10^{-4} \text{ m}^2/\text{s}) \exp\left[-\frac{130{,}000 \text{ J/mol}}{(8.31 \text{ J/mol-K})(550 + 273 \text{ K})}\right]$$

$$= 6.67 \times 10^{-13} \text{ m}^2/\text{s}$$

Thus, solving for the diffusion time at 550°C yields

$$t_{550} = \frac{D_{450} t_{450}}{D_{550}}$$

$$= \frac{(4.81 \times 10^{-14} \text{m}^2/\text{s})(15 \text{h})}{(6.67 \times 10^{-13} \text{m}^2/\text{s})} = 1.08 \text{ h}$$

5.36 *A copper–nickel diffusion couple similar to that shown in Figure 5.1a is fashioned. After a 500-h heat treatment at 1000°C (1273 K) the concentration of Ni is 3.0 wt% at the 1.0-mm position within the copper. At what temperature should the diffusion couple be heated to produce this same concentration (i.e., 3.0 wt% Ni) at a 2.0-mm position after 500 h? The preexponential and activation energy for the diffusion of Ni in Cu are 1.9 ×* 10^{-4} m^2*/s and 230,000 J/mol, respectively.*

Solution

In order to determine the temperature to which the diffusion couple must be heated so as to produce a concentration of 3.0 wt% Ni at the 2.0-mm position, we must first utilize Equation 5.6b with time *t* being a constant. That is, because time (*t*) is a constant, then

$$\frac{x^2}{D} = \text{constant}$$

Or

$$\frac{x_{1000}^2}{D_{1000}} = \frac{x_T^2}{D_T}$$

Now, solving for D_T from this equation, yields

$$D_T = \frac{x_T^2 D_{1000}}{x_{1000}^2}$$

and incorporating into this expressions the temperature dependence of D_{1000} utilizing Equation 5.8, yields

$$D_T = \frac{\left(x_T^2\right)\left[D_0 \exp\left(-\frac{Q_d}{RT}\right)\right]}{x_{1000}^2}$$

$$= \frac{(2\text{ mm})^2\left[(1.9 \times 10^{-4}\text{ m}^2/\text{s})\exp\left(-\frac{230{,}000\text{ J/mol}}{(8.31\text{ J/mol-K})(1273\text{ K})}\right)\right]}{(1\text{ mm})^2}$$

$$= 2.74 \times 10^{-13}\text{ m}^2/\text{s}$$

We now need to find the temperature *T* at which *D* has this value. This is accomplished by rearranging Equation 5.9a and solving for *T* as

$$T = \frac{Q_d}{R\left(\ln D_0 - \ln D\right)}$$

$$= \frac{230{,}000 \text{ J/mol}}{(8.31 \text{ J/mol-K})\left[\ln\left(1.9 \times 10^{-4} \text{ m}^2\text{/s}\right) - \ln\left(2.74 \times 10^{-13} \text{ m}^2\text{/s}\right)\right]}$$

= 1360 K = 1087°C

5.37 *A diffusion couple similar to that shown in Figure 5.1a is prepared using two hypothetical metals A and B. After a 20-h heat treatment at 800°C (and subsequently cooling to room temperature) the concentration of B in A is 2.5 wt% at the 5.0-mm position within metal A. If another heat treatment is conducted on an identical diffusion couple, but at 1000°C for 20 h, at what position will the composition be 2.5 wt% B? Assume that the preexponential and activation energy for the diffusion coefficient are 1.5 × 10*$^{-4}$ *m*^{2}*/s and 125,000 J/mol, respectively.*

Solution

In order to determine the position within the diffusion couple at which the concentration of A in B is 2.5 wt%, we must employ Equation 5.6b with *t* constant. That is

$$\frac{x^2}{D} = \text{constant}$$

Or

$$\frac{x_{800}^2}{D_{800}} = \frac{x_{1000}^2}{D_{1000}}$$

It is first necessary to compute values for both D_{800} and D_{1000}; this is accomplished using Equation 5.8 as follows:

$$D_{800} = (1.5 \times 10^{-4}\ \text{m}^2/\text{s})\exp\left[-\frac{125{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(800 + 273\ \text{K})}\right]$$

$$1.22 \times 10^{-10}\ \text{m}^2/\text{s}$$

$$D_{1000} = (1.5 \times 10^{-4}\ \text{m}^2/\text{s})\exp\left[-\frac{125{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(1000 + 273\ \text{K})}\right]$$

$$1.11 \times 10^{-9}\ \text{m}^2/\text{s}$$

Now, solving the above expression for x_{1000} yields

$$x_{1000} = x_{800}\sqrt{\frac{D_{1000}}{D_{800}}}$$

$$= (5\ \text{mm})\sqrt{\frac{1.11 \times 10^{-9}\ \text{m}^2/\text{s}}{1.22 \times 10^{-10}\ \text{m}^2/\text{s}}}$$

$= 15.1$ mm

5.38 *Consider the diffusion of some hypothetical metal Y into another hypothetical metal Z at 950°C; after 10 h the concentration at the 0.5 mm position (in metal Z) is 2.0 wt% Y. At what position will the concentration also be 2.0 wt% Y after a 17.5 h heat treatment again at 950°C? Assume preexponential and activation energy values of 4.3 × 10*$^{-4}$ *m*^{2}*/s and 180,000 J/mol, respectively, for this diffusion system.*

Solution

In order to determine the position within this diffusion system at which the concentration of X in Y is 2.0 wt% after 17.5 h, we must employ Equation 5.6b with *D* constant (since the temperature is constant). (Inasmuch as *D* is constant it is not necessary to employ preexponential and activation energy values cited in the problem statement.) Under these circumstances, Equation 5.6b takes the form

$$\frac{x^2}{t} = \text{constant}$$

Or

$$\frac{x_1^2}{t_1} = \frac{x_2^2}{t_2}$$

If we assume the following:

x_1 = 0.5 mm

t_1 = 10 h

t_2 = 17.5 h

Now upon solving the above expression for x_2 and incorporation of these values we have

$$x_2 = \sqrt{\frac{x_1^2 t_2}{t_1}}$$

$$= \sqrt{\frac{(0.5\text{ mm})^2(17.5\text{ h})}{10\text{ h}}}$$

$$= 0.66\text{ mm}$$

5.39 *A diffusion couple similar to that shown in Figure 5.1a is prepared using two hypothetical metals R and S. After a 2.5-h heat treatment at 750°C the concentration of R is 4 at% at the 4-mm position within S. Another heat treatment is conducted on an identical diffusion couple at 900°C and the time required to produce this same diffusion result (viz., 4 at% R at the 4-mm position within S) is 0.4 h. If it is known that the diffusion coefficient at 750°C is* 2.6×10^{-17} *m*^{2}*/s determine the activation energy for the diffusion of R in S.*

Solution

In order to determine the activation energy for this diffusion system it is first necessary to compute the diffusion coefficient at 900°C. Inasmuch as x is the same for both heat treatments, Equation 5.6b takes the form

$$Dt = \text{constant}$$

Or that

$$D_{750} t_{750} = D_{900} t_{900}$$

It is possible to solve for D_{900} inasmuch as values for the other parameters are provided in the problem statement; i.e.,

$t_{750} = 2.5$ h
$D_{750} = 2.6 \times 10^{-17}$ m^2/s
$t_{900} = 0.4$ h

Solving for D_{900} from the above equation leads to

$$D_{900} = \frac{D_{750} t_{750}}{t_{900}}$$

$$= \frac{(2.6 \times 10^{-17} \text{ m}^2/\text{s})(2.5 \text{ h})}{0.4 \text{ h}}$$

$$1.6 \times 10^{-16} \text{ m}^2/\text{s}$$

Inasmuch as we know the values of D at both 750°C and 900°C—viz.,

$D_{750} = 2.6 \times 10^{-17}$ m^2/s
$D_{900} = 1.6 \times 10^{-16}$ m^2/s

it is possible to solve for the activation energy Q_d using the following equation, which is derived in Example Problem 5.5. In this expression, if we assign $D_{750} = D_1$ and $D_{900} = D_2$, then the activation energy is equal to

$$Q_d = -2.3R\left[\frac{\log D_1 - \log D_2}{\frac{1}{T_1} - \frac{1}{T_2}}\right]$$

$$= -(2.3)(8.31\ \mathrm{J/mol \cdot K})\left[\frac{\log(2.6 \times 10^{-17}\ \mathrm{m^2/s}) - \log(1.6 \times 10^{-16}\ \mathrm{m^2/s})}{\frac{1}{(750 + 273\ \mathrm{K})} - \frac{1}{(900 + 273\ \mathrm{K})}}\right]$$

$$= 120{,}700\ \mathrm{J/mol}$$

5.40 *The outer surface of a steel gear is to be hardened by increasing its carbon content; the carbon is to be supplied from an external carbon-rich atmosphere maintained at an elevated temperature. A diffusion heat treatment at 600°C (873 K) for 100 min increases the carbon concentration to 0.75 wt% at a position 0.5 mm below the surface. Estimate the diffusion time required at 900°C (1173 K) to achieve this same concentration also at a 0.5-mm position. Assume that the surface carbon content is the same for both heat treatments, which is maintained constant. Use the diffusion data in Table 5.2 for C diffusion in α-Fe.*

Solution

In order to compute the diffusion time at 900°C to produce a carbon concentration of 0.75 wt% at a position 0.5 mm below the surface we must employ Equation 5.6b with position constant; that is

$$Dt = \text{constant}$$

since x is a constant (0.5 mm). This means that

$$D_{600}t_{600} = D_{900}t_{900}$$

In addition, it is necessary to compute values for both D_{600} and D_{900} using Equation 5.8. From Table 5.2, for the diffusion of C in α-Fe, Q_d = 87,400 J/mol and $D_0 = 1.1 \times 10^{-6}$ m^2/s. Therefore,

$$D_{600} = (1.1 \times 10^{-6}\ \mathrm{m^2/s})\exp\left[-\frac{87{,}400\ \mathrm{J/mol}}{(8.31\ \mathrm{J/mol\text{-}K})(600 + 273\ \mathrm{K})}\right]$$

$$6.45 \times 10^{-12}\ \mathrm{m^2/s}$$

$$D_{900} = (1.1 \times 10^{-6}\ \mathrm{m^2/s})\exp\left[-\frac{87{,}400\ \mathrm{J/mol}}{(8.31\ \mathrm{J/mol\text{-}K})(900 + 273\ \mathrm{K})}\right]$$

$$1.40 \times 10^{-10}\ \mathrm{m^2/s}$$

Now, solving the original equation for t_{900} gives

$$t_{900} = \frac{D_{600}t_{600}}{D_{900}}$$

$$= \frac{(6.45 \times 10^{-12}\ \mathrm{m^2/s})(100\ \mathrm{min})}{1.40 \times 10^{-10}\ \mathrm{m^2/s}}$$

$= 4.61 \text{ min}$

5.41 *An FCC iron–carbon alloy initially containing 0.10 wt% C is carburized at an elevated temperature and in an atmosphere in which the surface carbon concentration is maintained at 1.10 wt%. If after 48 h the concentration of carbon is 0.30 wt% at a position 3.5 mm below the surface, determine the temperature at which the treatment was carried out.*

Solution

This problem asks us to compute the temperature at which a nonsteady-state 48 h diffusion anneal was carried out in order to give a carbon concentration of 0.30 wt% C in FCC Fe at a position 3.5 mm below the surface. From Equation 5.5

$$\frac{C_x - C_0}{C_s - C_0} = \frac{0.30 - 0.10}{1.10 - 0.10} = 0.2000 = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Or

$$\operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = 0.8000$$

Now it becomes necessary, using the data in Table 5.1 and linear interpolation, to determine the value of $\frac{x}{2\sqrt{Dt}}$.

Thus

z	erf (z)
0.90	0.7970
y	0.8000
0.95	0.8209

$$\frac{y - 0.90}{0.95 - 0.90} = \frac{0.8000 - 0.7970}{0.8209 - 0.7970}$$

From which

$$y = 0.9063$$

Thus,

$$\frac{x}{2\sqrt{Dt}} = 0.9063$$

And since t = 48 h (172,800 s) and x = 3.5 mm (3.5×10^{-3} m), solving for D from the above equation yields

$$D = \frac{x^2}{(4t)(0.9063)^2}$$

$$= \frac{(3.5 \times 10^{-3}\text{ m})^2}{(4)(172{,}800\text{ s})(0.821)} = 2.16 \times 10^{-11}\text{ m}^2/\text{s}$$

Now, in order to determine the temperature at which D has the above value, we must employ Equation 5.9a; solving this equation for T yields

$$T = \frac{Q_d}{R(\ln D_0 - \ln D)}$$

From Table 5.2, D_0 and Q_d for the diffusion of C in FCC Fe are 2.3×10^{-5} m^2/s and 148,000 J/mol, respectively. Therefore

$$T = \frac{148{,}000\text{ J/mol}}{(8.31\text{ J/mol-K})\left[\ln(2.3 \times 10^{-5}\text{ m}^2/\text{s}) - \ln(2.16 \times 10^{-11}\text{ m}^2/\text{s})\right]}$$

$$= 1283\text{ K} = 1010°\text{C}$$

Diffusion in Semiconducting Materials

5.42 *For the predeposition heat treatment of a semiconducting device, gallium atoms are to be diffused into silicon at a temperature of 1150°C for 2.5 h. If the required concentration of Ga at a position 2 μm below the surface is 8 × 10^{23} atoms/m^3, compute the required surface concentration of Ga. Assume the following:*

(i) The surface concentration remains constant

(ii) The background concentration is 2 × 10^{19} Ga atoms/m^3

(iii) Preexponential and activation energy values are 3.74 × 10^{-5} m^2/s and 3.39 eV/atom, respectively.

Solution

This problem requires that we solve for the surface concentration, C_s of Equation 5.5 given the following:

$C_x = 8 \times 10^{23}$ atoms/m^3
$C_0 = 2 \times 10^{19}$ atoms/m^3
$x = 2$ μm $= 2 \times 10^{-6}$ m
$T = 1150$°C
$t = 2.5$ h $= 9000$ s
$D_0 = 3.74 \times 10^{-5}$ m^2/s
$Q_d = 3.39$ eV/atom

Equation 5.5 calls for a value of the diffusion coefficient D, which is determined at 1150°C using Equation 5.8. Thus

$$D = D_0 \exp\left(-\frac{Q_d}{RT}\right)$$

$$= (3.74 \times 10^{-5} \text{ m}^2/\text{s}) \exp\left[-\frac{3.39 \text{ eV/atom}}{(8.62 \times 10^{-5} \text{ eV/atom} \cdot \text{K})(1150°\text{C} + 273 \text{ K})}\right]$$

$$= 3.72 \times 10^{-17} \text{ m}^2/\text{s}$$

Now it is required that we solve for C_s in Equation 5.5:

$$\frac{C_x - C_0}{C_s - C_0} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

And solving for C_s from this expression and incorporation of values for all of the other parameters leads to

$$C_s = C_0 + \frac{C_x - C_0}{1 - \operatorname{erf}\left(\dfrac{x}{2\sqrt{Dt}}\right)}$$

$$= (2 \times 10^{19}\ \text{atoms/m}^3) + \frac{(8 \times 10^{23}\ \text{atoms/m}^3) - (2 \times 10^{19}\ \text{atoms/m}^3)}{1 - \operatorname{erf}\left[\dfrac{2 \times 10^{-6}\ \text{m}}{2\sqrt{(3.72 \times 10^{-17}\ \text{m}^2/\text{s})(9000\ \text{s})}}\right]}$$

$$= (2 \times 10^{19}\ \text{atoms/m}^3) + \frac{(8 \times 10^{23}\ \text{atoms/m}^3)}{1 - \operatorname{erf}(1.7283)}$$

At this point it becomes necessary to conduct an interpolation—we know the *z* and need to determine the value of erf(*z*). This interpolation is conducted using data found in Table 5.1 as follows:

erf(*z*)	*z*
0.9838	1.7
erf(*z*)	1.7283
0.9891	1.8

$$\frac{1.8000 - 1.7283}{1.8000 - 1.7000} = \frac{0.9891 - \operatorname{erf}(z)}{0.9891 - 0.9838}$$

And solving this expression for erf(*z*) leads to

$$\operatorname{erf}(z) = 0.9853$$

Inserting this value into the above equation in which we are solving for C_s yields

$$C_s = (2 \times 10^{19}\ \text{atoms/m}^3) + \frac{(8 \times 10^{23}\ \text{atoms/m}^3)}{1 - \operatorname{erf}(1.7283)}$$

$$= (2 \times 10^{19}\ \text{atoms/m}^3) + \frac{(8 \times 10^{23}\ \text{atoms/m}^3)}{1 - 0.9853}$$

$$= 5.44 \times 10^{25}\ \text{Ga atoms/m}^3$$

5.43 *Antimony atoms are to be diffused into a silicon wafer using both predeposition and drive-in heat treatments; the background concentration of Sb in this silicon material is known to be 2 × 10^{20} atoms/m^3. The predeposition treatment is to be conducted at 900°C for 1 h; the surface concentration of Sb is to be maintained at a constant level of 8.0 × 10^{25} atoms/m^3. Drive-in diffusion will be carried out at 1200°C for a period of 1.75 h. For the diffusion of Sb in Si, values of Q_d and D_0 are 3.65 eV/atom and 2.14 × 10^{-5} m^2/s, respectively.*

(a) Calculate the value of Q_0.

(b) Determine the value of x_j for the drive-in diffusion treatment.

(c) Also, for the drive-in treatment, compute the position x at which the concentration of Sb atoms is 5 × 10^{23}/m^3.

Solution

(a) For this portion of the problem we are asked to determine the value of Q_0. This is possible using Equation 5.12. However, it is first necessary to determine the value of D for the predeposition treatment [D_p at T_p = 900°C (1173 K)] using Equation 5.8. Thus

$$D_p = D_0 \exp\left(-\frac{Q_d}{kT_p}\right)$$

$$= (2.14 \times 10^{-5}\ \mathrm{m^2/s}) \exp\left[-\frac{3.65\ \mathrm{eV}}{(8.62 \times 10^{-5}\ \mathrm{eV/atom \cdot K})(1173\ \mathrm{K})}\right]$$

$$= 4.5 \times 10^{-21}\ \mathrm{m^2/s}$$

The value of Q_0 is determined (using Equation 5.12) as follows:

$$Q_0 = 2C_s \sqrt{\frac{D_p t_p}{\pi}}$$

$$= (2)(8.0 \times 10^{25}\ \mathrm{atoms/m^3}) \sqrt{\frac{(4.5 \times 10^{-21}\ \mathrm{m^2/s})(1\ \mathrm{h})(60\ \mathrm{min/h})(60\ \mathrm{s/min})}{\pi}}$$

$$= 3.63 \times 10^{17}\ \mathrm{atoms/m^2}$$

(b) Computation of the junction depth requires that we use Equation 5.13. However, before this is possible it is necessary to calculate D at the temperature of the drive-in treatment [D_d at 1200°C (1473 K)]. Thus,

$$D_d = D_0 \exp\left(-\frac{Q_d}{kT_d}\right)$$

$$= (2.14 \times 10^{-5}\ \mathrm{m^2/s}) \exp\left[-\frac{3.65\ \mathrm{eV}}{(8.62 \times 10^{-5}\ \mathrm{eV/atom \cdot K})(1473\ K)}\right]$$

$$= 7.02 \times 10^{-18}\ \mathrm{m^2/s}$$

Now from Equation 5.13

$$x_j = \left[(4D_d t_d) \ln\left(\frac{Q_0}{C_B\sqrt{\pi D_d t_d}}\right)\right]^{1/2}$$

$$= \left\{(4)(7.02 \times 10^{-18}\ \mathrm{m^2/s})(1.75\ \mathrm{h})(60\ \mathrm{min/h})(60\ \mathrm{s/min}) \ln\left[\frac{3.63 \times 10^{17}\ \mathrm{atoms/m^2}}{(2 \times 10^{20}\ \mathrm{atoms/m^3})\sqrt{(\pi)(7.02 \times 10^{-18}\ \mathrm{m^2/s})(1.75\ \mathrm{h})(60\ \mathrm{min/h})(60\ \mathrm{s/min})}}\right]\right\}^{1/2}$$

$$= 1.23 \times 10^{-6}\ \mathrm{m} = 1.23\ \mu\mathrm{m}$$

(c) For a concentration of 5×10^{23} Sb atoms/m^3 for the drive-in treatment, we compute the value of x using Equation 5.11. However, it is first necessary to manipulate Equation 5.11 so that x is the dependent variable. Taking natural logarithms of both sides leads to

$$\ln C(x,t) = \ln\left(\frac{Q_0}{\sqrt{\pi D_d t_d}}\right) - \frac{x^2}{4D_d t_d}$$

Now, rearranging and solving for x leads to

$$x = \left\{(4D_d t_d) \ln\left[\frac{Q_0}{C(x,t)\sqrt{\pi D_d t_d}}\right]\right\}^{1/2}$$

Now, incorporating values for Q_0 and D_d determined above and taking $C(x,t) = 5 \times 10^{23}$ Sb atoms/m^3 yields

$$x = \left\{ (4)(7.02 \times 10^{-18})(6300) \ln \left[\frac{3.63 \times 10^{17}}{(5 \times 10^{23})\sqrt{(\pi)(7.02 \times 10^{-18})(6300)}} \right] \right\}^{1/2}$$

$$= 3.43 \times 10^{-7} \text{ m} = 0.343 \ \mu\text{m}$$

5.44 *Indium atoms are to be diffused into a silicon wafer using both predeposition and drive-in heat treatments; the background concentration of In in this silicon material is known to be 2 × 10^{20} atoms/m^3. The drive-in diffusion treatment is to be carried out at 1175°C for a period of 2.0 h, which gives a junction depth x_j of 2.35 μm. Compute the predeposition diffusion time at 925°C if the surface concentration is maintained at a constant level of 2.5 × 10^{26} atoms/m^3. For the diffusion of In in Si, values of Q_d and D_0 are 3.63 eV/atom and 7.85 × 10^{-5} m^2/s, respectively.*

Solution

This problem asks that we compute the time for the predeposition heat treatment for the diffusion of In in Si. In order to do this it is first necessary to determine the value of Q_0 from Equation 5.13. However, before doing this we must first calculate D_d, using Equation 5.8. Therefore

$$D_d = D_0 \exp\left(-\frac{Q_d}{kT_d}\right)$$

$$= (7.85 \times 10^{-5}\ \mathrm{m^2/s}) \exp\left[-\frac{3.63\ \mathrm{eV}}{(8.62 \times 10^{-5}\ \mathrm{eV/atom \cdot K})(1175°\mathrm{C} + 273\ \mathrm{K})}\right]$$

$$= 1.84 \times 10^{-17}\ \mathrm{m^2/s}$$

Now, solving for Q_0 in Equation 5.13 leads to

$$Q_0 = \left(C_B \sqrt{\pi D_d t_d}\right) \exp\left(\frac{x_j^2}{4D_d t_d}\right)$$

In the problem statement we are given the following values:

C_B = 2 × 10^{20} atoms/m^3

t_d = 2 h (7,200 s)

x_j = 2.35 μm = 2.35 × 10^{-6} m

Therefore, incorporating these values into the above equation yields

$$Q_0 = \left[(2 \times 10^{20}\ \mathrm{atoms/m^3})\sqrt{(\pi)(1.84 \times 10^{-17}\ \mathrm{m^2/s})(7,200\ \mathrm{s})}\right] \exp\left[\frac{(2.35 \times 10^{-6}\ \mathrm{m})^2}{(4)(1.84 \times 10^{-17}\ \mathrm{m^2/s})(7,200\ \mathrm{s})}\right]$$

$$= 4.33 \times 10^{18}\ \mathrm{atoms/m^2}$$

We may now compute the value of t_p using Equation 5.12. However, before this is possible it is necessary to determine D_p (at 925°C) using Equation 5.8. Thus

$$D_p = (7.85 \times 10^{-5}\ \mathrm{m^2/s}) \exp\left[-\frac{3.63\ \mathrm{eV}}{(8.62 \times 10^{-5}\ \mathrm{eV/atom \cdot K})(925^\circ\mathrm{C} + 273\ \mathrm{K})}\right]$$

$$= 4.25 \times 10^{-20}\ \mathrm{m^2/s}$$

Now, solving for t_p in Equation 5.12 we get

$$t_p = \frac{\pi Q_0^2}{4 C_s^2 D_p}$$

And incorporating the value of C_s provided in the problem statement (2×10^{25} atoms/m^3) as well as values for Q_0 and D_p determined above, leads to

$$t_p = \frac{\pi \left(4.33 \times 10^{18}\ \mathrm{atoms/m^2}\right)^2}{(4)\left(2.5 \times 10^{26}\ \mathrm{atoms/m^3}\right)^2 (4.25 \times 10^{-20}\ \mathrm{m^2/s})}$$

$$= 5.54 \times 10^3\ \mathrm{s} = 92.3\ \mathrm{min} = 1.53\ \mathrm{h}$$

DESIGN PROBLEMS

Fick's First Law

5.D1 *It is desired to enrich the partial pressure of hydrogen in a hydrogen–nitrogen gas mixture for which the partial pressures of both gases are 0.1013 MPa (1 atm). It has been proposed to accomplish this by passing both gases through a thin sheet of some metal at an elevated temperature; inasmuch as hydrogen diffuses through the plate at a higher rate than does nitrogen, the partial pressure of hydrogen will be higher on the exit side of the sheet. The design calls for partial pressures of 0.051 MPa (0.5 atm) and 0.01013 MPa (0.1 atm), respectively, for hydrogen and nitrogen. The concentrations of hydrogen and nitrogen (C_H and C_N, in mol/m^3) in this metal are functions of gas partial pressures (p_{H_2} and p_{N_2}, in MPa) and absolute temperature and are given by the following expressions:*

$$C_{\mathrm{H}} = 2.5 \times 10^3 \sqrt{p_{\mathrm{H}_2}} \exp\left(-\frac{27{,}800 \text{ J/mol}}{RT}\right) \qquad (5.16a)$$

$$C_{\mathrm{N}} = 2.75 \times 10^3 \sqrt{p_{\mathrm{N}_2}} \exp\left(-\frac{37{,}600 \text{ J/mol}}{RT}\right) \qquad (5.16b)$$

Furthermore, the diffusion coefficients for the diffusion of these gases in this metal are functions of the absolute temperature as follows:

$$D_{\mathrm{H}}(\mathrm{m}^2/\mathrm{s}) = 1.4 \times 10^{-7} \exp\left(-\frac{13{,}400 \text{ J/mol}}{RT}\right) \qquad (5.17a)$$

$$D_{\mathrm{N}}(\mathrm{m}^2/\mathrm{s}) = 3.0 \times 10^{-7} \exp\left(-\frac{76{,}150 \text{ J/mol}}{RT}\right) \qquad (5.17b)$$

Is it possible to purify hydrogen gas in this manner? If so, specify a temperature at which the process may be carried out, and also the thickness of metal sheet that would be required. If this procedure is not possible, then state the reason(s) why.

Solution

Since this situation involves steady-state diffusion, we employ Fick's first law, Equation 5.2. Inasmuch as the partial pressures on the high-pressure side of the sheet are the same, and the pressure of hydrogen on the low pressure side is 5 times that of nitrogen, and concentrations are proportional to the square root of the partial pressure, the diffusion flux of hydrogen, J_{H}, is the square root of 5 times the diffusion flux of nitrogen J_{N}--i.e.

$$J_{\mathrm{H}} = \sqrt{5}\,J_{\mathrm{N}}$$

Let us begin by producing expressions for the diffusion flux of both hydrogen and nitrogen, and then use them to satisfy the above equation. Fick's first law describing the flux of hydrogen, J_{H}, is as follows:

$$J_{\mathrm{H}} = -D_{\mathrm{H}}\frac{\Delta C_{\mathrm{H}}}{\Delta x}$$

$$= -\left(\frac{1}{\Delta x}\right)(1.4 \times 10^{-7})\left[\exp\left(-\frac{13{,}400\ \mathrm{J/mol}}{RT}\right)\right]\left[C_{\mathrm{H}}(\mathrm{Lo}) - C_{\mathrm{H}}(\mathrm{Hi})\right]$$

where $C_{\mathrm{H}}(\mathrm{Lo})$ and $C_{\mathrm{H}}(\mathrm{Hi})$ designate values of the concentrations of hydrogen on low and high pressure sides of the plate. Expressions for these two parameters, as determined using Equation 5.16a, are as follows:

$$C_{\mathrm{H}}(\mathrm{Lo}) = (2.5 \times 10^{3})\left(\sqrt{0.051\ \mathrm{MPa}}\right)\left[\exp\left(-\frac{27{,}800\ \mathrm{J/mol}}{RT}\right)\right]$$

$$C_{\mathrm{H}}(\mathrm{Hi}) = (2.5 \times 10^{3})\left(\sqrt{0.1013\ \mathrm{MPa}}\right)\left[\exp\left(-\frac{27{,}800\ \mathrm{J/mol}}{RT}\right)\right]$$

Now, the expression for $C_{\mathrm{H}}(\mathrm{Lo}) - C_{\mathrm{H}}(\mathrm{Hi})$ may be written as follows:

$$C_{\mathrm{H}}(\mathrm{Lo}) - C_{\mathrm{H}}(\mathrm{Hi}) = (2.5 \times 10^{3})\left(\sqrt{0.051\ \mathrm{MPa}} - \sqrt{0.1013\ \mathrm{MPa}}\right)\left[\exp\left(-\frac{27{,}800\ \mathrm{J/mol}}{RT}\right)\right]$$

Hence, the expression for J_{H} reads as follows

$$J_{\mathrm{H}} = -\left(\frac{1}{\Delta x}\right)(1.4 \times 10^{-7})\left[\exp\left(-\frac{13{,}400\ \mathrm{J/mol}}{RT}\right)\right](2.5 \times 10^{3})\left(\sqrt{0.051\ \mathrm{MPa}} - \sqrt{0.1013\ \mathrm{MPa}}\right)\left[\exp\left(-\frac{27{,}800\ \mathrm{J/mol}}{RT}\right)\right]$$

A Fick's first law expression for the diffusion flux of nitrogen may be formulated in a similar manner, which reads as follows:

$$J_{\mathrm{N}} = -D_{\mathrm{N}}\frac{\Delta C_{\mathrm{N}}}{\Delta x}$$

$$= -\left(\frac{1}{\Delta x}\right)(3.0 \times 10^{-7})\left[\exp\left(-\frac{76{,}150\ \mathrm{J/mol}}{RT}\right)\right](2.75 \times 10^{3})(\sqrt{0.01013\ \mathrm{MPa}} - \sqrt{0.1013\ \mathrm{MPa}})\left[\exp\left(-\frac{37{,}600\ \mathrm{J/mol}}{RT}\right)\right]$$

And, finally, as noted above, we want to equate these two expressions such that they satisfy the following relationship:

$$J_{\mathrm{H}} = \sqrt{5}\,J_{\mathrm{N}}$$

and then solve this relationship for the temperature T (taking the value of R to be 8.31 J/mol-K). Following through this procedure results in a temperature of

$$T = 3467\ \mathrm{K}$$

which value is extremely high (surely above the vaporization point of most metals). Thus, such a diffusion process is *not possible*.

5.D2 *A gas mixture is found to contain two diatomic A and B species (A_2 and B_2), the partial pressures of both of which are 0.1013 MPa (1 atm). This mixture is to be enriched in the partial pressure of the A species by passing both gases through a thin sheet of some metal at an elevated temperature. The resulting enriched mixture is to have a partial pressure of 0.051 MPa (0.5 atm) for gas A and 0.0203 MPa (0.2 atm) for gas B. The concentrations of A and B (C_A and C_B, in mol/m^3) are functions of gas partial pressures (p_{A_2} and p_{B_2}, in MPa) and absolute temperature according to the following expressions:*

$$C_{\mathrm{A}} = 1.5 \times 10^3 \sqrt{p_{\mathrm{A}_2}} \exp\left(-\frac{20{,}000\ \mathrm{J/mol}}{RT}\right) \tag{5.18a}$$

$$C_{\mathrm{B}} = 2.0 \times 10^3 \sqrt{p_{\mathrm{B}_2}} \exp\left(-\frac{27{,}000\ \mathrm{J/mol}}{RT}\right) \tag{5.18b}$$

Furthermore, the diffusion coefficients for the diffusion of these gases in the metal are functions of the absolute temperature as follows:

$$D_{\mathrm{A}}(\mathrm{m^2/s}) = 5.0 \times 10^{-7} \exp\left(-\frac{13{,}000\ \mathrm{J/mol}}{RT}\right) \tag{5.19a}$$

$$D_{\mathrm{B}}(\mathrm{m^2/s}) = 3.0 \times 10^{-6} \exp\left(-\frac{21{,}000\ \mathrm{J/mol}}{RT}\right) \tag{5.19b}$$

Is it possible to purify the A gas in this manner? If so, specify a temperature at which the process may be carried out, and also the thickness of metal sheet that would be required. If this procedure is not possible, then state the reason(s) why.

<u>Solution</u>

Since this situation involves steady-state diffusion, we employ Fick's first law, Equation 5.2. Inasmuch as the partial pressures on the high-pressure side of the sheet are the same, and the pressure of A_2 on the low pressure side is 2.5 times that of B_2, and concentrations are proportional to the square root of the partial pressure, the diffusion flux of A, J_A, is the square root of 2.5 times the diffusion flux of nitrogen J_B--i.e.

$$J_{\mathrm{A}} = \sqrt{2.5}\, J_{\mathrm{B}}$$

Let us begin by producing expressions for the diffusion flux of both A and B, and then use them to satisfy the above equation. Fick's first law describing the flux of A, J_A, is as follows:

$$J_A = -D_A \frac{\Delta C_A}{\Delta x}$$

$$= -\left(\frac{1}{\Delta x}\right)(5.0 \times 10^{-7})\left[\exp\left(-\frac{13{,}000 \text{ J/mol}}{RT}\right)\right]\left[C_A(\text{Lo}) - C_A(\text{Hi})\right]$$

where $C_A(\text{Lo})$ and $C_A(\text{Hi})$ designate values of the concentrations of species A on low and high pressure sides of the plate, respectively. Expressions for these two parameters, as determined using Equation 5.18a, are as follows:

$$C_A(\text{Lo}) = (1.5 \times 10^3)\left(\sqrt{0.051 \text{ MPa}}\right)\left[\exp\left(-\frac{20{,}000 \text{ J/mol}}{RT}\right)\right]$$

$$C_A(\text{Hi}) = (1.5 \times 10^3)\left(\sqrt{0.1013 \text{ MPa}}\right)\left[\exp\left(-\frac{20{,}000 \text{ J/mol}}{RT}\right)\right]$$

Now, the expression for $C_A(\text{Lo}) - C_A(\text{Hi})$ may be written as follows:

$$C_A(\text{Lo}) - C_A(\text{Hi}) = (1.5 \times 10^3)\left(\sqrt{0.051 \text{ MPa}} - \sqrt{0.1013 \text{ MPa}}\right)\left[\exp\left(-\frac{20{,}000 \text{ J/mol}}{RT}\right)\right]$$

Hence, the expression for J_A reads as follows

$$J_A = -\left(\frac{1}{\Delta x}\right)(5.0 \times 10^{-7})\left[\exp\left(-\frac{13{,}000 \text{ J/mol}}{RT}\right)\right](1.5 \times 10^3)\left(\sqrt{0.051 \text{ MPa}} - \sqrt{0.1013 \text{ MPa}}\right)\left[\exp\left(-\frac{20{,}000 \text{ J/mol}}{RT}\right)\right]$$

An expression for the diffusion flux for species B may be formulated in a similar manner, which reads as follows:

$$J_B = -D_B \frac{\Delta C_B}{\Delta x}$$

$$= -\left(\frac{1}{\Delta x}\right)(3.0 \times 10^{-6})\left[\exp\left(-\frac{21{,}000 \text{ J/mol}}{RT}\right)\right](2.0 \times 10^3)\left(\sqrt{0.0203 \text{ MPa}} - \sqrt{0.1013 \text{ MPa}}\right)\left[\exp\left(-\frac{27{,}000 \text{ J/mol}}{RT}\right)\right]$$

And, finally, as noted above, we want to equate these two expressions such that they satisfy the following relationship:

$$J_{\mathbf{A}} = \sqrt{2.5}\, J_{\mathbf{B}}$$

and then solve this relationship for the temperature T (taking the value of R to be 8.31 J/mol-K). Following through this procedure results in a temperature of

$$T = 568 \text{ K } (295°\text{C})$$

Thus, this purification *process is possible*, which may be carried out at 568 K; furthermore, it is independent of sheet thickness.

Fick's Second Law—Nonsteady-State Diffusion

5.D3 *The wear resistance of a steel shaft is to be improved by hardening its surface by increasing the nitrogen content within an outer surface layer as a result of nitrogen diffusion into the steel; the nitrogen is to be supplied from an external nitrogen-rich gas at an elevated and constant temperature. The initial nitrogen content of the steel is 0.0025 wt%, whereas the surface concentration is to be maintained at 0.45 wt%. For this treatment to be effective, a nitrogen content of 0.12 wt% must be established at a position 0.45 mm below the surface. Specify an appropriate heat treatment in terms of temperature and time for a temperature between 475°C and 625°C. The preexponential and activation energy for the diffusion of nitrogen in iron are 5 × 10^{-7} m^2/s and 77,000 J/mol, respectively, over this temperature range.*

Solution

In order to specify time-temperature combinations for this nonsteady-state diffusion situation, it is necessary to employ Equation 5.5, utilizing the following values for the concentration parameters:

$$C_0 = 0.0025 \text{ wt\% N}$$
$$C_s = 0.45 \text{ wt\% N}$$
$$C_x = 0.12 \text{ wt\% N}$$

Therefore, Equation 5.5

$$\frac{C_x - C_0}{C_s - C_0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

takes the form

$$\frac{C_x - C_0}{C_s - C_0} = \frac{0.12 - 0.0025}{0.45 - 0.0025}$$

$$= 0.2626 = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Thus

$$1 - 0.2626 = 0.7374 = \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Using linear interpolation and the data presented in Table 5.1

z	erf (z)
0.7500	0.7112
y	0.7374
0.8000	0.7421

$$\frac{0.7374 - 0.7112}{0.7421 - 0.7112} = \frac{y - 0.7500}{0.8000 - 0.7500}$$

From which

$$y = \frac{x}{2\sqrt{Dt}} = 0.7924$$

The problem stipulates that $x = 0.45 \text{ mm} = 4.5 \times 10^{-4}$ m. Therefore

$$\frac{4.5 \times 10^{-4} \text{ m}}{2\sqrt{Dt}} = 0.7924$$

Which leads to

$$Dt = 8.06 \times 10^{-8} \text{ m}^2$$

Furthermore, the diffusion coefficient depends on temperature according to Equation 5.8; and, as stipulated in the problem statement, $D_0 = 5 \times 10^{-7}$ m^2/s and Q_d = 77,000 J/mol. Hence

$$Dt = D_0 \exp\left(-\frac{Q_d}{RT}\right)(t) = 8.06 \times 10^{-8} \text{ m}^2$$

$$(5.0 \times 10^{-7} \text{ m}^2/\text{s}) \exp\left[-\frac{77{,}000 \text{ J/mol}}{(8.31 \text{ J/mol-K})(T)}\right](t) = 8.06 \times 10^{-8} \text{ m}^2$$

And solving for the time *t*

$$t \text{ (in s)} = \frac{0.161}{\exp\left(-\frac{9265.9}{T}\right)}$$

Thus, the required diffusion time may be computed for some specified temperature (in K). Below are tabulated *t* values for three different temperatures that lie within the range stipulated in the problem.

Temperature (°C)	Time	
	s	h
500	25,860	7.2
550	12,485	3.5
600	6,550	1.8

5.D4 *The wear resistance of a steel gear is to be improved by hardening its surface, as described in Design Example 5.1. However, in this case the initial carbon content of the steel is 0.15 wt%, and a carbon content of 0.75 wt% is to be established at a position 0.65 mm below the surface. Furthermore, the surface concentration is to be maintained constant, but may be varied between 1.2 and 1.4 wt% C. Specify an appropriate heat treatment in terms of surface carbon concentration and time, and for a temperature between 1000°C and 1200°C.*

Solution

This is a nonsteady-state diffusion situation; thus, it is necessary to employ Equation 5.5, utilizing values/value ranges for the following parameters:

$$C_0 = 0.15 \text{ wt\% C}$$

$$1.2 \text{ wt\% C} \le C_s \le 1.4 \text{ wt\% C}$$

$$C_x = 0.75 \text{ wt\% C}$$

$$x = 0.65 \text{ mm}$$

$$1000^\circ\text{C} \le T \le 1200^\circ\text{C}$$

Let us begin by assuming a specific value for the surface concentration within the specified range—say 1.2 wt% C. Therefore, Equation 5.5 takes the form

$$\frac{C_x - C_0}{C_s - C_0} = \frac{0.75 - 0.15}{1.20 - 0.15}$$

$$= 0.5714 = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Thus

$$1 - 0.5714 = 0.4286 = \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Using linear interpolation and the data presented in Table 5.1

z	erf (z)
0.4000	0.4284
y	0.4286
0.4500	0.4755

$$\frac{0.4286 - 0.4284}{0.4755 - 0.4284} = \frac{y - 0.4000}{0.4500 - 0.4000}$$

from which

$$y = \frac{x}{2\sqrt{Dt}} = 0.4002$$

The problem statement stipulates that $x = 0.65$ mm $= 6.5 \times 10^{-4}$ m. Therefore

$$\frac{6.5 \times 10^{-4}\ \mathrm{m}}{2\sqrt{Dt}} = 0.4002$$

Which leads to

$$Dt = 6.59 \times 10^{-7}\ \mathrm{m}^2$$

Furthermore, the diffusion coefficient depends on temperature according to Equation 5.8; and, as noted in Design Example 5.1, $D_0 = 2.3 \times 10^{-5}$ m^2/s and $Q_d = 148{,}000$ J/mol. Hence

$$Dt = D_0 \exp\left(-\frac{Q_d}{RT}\right)(t) = 6.59 \times 10^{-7}\ \mathrm{m}^2$$

$$= \left(2.3 \times 10^{-5}\ \mathrm{m}^2/\mathrm{s}\right)\exp\left[-\frac{148{,}000\ \mathrm{J/mol}}{(8.31\ \mathrm{J/mol\text{-}K})(T)}\right](t) = 6.59 \times 10^{-7}\ \mathrm{m}^2$$

And solving for the time t

$$t\ (\mathrm{in\ s}) = \frac{2.86 \times 10^{-2}}{\exp\left(-\frac{17{,}810}{T}\right)}$$

Thus, the required diffusion time may be computed for some specified temperature (in K). Below are tabulated t values for three different temperatures that lie within the range stipulated in the problem.

Temperature (°C)	Time	
	s	h
1000	34,100	9.5
1100	12,300	3.4
1200	5,100	1.4

Now, let us repeat the above procedure for two other values of the surface concentration, say 1.3 wt% C and 1.4 wt% C. Below is a tabulation of the results, again using temperatures of 1000°C, 1100°C, and 1200°C.

C_s (wt% C)	Temperature (°C)	Time	
		s	h
1.3	1000	26,700	7.4
	1100	9,600	2.7
	1200	4,000	1.1
1.4	1000	21,100	6.1
	1100	7,900	2.2
	1200	1,500	0.9

Diffusion in Semiconducting Materials

5.D5 *One integrated circuit design calls for the diffusion of aluminum into silicon wafers; the background concentration of Al in Si is 1.75 × 10^{19} atoms/m^3. The predeposition heat treatment is to be conducted at 975°C for 1.25 h, with a constant surface concentration of 4 × 10^{26} Al atoms/m^3. At a drive-in treatment temperature of 1050°C, determine the diffusion time required for a junction depth of 1.75 μm. For this system, values of Q_d and D_0 are 3.41 eV/atom and 1.38 × 10^{-4} m^2/s, respectively.*

Solution

This problem asks that we compute the drive-in diffusion time for aluminum diffusion in silicon. Values of parameters given in the problem statement are as follows:

$C_B = 1.75 \times 10^{19}$ atoms/m^3

$C_s = 4 \times 10^{26}$ atoms/m^3

$x_j = 1.75$ μm $= 1.75 \times 10^{-6}$ m

$T_p = 975°\text{C} = 1248$ K

$T_d = 1050°\text{C} = 1323$ K

$t_p = 1.25$ h $= 4500$ s

$Q_d = 3.41$ eV/atom

$D_0 = 1.38 \times 10^{-4}$ m^2/s

It is first necessary to determine the value of Q_0 using Equation 5.12. But before this is possible, the value of D_p at 975°C must be computed with the aid of Equation 5.8. Thus,

$$D_p = D_0 \exp\left(-\frac{Q_d}{kT_p}\right)$$

$$= (1.38 \times 10^{-4} \text{ m}^2/\text{s}) \exp\left[-\frac{3.41 \text{ eV}}{(8.62 \times 10^{-5} \text{ eV/atom}\cdot\text{K})(975°\text{C} + 273 \text{ K})}\right]$$

$$= 2.36 \times 10^{-18} \text{ m}^2/\text{s}$$

Now for the computation of Q_0 using Equation 5.12:

$$Q_0 = 2C_s\sqrt{\frac{D_p t_p}{\pi}}$$

$$= (2)(4 \times 10^{26}\ \text{atoms/m}^3)\sqrt{\frac{(2.36 \times 10^{-18}\ \text{m}^2/\text{s})(1.25\ \text{h})(60\ \text{min/h})(60\ \text{s/min})}{\pi}}$$

$$= 4.65 \times 10^{19}\ \text{atoms/m}^2$$

We now desire to calculate t_d in Equation 5.13. Algebraic manipulation and rearrangement of this expression leads to

$$\exp\left(\frac{x_j^2}{4D_d t_d}\right) = \frac{Q_0}{C_B\sqrt{\pi D_d t_d}}$$

At this point it is necessary to determine the value of D_d (at 1050°C). This possible using Equation 5.8 as follows:

$$D_d = (1.38 \times 10^{-4}\ \text{m}^2/\text{s})\exp\left[-\frac{3.41\ \text{eV}}{(8.62 \times 10^{-5}\ \text{eV/atom}\cdot\text{K})(1050°\text{C} + 273\ \text{K})}\right]$$

$$= 1.426 \times 10^{-17}\ \text{m}^2/\text{s}$$

And incorporation of values of all parameters except t_d in the expression cited above—i.e.,

$$\exp\left(\frac{x_j^2}{4D_d t_d}\right) = \frac{Q_0}{C_B\sqrt{\pi D_d t_d}}$$

yields

$$\exp\left[\frac{(1.75 \times 10^{-6}\ \text{m})^2}{(4)(1.426 \times 10^{-17}\ \text{m}^2/\text{s})t_d}\right] = \frac{4.65 \times 10^{19}\ \text{atoms/m}^2}{(1.75 \times 10^{19}\ \text{atoms/m}^3)\sqrt{(\pi)(1.426 \times 10^{-17}\ \text{m}^2/\text{s})t_d}}$$

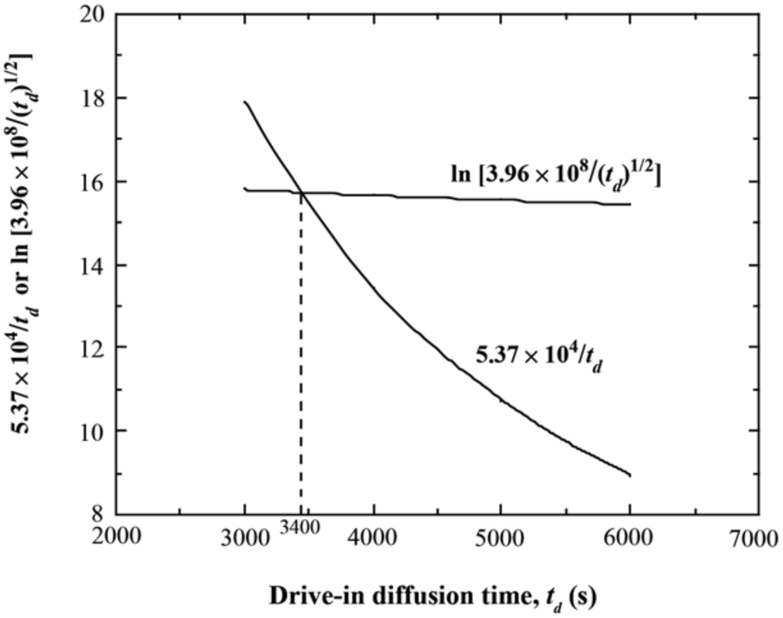
which expression reduces to

$$\exp\left(\frac{5.37 \times 10^4\ \text{s}}{t_d}\right) = \frac{3.96 \times 10^8\ \text{s}^{1/2}}{\sqrt{t_d}}$$

Solving for t_d is this expression is not a simple matter. One possibility is to use a graphing technique. Let us take the logarithm of both sides of the above equation, which gives

$$\frac{5.37 \times 10^4 \text{ s}}{t_d} = \ln\left(\frac{3.96 \times 10^8 \text{ s}^{1/2}}{\sqrt{t_d}}\right)$$

Now if we plot the terms on both left and right hand sides of this equation versus t_d, the value of t_d at the point of intersection of the two resulting curves is correct answer. Below is such a plot:



As noted, the two curves intersect at about 3400 s, which corresponds to t_d = 0.94 h.

FUNDAMENTALS OF ENGINEERING QUESTIONS AND PROBLEMS

5.1FE *Atoms of which of the following elements will diffuse most rapidly in iron?*

(A) Mo	*(C) Cr*
(B) C	*(D) W*

Solution

The correct answer is B. Carbon atoms diffuse most rapidly because they are smaller than atoms of Mo, Cr, and W. Furthermore, diffusion of C in Fe is via an interstitial mechanism, whereas for Mo, Cr, and W the mechanism is vacancy diffusion.

5.2FE *Calculate the diffusion coefficient for copper in aluminum at 600°C. Preexponential and activation energy values for this system are* 6.5×10^{-5} *m²/s and 136,000 J/mol, respectively.*

(A) 5.7×10^{-2} *m²/s*

(B) 9.4×10^{-17} *m²/s*

(C) 4.7×10^{-13} *m²/s*

(D) 3.9×10^{-2} *m²/s*

Solution

We are asked to calculate the diffusion coefficient for Cu in Al at 600°C, given values for D_0 and Q_d. This determination is possible using Equation 5.8 as follows:

$$D = D_0 \exp\left(-\frac{Q_d}{RT}\right)$$

$$= (6.5 \times 10^{-5} \text{ m}^2/\text{s}) \exp\left[-\frac{136{,}000 \text{ J/mol}}{(8.31 \text{ J/mol-K})(600 + 273 \text{ K})}\right]$$

$$= 4.7 \times 10^{-13} \text{ m}^2/\text{s}$$

Therefore, the correct answer is C.

CHAPTER 6

MECHANICAL PROPERTIES OF METALS

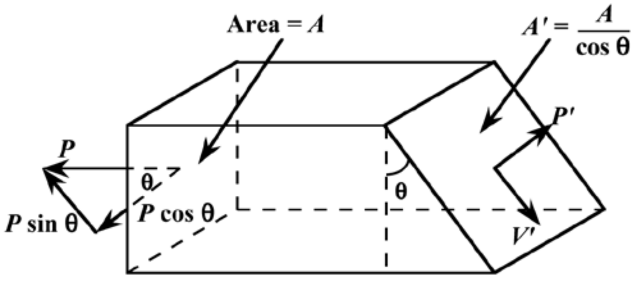
PROBLEM SOLUTIONS

Concepts of Stress and Strain

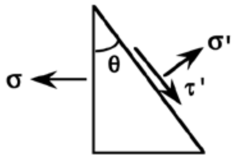
6.1 *Using mechanics-of-materials principles (i.e., equations of mechanical equilibrium applied to a free-body diagram), derive Equations 6.4a and 6.4b.*

Solution

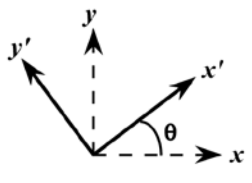
This problem asks that we derive Equations 6.4a and 6.4b, using mechanics of materials principles. In Figure (a) below is shown a block element of material of cross-sectional area *A* that is subjected to a tensile force *P*. Also represented is a plane that is oriented at an angle θ referenced to the plane perpendicular to the tensile axis; the area of this plane is *A'* = *A*/cos θ. In addition, the forces normal and parallel to this plane are labeled as *P'* and *V'*, respectively. Furthermore, on the left-hand side of this block element are shown force components that are tangential and perpendicular to the inclined plane. In Figure (b) are shown the orientations of the applied stress σ, the normal stress to this plane σ', as well as the shear stress τ' taken parallel to this inclined plane. In addition, two coordinate axis systems in represented in Figure (c): the primed *x* and *y* axes are referenced to the inclined plane, whereas the unprimed *x* axis is taken parallel to the applied stress.



(a)



(b)



(c)

Normal and shear stresses are defined by Equations 6.1 and 6.3, respectively. However, we now chose to express these stresses in terms (i.e., general terms) of normal and shear forces (*P* and *V*) as

$$\sigma = \frac{P}{A}$$

$$\tau = \frac{V}{A}$$

For static equilibrium in the *x′* direction the following condition must be met:

$$\sum F_{x'} = 0$$

which means that

$$P' - P\cos\theta = 0$$

Or that

$$P' = P\cos\theta$$

Now it is possible to write an expression for the stress σ' in terms of *P′* and *A′* using the above expression and the relationship between *A* and *A′* [Figure (a)]:

$$\sigma' = \frac{P'}{A'}$$

$$= \frac{P\cos\theta}{\frac{A}{\cos\theta}} = \frac{P}{A}\cos^2\theta$$

However, it is the case that *P/A* = σ; and, after making this substitution into the above expression, we have Equation 6.4a--that is

$$\sigma' = \sigma\cos^2\theta$$

Now, for static equilibrium in the *y′* direction, it is necessary that

$$\sum F_{y'} = 0$$

$$= -V' + P\sin\theta$$

Or

$$V' = P\sin\theta$$

We now write an expression for τ' as

$$\tau' = \frac{V'}{A'}$$

$$= \frac{\frac{P \sin\theta}{A}}{\cos\theta}$$

$$= \frac{P}{A} \sin\theta \cos\theta$$

$$= \sigma \sin\theta \cos\theta$$

which is just Equation 6.4b.

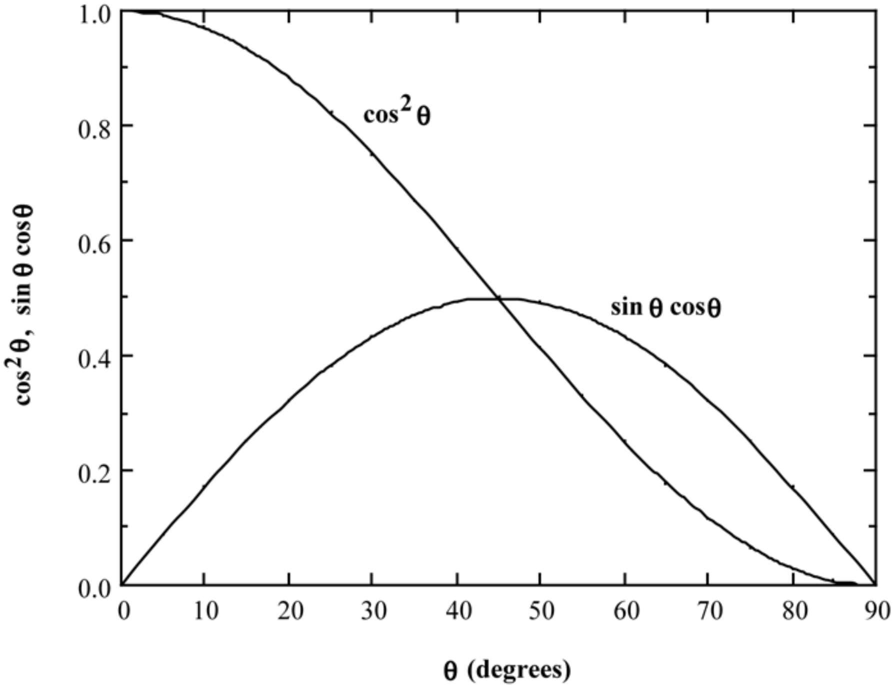
6.2 *(a) Equations 6.4a and 6.4b are expressions for normal (σ') and shear (τ') stresses, respectively, as a function of the applied tensile stress (σ) and the inclination angle of the plane on which these stresses are taken (θ of Figure 6.4). Make a plot showing the orientation parameters of these expressions (i.e., $\cos^2 \theta$ and $\sin \theta \cos \theta$) versus θ.*

(b) From this plot, at what angle of inclination is the normal stress a maximum?

(c) At what inclination angle is the shear stress a maximum?

Solution

(a) Below are plotted curves of $\cos^2\theta$ (for σ') and $\sin \theta \cos \theta$ (for τ') versus θ.



(b) The maximum normal stress occurs at an inclination angle of 0°.

(c) The maximum shear stress occurs at an inclination angle of 45°.

Stress–Strain Behavior

6.3 *A specimen of copper having a rectangular cross section 15.2 mm × 19.1 mm (0.60 in. × 0.75 in.) is pulled in tension with 44,500 N (10,000 lb$_f$) force, producing only elastic deformation. Calculate the resulting strain.*

Solution

This problem calls for us to calculate the elastic strain that results for a copper specimen stressed in tension. The cross-sectional area is just (15.2 mm) × (19.1 mm) = 290 mm^2 (= 2.90×10^{-4} m^2 = 0.45 in.^{2}); also, the elastic modulus for Cu is given in Table 6.1 as 110 GPa (or 110×10^9 N/m^2). Combining Equations 6.1 and 6.5 and solving for the strain yields

$$\varepsilon = \frac{\sigma}{E} = \frac{\frac{F}{A_0}}{E} = \frac{F}{A_0 E}$$

$$= \frac{44{,}500\ N}{(2.90 \times 10^{-4}\,\mathrm{m}^2)(110 \times 10^9\,\mathrm{N/m}^2)} = 1.39 \times 10^{-3}$$

6.4 *A cylindrical specimen of a nickel alloy having an elastic modulus of 207 GPa (30 × 10^6 psi) and an original diameter of 10.2 mm (0.40 in.) experiences only elastic deformation when a tensile load of 8900 N (2000 lb_f) is applied. Compute the maximum length of the specimen before deformation if the maximum allowable elongation is 0.25 mm (0.010 in.).*

Solution

We are asked to compute the maximum length of a cylindrical nickel specimen (before deformation) that is deformed elastically in tension. For a cylindrical specimen the original cross-sectional area A_0 is equal to

$$A_0 = \pi\left(\frac{d_0}{2}\right)^2$$

where d_0 is the original diameter. Combining Equations 6.1, 6.2, and 6.5 and solving for l_0 leads to

$$l_0 = \frac{\Delta l}{\varepsilon} = \frac{\Delta l}{\dfrac{\sigma}{E}} = \frac{\Delta l\, E}{\dfrac{F}{A_0}} = \frac{\Delta l\, E\pi\left(\dfrac{d_0}{2}\right)^2}{F} = \frac{\Delta l\, E\pi\, d_0^2}{4F}$$

Substitution into this expression, values of d_0, Δl, E, and F given in the problem statement yields the following

$$l_0 = \frac{(0.25 \times 10^{-3}\,\mathrm{m})(207 \times 10^9\,\mathrm{N/m^2})\,(\pi)(10.2 \times 10^{-3}\,\mathrm{m})^2}{(4)(8900\ \mathrm{N})}$$

$$= 0.475\ \mathrm{m} = 475\ \mathrm{mm}\ \ (18.7\ \mathrm{in.})$$

6.5 *An aluminum bar 125 mm (5.0 in.) long and having a square cross section 16.5 mm (0.65 in.) on an edge is pulled in tension with a load of 66,700 N (15,000 lb*$_f$*) and experiences an elongation of 0.43 mm (1.7 × 10*$^{-2}$ *in.). Assuming that the deformation is entirely elastic, calculate the modulus of elasticity of the aluminum.*

Solution

This problem asks us to compute the elastic modulus of aluminum. For a square cross-section, $A_0 = b_0^2$, where b_0 is the edge length. Combining Equations 6.1, 6.2, and 6.5 and solving for the modulus of elasticity, E, leads to

$$E = \frac{\sigma}{\varepsilon} = \frac{\dfrac{F}{A_0}}{\dfrac{\Delta l}{l_0}} = \frac{F l_0}{b_0^2 \Delta l}$$

Substitution into this expression, values of l_0, b_0 Δl, and F given in the problem statement yields the following

$$E = \frac{(66{,}700\ \text{N})(125 \times 10^{-3}\,\text{m})}{(16.5 \times 10^{-3}\,\text{m})^2 (0.43 \times 10^{-3}\,\text{m})}$$

$$= 71.2 \times 10^9\ \text{N/m}^2 = 71.2\ \text{GPa}\ \ (10.4 \times 10^6\ \text{psi})$$

6.6 *Consider a cylindrical nickel wire 2.0 mm (0.08 in.) in diameter and 3 × 10^4 mm (1200 in.) long. Calculate its elongation when a load of 300 N (67 lb_f) is applied. Assume that the deformation is totally elastic.*

Solution

In order to compute the elongation of the Ni wire when the 300 N load is applied we must employ Equations 6.2, 6.5, and 6.1. Combining these equations and solving for Δl leads to the following

$$\Delta l = l_0 \varepsilon = l_0 \frac{\sigma}{E} = \frac{l_0 F}{E A_0} = \frac{l_0 F}{E\pi \left(\frac{d_0}{2}\right)^2} = \frac{4 l_0 F}{E \pi d_0^2}$$

since the cross-sectional area A_0 of a cylinder of diameter d_0 is equal to

$$A_0 = \pi \left(\frac{d_0}{2}\right)^2$$

Incorporating into this expression values for l_0, F, and d_0 in the problem statement, and realizing that for Ni, E = 207 GPa (30 × 10^6 psi) (Table 6.1), and that 3 × 10^4 mm = 30m, the wire elongation is

$$\Delta l = \frac{(4)(30\text{ m})(300\text{ N})}{(207 \times 10^9\text{ N/m}^2)(\pi)(2 \times 10^{-3}\text{ m})^2} = 0.0138\text{ m} = 13.8\text{ mm}\ \ (0.53\text{ in.})$$

6.7 *For a brass alloy, the stress at which plastic deformation begins is 345 MPa (50,000 psi), and the modulus of elasticity is 103 GPa (15.0 × 10^6 psi).*

(a) What is the maximum load that can be applied to a specimen with a cross-sectional area of 130 mm^2 (0.2 $in.^2$) without plastic deformation?

(b) If the original specimen length is 76 mm (3.0 in.), what is the maximum length to which it can be stretched without causing plastic deformation?

Solution

(a) This portion of the problem calls for a determination of the maximum load that can be applied without plastic deformation (F_y). Taking the yield strength to be 345 MPa, and employment of Equation 6.1 leads to

$$F_y = \sigma_y A_0 = (345 \times 10^6 \text{ N/m}^2)(133 \text{ mm}^2)\left(\frac{1 \text{ m}}{10^3 \text{ mm}}\right)^2$$

$$= 44{,}850 \text{ N} \quad (10{,}000 \text{ lb}_f)$$

(b) The maximum length to which the sample may be deformed without plastic deformation is determined by combining Equations 6.2 and 6.5 as

$$l_i = \varepsilon l_0 + l_0 = l_0(\varepsilon + 1)$$

$$l_i = l_0\left(\frac{\sigma}{E} + 1\right)$$

Incorporating values of l_0, σ, and E provided in the problem statement leads to the computation of l_i as follows:

$$l_i = (76 \text{ mm})\left[\frac{345 \text{ MPa}}{103 \times 10^3 \text{ MPa}} + 1\right] = 76.25 \text{ mm} \quad (3.01 \text{ in.})$$

6.8 *A cylindrical rod of steel (E = 207 GPa, 30 × 10^6 psi) having a yield strength of 310 MPa (45,000 psi) is to be subjected to a load of 11,100 N (2500 lb_f). If the length of the rod is 500 mm (20.0 in.), what must be the diameter to allow an elongation of 0.38 mm (0.015 in.)?*

Solution

This problem asks us to compute the diameter of a cylindrical specimen of steel in order to allow an elongation of 0.38 mm. Employing Equations 6.1, 6.2, and 6.5, assuming that deformation is entirely elastic, we may write the following expression:

$$\sigma = \frac{F}{A_0} = \frac{F}{\pi\left(\frac{d_0^2}{4}\right)}$$

$$= E\varepsilon = E\frac{\Delta l}{l_0}$$

And upon simplification

$$\frac{F}{\pi\left(\frac{d_0^2}{4}\right)} = E\frac{\Delta l}{l_0}$$

Solving for the original cross-sectional area, d_0, leads to

$$d_0 = \sqrt{\frac{4 l_0 F}{\pi E \Delta l}}$$

Incorporation of values for l_0, F, E, and Δl provided in the problem statement yields the following:

$$d_0 = \sqrt{\frac{(4)(500 \times 10^{-3}\,\mathrm{m})(11{,}100\ \mathrm{N})}{(\pi)(207 \times 10^9\ \mathrm{N/m^2})(0.38 \times 10^{-3}\,\mathrm{m})}}$$

$$= 9.5 \times 10^{-3}\ \mathrm{m} = 9.5\ \mathrm{mm}\ \ (0.376\ \mathrm{in.})$$

6.9 *Compute the elastic moduli for the following metal alloys, whose stress-strain behaviors may be observed in the Tensile Tests module of Virtual Materials Science and Engineering* (VMSE)*: (a) titanium, (b) tempered steel, (c) aluminum, and (d) carbon steel. How do these values compare with those presented in Table 6.1 for the same metals?*

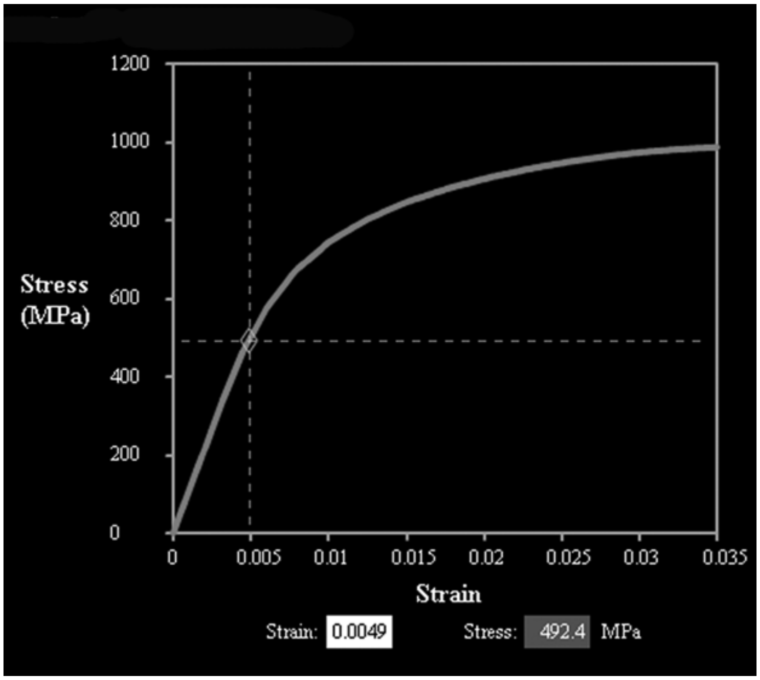
Solution

The elastic modulus is the slope in the linear elastic region (Equation 6.10) as

$$E = \frac{\Delta\sigma}{\Delta\varepsilon} = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1}$$

Since stress-strain curves for all of the metals/alloys pass through the origin, we make take σ_1 = 0 and ε_1 = 0. Determinations of σ_2 and ε_2 are possible by moving the cursor to some arbitrary point in the linear region of the curve and then reading corresponding values in the "Stress" and "Strain" windows that are located below the plot.

(a) A screenshot for the titanium alloy in the elastic region is shown below.



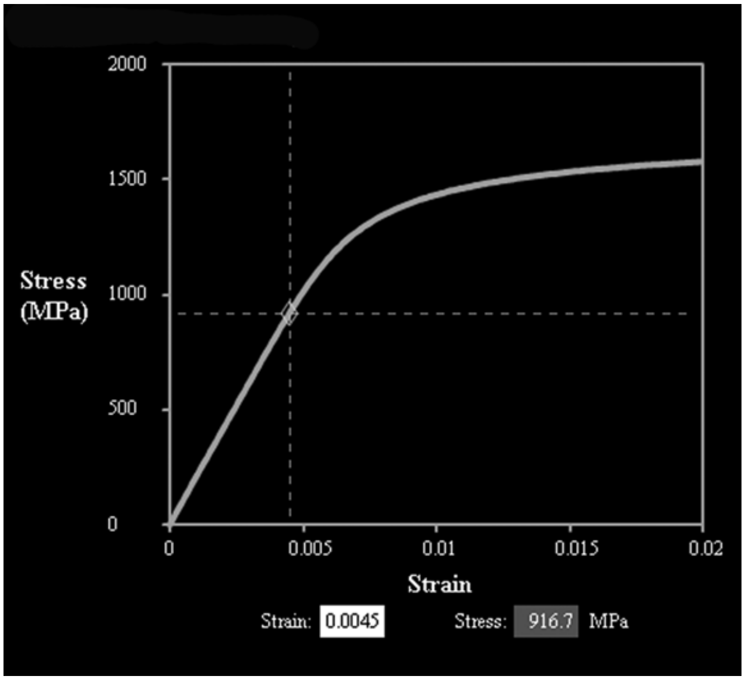
Strain: 0.0049 Stress: 492.4 MPa

Here the cursor point resides in the elastic region at a stress of 492.4 MPa (which is the value of σ_2) at a strain of 0.0049 (which is the value of ε_2). Thus, the elastic modulus is equal to

$$E = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1} = \frac{492.4\text{ MPa} - 0\text{ MPa}}{0.0049 - 0} = 100{,}500\text{ MPa} = 100.5\text{ GPa}$$

The elastic modulus for titanium given in Table 6.1 is 107 GPa, which is in reasonably good agreement with this value.

(b) A screenshot for the tempered steel alloy in the elastic region is shown below.

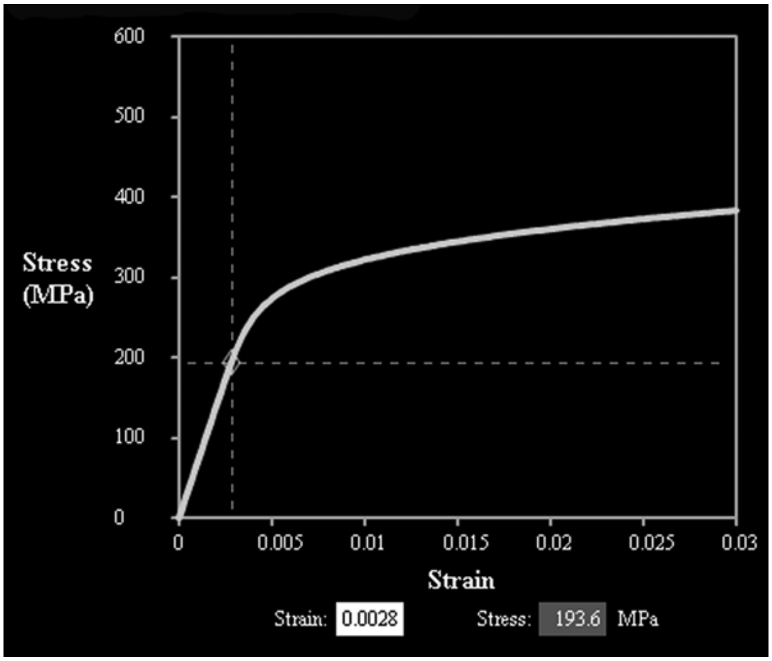


Here the cursor point resides in the elastic region at a stress of 916.7 MPa (which is the value of σ_2) at a strain of 0.0045 (which is the value of ε_2). Thus, the elastic modulus is equal to

$$E = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1} = \frac{916.7\text{ MPa} - 0\text{ MPa}}{0.0045 - 0} = 203{,}700\text{ MPa} = 203.7\text{ GPa}$$

The elastic modulus for steel given in Table 6.1 is 207 GPa, which is in good agreement with this value.

(c) A screenshot for the aluminum alloy in the elastic region is shown below.

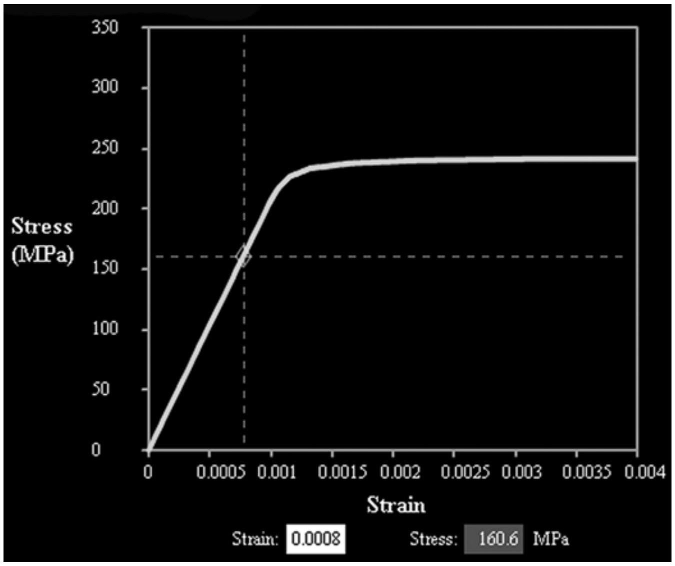


Here the cursor point resides in the elastic region at a stress of 193.6 MPa (which is the value of σ_2) at a strain of 0.0028 (which is the value of ε_2). Thus, the elastic modulus is equal to

$$E = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1} = \frac{193.6\text{ MPa} - 0\text{ MPa}}{0.0028 - 0} = 69{,}100\text{ MPa} = 69.1\text{ GPa}$$

The elastic modulus for aluminum given in Table 6.1 is 69 GPa, which is in excellent agreement with this value.

(d) A screenshot for the carbon steel alloy in the elastic region is shown below.



Here the cursor point resides in the elastic region at a stress of 160.6 MPa (which is the value of σ_2) at a strain of 0.0008 (which is the value of ε_2). Thus, the elastic modulus is equal to

$$E = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1} = \frac{160.6 \text{ MPa} - 0 \text{ MPa}}{0.0008 - 0} = 200{,}800 \text{ MPa} = 200.8 \text{ GPa}$$

The elastic modulus for steel given in Table 6.1 is 207 GPa, which is in reasonable agreement with this value.

6.10 *Consider a cylindrical specimen of a steel alloy (Figure 6.22) 8.5 mm (0.33 in.) in diameter and 80 mm (3.15 in.) long that is pulled in tension. Determine its elongation when a load of 65,250 N (14,500 lb_f) is applied.*

Solution

This problem asks that we calculate the elongation Δl of a specimen of steel the stress-strain behavior of which is shown in Figure 6.22. First it becomes necessary to compute the stress when a load of 65,250 N is applied using Equation 6.1 as

$$\sigma = \frac{F}{A_0} = \frac{F}{\pi\left(\frac{d_0}{2}\right)^2} = \frac{65{,}250\ \mathrm{N}}{\pi\left(\frac{8.5 \times 10^{-3}\ \mathrm{m}}{2}\right)^2} = 1.15\ \times\ 10^9\ \mathrm{N/m^2} = 1150\ \mathrm{MPa}\ \ (170{,}000\ \mathrm{psi})$$

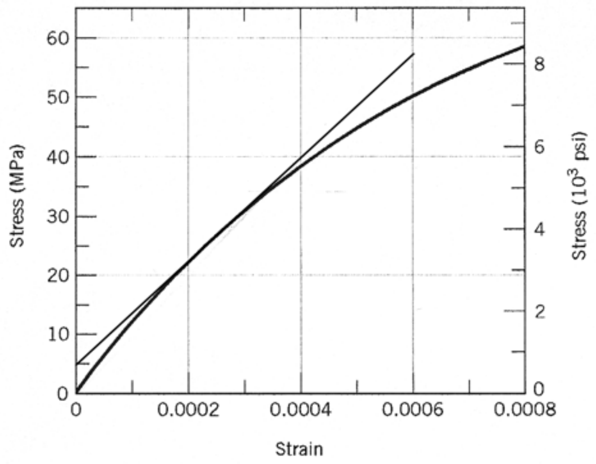
Referring to Figure 6.22, at this stress level we are in the elastic region (shown in the inset) on the stress-strain curve, which corresponds to a strain of 0.0054. Now, utilization of Equation 6.2 to compute the value of Δl:

$$\Delta l = \varepsilon l_0 = (0.0054)(80\ \mathrm{mm}) = 0.43\ \mathrm{mm}\ \ (0.017\ \mathrm{in.})$$

6.11 *Figure 6.23 shows the tensile engineering stress–strain curve in the elastic region for a gray cast iron. Determine (a) the tangent modulus at 25 MPa (3625 psi) and (b) the secant modulus taken to 35 MPa (5000 psi).*

Solution

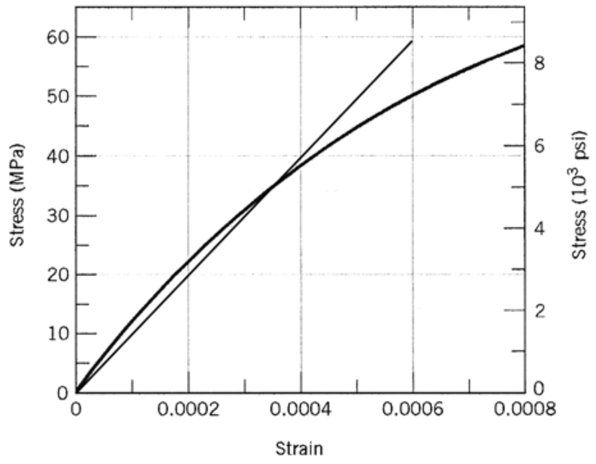
(a) This portion of the problem asks that the tangent modulus be determined for the gray cast iron, the stress-strain behavior of which is shown in Figure 6.23. In the figure below is shown a tangent draw on the curve at a stress of 25 MPa.



The slope of this line (i.e., $\Delta\sigma/\Delta\varepsilon$), the tangent modulus, is computed as follows:

$$\frac{\Delta\sigma}{\Delta\varepsilon} = \frac{57\text{ MPa} - 5\text{ MPa}}{0.0006 - 0} = 86{,}700\text{ MPa} = 86.7\text{ GPa}\ \ (12.6 \times 10^6\text{ psi})$$

(b) The secant modulus taken from the origin is calculated by taking the slope of a secant drawn from the origin through the stress-strain curve at 35 MPa (5,000 psi). This secant modulus is drawn on the curve shown below:



The slope of this line (i.e., $\Delta\sigma/\Delta\varepsilon$), the secant modulus, is computed as follows:

$$\frac{\Delta\sigma}{\Delta\varepsilon} = \frac{60\text{ MPa} - 0\text{ MPa}}{0.0006 - 0} = 100{,}000\text{ MPa} = 100\text{ GPa} \quad (14.5 \times 10^6\text{ psi})$$

6.12 *As noted in Section 3.15, for single crystals of some substances, the physical properties are anisotropic—that is, they depend on crystallographic direction. One such property is the modulus of elasticity. For cubic single crystals, the modulus of elasticity in a general [uvw] direction, E_{uvw}, is described by the relationship*

$$\frac{1}{E_{uvw}} = \frac{1}{E_{\langle 100\rangle}} - 3\left(\frac{1}{E_{\langle 100\rangle}} - \frac{1}{E_{\langle 111\rangle}}\right)\left(\alpha^2\beta^2 + \beta^2\gamma^2 + \gamma^2\alpha^2\right)$$

where $E_{\langle 100\rangle}$ *and* $E_{\langle 111\rangle}$ *are the moduli of elasticity in the* [100] *and* [111] *directions, respectively; α, β, and γ are the cosines of the angles between* [uvw] *and the respective* [100], [010], *and* [001] *directions. Verify that the* $E_{\langle 110\rangle}$ *values for aluminum, copper, and iron in Table 3.4 are correct.*

Solution

We are asked, using the equation given in the problem statement, to verify that the modulus of elasticity values along [110] directions given in Table 3.4 for aluminum, copper, and iron are correct. The α, β, and γ parameters in the equation correspond, respectively, to the cosines of the angles between the [110] direction and [100], [010] and [001] directions. Since these angles are 45°, 45°, and 90°, the values of α, β, and γ are 0.707, 0.707, and 0, respectively. Thus, the given equation takes the form

$$\frac{1}{E_{\langle 110\rangle}}$$

$$= \frac{1}{E_{\langle 100\rangle}} - 3\left(\frac{1}{E_{\langle 100\rangle}} - \frac{1}{E_{\langle 111\rangle}}\right)\left[(0.707)^2(0.707)^2 + (0.707)^2(0)^2 + (0)^2(0.707)^2\right]$$

$$= \frac{1}{E_{\langle 100\rangle}} - (0.75)\left(\frac{1}{E_{\langle 100\rangle}} - \frac{1}{E_{\langle 111\rangle}}\right)$$

Using the values of $E_{\langle 100\rangle}$ and $E_{\langle 111\rangle}$ from Table 3.4 for Al (63.7 GPa and 76.1 GPa, respectively)

$$\frac{1}{E_{\langle 110\rangle}} = \frac{1}{63.7\text{ GPa}} - (0.75)\left[\frac{1}{63.7\text{ GPa}} - \frac{1}{76.1\text{ GPa}}\right]$$

Which leads to, $E_{\langle 110\rangle}$ = 72.6 GPa, the value cited in the table.

For Cu, having values of 66.7 GPa and 191.1 GPa, respectively, for $E_{\langle 100\rangle}$ and $E_{\langle 111\rangle}$,

$$\frac{1}{E_{\langle 110\rangle}} = \frac{1}{66.7\text{ GPa}} - (0.75)\left[\frac{1}{66.7\text{ GPa}} - \frac{1}{191.1\text{ GPa}}\right]$$

Thus, $E_{\langle 110\rangle}$ = 130.3 GPa, which is also the value cited in the table.

Similarly, for Fe, having values of 125.0 GPa and 272.7 GPa, respectively, for $E_{\langle 100\rangle}$ and $E_{\langle 111\rangle}$,

$$\frac{1}{E_{\langle 110\rangle}} = \frac{1}{125.0\text{ GPa}} - (0.75)\left[\frac{1}{125.0\text{ GPa}} - \frac{1}{272.7\text{ GPa}}\right]$$

And $E_{\langle 110\rangle}$ = 210.5 GPa, which is also the value given in the table.

6.13 *In Section 2.6, it was noted that the net bonding energy E_N between two isolated positive and negative ions is a function of interionic distance r as follows:*

$$E_N = -\frac{A}{r} + \frac{B}{r^n} \tag{6.31}$$

where A, B, and n are constants for the particular ion pair. Equation 6.31 is also valid for the bonding energy between adjacent ions in solid materials. The modulus of elasticity E is proportional to the slope of the interionic force–separation curve at the equilibrium interionic separation; that is,

$$E \propto \left(\frac{dF}{dr}\right)_{r_o}$$

Derive an expression for the dependence of the modulus of elasticity on these A, B, and n parameters (for the two-ion system), using the following procedure:

1. Establish a relationship for the force F as a function of r, realizing that

$$F = \frac{dE_N}{dr}$$

2. Now take the derivative dF/dr.

3. Develop an expression for r_0, the equilibrium separation. Because r_0 corresponds to the value of r at the minimum of the E_N-versus-r curve (Figure 2.10b), take the derivative dE_N/dr, set it equal to zero, and solve for r, which corresponds to r_0.

4. Finally, substitute this expression for r_0 into the relationship obtained by taking dF/dr.

Solution

This problem asks that we derive an expression for the dependence of the modulus of elasticity, *E*, on the parameters *A*, *B*, and *n* in Equation 6.31. It is first necessary to take dE_N/dr in order to obtain an expression for the force *F*; this is accomplished as follows:

$$F = \frac{dE_N}{dr} = \frac{d\left(-\frac{A}{r}\right)}{dr} + \frac{d\left(\frac{B}{r^n}\right)}{dr}$$

$$= \frac{A}{r^{(1+1)}} - \frac{nB}{r^{(n+1)}}$$

The second step is to set this dE_N/dr expression equal to zero and then solve for r (= r_0). The algebra for this procedure is carried out in Problem 2.18, with the result that

$$r_0 = \left(\frac{A}{nB}\right)^{1/(1-n)}$$

Next it becomes necessary to take the derivative of the force (dF/dr), which is accomplished as follows:

$$\frac{dF}{dr} = \frac{d\left(\frac{A}{r^2}\right)}{dr} + \frac{d\left(-\frac{nB}{r^{n+1}}\right)}{dr}$$

$$-\frac{2A}{r^3} + \frac{(n)(n+1)B}{r^{(n+2)}}$$

Now, substitution of the above expression for r_0 into this equation yields

$$\left(\frac{dF}{dr}\right)_{r_0} = -\frac{2A}{\left(\frac{A}{nB}\right)^{3/(1-n)}} + \frac{(n)(n+1)B}{\left(\frac{A}{nB}\right)^{(n+2)/(1-n)}}$$

which is the expression to which the modulus of elasticity is proportional.

Elastic Properties of Materials

6.14 *Using the solution to Problem 6.13, rank the magnitudes of the moduli of elasticity for the following hypothetical X, Y, and Z materials from the greatest to the least. The appropriate A, B, and n parameters (Equation 6.31) for these three materials are tabulated below; they yield E_N in units of electron volts and r in nanometers:*

Material	***A***	***B***	***n***
X	*1.5*	*7.0×10^{-6}*	*8*
Y	*2.0*	*1.0×10^{-5}*	*9*
Z	*3.5*	*4.0×10^{-6}*	*7*

Solution

This problem asks that we rank the magnitudes of the moduli of elasticity of the three hypothetical metals X, Y, and Z. From Problem 6.13, it was shown for materials in which the bonding energy is dependent on the interatomic distance *r* according to Equation 6.31, that the modulus of elasticity *E* is proportional to

$$E \propto -\frac{2A}{\left(\dfrac{A}{nB}\right)^{3/(1-n)}} + \frac{(n)(n+1)B}{\left(\dfrac{A}{nB}\right)^{(n+2)/(1-n)}}$$

For metal X, *A* = 1.5, *B* = 7 × 10^{-6}, and *n* = 8. Therefore,

$$E \propto -\frac{(2)(1.5)}{\left[\dfrac{1.5}{(8)(7\times10^{-6})}\right]^{3/(1-8)}} + \frac{(8)(8+1)(7\times10^{-6})}{\left[\dfrac{1.5}{(8)(7\times10^{-6})}\right]^{(8+2)/(1-8)}}$$

$$= 830$$

For metal Y, *A* = 2.0, *B* = 1 × 10^{-5}, and *n* = 9. Hence

$$E \propto -\frac{(2)(2.0)}{\left[\dfrac{2.0}{(9)(1\times10^{-5})}\right]^{3/(1-9)}} + \frac{(9)(9+1)(1\times10^{-5})}{\left[\dfrac{2.0}{(9)(1\times10^{-5})}\right]^{(9+2)/(1-9)}}$$

$$= 683$$

And, for metal Z, A = 3.5, B = 4 × 10^{-6}, and n = 7. Thus

$$E \propto -\frac{(2)(3.5)}{\left[\dfrac{3.5}{(7)(4\times10^{-6})}\right]^{3/(1-7)}} + \frac{(7)(7+1)(4\times10^{-6})}{\left[\dfrac{3.5}{(7)(4\times10^{-6})}\right]^{(7+2)/(1-7)}}$$

$$= 7425$$

Therefore, metal Z has the highest modulus of elasticity.

6.15 *A cylindrical specimen of steel having a diameter of 15.2 mm (0.60 in.) and length of 250 mm (10.0 in.) is deformed elastically in tension with a force of 48,900 N (11,000 lb*$_f$*). Using the data contained in Table 6.1, determine the following:*

(a) The amount by which this specimen will elongate in the direction of the applied stress.

(b) The change in diameter of the specimen. Will the diameter increase or decrease?

Solution

(a) We are asked, in this portion of the problem, to determine the elongation of a cylindrical specimen of steel. To solve this part of the problem requires that we use Equations 6.1, 6.2 and 6.5. Equation 6.5 reads as follows:

$$\sigma = E\varepsilon$$

Substitution the expression for σ from Equation 6.1 and the expression for ε from Equation 6.2 leads to

$$\frac{F}{\pi\left(\frac{d_0^2}{4}\right)} = E\,\frac{\Delta l}{l_0}$$

In this equation d_0 is the original cross-sectional diameter. Now, solving for Δl yields

$$\Delta l = \frac{4 F l_0}{\pi d_0^2 E}$$

And incorporating values of F, l_0, and d_0, and realizing that E = 207 GPa (Table 6.1), leads to

$$\Delta l = \frac{(4)(48{,}900\ \mathrm{N})(250 \times 10^{-3}\,\mathrm{m})}{(\pi)(15.2 \times 10^{-3}\,\mathrm{m})^2(207 \times 10^9\ \mathrm{N/m^2})} = 3.25 \times 10^{-4}\ \mathrm{m} = 0.325\ \mathrm{mm} \quad (0.013\ \mathrm{in.})$$

(b) We are now called upon to determine the change in diameter, Δd. Using Equation 6.8 (the definition of Poisson's ratio)

$$\nu = -\frac{\varepsilon_x}{\varepsilon_z} = -\frac{\Delta d/d_0}{\Delta l/l_0}$$

From Table 6.1, for steel, the value of Poisson's ratio, ν, is 0.30. Now, solving the above expression for Δd yields

$$\Delta d = -\frac{\nu \Delta l\, d_0}{l_0} = -\frac{(0.30)(0.325\text{ mm})(15.2\text{ mm})}{250\text{ mm}}$$

$$= -5.9 \times 10^{-3}\text{ mm} \quad (-2.3 \times 10^{-4}\text{ in.})$$

The diameter will decrease since Δd is negative.

6.16 *A cylindrical bar of aluminum 19 mm (0.75 in.) in diameter is to be deformed elastically by application of a force along the bar axis. Using the data in Table 6.1, determine the force that produces an elastic reduction of 2.5 × 10^{-3} mm (1.0 × 10^{-4} in.) in the diameter.*

Solution

This problem asks that we calculate the force necessary to produce a reduction in diameter of 2.5 × 10^{-3} mm for a cylindrical bar of aluminum. For a cylindrical specimen, the cross-sectional area is equal to

$$A_0 = \frac{\pi d_0^2}{4}$$

Now, combining Equations 6.1 and 6.5 leads to

$$\sigma = \frac{F}{A_0} = \frac{F}{\dfrac{\pi d_0^2}{4}} = E\varepsilon_z$$

And, since from Equation 6.8

$$\varepsilon_z = -\frac{\varepsilon_x}{\nu} = -\frac{\dfrac{\Delta d}{d_0}}{\nu} = -\frac{\Delta d}{\nu d_0}$$

Substitution of this equation into the previous one gives

$$\frac{F}{\dfrac{\pi d_0^2}{4}} = E\left(-\frac{\Delta d}{\nu d_0}\right)$$

And, solving for F leads to

$$F = -\frac{d_0 \Delta d \pi E}{4\nu}$$

Incorporating into this equation values of d_0 and Δd from the problem statement and realizing that, for aluminum, ν = 0.33 and E = 69 GPa (Table 6.1) allows us to determine the value of the force F as follows:

$$F = -\frac{(19 \times 10^{-3}\,\text{m})(-2.5 \times 10^{-6}\,\text{m})(\pi)(69 \times 10^{9}\ \text{N/m}^2)}{(4)(0.33)}$$

$= 7{,}800\ \text{N} \quad (1{,}785\ \text{lb}_f)$

6.17 *A cylindrical specimen of a metal alloy 10 mm (0.4 in.) in diameter is stressed elastically in tension. A force of 15,000 N (3,370 lb$_f$) produces a reduction in specimen diameter of 7 × 10^{-3} mm (2.8 × 10^{-4} in.). Compute Poisson's ratio for this material if its elastic modulus is 100 GPa (14.5 × 10^6 psi).*

Solution

This problem asks that we compute Poisson's ratio for the metal alloy. From Equations 6.5 and 6.1

$$\varepsilon_z = \frac{\sigma}{E} = \frac{F}{A_0 E} = \frac{F}{\pi\left(\frac{d_0}{2}\right)^2 E} = \frac{4F}{\pi d_0^2 E}$$

Since the transverse strain ε_x is equal to

$$\varepsilon_x = \frac{\Delta d}{d_0}$$

and Poisson's ratio is defined by Equation 6.8, then

$$\upsilon = -\frac{\varepsilon_x}{\varepsilon_z} = -\frac{\Delta d / d_0}{\left(\frac{4F}{\pi d_0^2 E}\right)} = -\frac{d_0 \Delta d \pi E}{4F}$$

Now, incorporating values of d_0, Δd, E and F from the problem statement yields the following value for Poisson's ratio

$$\upsilon = -\frac{(10 \times 10^{-3}\ \text{m})(-7 \times 10^{-6}\ \text{m})(\pi)(100 \times 10^{9}\ \text{N/m}^2)}{(4)(15{,}000\ \text{N})} = 0.367$$

6.18 *A cylindrical specimen of a hypothetical metal alloy is stressed in compression. If its original and final diameters are 30.00 and 30.04 mm, respectively, and its final length is 105.20 mm, compute its original length if the deformation is totally elastic. The elastic and shear moduli for this alloy are 65.5 and 25.4 GPa, respectively.*

Solution

This problem asks that we compute the original length of a cylindrical specimen that is stressed in compression. It is first convenient to compute the lateral strain ε_x using the Poisson's ratio expression for this strain:

$$\varepsilon_x = \frac{\Delta d}{d_0} = \frac{30.04\ \text{mm} - 30.00\ \text{mm}}{30.00\ \text{mm}} = 1.33 \times 10^{-3}$$

In order to determine the longitudinal strain ε_z we need Poisson's ratio, which may be computed using Equation 6.9; using values for E and G in the problem statement and solving this equation for ν yields

$$\nu = \frac{E}{2G} - 1 = \frac{65.5 \times 10^3\ \text{MPa}}{(2)(25.4 \times 10^3\ \text{MPa})} - 1 = 0.289$$

Now ε_z may be computed from Equation 6.8 as

$$\varepsilon_z = -\frac{\varepsilon_x}{\nu} = -\frac{1.33 \times 10^{-3}}{0.289} = -4.60 \times 10^{-3}$$

Using this value of ε_z we solve for l_0 using Equation 6.2 and the value of l_i given in the problem statement:

$$l_0 = \frac{l_i}{1 + \varepsilon_z}$$

$$= \frac{105.20\ \text{mm}}{1 + (-4.60 \times 10^{-3})} = 105.69\ \text{mm}$$

6.19 *Consider a cylindrical specimen of some hypothetical metal alloy that has a diameter of 10.0 mm (0.39 in.). A tensile force of 1500 N (340 lb$_f$) produces an elastic reduction in diameter of 6.7 × 10^{-4} mm (2.64 × 10^{-5} in.). Compute the elastic modulus of this alloy, given that Poisson's ratio is 0.35.*

Solution

This problem asks that we calculate the modulus of elasticity of a metal that is stressed in tension. Combining Equations 6.5 and 6.1 leads to

$$E = \frac{\sigma}{\varepsilon_z} = \frac{\dfrac{F}{A_0}}{\varepsilon_z} = \frac{F}{A_0\varepsilon_z} = \frac{F}{\varepsilon_z \pi \left(\dfrac{d_0}{2}\right)^2} = \frac{4F}{\varepsilon_z \pi d_0^2}$$

From the definition of Poisson's ratio, (Equation 6.8) and realizing that for the transverse strain, $\varepsilon_x = \dfrac{\Delta d}{d_0}$ leads to

$$\varepsilon_z = -\frac{\varepsilon_x}{\nu} = -\frac{\Delta d/d_0}{\nu} = -\frac{\Delta d}{d_0 \nu}$$

Therefore, substitution of this expression for ε_z into the above equation for E yields

$$E = \frac{4F}{\varepsilon_z \pi d_0^2} = \frac{4F}{\left(-\dfrac{\Delta d}{d_0 \nu}\right)\pi d_0^2} = -\frac{4F\nu}{\pi d_0 \Delta d}$$

Incorporation of values for F, ν, d_0, and Δd given in the problem statement (and realizing that Δd is negative) allows us to calculate the modulus of elasticity as follows:

$$E = -\frac{(4)(1500\ \mathrm{N})(0.35)}{\pi\left(10 \times 10^{-3}\ \mathrm{m}\right)\left(-6.7 \times 10^{-7}\ \mathrm{m}\right)} = 10^{11}\ \mathrm{Pa} = 100\ \mathrm{GPa} \quad (14.7 \times 10^6\ \mathrm{psi})$$

6.20 *A brass alloy is known to have a yield strength of 240 MPa (35,000 psi), a tensile strength of 310 MPa (45,000 psi), and an elastic modulus of 110 GPa (16.0 × 10^6 psi). A cylindrical specimen of this alloy 15.2 mm (0.60 in.) in diameter and 380 mm (15.0 in.) long is stressed in tension and found to elongate 1.9 mm (0.075 in.). On the basis of the information given, is it possible to compute the magnitude of the load necessary to produce this change in length? If so, calculate the load; if not, explain why.*

Solution

We are asked to ascertain whether or not it is possible to compute, for brass, the magnitude of the load necessary to produce an elongation of 1.9 mm (0.075 in.). It is first necessary to compute the strain at yielding from the yield strength and the elastic modulus, and then the strain experienced by the test specimen. Then, if

$$\varepsilon(\text{test}) < \varepsilon(\text{yield})$$

deformation is elastic, and the load may be computed using Equations 6.1 and 6.5. However, if

$$\varepsilon(\text{test}) > \varepsilon(\text{yield})$$

computation of the load is not possible inasmuch as deformation is plastic and we have neither a stress-strain plot nor a mathematical expression relating plastic stress and strain. The value of ε(test) is determined using Equation 6.2 as follows:

$$\varepsilon(\text{test}) = \frac{\Delta l}{l_0} = \frac{1.9\ \text{mm}}{380\ \text{mm}} = 0.005$$

and for ε(yield), Equation 6.5 is used—i.e.,

$$\varepsilon(\text{yield}) = \frac{\sigma_y}{E} = \frac{240\ \text{MPa}}{110 \times 10^3\ \text{MPa}} = 0.0022$$

Therefore, computation of the load is *not possible* since ε(test) > ε(yield).

6.21 *A cylindrical metal specimen 15.0 mm (0.59 in.) in diameter and 150 mm (5.9 in.) long is to be subjected to a tensile stress of 50 MPa (7250 psi); at this stress level, the resulting deformation will be totally elastic.*

(a) If the elongation must be less than 0.072 mm (2.83 × 10^{-3} in.), which of the metals in Table 6.1 are suitable candidates? Why?

(b) If, in addition, the maximum permissible diameter decrease is 2.3 × 10^{-3} mm (9.1 × 10^{-5} in.) when the tensile stress of 50 MPa is applied, which of the metals that satisfy the criterion in part (a) are suitable candidates? Why?

Solution

(a) This part of the problem asks that we ascertain which of the metals in Table 6.1 experience an elongation of less than 0.072 mm when subjected to a tensile stress of 50 MPa. The maximum strain that may be sustained, (using Equation 6.2) is just

$$\varepsilon = \frac{\Delta l}{l_0} = \frac{0.072\ \text{mm}}{150\ \text{mm}} = 4.8 \times 10^{-4}$$

Since the stress level is given (50 MPa), using Equation 6.5 it is possible to compute the minimum modulus of elasticity that is required to yield this minimum strain. Hence

$$E = \frac{\sigma}{\varepsilon} = \frac{50\ \text{MPa}}{4.8 \times 10^{-4}} = 104.2\ \text{GPa}$$

Which means that those metals with moduli of elasticity greater than this value are acceptable candidates--namely, Cu, Ni, steel, Ti and W.

(b) This portion of the problem further stipulates that the maximum permissible diameter decrease is 2.3 × 10^{-3} mm when the tensile stress of 50 MPa is applied. This translates into a maximum lateral strain ε_x(max) as

$$\varepsilon_x(\text{max}) = \frac{\Delta d}{d_0} = \frac{-2.3 \times 10^{-3}\ \text{mm}}{15.0\ \text{mm}} = -1.53 \times 10^{-4}$$

But, since the specimen contracts in this lateral direction, and we are concerned that this strain be less than 1.53 × 10^{-4}, then the criterion for this part of the problem may be stipulated as $-\frac{\Delta d}{d_0} < 1.53 \times 10^{-4}$.

Now, Poisson’s ratio is defined by Equation 6.8 as

$$\nu = -\frac{\varepsilon_x}{\varepsilon_z}$$

For each of the metal alloys let us consider a possible lateral strain, $\varepsilon_x = \frac{\Delta d}{d_0}$. Furthermore, since the deformation is elastic, then, from Equation 6.5, the longitudinal strain, ε_z is equal to

$$\varepsilon_z = \frac{\sigma}{E}$$

Substituting these expressions for ε_x and ε_z into the definition of Poisson's ratio we have

$$\nu = -\frac{\varepsilon_x}{\varepsilon_z} = -\frac{\frac{\Delta d}{d_0}}{\frac{\sigma}{E}}$$

which leads to the following:

$$-\frac{\Delta d}{d_0} = \frac{\nu\sigma}{E}$$

Using values for ν and E found in Table 6.1 for the six metal alloys that satisfy the criterion for part (a), and for σ = 50 MPa, we are able to compute a $-\frac{\Delta d}{d_0}$ for each of Cu, Ni, steel, Ti and W as follows:

$$-\frac{\Delta d}{d_0}(\text{copper}) = \frac{(0.34)(50 \times 10^6 \text{ N/m}^2)}{110 \times 10^9 \text{ N/m}^2} = 1.55 \times 10^{-4}$$

$$-\frac{\Delta d}{d_0}(\text{titanium}) = \frac{(0.34)(50 \times 10^6 \text{ N/m}^2)}{107 \times 10^9 \text{ N/m}^2} = 1.59 \times 10^{-4}$$

$$-\frac{\Delta d}{d_0}(\text{nickel}) = \frac{(0.31)(50 \times 10^6 \text{ N/m}^2)}{207 \times 10^9 \text{ N/m}^2} = 7.49 \times 10^{-5}$$

$$-\frac{\Delta d}{d_0}(\text{steel}) = \frac{(0.30)(50 \times 10^6\ \text{N/m}^2)}{207 \times 10^9\ \text{N/m}^2} = 7.25 \times 10^{-5}$$

$$-\frac{\Delta d}{d_0}(\text{tungsten}) = \frac{(0.28)(50 \times 10^6\ \text{N/m}^2)}{407 \times 10^9\ \text{N/m}^2} = 3.44 \times 10^{-5}$$

Thus, copper and titanium alloys will experience a negative transverse strain greater than 1.53×10^{-4}. This means that the following alloys satisfy the criteria for both parts (a) and (b) of this problem: nickel, steel, and tungsten.

6.22 *A cylindrical metal specimen 10.7000 mm in diameter and 95.000 mm long is to be subjected to a tensile force of 6300 N; at this force level, the resulting deformation will be totally elastic.*

(a) If the final length must be less than 95.040 mm, which of the metals in Table 6.1 are suitable candidates? Why?

(b) If, in addition, the diameter must be no greater than 10.698 mm while the tensile force of 6300 N is applied, which of the metals that satisfy the criterion in part (a) are suitable candidates? Why?

Solution

(a) This part of the problem asks that we ascertain which of the metals in Table 6.1 experience an increase in length from 95.000 mm (l_0) to 95.040 mm (l_i) when subjected to a tensile force of 6300 N. We may make this determination by computing the minimum modulus of elasticity required using data given in the problem statement; those metals having values greater than this minimum satisfy the criterion. Modulus of elasticity is determined using Equation 6.5 ($\sigma = \varepsilon E$), which requires that we first compute values for the stress and strain.

The maximum strain that may be sustained, (using Equation 6.2) is just

$$\varepsilon = \frac{l_i - l_0}{l_0} = \frac{95.040\ \mathrm{mm} - 95.000\ \mathrm{mm}}{95.000\ \mathrm{mm}} = 4.21 \times 10^{-4}$$

The maximum stress level is computed using Equation 6.1; original cross-sectional area (A_0) may be determined from original specimen diameter (d_0 = 10.7000 mm). Thus, the stress is equal to

$$\sigma = \frac{F}{A_0} = \frac{F}{\pi\left(\frac{d_0}{2}\right)^2} = \frac{6300\ \mathrm{N}}{\pi\left(\frac{10.7000 \times 10^{-3}\ \mathrm{m}}{2}\right)^2}$$

$$70.1 \times 10^6\ \mathrm{N/m^2} = 70.1\ \mathrm{MPa}$$

We now calculate the minimum modulus of elasticity incorporating these stress and strain values into Equation 6.5. Hence

$$E = \frac{\sigma}{\varepsilon} = \frac{70.1\ \mathrm{MPa}}{4.21 \times 10^{-4}} = 167 \times 10^3\ \mathrm{MPa} = 167\ \mathrm{GPa}$$

Which means that those metals with moduli of elasticity greater than this value are acceptable candidates--namely, Ni, steel, and W.

(b) For this part of the problem it is necessary to ascertain which of nickel, steel, and tungsten will have diameters of no greater than 10.698 while the 6300 N force is being applied. This determination can be made by computing the maximum allowable Poisson's ratio (Equation 6.8) from the ratio of transverse and longitudinal strains (ε_x and ε_z, respectively). The strain calculated in part (a) is a longitudinal strain—i.e.,

$$\varepsilon_z = 4.21 \times 10^{-4}$$

Transverse strain (ε_x)is computed using the transverse analog of Equation 6.2—i.e.,

$$\varepsilon_x = \frac{d_i - d_0}{d_0}$$

In this equation d_i is the diameter while the stress is being applied—i.e., 10.698 mm. Thus

$$\varepsilon_x = \frac{10.698 \text{ mm} - 10.7000 \text{ mm}}{10.700 \text{ mm}} = \frac{-0.002 \text{ mm}}{10.700 \text{ mm}} = -1.87 \times 10^{-4}$$

We now compute Poisson's ratio using Equation 6.8 as follows:

$$\nu = -\frac{\varepsilon_x}{\varepsilon_z} = -\frac{-1.87 \times 10^{-4}}{4.21 \times 10^{-4}} = 0.444$$

This result means that for deformed diameters to be less than 10.698 mm, the value of Poisson's ratio must be less than 0.444—therefore, all of nickel ($\nu = 0.31$), steel ($\nu = 0.30$), and tungsten ($\nu = 0.28$) are candidates.

6.23 *Consider the brass alloy for which the stress–strain behavior is shown in Figure 6.12. A cylindrical specimen of this material 10.0 mm (0.39 in.) in diameter and 101.6 mm (4.0 in.) long is pulled in tension with a force of 10,000 N (2250 lb*$_f$*). If it is known that this alloy has a value for Poisson's ratio of 0.35, compute (a) the specimen elongation and (b) the reduction in specimen diameter.*

Solution

(a) This portion of the problem asks that we compute the elongation of the brass specimen. The first calculation necessary is that of the applied stress using Equation 6.1, as

$$\sigma = \frac{F}{A_0} = \frac{F}{\pi\left(\frac{d_0}{2}\right)^2} = \frac{10{,}000 \text{ N}}{\pi\left(\frac{10 \times 10^{-3}\text{ m}}{2}\right)^2} = 127 \text{ MPa} \quad (17{,}900 \text{ psi})$$

From the stress-strain plot in Figure 6.12, this stress corresponds to a strain of about 1.5 × 10^{-3}. From the definition of strain, Equation 6.2

$$\Delta l = \varepsilon l_0 = (1.5 \times 10^{-3})(101.6 \text{ mm}) = 0.15 \text{ mm} \quad (6.0 \times 10^{-3} \text{ in.})$$

(b) In order to determine the reduction in diameter Δ*d*, it is necessary to use Equation 6.8 and the definition of lateral strain (i.e., $\varepsilon_x = \Delta d/d_0$) as follows

$$\Delta d = d_0\varepsilon_x = -d_0\nu\varepsilon_z = -(10 \text{ mm})(0.35)(1.5 \times 10^{-3})$$

$$= -5.25 \times 10^{-3} \text{ mm} \quad (-2.05 \times 10^{-4} \text{ in.})$$

6.24 *A cylindrical rod 120 mm long and having a diameter of 15.0 mm is to be deformed using a tensile load of 35,000 N. It must not experience either plastic deformation or a diameter reduction of more than 1.2 × 10^{-2} mm. Of the following materials listed, which are possible candidates? Justify your choice(s).*

Material	***Modulus of Elasticity* (*GPa*)**	***Yield Strength* (*MPa*)**	***Poisson's Ratio***
Aluminum alloy	70	250	0.33
Titanium alloy	105	850	0.36
Steel alloy	205	550	0.27
Magnesium alloy	45	170	0.35

Solution

This problem asks that we assess the four alloys relative to the two criteria presented. The first criterion is that the material not experience plastic deformation when the tensile load of 35,000 N is applied; this means that the stress corresponding to this load not exceed the yield strength of the material. Upon computing the stress

$$\sigma = \frac{F}{A_0} = \frac{F}{\pi\left(\frac{d_0}{2}\right)^2} = \frac{35{,}000\ \text{N}}{\pi\left(\frac{15 \times 10^{-3}\ \text{m}}{2}\right)^2} = 200 \times 10^6\ \text{N/m}^2 = 200\ \text{MPa}$$

Of the alloys listed, the Al, Ti and steel alloys have yield strengths greater than 200 MPa.

Relative to the second criterion (i.e., that Δd be less than 1.2 × 10^{-2} mm), it is necessary to calculate the change in diameter Δd for these three alloys. It is first necessary to generate an expression for Poisson's ratio from Equation 6.8, where $\varepsilon_x = \Delta d/d_0$, and, from Equation 6.5, $\varepsilon_y = \sigma/E$. Thus

$$\nu = -\frac{\varepsilon_x}{\varepsilon_z} = -\frac{\frac{\Delta d}{d_0}}{\frac{\sigma}{E}} = -\frac{E\Delta d}{\sigma d_0}$$

Now, solving for Δd from this expression,

$$\Delta d = -\frac{\nu \sigma d_0}{E}$$

From the data presented in the table in the problem statement, we now compute the value of Δd for each of the four alloys.

For the aluminum alloy (E = 70 GPa, ν = 0.33, and taking the stress σ to be 200 MPa)

$$\Delta d = -\frac{(0.33)(200\ \mathrm{MPa})(15\ \mathrm{mm})}{70 \times 10^3\ \mathrm{MPa}} = -1.41 \times 10^{-3}\ \mathrm{mm}$$

Therefore, the Al alloy is not a candidate because its Δ*d* is greater than 1.2×10^{-2} mm.

For the steel alloy (E = 205 GPa, ν = 0.27)

$$\Delta d = -\frac{(0.27)(200\ \mathrm{MPa})(15\ \mathrm{mm})}{205 \times 10^3\ \mathrm{MPa}} = -0.40 \times 10^{-2}\ \mathrm{mm}$$

Therefore, the steel is a candidate.

For the Ti alloy (E = 105 GPa, ν = 0.36)

$$\Delta d = -\frac{(0.36)(200\ \mathrm{MPa})(15\ \mathrm{mm})}{105 \times 10^3\ \mathrm{MPa}} = -1.0 \times 10^{-2}\ \mathrm{mm}$$

Hence, the titanium alloy is also a candidate.

6.25 *A cylindrical rod 500 mm (20.0 in.) long and having a diameter of 12.7 mm (0.50 in.) is to be subjected to a tensile load. If the rod is to experience neither plastic deformation nor an elongation of more than 1.3 mm (0.05 in.) when the applied load is 29,000 N (6500 lb* $_f$*), which of the four metals or alloys listed in the following table are possible candidates? Justify your choice(s).*

Material	***Modulus of Elasticity (GPa)***	***Yield Strength (MPa)***	***Tensile Strength (MPa)***
Aluminum alloy	70	255	420
Brass alloy	100	345	420
Copper	110	210	275
Steel alloy	207	450	550

Solution

This problem asks that we ascertain which of four metal alloys will not (1) experience plastic deformation, and (2) elongate more than 1.3 mm when a tensile load of 29,000 N is applied. It is first necessary to compute the stress using Equation 6.1; a material to be used for this application must necessarily have a yield strength greater than this value. Thus,

$$\sigma = \frac{F}{A_0} = \frac{F}{\pi\left(\frac{d_0}{2}\right)^2} = \frac{29{,}000\ \text{N}}{\pi\left(\frac{12.7\ \times\ 10^{-3}\text{m}}{2}\right)^2} = 230\ \text{MPa}$$

Of the metal alloys listed, aluminum, brass and steel have yield strengths greater than this stress.

Next, we must compute the elongation produced in each of aluminum, brass, and steel by combining Equations 6.2 and 6.5 in order to determine whether or not this elongation is less than 1.3 mm. For aluminum (E = 70 GPa = 70 × 10^3 MPa)

$$\Delta l = \varepsilon l_0 = \frac{\sigma l_0}{E} = \frac{(230\ \text{MPa})(500\ \text{mm})}{70\ \times\ 10^3\ \text{MPa}} = 1.64\ \text{mm}$$

Thus, aluminum is not a candidate because its Δl is greater than 1.3 mm.

For brass (E = 100 GPa = 100 × 10^3 MPa)

$$\Delta l = \frac{\sigma l_0}{E} = \frac{(230\ \text{MPa})(500\ \text{mm})}{100\ \times\ 10^3\ \text{MPa}} = 1.15\ \text{mm}$$

Thus, brass is a candidate. And, for steel (E = 207 GPa = 207 × 10^3 MPa)

$$\Delta l = \frac{\sigma l_0}{E} = \frac{(230\text{ MPa})(500\text{ mm})}{207 \times 10^3\text{ MPa}} = 0.56\text{ mm}$$

Therefore, of these four alloys, only brass and steel satisfy the stipulated criteria.

Tensile Properties

6.26 *Figure 6.22 shows the tensile engineering stress–strain behavior for a steel alloy.*

(a) What is the modulus of elasticity?

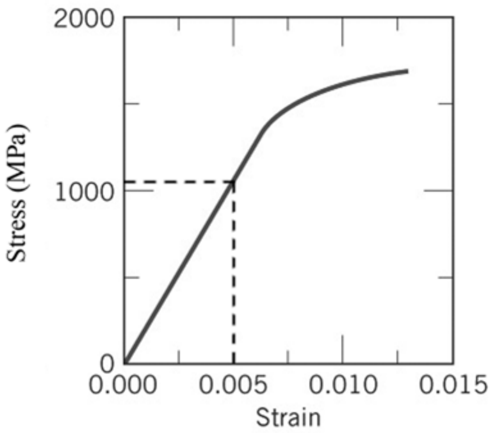
(b) What is the proportional limit?

(c) What is the yield strength at a strain offset of 0.002?

(d) What is the tensile strength?

Solution

(a) Shown below is the inset of Figure 6.22.



The elastic modulus is just the slope of the initial linear portion of the curve; or, from Equation 6.10

$$E = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1}$$

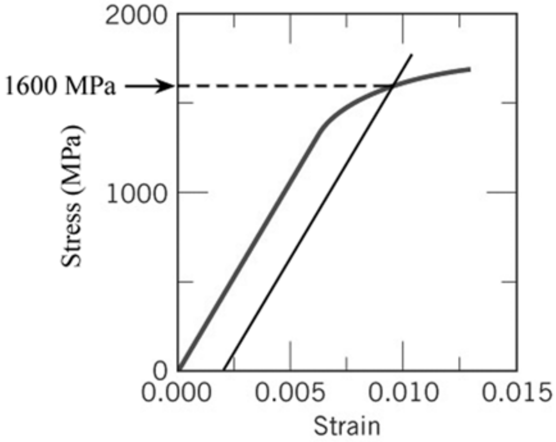
Inasmuch as the linear segment passes through the origin, let us take both σ_1 and ε_1 to be zero. If we arbitrarily take ε_2 = 0.005, as noted in the above plot, σ_2 = 1050 MPa. Using these stress and strain values we calculate the elastic modulus as follows:

$$E = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1} = \frac{1050\text{ MPa} - 0\text{ MPa}}{0.005 - 0} = 210 \times 10^3\text{ MPa} = 210\text{ GPa}$$

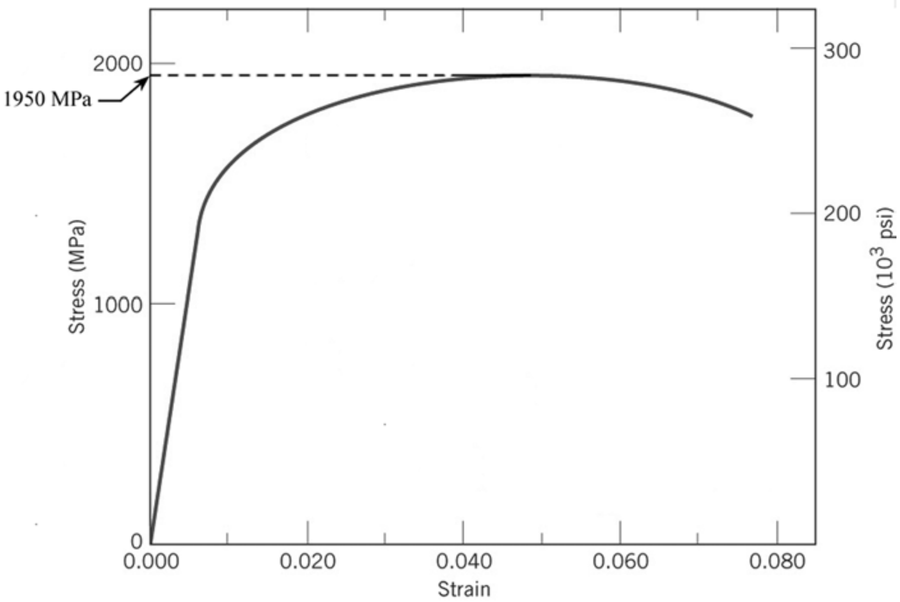
The value given in Table 6.1 is 207 GPa.

(b) The proportional limit is the stress level at which linearity of the stress-strain curve ends, which is approximately 1370 MPa (200,000 psi).

(c) As noted in the plot below, the 0.002 strain offset line intersects the stress-strain curve at approximately 1600 MPa (232,000 psi).



(d) The tensile strength (the maximum on the curve) is approximately 1950 MPa (283,000 psi), as noted in the following plot.



6.27 *A cylindrical specimen of a brass alloy having a length of 100 mm (4 in.) must elongate only 5 mm (0.2 in.) when a tensile load of 100,000 N (22,500 lb$_f$) is applied. Under these circumstances, what must be the radius of the specimen? Consider this brass alloy to have the stress–strain behavior shown in Figure 6.12.*

Solution

We are asked to calculate the radius of a cylindrical brass specimen in order to produce an elongation of 5 mm when a load of 100,000 N is applied. It first becomes necessary to compute the strain corresponding to this elongation using Equation 6.2 as

$$\varepsilon = \frac{\Delta l}{l_0} = \frac{5 \text{ mm}}{100 \text{ mm}} = 5 \times 10^{-2}$$

From Figure 6.12, a stress of 335 MPa (49,000 psi) corresponds to this strain. Since for a cylindrical specimen, stress, force, and initial radius r_0 are related (Equation 6.1) as

$$\sigma = \frac{F}{A_0} = \frac{F}{\pi r_0^2}$$

then taking F = 10,000 N and σ = 335 MPa = 335 × 10^6 N/m^2, r_0 is calculated as follows

$$r_0 = \sqrt{\frac{F}{\pi\sigma}} = \sqrt{\frac{100{,}000 \text{ N}}{\pi(335 \times 10^6 \text{ N/m}^2)}} = 0.0097 \text{ m} = 9.7 \text{ mm} \quad (0.38 \text{ in.})$$

6.28 *A load of 140,000 N (31,500 lb$_f$) is applied to a cylindrical specimen of a steel alloy (displaying the stress–strain behavior shown in Figure 6.22) that has a cross-sectional diameter of 10 mm (0.40 in.).*

(a) Will the specimen experience elastic and/or plastic deformation? Why?

(b) If the original specimen length is 500 mm (20 in.), how much will it increase in length when this load is applied?

Solution

This problem asks us to determine the deformation characteristics of a steel specimen, the stress-strain behavior for which is shown in Figure 6.22.

(a) In order to ascertain whether the deformation is elastic or plastic, we must first compute the stress, then locate it on the stress-strain curve, and, finally, note whether this point is on the elastic or elastic + plastic region. Thus, from Equation 6.1

$$\sigma = \frac{F}{A_0} = \frac{F}{\pi\left(\frac{d_0}{2}\right)^2} = \frac{140{,}000\ \text{N}}{\pi\left(\frac{10 \times 10^{-3}\ \text{m}}{2}\right)^2} = 1{,}782\ \text{MPa}\quad (250{,}000\ \text{psi})$$

The 1782 MPa point is beyond the linear portion of the curve, and, therefore, the deformation will be both elastic and plastic.

(b) This portion of the problem asks us to compute the increase in specimen length. From the stress-strain curve, the strain at 1782 MPa is approximately 0.017. Thus, from Equation 6.2

$$\Delta l = \varepsilon l_0 = (0.017)(500\ \text{mm}) = 8.5\ \text{mm}\quad (0.34\ \text{in.})$$

6.*29 A bar of a steel alloy that exhibits the stress–strain behavior shown in Figure 6.22 is subjected to a tensile load; the specimen is 375 mm (14.8 in.) long and has a square cross section 5.5 mm (0.22 in.) on a side.*

(a) Compute the magnitude of the load necessary to produce an elongation of 2.25 mm (0.088 in.).

(b) What will be the deformation after the load has been released?

Solution

(a) We are asked to compute the magnitude of the load necessary to produce an elongation of 2.25 mm for the steel displaying the stress-strain behavior shown in Figure 6.22. First, calculate the strain, and then the corresponding stress from the plot. Using Equation 6.2, the strain ε is equal to

$$\varepsilon = \frac{\Delta l}{l_0} = \frac{2.25 \text{ mm}}{375 \text{ mm}} = 0.006$$

This is within the elastic region; from the inset of Figure 6.22, this corresponds to a stress of about 1250 MPa (180,000 psi). Now, from Equation 6.1

$$F = \sigma A_0 = \sigma b^2$$

in which *b* is the cross-section side length. Thus,

$$F = \left(1250 \times 10^6 \text{ N/m}^2\right)\left(5.5 \times 10^{-3} \text{ m}\right)^2 = 37{,}800 \text{ N} \quad (8500 \text{ lb}_\text{f})$$

(b) After the load is released there will be no net deformation since the material was strained only elastically when the load was applied.

6.30 *A cylindrical specimen of stainless steel having a diameter of 12.8 mm (0.505 in.) and a gauge length of 50.800 mm (2.000 in.) is pulled in tension. Use the load–elongation characteristics shown in the following table to complete parts (a) through (f).*

Load		***Length***	
N	***lb$_f$***	***mm***	***in.***
0	*0*	*50.800*	*2.000*
12,700	*2,850*	*50.825*	*2.001*
25,400	*5,710*	*50.851*	*2.002*
38,100	*8,560*	*50.876*	*2.003*
50,800	*11,400*	*50.902*	*2.004*
76,200	*17,100*	*50.952*	*2.006*
89,100	*20,000*	*51.003*	*2.008*
92,700	*20,800*	*51.054*	*2.010*
102,500	*23,000*	*51.181*	*2.015*
107,800	*24,200*	*51.308*	*2.020*
119,400	*26,800*	*51.562*	*2.030*
128,300	*28,800*	*51.816*	*2.040*
149,700	*33,650*	*52.832*	*2.080*
159,000	*35,750*	*53.848*	*2.120*
160,400	*36,000*	*54.356*	*2.140*
159,500	*35,850*	*54.864*	*2.160*
151,500	*34,050*	*55.880*	*2.200*
124,700	*28,000*	*56.642*	*2.230*
	Fracture		

(a) Plot the data as engineering stress versus engineering strain.

(b) Compute the modulus of elasticity.

(c) Determine the yield strength at a strain offset of 0.002.

(d) Determine the tensile strength of this alloy.

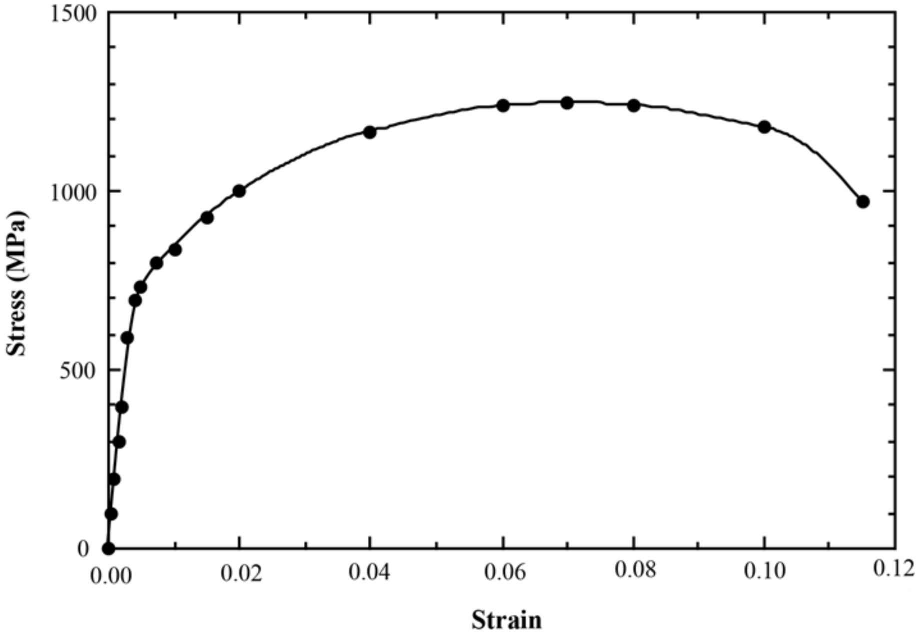
(e) What is the approximate ductility, in percent elongation?

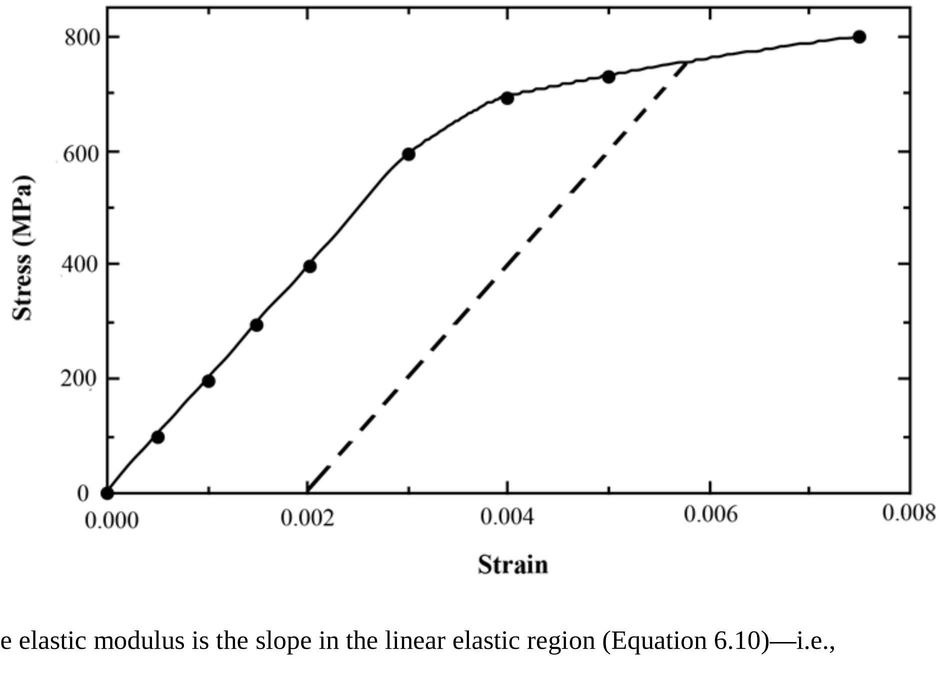
(f) Compute the modulus of resilience.

Solution

This problem calls for us to make a stress-strain plot for stainless steel, given its tensile load-length data, and then to determine some of its mechanical characteristics.

(a) The data are plotted below on two plots: the first corresponds to the entire stress-strain curve, while for the second, the curve extends to just beyond the elastic region of deformation.





(b) The elastic modulus is the slope in the linear elastic region (Equation 6.10)—i.e.,

$$E = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1}$$

Because the stress-strain curve passes through the origin, to simplify the computation let us take both σ_1 and ε_1 to be zero. If we select σ_2 = 400 MPa, its corresponding strain on the plot ε_2 is about 0.002. Thus the elastic modulus is equal to

$$E = \frac{400\ \text{MPa} - 0\ \text{MPa}}{0.002 - 0} = 200 \times 10^3\ \text{MPa} = 200\ \text{GPa} \quad (29 \times 10^6\ \text{psi})$$

(c) For the yield strength, the 0.002 strain offset line is drawn dashed in the lower plot. It intersects the stress-strain curve at approximately 750 MPa (112,000 psi).

(d) The tensile strength is approximately 1250 MPa (180,000 psi), corresponding to the maximum stress on the complete stress-strain plot.

(e) Ductility, in percent elongation, is just the plastic strain at fracture, multiplied by one-hundred. The total fracture strain at fracture is 0.115; subtracting out the elastic strain (which is about 0.003) leaves a plastic strain of 0.112. Thus, the ductility is about 11.2%EL.

(f) From Equation 6.14, the modulus of resilience is just

$$U_r = \frac{\sigma_y^2}{2E}$$

which, using values of σ_y and E computed above, (750 MPa = 750 × 10^6 N/m^2 and 200 GPa = 200 × 10^9 N/m^2, respectively) give a modulus of resilience of

$$U_r = \frac{(750 \times 10^6\ \text{N/m}^2)^2}{(2)\left(200 \times 10^9\ \text{N/m}^2\right)} = 1.40 \times 10^6\ \text{N/m}^2 = 1.40 \times 10^6\ \text{J/m}^3 \quad \left(210\ \text{in.-lb}_\text{f}/\text{in.}^3\right)$$

6.31 *A specimen of magnesium having a rectangular cross section of dimensions 3.2 mm × 19.1 mm ($\frac{1}{8}$ in. × $\frac{3}{4}$ in.) is deformed in tension. Using the load–elongation data shown in the following table, complete parts (a) through (f).*

Load		***Length***	
lb$_f$	***N***	***in.***	***mm***
0	*0*	*2.500*	*63.50*
310	*1380*	*2.501*	*63.53*
625	*2780*	*2.502*	*63.56*
1265	*5630*	*2.505*	*63.62*
1670	*7430*	*2.508*	*63.70*
1830	*8140*	*2.510*	*63.75*
2220	*9870*	*2.525*	*64.14*
2890	*12,850*	*2.575*	*65.41*
3170	*14,100*	*2.625*	*66.68*
3225	*14,340*	*2.675*	*67.95*
3110	*13,830*	*2.725*	*69.22*
2810	*12,500*	*2.775*	*70.49*
Fracture			

(a) Plot the data as engineering stress versus engineering strain.

(b) Compute the modulus of elasticity.

(c) Determine the yield strength at a strain offset of 0.002.

(d) Determine the tensile strength of this alloy.

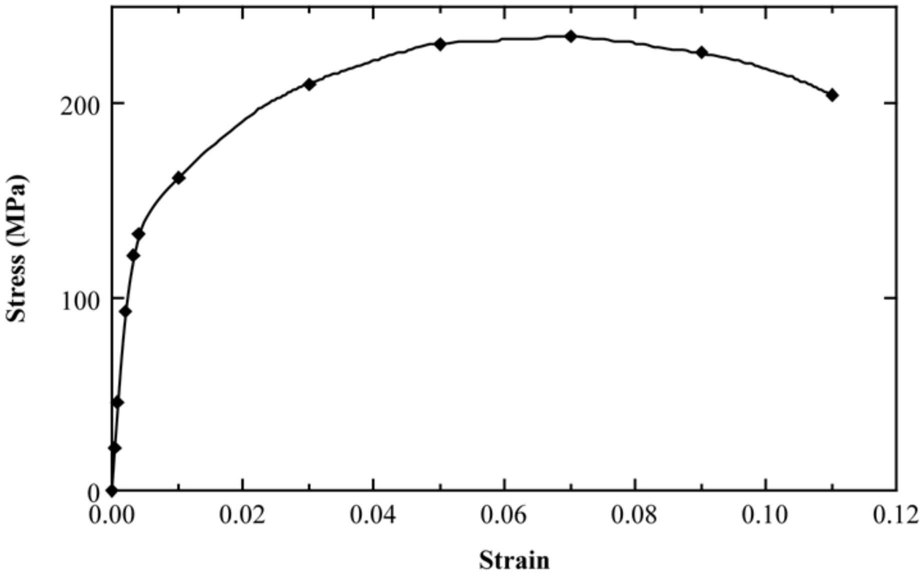
(e) Compute the modulus of resilience.

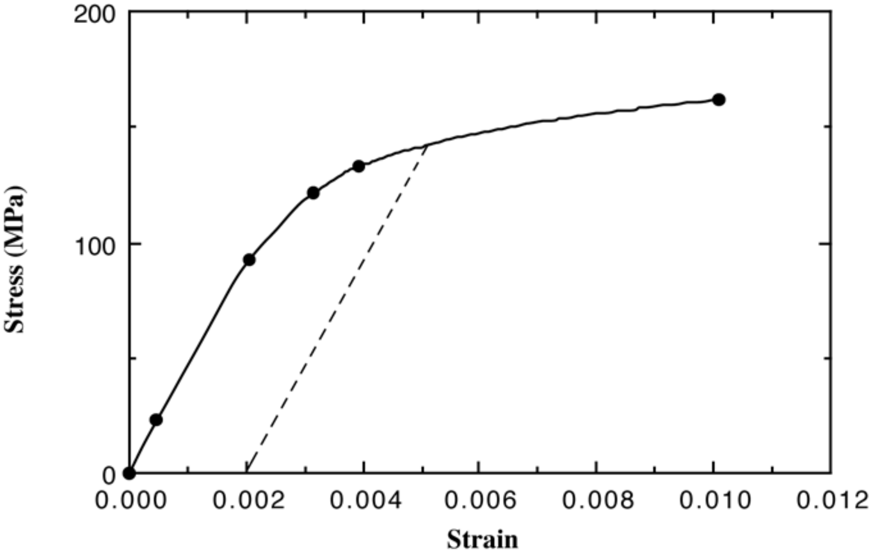
(f) What is the ductility, in percent elongation?

Solution

This problem calls for us to make a stress-strain plot for a magnesium, given its tensile load-length data, and then to determine some of its mechanical characteristics.

(a) The data are plotted below on two plots: the first corresponds to the entire stress-strain curve, while for the second, the curve extends just beyond the elastic region of deformation.





(b) The elastic modulus is the slope in the linear elastic region (Equation 6.10)—i.e.,

$$E = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1}$$

Because the stress-strain curve passes through the origin, to simplify the computation let us take both σ_1 and ε_1 to be zero. If we select σ_2 = 50 MPa, its corresponding strain on the plot ε_2 is about 0.001. Thus the elastic modulus is equal to

$$E = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1} = \frac{50\ \text{MPa} - 0\ \text{MPa}}{0.001 - 0} = 50 \times 10^3\ \text{MPa} = 50\ \text{GPa} \quad (7.3 \times 10^6\ \text{psi})$$

(c) For the yield strength, the 0.002 strain offset line is drawn dashed. It intersects the stress-strain curve at approximately 140 MPa (20,300 psi).

(d) The tensile strength is approximately 230 MPa (33,350 psi), corresponding to the maximum stress on the complete stress-strain plot.

(e) From Equation 6.14, the modulus of resilience is just

$$U_r = \frac{\sigma_y^2}{2E}$$

which, using data computed above, yields a value of

$$U_r = \frac{(140 \times 10^6\ \text{N/m}^2)^2}{(2)(50 \times 10^9\ \text{N/m}^2)} = 1.96 \times 10^5\ \text{N/m}^2 = 1.96 \times 10^5\ \text{J/m}^3 \quad (28.4\ \text{in.-lb}_\text{f}/\text{in.}^3)$$

(f) The ductility, in percent elongation, is just the plastic strain at fracture, multiplied by one-hundred. The total fracture strain at fracture is 0.110; subtracting out the elastic strain (which is about 0.003) leaves a plastic strain of 0.107. Thus, the ductility is about 10.7%EL.

6.32 *A cylindrical metal specimen 15.00 mm in diameter and 120 mm long is to be subjected to a tensile force of 15,000 N.*

(a) If this metal must not experience any plastic deformation, which of aluminum, copper, brass, nickel, steel, and titanium (Table 6.2) are suitable candidates? Why?

(b) If, in addition, the specimen must elongate no more than 0.070 mm, which of the metals that satisfy the criterion in part (a) are suitable candidates? Why? Base your choices on data found in Table 6.1.

Solution

(a) In order to determine which of the metals in Table 6.2 do not experience plastic deformation we need to compute the applied engineering stress; any metal in the table that has a yield strength greater than this value will not plastically deform.

The applied engineering stress is computed using Equation 6.1 as follows:

$$\sigma = \frac{F}{A_0}$$

which, for a cylindrical specimen of diameter d_0 takes the form:

$$\sigma = \frac{F}{\pi\left(\frac{d_0}{2}\right)^2}$$

For F = 15,000 N and d_0 = 15.00 mm (15×10^{-3} m) the stress is equal to

$$\sigma = \frac{15{,}000\ \mathrm{N}}{\pi\left(\frac{15 \times 10^{-3}\ \mathrm{m}}{2}\right)^2} = 84.9 \times 10^6\ \mathrm{N/m^2} = 84.9\ \mathrm{MPa}$$

Of those 6 alloys in Table 6.2, only nickel, steel, and titanium have yield strengths greater than 84.9 MPa.

(b) Because none of these three metals has experienced plastic deformation it is possible to compute the elongation Δl by combining Equations 6.2 and 6.5. From Equation 6.5 it is the case that

$$\varepsilon = \frac{\sigma}{E}$$

in which E is the modulus of elasticity. If we incorporate the definition of the strain (Equation 6.2) into this expression, the following results:

$$\frac{\Delta l}{l_0} = \frac{\sigma}{E}$$

And solving for the elongation Δl leads to

$$\Delta l = \frac{l_0 \sigma}{E}$$

In order to calculate the elongation for each of these metals we incorporate the original length 120 mm (120×10^{-3} m), the stress computed above (84.9 MPa = 84.9×10^6 N/m^2), and, for each of the three metals, its modulus of elasticity found in Table 6.1.

For Ni (E = 207 GPa = 207×10^9 N/m^2), therefore:

$$\Delta l = \frac{(120 \times 10^{-3}\ \mathrm{m})(84.9 \times 10^6\ \mathrm{N/m^2})}{207 \times 10^9\ \mathrm{N/m^2}} = 4.9 \times 10^{-5}\ \mathrm{m} = 0.049\ \mathrm{mm}$$

Thus, Ni satisfies this criterion since its elongation is less than 0.070 mm.

For steel (E = 207 GPa = 207×10^9 N/m^2) the elongation will also be 0.049 mm since its elastic modulus is the same as Ni—i.e., steel meets the criterion).

For titanium (E = 107 GPa = 107×10^9 N/m^2)

$$\Delta l = \frac{(120 \times 10^{-3}\ \mathrm{m})(84.9 \times 10^6\ \mathrm{N/m^2})}{107 \times 10^9\ \mathrm{N/m^2}} = 9.5 \times 10^{-5}\ \mathrm{m} = 0.095\ \mathrm{mm}$$

And, titanium does not satisfy the criterion because its elongation (0.095 mm) is greater than 0.070 mm.

6.33 *For the titanium alloy whose stress–strain behavior can be observed in the Tensile Tests module of* Virtual Materials Science and Engineering (VMSE), *determine the following:*

(a) the approximate yield strength (0.002 strain offset)

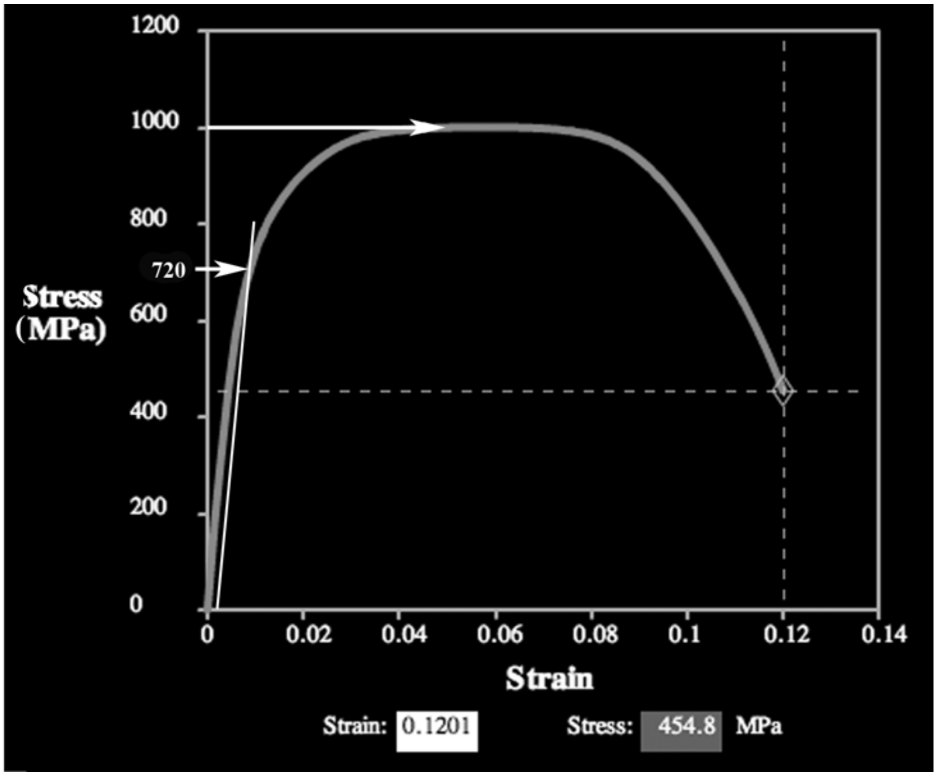
(b) the tensile strength

(c) the approximate ductility, in percent elongation

How do these values compare with those for the two Ti-6Al-4V alloys presented in Table B.4 of Appendix B?

Solution

(a) A screenshot of the entire stress-strain curve for the Ti alloy is shown below.



The intersection of the straight line drawn parallel to the initial linear region of the curve and offset at a strain of 0.002 with this curve is at approximately 720 MPa.

(b) The maximum stress on the stress-strain curve is 1000 MPa, the value of the tensile strength.

(c) The approximate percent elongation corresponds to the strain at fracture multiplied by 100 (i.e., 12%) minus the maximum elastic strain (i.e., value of strain at which the linearity of the curve ends multiplied by 100—in this case about 0.5%); this gives a value of about 11.5%EL.

From Table B.4 in Appendix B, yield strength, tensile strength, and percent elongation values for the annealed Ti-6Al-4V are 830 MPa, 900 MPa, and 14%EL, while for the solution heat treated and aged alloy, the corresponding values are 1103 MPa, 1172 MPa, and 10%EL. Thus, tensile strength and percent elongation values for the *VMSE* alloy are slightly lower than for the annealed material in Table B.4 (720 vs 830 MPa, and 11.5 vs. 14 %EL), whereas the tensile strength is slightly higher (1000 vs. 900 MPa).

6.34 *For the tempered steel alloy whose stress-strain behavior can be observed in the Tensile Tests module of* Virtual Materials Science and Engineering (VMSE), *determine the following:*

(a) the approximate yield strength (0.002 strain offset)

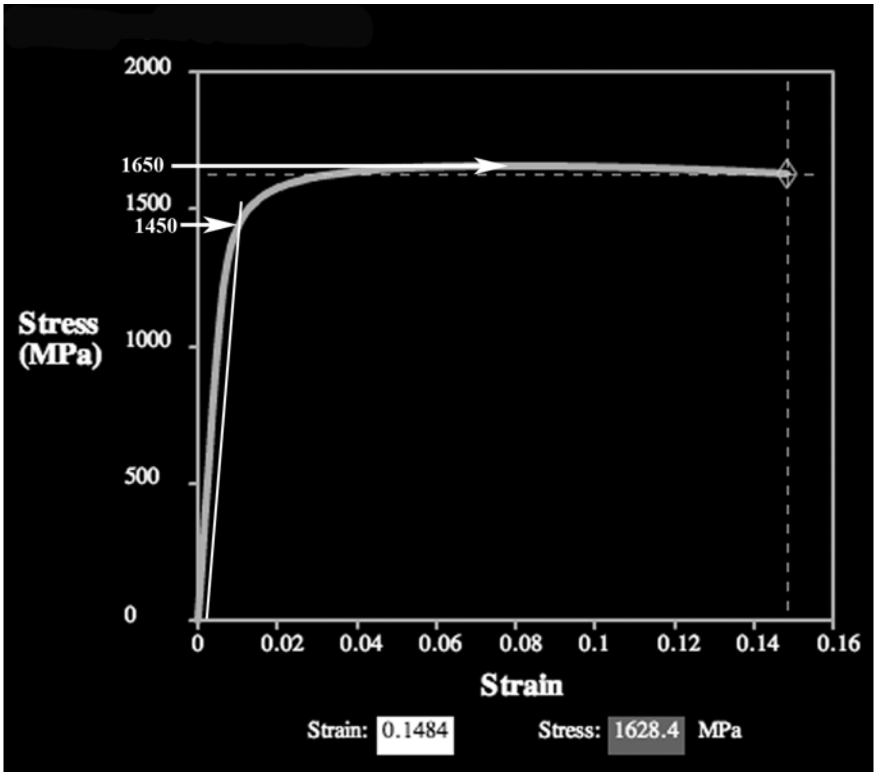
(b) the tensile strength

(c) the approximate ductility, in percent elongation

How do these values compare with those for the oil-quenched and tempered 4140 and 4340 steel alloys presented in Table B.4 of Appendix B?

Solution

(a) A screenshot of the entire stress-strain curve for the tempered steel alloy is shown below.



Strain: 0.1484 Stress: 1628.4 MPa

The intersection of the straight line drawn parallel to the initial linear region of the curve and offset at a strain of 0.002 with this curve is at approximately 1450 MPa.

(b) As noted on this stress-strain curve, the maximum stress is about 1650 MPa, the value of the tensile strength.

(c) The approximate percent elongation corresponds to the strain at fracture multiplied by 100 (i.e., 14.8%) minus the maximum elastic strain (i.e., value of strain at which the linearity of the curve ends multiplied by 100—in this case about 0.8%); this gives a value of about 14.0%EL.

For the oil-quenched and tempered 4140 and 4340 steel alloys, yield strength values presented in Table B.4 of Appendix B are 1570 MPa and 1620 MPa, respectively; these values are somewhat larger than the 1450 MPa for the tempered steel alloy of *VMSE*. Tensile strength values for these 4140 and 4340 alloys are, respectively 1720 MPa and 1760 MPa (compared to 1650 MPa for the *VMSE* steel). And, finally, the respective ductilities for the 4140 and 4340 alloys are 11.5%EL and 12%EL, which are slightly lower than the 14%EL value for the *VMSE* steel.

6.35 *For the aluminum alloy whose stress strain behavior can be observed in the Tensile Tests module of Virtual Materials Science and Engineering (VMSE), determine the following:*

(a) the approximate yield strength (0.002 strain offset)

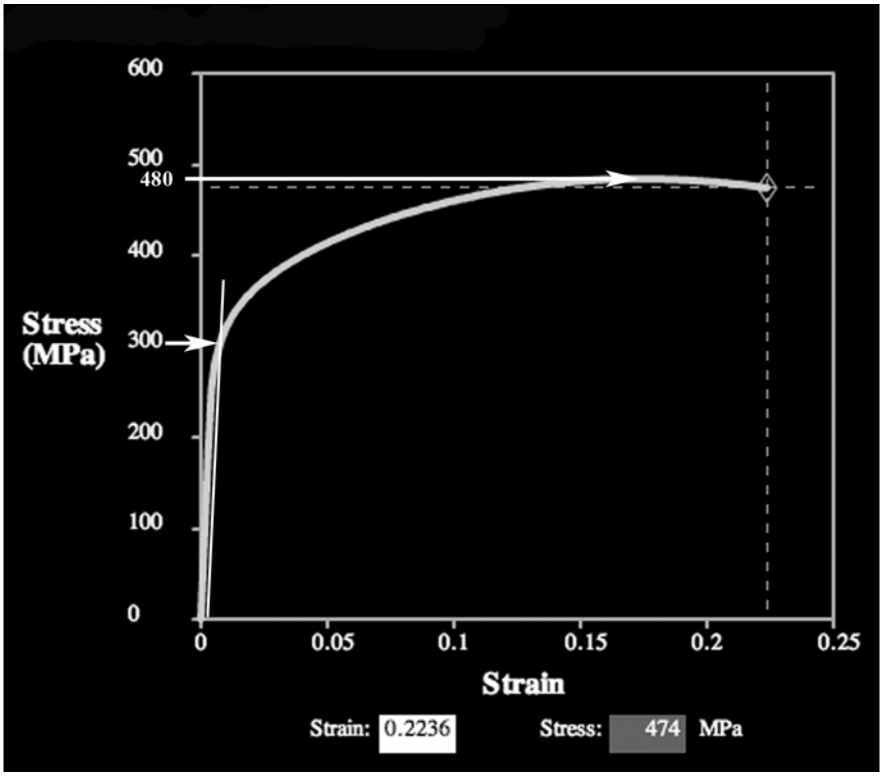
(b) the tensile strength

(c) the approximate ductility, in percent elongation

How do these values compare with those for the 2024 aluminum alloy (T351 temper) presented in Table B.4 of Appendix B?

Solution

(a) A screenshot of the entire stress-strain curve for the aluminum alloy is shown below.



The intersection of a straight line drawn parallel to the initial linear region of the curve and offset at a strain of 0.002 with this curve is at approximately 300 MPa.

(b) As noted on this stress-strain curve, the maximum stress is about 480 MPa, the value of the tensile strength.

(c) The approximate percent elongation corresponds to the strain at fracture multiplied by 100 (i.e., 22.4%) minus the maximum elastic strain (i.e., value of strain at which the linearity of the curve ends multiplied by 100—in this case about 0.5%); this gives a value of about 21.9%EL.

For the 2024 aluminum alloy (T351 temper), the yield strength value presented in Table B.4 of Appendix B is 325, which is slightly larger than the 300 MPa for the aluminum alloy of *VMSE*. The tensile strength value for the 2024-T351 is 470 MPa (compared to 480 MPa for the *VMSE* alloy). And, finally, the ductility for 2024-T351 is 20%EL, which is about the same as for the *VMSE* aluminum (21.9%EL).

6.36 *For the (plain) carbon steel alloy whose stress-strain behavior can be observed in the Tensile Tests module of Virtual Materials Science and Engineering (VMSE), determine the following:*

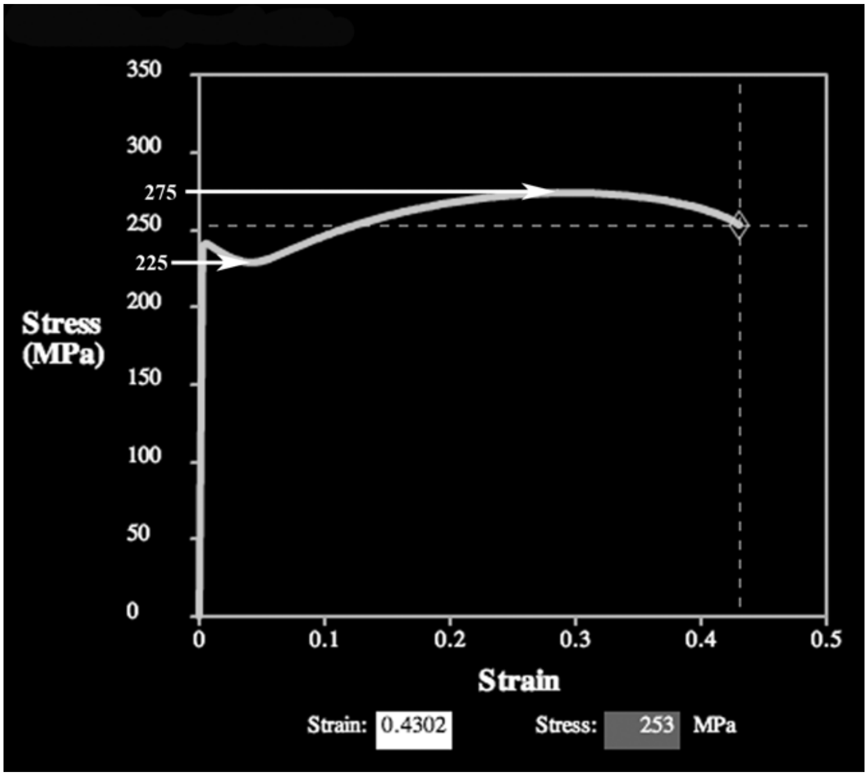
(a) the approximate yield strength

(b) the tensile strength

(c) the approximate ductility, in percent elongation

Solution

(a) A screenshot of the entire stress-strain curve for the plain carbon steel alloy is shown below.



Strain: 0.4302

Stress: 253 MPa

Inasmuch as the stress-strain curve displays the yield point phenomenon, we take the yield strength as the lower yield point, which, for this steel, is about 225 MPa.

(b) As noted on this stress-strain curve, the maximum stress is about 275 MPa, the value of the tensile strength.

(c) The approximate percent elongation corresponds to the strain at fracture multiplied by 100 (i.e., 43.0%) minus the maximum elastic strain (i.e., value of strain at which the linearity of the curve ends multiplied by 100—in this case about 0.6%); this gives a value of about 42.4%EL.

6.37 *A cylindrical metal specimen having an original diameter of 12.8 mm (0.505 in.) and gauge length of 50.80 mm (2.000 in.) is pulled in tension until fracture occurs. The diameter at the point of fracture is 8.13 mm (0.320 in.), and the fractured gauge length is 74.17 mm (2.920 in.). Calculate the ductility in terms of percent reduction in area and percent elongation.*

Solution

This problem calls for the computation of ductility in both percent reduction in area and percent elongation. Percent reduction in area, for a cylindrical specimen, is computed using Equation 6.12 as

$$\%\mathrm{RA} = \left(\frac{A_0 - A_f}{A_0}\right) \times 100 = \frac{\pi\left(\frac{d_0}{2}\right)^2 - \pi\left(\frac{d_f}{2}\right)^2}{\pi\left(\frac{d_0}{2}\right)^2} \times 100$$

in which d_0 and d_f are, respectively, the original and fracture cross-sectional areas. Thus,

$$\%\mathrm{RA} = \frac{\pi\left(\frac{12.8\text{ mm}}{2}\right)^2 - \pi\left(\frac{8.13\text{ mm}}{2}\right)^2}{\pi\left(\frac{12.8\text{ mm}}{2}\right)^2} \times 100 = 60\%$$

While, for percent elongation, we use Equation 6.11 as

$$\%\mathrm{EL} = \left(\frac{l_f - l_0}{l_0}\right) \times 100$$

$$= \frac{74.17\text{ mm} - 50.80\text{ mm}}{50.80\text{ mm}} \times 100 = 46\%$$

6.38 *Calculate the moduli of resilience for the materials having the stress–strain behaviors shown in Figures 6.12 and 6.22.*

<u>Solution</u>

This problem asks us to calculate the moduli of resilience for the materials having the stress-strain behaviors shown in Figures 6.12 and 6.22. According to Equation 6.14, the modulus of resilience U_r is a function of the yield strength and the modulus of elasticity as

$$U_r = \frac{\sigma_y^2}{2E}$$

The values for σ_y and E for the brass in Figure 6.12 are determined in Example Problem 6.3 as 250 MPa (36,000 psi) and 93.8 GPa (13.6 × 10^6 psi), respectively. Thus

$$U_r = \frac{(250 \text{ MPa})^2}{(2)(93.8 \text{ GPa})} = \frac{(250 \times 10^6 \text{ N/m}^2)^2}{(2)(93.8 \times 10^9 \text{ N/m}^2)}$$

$$= 3.32 \times 10^5 \text{ N/m}^2 = 3.32 \times 10^5 \text{ J/m}^3 \quad (48.2 \text{ in.-lb}_\text{f}/\text{in.}^3)$$

Values of the corresponding parameters for the steel alloy (Figure 6.22) are determined in Problem 6.26 as 1600 MPa (232,000 psi) and 210 GPa (30.5 × 10^6 psi), respectively, and therefore

$$U_r = \frac{(1600 \text{ MPa})^2}{(2)(210 \text{ GPa})} = \frac{(1600 \times 10^6 \text{ N/m}^2)^2}{(2)(210 \times 10^9 \text{ N/m}^2)}$$

$$= 6.10 \times 10^6 \text{ N/m}^2 = 6.10 \times 10^6 \text{ J/m}^3 \quad (882 \text{ in.-lb}_\text{f}/\text{in.}^3)$$

6.39 *Determine the modulus of resilience for each of the following alloys:*

	Yield Strength	
Material	***MPa***	***psi***
Steel alloy	*830*	*120,000*
Brass alloy	*380*	*55,000*
Aluminum alloy	*275*	*40,000*
Titanium alloy	*690*	*100,000*

Use the modulus of elasticity values in Table 6.1.

Solution

The moduli of resilience of the alloys listed in the table may be determined using Equation 6.14, that is

$$U_r = \frac{\sigma_y^2}{2E}$$

Yield strength values are provided in this table, whereas the elastic moduli are tabulated in Table 6.1.

For steel (E = 207 GPa)

$$U_r = \frac{(830\ \text{MPa})^2}{(2)(207\ \text{GPa})} = \frac{(830 \times 10^6\ \text{N/m}^2)^2}{(2)\left(207 \times 10^9\ \text{N/m}^2\right)}$$

$$= 1.66 \times 10^6\ \text{N/m}^2 = 1.66 \times 10^6\ \text{J/m}^3 \quad \left(240\ \text{in.-lb}_\text{f}/\text{in.}^3\right)$$

For the brass (E = 97 GPa)

$$U_r = \frac{(380\ \text{MPa})}{(2)(97\ \text{GPa})} = \frac{(380 \times 10^6\ \text{N/m}^2)^2}{(2)\left(97 \times 10^9\ \text{N/m}^2\right)}$$

$$= 7.44 \times 10^5\ \text{N/m}^2 = 7.44 \times 10^5\ \text{J/m}^3 \quad \left(108\ \text{in.-lb}_\text{f}/\text{in.}^3\right)$$

For the aluminum alloy (E = 69 GPa)

$$U_r = \frac{(275\ \text{MPa})^2}{(2)(69\ \text{GPa})} = \frac{(275 \times 10^6\ \text{N/m}^2)^2}{(2)\left(69 \times 10^9\ \text{N/m}^2\right)}$$

$$= 5.48 \times 10^5\ \text{N/m}^2 = 5.48 \times 10^5\ \text{J/m}^3 \quad \left(80.0\ \text{in.-lb}_\text{f}/\text{in.}^3\right)$$

And, for the titanium alloy (E = 107 GPa)

$$U_r = \frac{(690\text{ MPa})^2}{(2)(107\text{ GPa})} = \frac{(690 \times 10^6\text{ N/m}^2)^2}{(2)(107 \times 10^9\text{ N/m}^2)}$$

$$= 2.22 \times 10^6\text{ N/m}^2 = 2.22 \times 10^6\text{ J/m}^3 \quad (323\text{ in.-lb}_f/\text{in.}^3)$$

6.40 *A steel alloy to be used for a spring application must have a modulus of resilience of at least 2.07 MPa (300 psi). What must be its minimum yield strength?*

Solution

The modulus of resilience, yield strength, and elastic modulus of elasticity are related to one another through Equation 6.14, that is

$$U_r = \frac{\sigma_y^2}{2E}$$

Solving for σ_y from this expression yields

$$\sigma_y = \sqrt{2U_rE}$$

The value of *E* for steel given in Table 6.1 is 207 GPa. Using this elastic modulus value leads to a yield strength of

$$\sigma_y = \sqrt{2U_rE} = \sqrt{(2)(2.07\ \mathbf{MPa})(207 \times 10^3\ \mathbf{MPa})}$$

$$= 926\ \text{MPa}\ \ (134{,}000\ \text{psi})$$

6.41 *Using data found in Appendix B, estimate the modulus of resilience (in MPa) of cold-rolled 17-7PH stainless steel.*

Solution

To solve this problem it is necessary to use Equation 6.14—viz.

$$U_r = \frac{\sigma_y^2}{2E}$$

From Table B.2 (Appendix B) the modulus of elasticity for 17-7PH stainless steel is 204 GPa (204 × 10^3 MPa). Furthermore, the yield strength for this cold-rolled stainless steel is 1210 MPa (Table B.4). Insertion of these two values into Equation 6.14 leads to the following:

$$U_r = \frac{(1210\ \text{MPa})^2}{(2)(204 \times 10^3\ \text{MPa})} = 3.59\ \text{MPa}$$

True Stress and Strain

6.42 *Show that Equations 6.18a and 6.18b are valid when there is no volume change during deformation.*

Solution

To show that Equation 6.18a is valid, we must first rearrange Equation 6.17 as

$$A_i = \frac{A_0 l_0}{l_i}$$

Substituting this expression into Equation 6.15 yields

$$\sigma_T = \frac{F}{A_i} = \frac{F}{\frac{A_0 l_0}{l_i}} = \frac{F}{A_0}\left(\frac{l_i}{l_0}\right) = \sigma\left(\frac{l_i}{l_0}\right)$$

From Equation 6.2

$$\varepsilon = \frac{l_i - l_0}{l_0} = \frac{l_i}{l_0} - 1$$

Or

$$\frac{l_i}{l_0} = 1 + \varepsilon \qquad (6.2b)$$

Substitution of this expression into the equation above leads to

$$\sigma_T = \sigma\left(\frac{l_i}{l_0}\right) = \sigma(1 + \varepsilon)$$

which is Equation 6.18a.

For Equation 6.18b, true strain is defined in Equation 6.16 as

$$\varepsilon_T = \ln\left(\frac{l_i}{l_0}\right)$$

Substitution the of the l_i-l_0 ratio of Equation 6.2b leads to Equation 6.18b—viz.

$$\varepsilon_T = \ln(1 + \varepsilon)$$

6.43 *Demonstrate that Equation 6.16, the expression defining true strain, may also be represented by*

$$\epsilon_T = \ln\left(\frac{A_0}{A_i}\right)$$

when the specimen volume remains constant during deformation. Which of these two expressions is more valid during necking? Why?

Solution

This problem asks us to demonstrate that true strain may also be represented by

$$\varepsilon_T = \ln\left(\frac{A_0}{A_i}\right)$$

Rearrangement of Equation 6.17 yields

$$\frac{l_i}{l_0} = \frac{A_0}{A_i}$$

Substitution of A_0/A_i for l_i/l_0 in the definition of true strain, Equation 6.16 leads to

$$\varepsilon_T = \ln\left(\frac{l_i}{l_0}\right) = \ln\left(\frac{A_0}{A_i}\right)$$

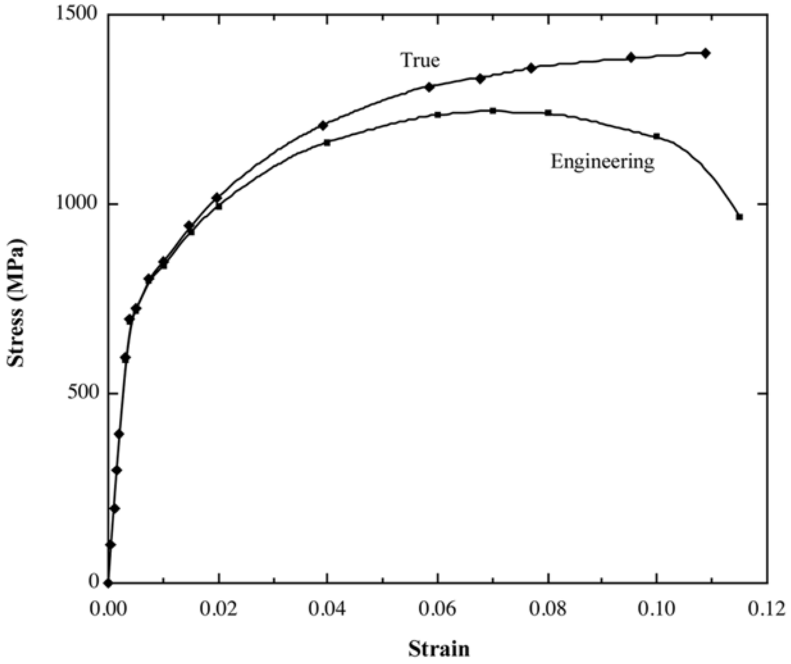
The expression $\varepsilon_T = \ln\left(\frac{A_0}{A_i}\right)$ is more valid during necking because A_i is taken as the area of the neck.

6.44 *Using the data in Problem 6.30 and Equations 6.15, 6.16, and 6.18a, generate a true stress–true strain plot for stainless steel. Equation 6.18a becomes invalid past the point at which necking begins; therefore, measured diameters are given in the following table for the last three data points, which should be used in true stress computations.*

Load		***Length***		***Diameter***	
N	***lb_f***	***mm***	***in.***	***mm***	***in.***
159,500	*35,850*	*54.864*	*2.160*	*12.22*	*0.481*
151,500	*34,050*	*55.880*	*2.200*	*11.80*	*0.464*
124,700	*28,000*	*56.642*	*2.230*	*10.65*	*0.419*

<u>Solution</u>

Both true and engineering stress-strain data for this stainless steel are plotted below.



6.45 *A tensile test is performed on a metal specimen, and it is found that a true plastic strain of 0.16 is produced when a true stress of 500 MPa (72,500 psi) is applied; for the same metal, the value of K in Equation 6.19 is 825 MPa (120,000 psi). Calculate the true strain that results from the application of a true stress of 600 MPa (87,000 psi).*

Solution

We are asked to compute the true strain that results from the application of a true stress of 600 MPa (87,000 psi); other true stress-strain data are also given. It first becomes necessary to solve for *n* in Equation 6.19. Taking logarithms of this expression leads to

$$\log \sigma_T = \log K + n \log \varepsilon_T$$

Next we rearrange this equation such that *n* is the dependent variable:

$$n = \frac{\log \sigma_T - \log K}{\log \varepsilon_T}$$

We now solve for *n* using the following data given in the problem statement:

σ_T = 500 MPa

ε_T = 0.16

K = 825 MPa

Thus

$$n = \frac{\log (500 \text{ MPa}) - \log (825 \text{ MPa})}{\log (0.16)} = 0.273$$

We now rearrange Equation 6.19 such that ε_T is the dependent variable; we first divide both sides of the Equation 6.19 by *K*, which leads to the following expression:

$$\varepsilon_T^n = \frac{\sigma_T}{K}$$

ε_T becomes the dependent variable by taking the 1/*n* root of both sides of this expression, as

$$\varepsilon_T = \left(\frac{\sigma_T}{K}\right)^{1/n}$$

Finally, using values of *K* and *n*, we solve for the true strain at a true stress of 600 MPa:

$$\varepsilon_T = \left(\frac{\sigma_T}{K}\right)^{1/n} = \left(\frac{600\ \text{MPa}}{825\ \text{MPa}}\right)^{1/0.273} = 0.311$$

6.46 *For some metal alloy, a true stress of 345 MPa (50,000 psi) produces a plastic true strain of 0.02. How much does a specimen of this material elongate when a true stress of 415 MPa (60,000 psi) is applied if the original length is 500 mm (20 in.)? Assume a value of 0.22 for the strain-hardening exponent, n.*

Solution

We are asked to compute how much elongation a metal specimen will experience when a true stress of 415 MPa is applied, given the value of *n* and that a given true stress produces a specific true strain. Solution of this problem requires that we utilize Equation 6.19. It is first necessary to solve for *K* from the given true stress and strain. Rearrangement of this Equation 6.19 so that *K* is the dependent parameter yields

$$K = \frac{\sigma_T}{(\varepsilon_T)^n}$$

The value of *K* is determined by substitution of the first set of data in the problem statement, as follows:

$$K = \frac{345\ \text{MPa}}{(0.02)^{0.22}} = 816\ \text{MPa}\ \ (118{,}000\ \text{psi})$$

Next we must solve for the true strain produced when a true stress of 415 MPa is applied, also using Equation 6.19. Algebraic manipulation of Equation 6.19 such that true strain is the dependent variable leads to

$$\varepsilon_T = \left(\frac{\sigma_T}{K}\right)^{1/n}$$

Incorporation into this expression the value of *K* and the applied true stress (415 MPa) results in the following value for true strain:

$$\varepsilon_T = \left(\frac{415\ \text{MPa}}{816\ \text{MPa}}\right)^{1/0.22} = 0.0463$$

And from the definition of true strain, Equation 6.16, we have

$$\varepsilon_T = \ln\left(\frac{l_i}{l_0}\right) = 0.0463$$

Another way to write this expression is as follows:

$$e^{0.0463} = \frac{l_i}{l_0}$$

Now, solving for l_i gives

$$l_i = l_0 e^{0.0463} = (500\ \text{mm})e^{0.0463} = 523.7\ \text{mm}\ \ (20.948\ \text{in.})$$

And, since $l_0 = 500$ mm, we solve for Δl as follows:

$$\Delta l = l_i - l_0 = 523.7\ \text{mm} - 500\ \text{mm} = 23.7\ \text{mm}\ \ (0.948\ \text{in.})$$

6.47 *The following true stresses produce the corresponding true plastic strains for a brass alloy:*

True Stress (psi)	***True Strain***
60,000	*0.15*
70,000	*0.25*

What true stress is necessary to produce a true plastic strain of 0.21?

Solution

For this problem, we are given two values of ε_T and σ_T, from which we are asked to calculate the true stress that produces a true plastic strain of 0.21. From Equation 6.19, we want to set up two simultaneous equations with two unknowns (the unknowns being *K* and *n*). Taking logarithms of both sides of Equation 6.19 leads to

$$\log \sigma_T = \log K + n \log \varepsilon_T$$

The two simultaneous equations using data provided in the problem statement are as follows:

$$\log\,(60{,}000\text{ psi}) = \log K + n\,\log\,(0.15)$$

$$\log\,(70{,}000\text{ psi}) = \log K + n\,\log\,(0.25)$$

Solving for *n* from these two expressions yields

$$n = \frac{\log\,(60{,}000) - \log\,(70{,}000)}{\log\,(0.15) - \log\,(0.25)} = 0.302$$

We solve for *K* by substitution of this value of *n* into the first simultaneous equation as

$$\log K = \log \sigma_T - n \log \varepsilon_T$$

$$= \log(60{,}000) - (0.302)[\log(0.15)] = 5.027$$

Thus, the value of *K* is equal to

$$K = 10^{5.027} = 106{,}400\text{ psi}$$

The true stress required to produce a true strain of 0.21 is determined using Equation 6.19 as follows:

$$\sigma_T = K(\varepsilon_T)^n = (106{,}400\text{ psi})(0.21)^{0.302} = 66{,}400\text{ psi}\ \ (460\text{ MPa})$$

6.48 For a brass alloy, the following engineering stresses produce the corresponding plastic engineering strains prior to necking:

Engineering Stress (MPa)	***Engineering Strain***
315	*0.105*
340	*0.220*

On the basis of this information, compute the engineering *stress necessary to produce an* engineering *strain of 0.28.*

Solution

For this problem we first need to convert engineering stresses and strains to true stresses and strains so that the constants *K* and *n* in Equation 6.19 may be determined. Since $\sigma_T = \sigma(1 + \varepsilon)$ (Equation 6.18a), we convert the two values of engineering stress into true stresses as follows:

$$\sigma_{T1} = (315 \text{ MPa})(1 + 0.105) = 348 \text{ MPa}$$

$$\sigma_{T2} = (340 \text{ MPa})(1 + 0.220) = 415 \text{ MPa}$$

Similarly for strains—we convert engineering strains to true strains using Equation 6.18b [i.e., $\varepsilon_T = \ln(1 + \varepsilon)$] as follows:

$$\varepsilon_{T1} = \ln(1 + 0.105) = 0.09985$$

$$\varepsilon_{T2} = \ln(1 + 0.220) = 0.19885$$

Taking logarithms of both sides of Equation 6.19 leads to

$$\log \sigma_T = \log K + n \log \varepsilon_T$$

which allows us to set up two simultaneous equations for the above pairs of true stresses and true strains, with *K* and *n* as unknowns. Thus

$$\log(348) = \log K + n \log(0.09985)$$

$$\log(415) = \log K + n \log(0.19885)$$

Solving for *n* from these two expressions yields

$$n = \frac{\log(348) - \log(415)}{\log(0.09985) - \log(0.19885)} = 0.256$$

We solve for *K* by substitution of this value of *n* into the first simultaneous equation as

$$\log K = \log \sigma_T - n \log \varepsilon_T$$

$$= \log(348) - (0.256)[\log(0.09985)] = 2.7977$$

Thus, the value of *K* is equal to

$$K = 10^{2.7977} = 628 \text{ MPa}$$

We now, converting $\varepsilon = 0.28$ to true strain using Equation 6.18b as follows:

$$\varepsilon_T = \ln(1 + 0.28) = 0.247$$

The corresponding σ_T to give this value of ε_T (using Equation 6.19) is just

$$\sigma_T = K\varepsilon_T^n = (628 \text{ MPa})(0.247)^{0.256} = 439 \text{ MPa}$$

Now converting this value of σ_T to an engineering stress using Equation 6.18a gives

$$\sigma = \frac{\sigma_T}{1 + \varepsilon} = \frac{439 \text{ MPa}}{1 + 0.28} = 343 \text{ MPa}$$

6.49 *Find the toughness (or energy to cause fracture) for a metal that experiences both elastic and plastic deformation. Assume Equation 6.5 for elastic deformation, that the modulus of elasticity is 103 GPa (15 × 10^6 psi), and that elastic deformation terminates at a strain of 0.007. For plastic deformation, assume that the relationship between stress and strain is described by Equation 6.19, in which the values for K and n are 1520 MPa (221,000 psi) and 0.15, respectively. Furthermore, plastic deformation occurs between strain values of 0.007 and 0.60, at which point fracture occurs.*

Solution

This problem calls for us to compute the toughness (or energy to cause fracture). This toughness is equal to the area beneath the entire stress-strain curve. The easiest way to make this computation is to perform integrations in both elastic and plastic regions using data given in the problem statement, and then add these values together. Thus, we may define toughness using the following equation:

$$\textbf{Toughness} = \int \sigma\, d\varepsilon$$

Toughness in the elastic region is determined by integration of Equation 6.5, integrating between strains of 0 and 0.007 (per the problem statement). Thus

$$\textbf{Toughness (elastic)} = \int_0^{0.007} E\varepsilon\, d\varepsilon$$

$$= \left. \frac{E\varepsilon^2}{2} \right|_0^{0.007}$$

$$= \frac{103 \times 10^9\ \text{N/m}^2}{2}\left[(0.007)^2 - (0)^2\right]$$

$$= 2.52 \times 10^6\ \text{N/m}^2 = 2.52 \times 10^6\ \text{J/m}^3$$

Now for the plastic region of the stress-strain curve, we integrate Equation 6.19 between the strain limits of 0.007 and 0.60, as follows:

$$\textbf{Toughness (plastic)} = \int_{0.007}^{0.60} K\varepsilon^n\, d\varepsilon$$

$$= \frac{K}{(n+1)} \varepsilon^{(n+1)} \Big|_{0.007}^{0.60}$$

$$= \frac{1520 \times 10^6 \text{ N/m}^2}{(1.0 + 0.15)} \left[(0.60)^{1.15} - (0.007)^{1.15} \right]$$

$$= 730 \times 10^6 \text{ N/m}^2 = 7.30 \times 10^6 \text{ J/m}^3$$

And, finally, the total toughness is the sum of elastic and plastic values, which is equal to

$$\text{Toughness} = \text{Toughness(elastic)} + \text{Toughness(plastic)}$$

$$= 2.52 \times 10^6 \text{ J/m}^3 + 730 \times 10^6 \text{ J/m}^3$$

$$= 733 \times 10^6 \text{ J/m}^3 = 7.33 \times 10^8 \text{ J/m}^3 \quad (1.07 \times 10^5 \text{ in.-lb}_f\text{/in.}^3)$$

6.50 *For a tensile test, it can be demonstrated that necking begins when*

$$\frac{d\sigma_T}{d\varepsilon_T} = \sigma_T \qquad (6.32)$$

Using Equation 6.19, determine an expression for the value of the true strain at this onset of necking.

Solution

This problem asks that we determine the value of ε_T for the onset of necking assuming that necking begins when

$$\frac{d\sigma_T}{d\varepsilon_T} = \sigma_T$$

Let us take the derivative of Equation 6.19, set it equal to σ_T, and then solve for ε_T from the resulting expression. Differentiating Equation 6.19 leads to the following:

$$\frac{d\left[K(\varepsilon_T)^n\right]}{d\varepsilon_T} = Kn(\varepsilon_T)^{(n-1)} = \sigma_T$$

However, from Equation 6.19, $\sigma_T = K(\varepsilon_T)^n$, which, when substituted into the above expression, yields

$$Kn(\varepsilon_T)^{(n-1)} = K(\varepsilon_T)^n$$

Now solving for ε_T from this equation leads to

$$\varepsilon_T = n$$

as the value of the true strain at the onset of necking.

6.51 *Taking the logarithm of both sides of Equation 6.19 yields*

$$\log \sigma_T = \log K + n \log \in_T \qquad (6.33)$$

Thus, a plot of log σ_T *versus log* $\in_T$ *in the plastic region to the point of necking should yield a straight line having a slope of n and an intercept (at log* σ_T *= 0) of log K.*

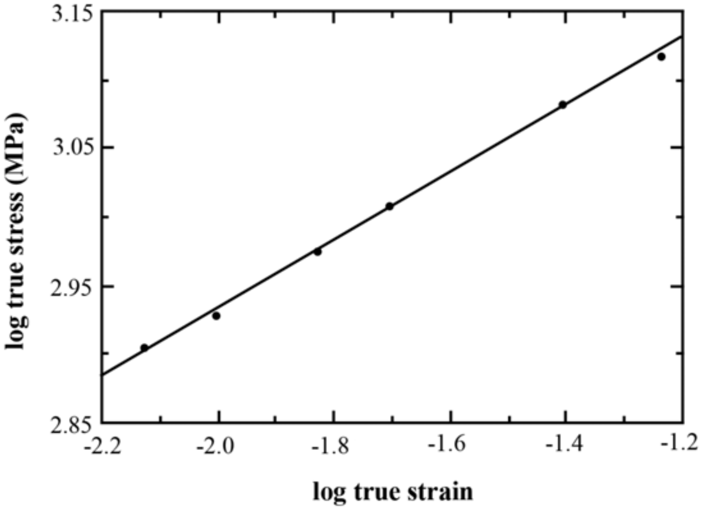
Using the appropriate data tabulated in Problem 6.30, make a plot of log σ_T *versus log* $\in_T$ *and determine the values of n and K. It will be necessary to convert engineering stresses and strains to true stresses and strains using Equations 6.18a and 6.18b.*

Solution

This problem calls for us to utilize the appropriate data from Problem 6.30 in order to determine the values of *n* and *K* for this material. From Equation 6.33 the slope of a log σ_T versus log ε_T plot will yield *n*. However, Equation 6.19 is only valid in the region of plastic deformation to the point of necking; thus, only the 8th, 9th, 10th, 11th, 12th, and 13th data points may be utilized. These data are tabulated below:

σ (MPa)	$\sigma_{\square}$ (MPa)	log $\sigma_{\square}$	ε	$\varepsilon_{\square}$	log $\varepsilon_{\square}$
797	803	2.905	0.0075	7.47×10^{-3}	–2.127
838	846	2.927	0.010	9.95×10^{-3}	–2.002
928	942	2.974	0.015	1.488×10^{-2}	–1.827
997	1017	3.007	0.020	1.980×10^{-2}	–1.703
1163	1210	3.083	0.040	3.92×10^{-2}	–1.407
1236	1310	3.117	0.060	5.83×10^{-2}	–1.234

The log-log plot with these data points is given below.



From Equation 6.33, the value of *n* is equal to the slope of the line that has been drawn through the data points; that is

$$n = \frac{\Delta \log \sigma_T}{\Delta \log \varepsilon_T}$$

From this line, values of log σ_T corresponding to log ε_T (1) = –2.20 and log ε_T (2) = –1.20 are, respectively, log σ_T (1) = 2.886 and log σ_T (2) = 3.131. Therefore, we determine the value of *n* as follows:

$$n = \frac{\Delta \log \sigma_T}{\Delta \log \varepsilon_T} = \frac{\log \sigma_T(1) - \log \sigma_T(2)}{\log \varepsilon_T(1) - \log \varepsilon_T(2)}$$

$$= \frac{2.886 - 3.131}{-2.20 - (-1.20)} = 0.245$$

In order to determine the value of *K* we rearrange Equation 6.33 to read as follows:

$$\log K = \log \sigma_T - n \log \varepsilon_T$$

It is possible to compute log *K* by inserting into this equation the value for a specific log σ_T and its corresponding log ε_T. (Of course we have already calculated the value of *n*.) If we use log σ_T (1) and log ε_T (1) values from above, then *K* is determined as follows:

$$\log K = \log \sigma_T(1) - n \log \varepsilon_T(1)$$

$$= 2.886 - (0.245)(-2.20) = 3.425$$

Which means that

$$K = 10^{3.425} = 2660\ \mathbf{MPa}$$

Elastic Recovery after Plastic Deformation

6.52 *A cylindrical specimen of a brass alloy 10.0 mm (0.39 in.) in diameter and 120.0 mm (4.72 in.) long is pulled in tension with a force of 11,750 N (2640 lb$_f$); the force is subsequently released.*

(a) Compute the final length of the specimen at this time. The tensile stress–strain behavior for this alloy is shown in Figure 6.12.

(b) Compute the final specimen length when the load is increased to 23,500 N (5280 lb$_f$) and then released.

Solution

(a) In order to determine the final length of the brass specimen when the load is released, it first becomes necessary to compute the applied stress using Equation 6.1; thus

$$\sigma = \frac{F}{A_0} = \frac{F}{\pi\left(\frac{d_0}{2}\right)^2} = \frac{11{,}750\ \mathrm{N}}{\pi\left(\frac{10 \times 10^{-3}\ \mathrm{m}}{2}\right)^2} = 150 \times 10^6\ \mathrm{N/m^2} = 150\ \mathrm{MPa}\ \ (22{,}000\ \mathrm{psi})$$

Upon locating this point on the stress-strain curve (Figure 6.12), we note that it is in the linear, elastic region; therefore, when the load is released the specimen will return to its original length of 120 mm (4.72 in.).

(b) In this portion of the problem we are asked to calculate the final length, after load release, when the load is increased to 23,500 N (5280 lb$_f$). Again, computing the stress

$$\sigma = \frac{23{,}500\ \mathrm{N}}{\pi\left(\frac{10 \times 10^{-3}\ \mathrm{m}}{2}\right)^2} = 300 \times 10^6\ \mathrm{N/m^2} = 300\ \mathrm{MPa}\ \ (44{,}200\ \mathrm{psi})$$

The point on the stress-strain curve corresponding to this stress is in the plastic region. We are able to estimate the amount of permanent strain by drawing a straight line parallel to the linear elastic region; this line intersects the strain axis at a strain of about 0.012 which is the amount of plastic strain. The final specimen length l_i may be determined from a rearranged form of Equation 6.2 as

$$l_i = l_0(1 + \varepsilon) = (120\ \mathrm{mm})(1 + 0.012) = 121.44\ \mathrm{mm}\ \ (4.78\ \mathrm{in.})$$

6.53 *A steel alloy specimen having a rectangular cross section of dimensions 19 mm × 3.2 mm ($\frac{3}{4}$ in. × $\frac{1}{8}$ in.) has the stress–strain behavior shown in Figure 6.22. This specimen is subjected to a tensile force of 110,000 N (25,000 lb_f).*

(a) Determine the elastic and plastic strain values.

(b) If its original length is 610 mm (24.0 in.), what will be its final length after the load in part (a) is applied and then released?

Solution

(a) We are asked to determine both the elastic and plastic strain values when a tensile force of 110,000 N (25,000 $\mathrm{lb_f}$) is applied to the steel specimen and then released. First it becomes necessary to determine the applied stress using Equation 6.1; thus

$$\sigma = \frac{F}{A_0} = \frac{F}{b_0 d_0}$$

where b_0 and d_0 are cross-sectional width and depth [19 mm (19×10^{-3} m) and 3.2 mm (3.2×10^{-3} m), respectively). Thus

$$\sigma = \frac{110{,}000\ \mathrm{N}}{(19 \times 10^{-3}\,\mathrm{m})(3.2 \times 10^{-3}\,\mathrm{m})} = 1.810 \times 10^9\ \mathrm{N/m^2} = 1810\ \mathrm{MPa}\ \ (265{,}000\ \mathrm{psi})$$

From Figure 6.22, this point is in the plastic region so the specimen will be both elastic and plastic strains. The total strain at this point, ε_t, is about 0.020. From this point on the stress-strain curve we are able to estimate the amount of strain recovery ε_e from Hooke's law, Equation 6.5 as

$$\varepsilon_e = \frac{\sigma}{E}$$

And, since E = 207 GPa for steel (Table 6.1)

$$\varepsilon_e = \frac{1810\ \mathrm{MPa}}{207\ \times 10^3\,\mathrm{MPa}} = 0.0087$$

The value of the plastic strain, ε_p is just the difference between the total and elastic strains; that is

$$\varepsilon_p = \varepsilon_t - \varepsilon_e = 0.020 - 0.0087 = 0.0113$$

(b) If the initial length is 610 mm (24.0 in.) then the final specimen length l_i may be determined from a rearranged form of Equation 6.2 using the plastic strain value as

$$l_i = l_0(1 + \varepsilon_p) = (610\text{ mm})(1 + 0.0113) = 616.9\text{ mm }(24.26\text{ in.})$$

Hardness

6.54 *(a) A 10-mm-diameter Brinell hardness indenter produced an indentation 2.50 mm in diameter in a steel alloy when a load of 1000 kg was used. Compute the HB of this material.*

(b) What will be the diameter of an indentation to yield a hardness of 300 HB when a 500-kg load is used?

Solution

(a) We are asked to compute the Brinell hardness for the given indentation. It is necessary to use the equation in Table 6.5 for HB, where P = 1000 kg, d = 2.50 mm, and D = 10 mm. Thus, the Brinell hardness is computed as

$$\mathrm{HB} = \frac{2P}{\pi D\left[D - \sqrt{D^2 - d^2}\right]}$$

$$= \frac{(2)(1000\ \mathrm{kg})}{(\pi)(10\ \mathrm{mm})\left[10\ \mathrm{mm} - \sqrt{(10\ \mathrm{mm})^2 - (2.50\ \mathrm{mm})^2}\right]} = 200.5$$

(b) This part of the problem calls for us to determine the indentation diameter d that will yield a 300 HB when P = 500 kg. Solving for d from the equation in Table 6.5 gives

$$d = \sqrt{D^2 - \left[D - \frac{2P}{(\mathrm{HB})\pi D}\right]^2}$$

$$= \sqrt{(10\ \mathrm{mm})^2 - \left[10\ \mathrm{mm} - \frac{(2)(500\ \mathrm{kg})}{(300)(\pi)(10\ \mathrm{mm})}\right]^2} = 1.45\ \mathrm{mm}$$

6.55 *(a) Calculate the Knoop hardness when a 500-g load yields an indentation diagonal length of 100 μm.*

(b) The measured HK of some material is 200. Compute the applied load if the indentation diagonal length is 0.25 mm.

Solution

(a) Knoop microhardness is related to the applied load (*P* in kg) and indentation length (*l* in mm) according to the equation given in Table 6.5—viz.

$$\mathrm{HK} = \frac{14.2P}{l^2}$$

The applied load is 500 g = 0.500 kg, whereas the indentation length is 100 μm = 0.100 mm. Incorporating these values into the equation above leads to

$$\mathrm{HK} = \frac{(14.2)(0.500\ \mathrm{kg})}{(0.100\ \mathrm{mm})^2} = 710$$

(b) This portion of the problem asks for the applied load for HK = 200 and *l* = 0.25 mm. Assigning *P* in the above equation to be the dependent variable yields the following expression:

$$P = \frac{(\mathrm{HK})l^2}{14.2}$$

When we insert the above values for HK and *l* into this expression, the value of the *P* is computed as follows:

$$P = \frac{(200)(0.25\ \mathrm{mm})^2}{14.2} = 0.880\ \mathrm{kg}$$

6.56 *(a) What is the indentation diagonal length when a load of 0.60 kg produces a Vickers HV of 400? (b) Calculate the Vickers hardness when a 700-g load yields an indentation diagonal length of 0.050 mm.*

Solution

(a) The equation given in Table 6.5 for Vickers microhardness is as follows:

$$\mathrm{HV} = \frac{1.854P}{d_1^2}$$

Here P is the applied load (in kg) and d_1 is the diagonal length (in mm). This portion of the problem asks that we compute the indentation diagonal length. Rearranging the above equation to make d_1 the dependent variable gives

$$d_1 = \sqrt{\frac{1.854P}{\mathrm{HV}}}$$

Using values for P and HV given in the problem statement yields the following value for d_1:

$$d_1 = \sqrt{\frac{(1.854)(0.60\ \mathrm{kg})}{400}} = 0.0527\ \mathrm{mm}$$

(b) For P = 700 g (0.700 kg) and d_1 = 0.050 mm, the Vickers hardness value is

$$\mathrm{HV} = \frac{1.854P}{d_1^2}$$

$$= \frac{(1.854)(0.700\ \mathrm{kg})}{(0.050\ \mathrm{mm})^2} = 519$$

6.57 *Estimate the Brinell and Rockwell hardnesses for the following:*

(a) The naval brass for which the stress–strain behavior is shown in Figure 6.12.

(b) The steel alloy for which the stress–strain behavior is shown in Figure 6.22.

Solution

This problem calls for estimations of Brinell and Rockwell hardnesses.

(a) For the brass specimen, the stress-strain behavior for which is shown in Figure 6.12, the tensile strength is 450 MPa (65,000 psi). From Figure 6.19, the hardness for brass corresponding to this tensile strength is about 125 HB or 85 HRB.

(b) The steel alloy (Figure 6.22) has a tensile strength of about 1950 MPa (283,000 psi) [Problem 6.26(d)]. This corresponds to a hardness of about 560 HB or ~55 HRC from the line (extended) for steels in Figure 6.19.

6.58 *Using the data represented in Figure 6.19, specify equations relating tensile strength and Brinell hardness for brass and nodular cast iron, similar to Equations 6.20a and 6.20b for steels.*

Solution

This problem calls for us to specify expressions similar to Equations 6.20a and 6.20b for nodular cast iron and brass. These equations, for a straight line, are of the form

$$TS = C + (E)(\mathrm{HB})$$

where TS is the tensile strength, HB is the Brinell hardness, and C and E are constants, which need to be determined.

One way to solve for C and E is analytically--establishing two equations using TS and HB data points on the plot, as

$$(TS)_1 = C + (E)(\mathrm{HB})_1$$
$$(TS)_2 = C + (E)(\mathrm{HB})_2$$

Solving for E from these two expressions yields

$$E = \frac{(TS)_1 - (TS)_2}{(\mathrm{HB})_2 - (\mathrm{HB})_1}$$

For nodular cast iron, if we make the arbitrary choice of $(\mathrm{HB})_1$ and $(\mathrm{HB})_2$ as 200 and 300, respectively, then, from Figure 6.19, $(TS)_1$ and $(TS)_2$ take on values of 600 MPa (87,000 psi) and 1100 MPa (160,000 psi), respectively. Substituting these values into the above expression and solving for E gives

$$E = \frac{600 \text{ MPa} - 1100 \text{ MPa}}{200 \text{ HB} - 300 \text{ HB}} = 5.0 \text{ MPa/HB} \quad (730 \text{ psi/HB})$$

We may determine the value for the constant C by inserting this value of E into either of the $(TS)_1$ or $(TS)_2$ equations cited above. Using the $(TS)_1$ expression, we solve for C as follows:

$$C = (TS)_1 - (E)(\mathrm{BH})_1$$

$$= 600 \text{ MPa} - (5.0 \text{ MPa/HB})(200 \text{ HB}) = -400 \text{ MPa } (-59{,}000 \text{ psi})$$

Thus, for nodular cast iron, these two equations take the form

$$TS(\mathrm{MPa}) = -400 + 5.0 \times \mathrm{HB}$$
$$TS(\mathrm{psi}) = -59{,}000 + 730 \times \mathrm{HB}$$

Now for brass, we take $(\mathrm{HB})_1$ and $(\mathrm{HB})_2$ as 100 and 200, respectively, then, from Figure 6.19, $(TS)_1$ and $(TS)_2$ take on values of 370 MPa (54,000 psi) and 660 MPa (95,000 psi), respectively. Substituting these values into the above expression for E gives

$$E = \frac{\mathbf{370\ MPa - 660\ MPa}}{\mathbf{100\ HB - 200\ HB}} = 2.9\ \mathbf{MPa/HB\ \ (410\ psi/HB)}$$

We determine the value of C in using the same procedure outlined above:

$$C = (TS)_1 - (E)(\mathrm{BH})_1$$

$$= 370\ \mathrm{MPa} - (2.9\ \mathrm{MPa/HB})(100\ \mathrm{HB}) = 80\ \mathrm{MPa}\ \ (13{,}000\ \mathrm{psi})$$

Thus, for brass these two equations that relate tensile strength and Brinell hardness take the form

$$TS(\mathrm{MPa}) = 80 + 2.9 \times \mathrm{HB}$$

$$TS(\mathrm{psi}) = 13{,}000 + 410 \times \mathrm{HB}$$

Variability of Material Properties

6.59 *Cite five factors that lead to scatter in measured material properties.*

Solution

The five factors that lead to scatter in measured material properties are the following: (1) test method; (2) variation in specimen fabrication procedure; (3) operator bias; (4) apparatus calibration; and (5) material inhomogeneities and/or compositional differences.

6.60 *The following table gives a number of Rockwell G hardness values that were measured on a single steel specimen. Compute average and standard deviation hardness values.*

47.3	*48.7*	*47.1*
52.1	*50.0*	*50.4*
45.6	*46.2*	*45.9*
49.9	*48.3*	*46.4*
47.6	*51.1*	*48.5*
50.4	*46.7*	*49.7*

Solution

The average of the given hardness values is calculated using Equation 6.21 as

$$\overline{\mathrm{HRG}} = \frac{\sum_{i=1}^{18} \mathrm{HRG}_i}{18}$$

$$= \frac{47.3 + 52.1 + 45.6 \ldots + 49.7}{18} = 48.4$$

And we compute the standard deviation using Equation 6.22 as follows:

$$s = \sqrt{\frac{\sum_{i=1}^{18} \left(\mathrm{HRG}_i - \overline{\mathrm{HRG}}\right)^2}{18 - 1}}$$

$$= \left[\frac{(47.3 - 48.4)^2 + (52.1 - 48.4)^2 + \ldots + (49.7 - 48.4)^2}{17}\right]^{1/2}$$

$$= \sqrt{\frac{64.95}{17}} = 1.95$$

6.61 *The following table gives a number of yield strength values* (*in MPa*) *that were measured on the same aluminum alloy. Compute average and standard deviation yield strength values.*

274.3	*277.1*	*263.8*
267.5	*258.6*	*271.2*
255.4	*266.9*	*257.6*
270.8	*260.1*	*264.3*
261.7	*279.4*	*260.5*

Solution

The average of the given yield strength values is calculated using Equation 6.21 as

$$\overline{\sigma_y} = \frac{\sum_{i=1}^{15} (\sigma_y)_i}{15}$$

$$= \frac{274.3 + 267.5 + 255.4 + \ldots + 260.5}{15} = 265.9 \text{ MPa}$$

And we compute the standard deviation using Equation 6.22 as follows:

$$s = \sqrt{\frac{\sum_{i=1}^{15} \left((\sigma_y)_i - \overline{\sigma_y}\right)^2}{15 - 1}}$$

$$= \left[\frac{(274.3 - 265.9)^2 + (267.5 - 265.9)^2 + \ldots + (260.5 - 265.9)^2}{14}\right]^{1/2}$$

$$= \sqrt{\frac{753.75}{14}} = 7.34 \text{ MPa}$$

Design/Safety Factors

6.62 *Upon what three criteria are factors of safety based?*

Solution

The criteria upon which factors of safety are based are (1) consequences of failure, (2) previous experience, (3) accuracy of measurement of mechanical forces and/or material properties, and (4) economics.

6.63 *Determine working stresses for the two alloys that have the stress–strain behaviors shown in Figures 6.12 and 6.22.*

Solution

The working stresses for the two alloys the stress-strain behaviors of which are shown in Figures 6.12 and 6.22 are calculated by dividing the yield strength by a factor of safety, which we will take to be 2. For the brass alloy (Figure 6.12), since σ_y = 250 MPa (36,000 psi), the working stress is 125 MPa (18,000 psi), whereas for the steel alloy (Figure 6.22), σ_y = 1600 MPa (232,000 psi) (from the solution to Problem 6.26), and, therefore, σ_w = 800 MPa (116,000 psi).

DESIGN PROBLEMS

6.D1 *A large tower is to be supported by a series of steel wires; it is estimated that the load on each wire will be 13,300 N (3000 lb*$_f$*). Determine the minimum required wire diameter, assuming a factor of safety of 2.0 and a yield strength of 860 MPa (125,000 psi) for the steel.*

Solution

For this problem the working stress is computed using Equation 6.24 with $N = 2$, as

$$\sigma_w = \frac{\sigma_y}{2} = \frac{860 \text{ MPa}}{2} = 430 \text{ MPa} \ \ (62{,}500 \text{ psi})$$

Since the force is given, the area may be determined from Equation 6.1, and subsequently the original diameter d_0 may be calculated as

$$A_0 = \frac{F}{\sigma_w} = \pi\left(\frac{d_0}{2}\right)^2$$

And

$$d_0 = \sqrt{\frac{4F}{\pi\sigma_w}} = \sqrt{\frac{(4)(13{,}300 \text{ N})}{\pi\left(430 \times 10^6 \text{ N/m}^2\right)}}$$

$$= 6.3 \times 10^{-3} \text{ m} = 6.3 \text{ mm} \ \ (0.25 \text{ in.})$$

6.D2 *(a) Consider a thin-walled cylindrical tube having a radius of 65 mm is to be used to transport pressurized gas. If inside and outside tube pressures are 100 and 2.0 atm (10.13 and 0.2026 MPa), respectively, compute the minimum required thickness for each of the following metal alloys. Assume a factor of safety of 3.5.*

(b) A tube constructed of which of the alloys will cost the least amount?

Alloy	*Yield Strength,* σ_y (*MPa*)	*Density,* ρ (*g/cm*^{3})	*Unit Mass Cost,* $\bar{c}$ (*$US/kg*)
Steel (plain)	*375*	*7.8*	*1.65*
Steel (alloy)	*1000*	*7.8*	*4.00*
Cast iron	*225*	*7.1*	*2.50*
Aluminum	*275*	*2.7*	*7.50*
Magnesium	*175*	*1.80*	*15.00*

Solution

(a) To solve this problem we use a procedure similar to that used for Design Example 6.2. Alloy yield strength, tube radius and thickness, and the inside-outside pressure difference are related according to Equation 6.26; furthermore, labels for the tube dimensions are represented in the sketch of Figure 6.21. For this problem all parameters in this equation are provided except for the tube thickness, *t*. Rearranging Equation 6.26 such that *t* is the dependent variable leads to

$$t = \frac{Nr\Delta p}{\sigma_y} \qquad (6.26b)$$

Tube wall thickness will vary from alloy to alloy since each alloy has a different yield strength, whereas *N*, *r*, and Δ*p* are constant. Their values are provided in the problem statement as follows:

$N = 3.5$

$r = 65 \text{ mm} = 65 \times 10^{-3} \text{ m}$

$\Delta p = 10.13 \text{ MPa} - 0.2026 \text{ MPa} = 9.927 \text{ MPa}$

Using Equation 6.26b, we compute the tube wall thickness for these five alloys as follows:

$$t \text{ (plain steel)} = \frac{(3.5)(65 \times 10^{-3} \text{ m})(9.927 \text{ MPa})}{375 \text{ MPa}} = 0.00602 \text{ m} = 6.02 \text{ mm}$$

$$t\ (\text{alloy steel}) = \frac{(3.5)(65\ \times\ 10^{-3}\ \text{m})(9.927\ \text{MPa})}{1000\ \text{MPa}} = \ 0.00226\ \text{m} = 2.26\ \text{mm}$$

$$t\ (\text{cast iron}) = \frac{(3.5)(65\ \times\ 10^{-3}\ \text{m})(9.927\ \text{MPa})}{225\ \text{MPa}} = \ 0.0100\ \text{m} = 10.0\ \text{mm}$$

$$t\ (\text{aluminum}) = \frac{(3.5)(65\ \times\ 10^{-3}\ \text{m})(9.927\ \text{MPa})}{275\ \text{MPa}} = \ 0.00821\ \text{m} = 8.21\ \text{mm}$$

$$t\ (\text{magnesium}) = \frac{(3.5)(65\ \times\ 10^{-3}\ \text{m})(9.927\ \text{MPa})}{175\ \text{MPa}} = \ 0.0129\ \text{m} = 12.9\ \text{mm}$$

(b) This portion of the problem asks that we determine at tube constructed of which of the alloys will cost the least amount. We begin by considering Equation 6.28, which gives tube volume as a function of *t*. Furthermore, when the expression for *t*, Equation 6.26b, is incorporated into Equation 6.28, the following equation for tube volume *V* results:

$$V = \pi(2rt + t^2)L$$

$$= \pi\left[2r\left(\frac{Nr\Delta p}{\sigma_y}\right) + \left(\frac{Nr\Delta p}{\sigma_y}\right)^2\right]L$$

Now tube cost per unit length is dependent on volume, alloy density, and cost per unit mass values according to Equation 6.29. Substitution of the above expression for *V* into Equation 6.29 yields

$$\text{Cost} = \left(\frac{V\rho}{1000}\right)(\bar{c})$$

$$= \frac{\left\{\pi\left[2r\left(\frac{Nr\Delta p}{\sigma_y}\right) + \left(\frac{Nr\Delta p}{\sigma_y}\right)^2\right]L\rho\right\}\bar{c}}{1000}$$

Using this equation, let us now determine the cost per unit length for the plain steel.

$$\text{Cost (plain steel)} =$$

$$\frac{\left\{\pi\left[(2)(65\times10^{-3}\text{ m})\left(\dfrac{(3.5)(65\times10^{-3}\text{ m})(9.927\text{ MPa})}{375\text{ MPa}}\right)+\left(\dfrac{(3.5)(65\times10^{-3}\text{ m})(9.927\text{ MPa})}{375\text{ MPa}}\right)^2\right](10^6\text{ cm}^3/\text{m}^3)(1\text{ m})(7.8\text{ g/cm}^3)\right\}(1.65\text{ \$US/kg})}{1000\text{ g/kg}}$$

$$= \$33.10$$

We will not present cost computations for the other alloys. However, the following table lists costs for all five alloys (along with wall thickness values calculated above.

Alloy	*t* (mm)	Cost ($US)
Steel (plain)	6.02	33.10
Steel (alloy)	2.26	29.30
Cast iron	10.0	78.40
Aluminum	8.21	72.20
Magnesium	12.9	156.50

Hence, the alloy steel is the least expensive, the plain steel is next; the most expensive is the magnesium alloy.

6.D3 *(a) Gaseous hydrogen at a constant pressure of 0.658 MPa (5 atm) is to flow within the inside of a thin-walled cylindrical tube of nickel that has a radius of 0.125 m. The temperature of the tube is to be 350°C and the pressure of hydrogen outside of the tube will be maintained at 0.0127 MPa (0.125 atm). Calculate the minimum wall thickness if the diffusion flux is to be no greater than* 1.25×10^{-7} *mol/m*^{2}*·s. The concentration of hydrogen in the nickel,* C_H *(in moles hydrogen per cubic meter of Ni), is a function of hydrogen pressure,* P_{H_2} *(in MPa), and absolute temperature T according to*

$$C_{\mathrm{H}} = 30.8\sqrt{p_{\mathrm{H}_2}}\exp\left(-\frac{12{,}300\ \mathrm{J/mol}}{RT}\right) \qquad (6.34)$$

Furthermore, the diffusion coefficient for the diffusion of H in Ni depends on temperature as

$$D_{\mathrm{H}}(\mathrm{m^2/s}) = (4.76 \times 10^{-7})\exp\left(-\frac{39{,}560\ \mathrm{J/mol}}{RT}\right) \qquad (6.35)$$

(b) For thin-walled cylindrical tubes that are pressurized, the circumferential stress is a function of the pressure difference across the wall (Δp*), cylinder radius (r), and tube thickness (*Δx*) according to Equation 6.25—that is*

$$\sigma = \frac{r\Delta p}{\Delta x} \qquad (6.25a)$$

Compute the circumferential stress to which the walls of this pressurized cylinder are exposed.
(Note: the symbol t is used for cylinder wall thickness in Equation 6.25 found in Design Example 6.2; in this version of Equation 6.25 (i.e., 6.25a) we denote wall thickness by Δx*.)*

(c) The room-temperature yield strength of Ni is 100 MPa (15,000 psi), and σ_y *diminishes about 5 MPa for every 50°C rise in temperature. Would you expect the wall thickness computed in part (b) to be suitable for this Ni cylinder at 350°C? Why or why not?*

(d) If this thickness is found to be suitable, compute the minimum thickness that could be used without any deformation of the tube walls. How much would the diffusion flux increase with this reduction in thickness? However, if the thickness determined in part (c) is found to be unsuitable, then specify a minimum thickness that you would use. In this case, how much of a decrease in diffusion flux would result?

Solution

(a) This portion of the problem asks for us to compute the wall thickness of a thin-walled cylindrical Ni tube at 350°C through which hydrogen gas diffuses. The inside and outside pressures are, respectively, 0.658 and 0.0127 MPa, and the diffusion flux is to be no greater than 1.25×10^{-7} mol/m^2-s. This is a steady-state diffusion problem, which necessitates that we employ Equation 5.2. The concentrations at the inside and outside wall faces may be determined using Equation 6.34, and, furthermore, the diffusion coefficient is computed using Equation 6.35. Solving for Δx (using Equation 5.2)

$$\Delta x = -\frac{D\Delta C}{J}$$

$$= -\frac{1}{1.25 \times 10^{-7}\ \mathrm{mol/m^2\text{-}s}} \times$$

$$\left(4.76 \times 10^{-7}\right)\exp\left(-\frac{39{,}560\ \mathrm{J/mol}}{(8.31\ \mathrm{J/mol\text{-}K})(350 + 273\ \mathrm{K})}\right) \times$$

$$(30.8)\exp\left(-\frac{12{,}300\ \mathrm{J/mol}}{(8.31\ \mathrm{J/mol\text{-}K})(350 + 273\ \mathrm{K})}\right)\left(\sqrt{0.0127\ \mathrm{MPa}} - \sqrt{0.658\ \mathrm{MPa}}\right)$$

$$= 0.00366\ \mathrm{m} = 3.66\ \mathrm{mm}$$

(b) Now we are asked to determine the circumferential stress:

$$\sigma = \frac{r\,\Delta p}{\Delta x}$$

$$= \frac{(0.125\ \mathrm{m})(0.658\ \mathrm{MPa} - 0.0127\ \mathrm{MPa})}{0.00366\ \mathrm{m}}$$

$$= 22.0\ \mathrm{MPa}$$

(c) Now we are to compare this value of stress to the yield strength of Ni at 350°C, from which it is possible to determine whether or not the 3.66 mm wall thickness is suitable. From the information given in the problem, we may write an equation for the dependence of yield strength (σ_y) on temperature (T) as follows:

$$\sigma_y = 100\ \mathrm{MPa} - \frac{5\ \mathrm{MPa}}{50°\mathrm{C}}\left(T - T_r\right)$$

where T_r is room temperature and for temperature in degrees Celsius. Thus, at 350°C

$$\sigma_y = 100\ \mathrm{MPa} - \left(\frac{5\ \mathrm{MPa}}{50°\mathrm{C}}\right)(350°\mathrm{C} - 20°\mathrm{C}) = 67\ \mathrm{MPa}$$

Inasmuch as the circumferential stress (22.0 MPa) is much less than the yield strength (67 MPa), this thickness is entirely suitable.

(d) And, finally, this part of the problem asks that we specify how much this thickness may be reduced and still retain a safe design. Let us use a working stress by dividing the yield stress by a factor of safety, according to Equation 6.24. On the basis of our experience, let us use a value of 2.0 for *N*. Thus

$$\sigma_w = \frac{\sigma_y}{N} = \frac{67\text{ MPa}}{2} = 33.5\ \text{MPa}$$

Using this value for σ_w and Equation 6.25a, we now compute the tube thickness as

$$\Delta x = \frac{r\,\Delta p}{\sigma_w}$$

$$= \frac{(0.125\text{ m})(0.658\text{ MPa} - 0.0127\text{ MPa})}{(33.5\text{ MPa})}$$

$$= 0.00241\text{ m} = 2.41\text{ mm}$$

Substitution of this value into Fick's first law we calculate the diffusion flux as follows:

$$J = -D\frac{\Delta C}{\Delta x}$$

$$= -\left(4.76 \times 10^{-7}\right)\exp\left[-\frac{39{,}560\ \text{J/mol}}{(8.31\ \text{J/mol-K})(350 + 273\text{ K})}\right] \times$$

$$\frac{(30.8)\exp\left[-\frac{12{,}300\ \text{J/mol}}{(8.31\ \text{J/mol-K})(350 + 273\text{ K})}\right]\left(\sqrt{0.0127\text{ MPa}} - \sqrt{0.658\text{ MPa}}\right)}{0.00241\text{ m}}$$

$$= 1.90 \times 10^{-7}\ \text{mol/m}^2\text{-s}$$

Thus, the flux increases by approximately a factor of 1.5, from 1.25×10^{-7} to 1.90×10^{-7} mol/m^2-s with this reduction in thickness.

6.D4 *Consider the steady-state diffusion of hydrogen through the walls of a cylindrical nickel tube as described in Problem 6.D3. One design calls for a diffusion flux of 2.5 ×* 10^{-8} *mol/*m^2*•s, a tube radius of 0.100 m, and inside and outside pressures of 1.015 MPa (10 atm) and 0.01015 MPa (0.1 atm), respectively; the maximum allowable temperature is 300°C. Specify a suitable temperature and wall thickness to give this diffusion flux and yet ensure that the tube walls will not experience any permanent deformation.*

Solution

This problem calls for the specification of a temperature and cylindrical tube wall thickness that will give a diffusion flux of 2.5 × 10^{-8} mol/m^2-s for the diffusion of hydrogen in nickel; the tube radius is 0.100 m and the inside and outside pressures are 1.015 and 0.01015 MPa, respectively. There are probably several different approaches that may be used; and there is not one unique solution. Let us employ the following procedure to solve this problem: (1) assume some wall thickness, and, then, using Fick's first law for diffusion (which also employs Equations 5.2 and 6.35), compute the temperature at which the diffusion flux is that required; (2) compute the yield strength of the nickel at this temperature using the dependence of yield strength on temperature as stated in Problem 6.D3; (3) calculate the circumferential stress on the tube walls using Equation 6.25a; and (4) compare the yield strength and circumferential stress values--the yield strength should probably be at least twice the stress in order to make certain that no permanent deformation occurs. If this condition is not met then another iteration of the procedure should be conducted with a more educated choice of wall thickness.

As a starting point, let us arbitrarily choose a wall thickness of 2 mm (2 × 10^{-3} m). The steady-state diffusion equation, Equation 5.2, takes the form

$$J = -D\frac{\Delta C}{\Delta x}$$

$$= 2.5 \times 10^{-8} \text{ mol/m}^2\text{-s}$$

$$= -\left(4.76 \times 10^{-7}\right)\exp\left[-\frac{39{,}560 \text{ J/mol}}{(8.31 \text{ J/mol-K})(T)}\right] \times$$

$$\frac{(30.8)\exp\left[-\dfrac{12{,}300 \text{ J/mol}}{(8.31 \text{ J/mol-K})(T)}\right]\left(\sqrt{0.01015 \text{ MPa}} - \sqrt{1.015 \text{ MPa}}\right)}{0.002 \text{ m}}$$

Solving this expression for the temperature T gives T = 500 K = 227°C; this value is satisfactory inasmuch as it is less than the maximum allowable value (300°C).

The next step is to compute the stress on the wall using Equation 6.25a; thus

$$\sigma = \frac{r\,\Delta p}{\Delta x}$$

$$= \frac{(0.100 \text{ m})(1.015 \text{ MPa} - 0.01015 \text{ MPa})}{(2 \times 10^{-3} \text{ m})}$$

50.2 MPa

Now, the yield strength (σ_y) of Ni at this temperature may be computed using the expression

$$\sigma_y = 100 \text{ MPa} - \frac{5 \text{ MPa}}{50°\text{C}}(T - T_r)$$

where T_r is room temperature. Thus,

$$\sigma_y = 100 \text{ MPa} - 0.1 \text{ MPa/°C } (227°\text{C} - 20°\text{C}) = 79.3 \text{ MPa}$$

Inasmuch as this yield strength is about 50% greater than the circumferential stress, a wall thickness of 2 mm is a satisfactory design parameter; furthermore, 227°C is a satisfactory operating temperature.

FUNDAMENTALS OF ENGINEERING QUESTIONS AND PROBLEMS

6.1FE *A steel rod is pulled in tension with a stress that is less than the yield strength. The modulus of elasticity may be calculated as*

(A) Axial stress divided by axial strain
(B) Axial stress divided by change in length
(C) Axial stress times axial strain
(D) Axial load divided by change in length

Solution

The modulus of elasticity of a steel rod placed under a tensile stress that is less than the yield strength (i.e., when deformation is totally elastic) may be calculated using Equation 6.5 as

$$E = \frac{\sigma}{\varepsilon}$$

That is, the modulus is equal to the axial stress divided by axial strain. Therefore, the correct answer is A.

6.2FE *A cylindrical specimen of brass that has a diameter of 20 mm, a tensile modulus of 110 GPa, and a Poisson's ratio of 0.35 is pulled in tension with force of 40,000 N. If the deformation is totally elastic, what is the strain experienced by the specimen?*

(A) 0.00116 *(C) 0.00463*

(B) 0.00029 *(D) 0.01350*

Solution

This problem calls for us to calculate the elastic strain that results for a brass specimen stressed in tension. The cross-sectional area A_0 is equal to

$$A_0 = \pi\left(\frac{d_0}{2}\right)^2 = \pi\left(\frac{20 \times 10^{-3}\ \text{m}}{2}\right)^2 = 3.14 \times 10^{-4}\,\text{m}^2$$

Here d_0 is the original cross-sectional diameter. Also, the elastic modulus for brass is given in the problem statement as 110 GPa (or 110 × 10^9 N/m^2). Combining Equations 6.1 and 6.5 and solving for the strain yields

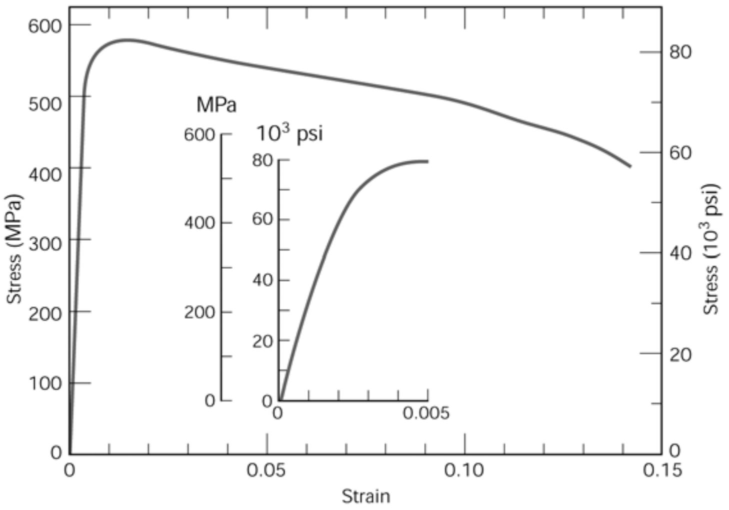
$$\varepsilon = \frac{\sigma}{E} = \frac{F}{A_0 E}$$

Now incorporating values for stress, cross-sectional area, and modulus of elasticity into this expression leads to the following value of strain:

$$\varepsilon = \frac{40{,}000\ \text{N}}{(3.14 \times 10^{-4}\,\text{m}^2)(110 \times 10^9\,\text{N/m}^2)} = 1.16 \times 10^{-3} = 0.00116$$

which is answer A.

6.3FE *The following figure shows the tensile stress-strain curve for a plain-carbon steel.*



(a) What is this alloy's tensile strength?

(A) 650 MPa *(C) 570 MPa*

(B) 300 MPa *(D) 3,000 MPa*

(b) What is its modulus of elasticity?

(A) 320 GPa *(C) 500 GPa*

(B) 400 GPa *(D) 215 GPa*

(c) What is the yield strength?

(A) 550 MPa *(C) 600 MPa*

(B) 420 MPa *(D) 1000 MPa*

Solution

(a) The tensile strength (the maximum on the curve) is approximately 570 MPa. Therefore, C is the correct answer.

(b) The elastic modulus is just the slope of the initial linear portion of the curve, which may be determined using Equation 6.10:

$$E = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1}$$

If we take σ_1 and ε_1 to be zero and σ_2 = 300 MPa, then its corresponding strain ε_2 (from the inset) is about 0.0014. Thus, we calculate the modulus of elasticity as follows:

$$E = \frac{300 \text{ MPa} - 0 \text{ MPa}}{0.0014 - 0} = 215 \times 10^3 \text{ MPa} = 215 \text{ GPa}$$

Thus, D is the correct answer.

(c) The 0.002 strain offset line intersects the stress-strain curve at approximately 550 MPa, which means that the correct answer is A.

6.4FE *A specimen of steel has a rectangular cross section 20 mm wide and 40 mm thick, an elastic modulus of 207 GPa, and a Poisson's ratio of 0.30. If this specimen is pulled in tension with a force of 60,000 N, what is the change in width if deformation is totally elastic?*

(A) Increase in width of 3.62×10^{-6} *m*

(B) Decrease in width of 7.24×10^{-6} *m*

(C) Increase in width of 7.24×10^{-6} *m*

(D) Decrease in width of 2.18×10^{-6} *m*

Solution

This problem calls for us to calculate the change in width that results for a steel specimen stressed in tension. The first step is to calculate the tensile strain. The cross-sectional area is (20 mm) × (40 mm) = 800 mm^2 = 8×10^{-4} m^2; also, the elastic modulus for steel is given as 207 GPa (or 207×10^9 N/m^2). Combining Equations 6.1 and 6.5 leads to the following:

$$\varepsilon_z = \frac{\sigma}{E} = \frac{\dfrac{F}{A_0}}{E} = \frac{F}{A_0 E}$$

Incorporation of values for force, cross-sectional area, and the modulus of elasticity yields the following for the axial strain:

$$\varepsilon_z = \frac{60{,}000 \text{ N}}{(8.0 \times 10^{-4} \text{ m}^2)(207 \times 10^9 \text{ N/m}^2)} = 3.62 \times 10^{-4}$$

The lateral strain is calculated by rearranging Equation 6.8 to give

$$\varepsilon_x = -\nu\varepsilon_z = -(0.30)(3.62 \times 10^{-4}) = -1.09 \times 10^{-4}$$

Finally, the change in width, Δw, is calculated using a rearranged and modified form of Equation 6.2 as

$$\Delta w = w_0 \varepsilon_x$$

Here w_0 is the original specimen width (20 mm). Therefore, using the above equation, Δw is calculated as

$$\Delta w = (20 \text{ mm})(-1.09 \times 10^{-4}) = -2.18 \times 10^{-3} \text{ mm} = -2.18 \times 10^{-6} \text{ m}$$

Therefore, the width decreases (a minus Δw) by 2.18×10^{-6} m, which means that the correct answer is D.

6.5FE *A cylindrical specimen of undeformed brass that has a radius of 300 mm is elastically deformed to a tensile strain of 0.001. If Poisson's ratio for this brass is 0.35, what is the change in specimen diameter?*

(A) Increase by 0.028 mm

(B) Decrease by 1.05 $\times 10^{-4}$ *m*

(C) Decrease by 3.00 $\times 10^{-4}$ *m*

(D) Increase by 1.05 $\times 10^{-4}$ *m*

Solution

This problem calls for us to calculate the change in diameter that results for a brass specimen stressed in tension. The lateral strain (ε_x) is calculated using a rearranged form of Equation 6.8 as

$$\varepsilon_x = -\nu\varepsilon_z = -(0.35)(1.00 \times 10^{-3}) = -3.50 \times 10^{-4}$$

The change in diameter, Δd, is calculated using a modified and rearranged form of Equation 6.2:

$$\Delta d = d_0\varepsilon_x$$

where d_0 is the original diameter (300 mm). Now we determine the change in diameter using the above equation as follows:

$$\Delta d = (300 \text{ mm})(-3.5 \times 10^{-4}) = -0.105 \text{ mm} = -1.05 \times 10^{-4} \text{ m}$$

Therefore, the diameter decreases (a minus Δd) by 1.05 × 10^{-4} m, which means that the correct answer is B.

CHAPTER 7

DISLOCATIONS AND STRENGTHENING MECHANISMS

PROBLEM SOLUTIONS

Basic Concepts of Dislocations
Characteristics of Dislocations

7.1 *To provide some perspective on the dimensions of atomic defects, consider a metal specimen with a dislocation density of* 10^5 *mm*$^{-2}$*. Suppose that all the dislocations in 1000 mm*^{3} *(1 cm*^{3}*) were somehow removed and linked end to end. How far (in miles) would this chain extend? Now suppose that the density is increased to* 10^9 *mm*$^{-2}$ *by cold working. What would be the chain length of dislocations in 1000 mm*^{3} *of material?*

Solution

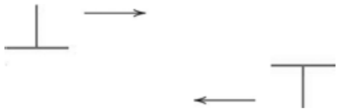
The dislocation density is just the total dislocation length per unit volume of material (in this case per cubic millimeters). Thus, the total length in 1000 mm^3 of material having a density of 10^5 mm^{-2} is just

$$\left(10^5\ \text{mm}^{-2}\right)\left(1000\ \text{mm}^3\right) = 10^8\,\text{mm} = 10^5\ \text{m} = 62\ \text{mi}$$

Similarly, for a dislocation density of 10^9 mm^{-2}, the total length is

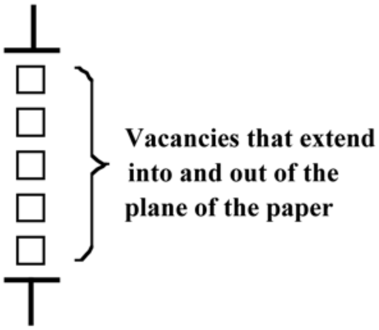
$$\left(10^9\ \text{mm}^{-2}\right)\left(1000\ \text{mm}^3\right) = 10^{12}\ \text{mm} = 10^9\ \text{m} = 6.2\ \times\ 10^5\ \text{mi}$$

7.2 *Consider two edge dislocations of opposite sign and having slip planes that are separated by several atomic distances, as indicated in the following diagram. Briefly describe the defect that results when these two dislocations become aligned with each other.*



Answer

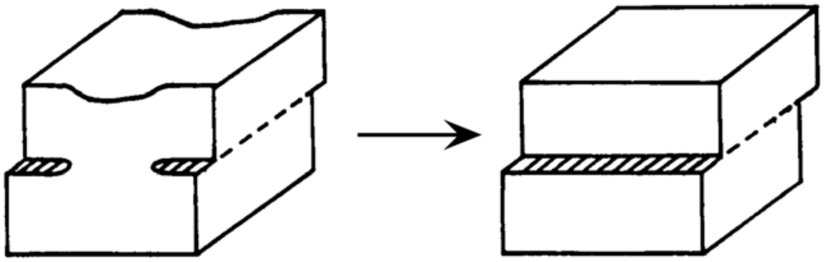
When the two edge dislocations become aligned, a planar region of vacancies will exist between the dislocations as:



7.3 *Is it possible for two screw dislocations of opposite sign to annihilate each other? Explain your answer.*

Answer

It is possible for two screw dislocations of opposite sign to annihilate one another if their dislocation lines are parallel. This is demonstrated in the figure below.



7.4 *For each of edge, screw, and mixed dislocations, cite the relationship between the direction of the applied shear stress and the direction of dislocation line motion.*

Answer

For the various dislocation types, the relationships between the direction of the applied shear stress and the direction of dislocation line motion are as follows:

edge dislocation—parallel
screw dislocation—perpendicular
mixed dislocation--neither parallel nor perpendicular

Slip Systems

7.5 *(a) Define a slip system.*

(b) Do all metals have the same slip system? Why or why not?

<u>Answer</u>

(a) A slip system is a crystallographic plane, and, within that plane, a direction along which dislocation motion (or slip) occurs.

(b) All metals do not have the same slip system. The reason for this is that for most metals, the slip system will consist of the most densely packed crystallographic plane, and within that plane the most closely packed direction. This plane and direction will vary from crystal structure to crystal structure.

7.6 (*a) Compare planar densities (Section 3.11 and Problem 3.60) for the (100), (110), and (111) planes for FCC.*

(b) Compare planar densities (Problem 3.61) for the (100), (110), and (111) planes for BCC.

Solution

(a) For the FCC crystal structure, the planar density for the (110) plane is given in Equation 3.19 as

$$\mathrm{PD}_{110}(\mathrm{FCC}) = \frac{1}{4R^2\sqrt{2}} = \frac{0.177}{R^2}$$

Furthermore, the planar densities of the (100) and (111) planes are calculated in Homework Problem 3.60, which are as follows:

$$\mathrm{PD}_{100}(\mathrm{FCC}) = \frac{1}{4R^2} = \frac{0.25}{R^2}$$

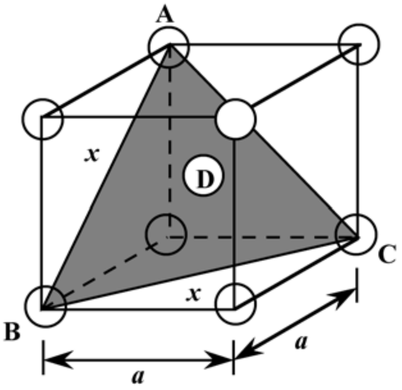
$$\mathrm{PD}_{111}(\mathrm{FCC}) = \frac{1}{2R^2\sqrt{3}} = \frac{0.29}{R^2}$$

(b) For the BCC crystal structure, the planar densities of the (100) and (110) planes were determined in Homework Problem 3.61, which are as follows:

$$\mathrm{PD}_{100}(\mathrm{BCC}) = \frac{3}{16R^2} = \frac{0.19}{R^2}$$

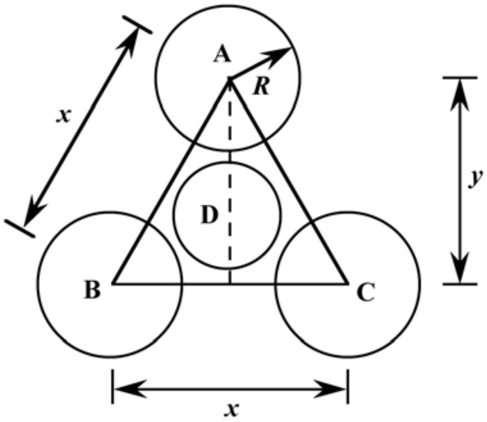
$$\mathrm{PD}_{110}(\mathrm{BCC}) = \frac{3}{8R^2\sqrt{2}} = \frac{0.27}{R^2}$$

Below is a BCC unit cell, within which is shown a (111) plane.



(*a*)

The centers of the three corner atoms, denoted by A, B, and C lie on this plane. Furthermore, the (111) plane does not pass through the center of atom D, which is located at the unit cell center. The atomic packing of this plane is presented in the following figure; the corresponding atom positions from the Figure (*a*) are also noted.



(*b*)

Inasmuch as this plane does not pass through the center of atom D, it is not included in the atom count. One sixth of each of the three atoms labeled A, B, and C is associated with this plane, which gives an equivalence of one-half atom.

In Figure (*b*) the triangle with A, B, and C at its corners is an equilateral triangle. And, from Figure (*b*), the area of this triangle is $\frac{xy}{2}$. The triangle edge length, *x*, is equal to the length of a face diagonal, as indicated in Figure (*a*). And its length is related to the unit cell edge length, *a*, as

$$x^2 = a^2 + a^2 = 2a^2$$

or

$$x = a\sqrt{2}$$

For BCC, $a = \frac{4R}{\sqrt{3}}$ (Equation 3.4), and, therefore,

$$x = \frac{4R\sqrt{2}}{\sqrt{3}}$$

Also, from Figure (*b*), with respect to the length *y* we may write

$$y^2 + \left(\frac{x}{2}\right)^2 = x^2$$

which leads to $y = \frac{x\sqrt{3}}{2}$. And, substitution for the above expression for x yields

$$y = \frac{x\sqrt{3}}{2} = \left(\frac{4R\sqrt{2}}{\sqrt{3}}\right)\left(\frac{\sqrt{3}}{2}\right) = \frac{4R\sqrt{2}}{2}$$

Thus, the area of this triangle is equal to

$$\text{AREA} = \frac{1}{2}x\,y = \left(\frac{1}{2}\right)\left(\frac{4R\sqrt{2}}{\sqrt{3}}\right)\left(\frac{4R\sqrt{2}}{2}\right) = \frac{8R^2}{\sqrt{3}}$$

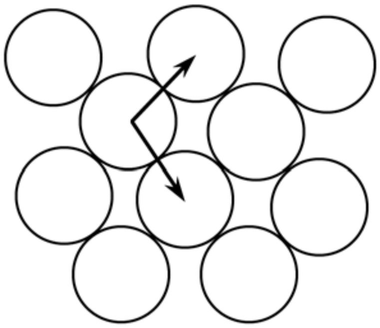
And, finally, the planar density for this (111) plane is

$$\text{PD}_{111}(\text{BCC}) = \frac{0.5 \text{ atom}}{\dfrac{8R^2}{\sqrt{3}}} = \frac{\sqrt{3}}{16R^2} = \frac{0.11}{R^2}$$

7.7 *One slip system for the BCC crystal structure is* $\{110\}\langle 111\rangle$. *In a manner similar to Figure 7.6b, sketch a {110}-type plane for the BCC structure, representing atom positions with circles. Now, using arrows, indicate two different* $\langle 111\rangle$ *slip directions within this plane.*

Solution

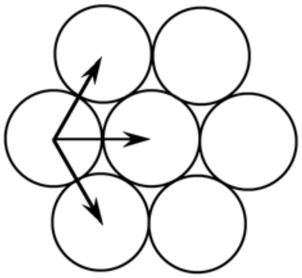
Below is shown the atomic packing for a BCC {110}-type plane. The arrows indicate two different $\langle 111\rangle$ type directions.



7.8 *One slip system for the HCP crystal structure is* $\{0001\}\langle 11\bar{2}0\rangle$. *In a manner similar to Figure 7.6b, sketch a {0001}-type plane for the HCP structure and, using arrows, indicate three different* $\langle 11\bar{2}0\rangle$ *slip directions within this plane. You may find Figure 3.9 helpful.*

Solution

Below is shown the atomic packing for an HCP {0001}-type plane. The arrows indicate three different $\langle 11\bar{2}0\rangle$-type directions.



7.9 *Equations 7.1a and 7.1b, expressions for Burgers vectors for FCC and BCC crystal structures, are of the form*

$$\boldsymbol{b} = \frac{a}{2}\langle uvw \rangle$$

where a is the unit cell edge length. The magnitudes of these Burgers vectors may be determined from the following equation:

$$|\mathbf{b}| = \frac{a}{2}(u^2 + v^2 + w^2)^{1/2} \qquad (7.11)$$

*determine the values of |**b**| for copper and iron. You may want to consult Table 3.1.*

Solution

This problem asks that we compute the magnitudes of the Burgers vectors for copper and iron. For Cu, which has an FCC crystal structure, R = 0.1278 nm (Table 3.1) and, from Equation 3.1

$$a = 2R\sqrt{2} = (2)(0.1278 \text{ nm})(\sqrt{2})$$

0.3615 nm

Also, from Equation 7.1a, the Burgers vector for FCC metals is

$$\mathbf{b} = \frac{a}{2}\langle 110 \rangle$$

Therefore, the values for u, v, and w in Equation 7.11 are 1, 1, and 0, respectively. Hence, the magnitude of the Burgers vector for Cu is

$$|\mathbf{b}| = \frac{a}{2}\sqrt{u^2 + v^2 + w^2}$$

$$= \frac{0.3615 \text{ nm}}{2}\sqrt{(1)^2 + (1)^2 + (0)^2} = 0.2556 \text{ nm}$$

For Fe which has a BCC crystal structure, R = 0.1241 nm (Table 3.1) and, from Equation 3.4

$$a = \frac{4R}{\sqrt{3}} = \frac{(4)(0.1241 \text{ nm})}{\sqrt{3}}$$

=0.2866 nm

Also, from Equation 7.1b, the Burgers vector for BCC metals is

$$\mathbf{b} = \frac{a}{2}\langle 111 \rangle$$

Therefore, the values for *u*, *v*, and *w* in Equation 7.11 are 1, 1, and 1, respectively. Hence, the magnitude of the Burgers vector for Fe is

$$|\mathbf{b}| = \frac{0.2866\ \text{nm}}{2}\sqrt{(1)^2 + (1)^2 + (1)^2} = 0.2482\ \text{nm}$$

7.10 *(a) In the manner of Equations 7.1a to 7.1c, specify the Burgers vector for the simple cubic crystal structure whose unit cell is shown in Figure 3.3. Also, simple cubic is the crystal structure for the edge dislocation of Figure 4.4, and for its motion as presented in Figure 7.1. You may also want to consult the answer to Concept Check 7.1.*

*(b) On the basis of Equation 7.11, formulate an expression for the magnitude of the Burgers vector, |**b**|, for the simple cubic crystal structure.*

Solution

(a) This part of the problem asks that we specify the Burgers vector for the simple cubic crystal structure (and suggests that we consult the answer to Concept Check 7.1). This Concept Check asks that we select the slip system for simple cubic from four possibilities. The correct answer is $\{100\}\langle 010\rangle$. Thus, the Burgers vector will lie in a $\langle 010\rangle$-type direction. Also, the unit slip distance is *a* (i.e., the unit cell edge length, Figures 4.4 and 7.1). Therefore, the Burgers vector for simple cubic is

$$\mathbf{b} = a\langle 010\rangle$$

Or, equivalently

$$\mathbf{b} = a\langle 100\rangle$$

(b) The magnitude of the Burgers vector, |**b**|, for simple cubic is

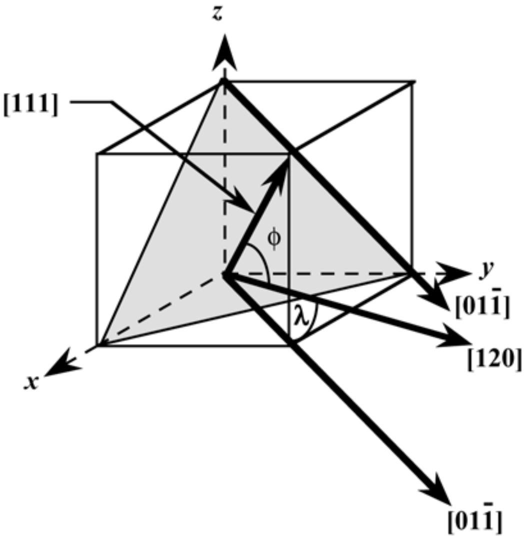
$$|\mathbf{b}| = a(1^2 + 0^2 + 0^2)^{1/2} = a$$

Slip in Single Crystals

7.11 *Sometimes* $\cos\phi\cos\lambda$ *in Equation 7.2 is termed the Schmid factor. Determine the magnitude of the Schmid factor for an FCC single crystal oriented with its [120] direction parallel to the loading axis.*

Solution

We are asked to compute the *Schmid factor* for an FCC crystal oriented with its [120] direction parallel to the loading axis. With this scheme, slip may occur on the (111) plane and in the $[01\bar{1}]$ direction as noted in the figure below.



The angle between the [120] and $[01\bar{1}]$ directions, λ, may be determined using Equation 7.6

$$\lambda = \cos^{-1}\left[\frac{u_1u_2 + v_1v_2 + w_1w_2}{\sqrt{\left(u_1^2 + v_1^2 + w_1^2\right)\left(u_2^2 + v_2^2 + w_2^2\right)}}\right]$$

where (for [120]) $u_1 = 1$, $v_1 = 2$, $w_1 = 0$, and (for $[01\bar{1}]$) $u_2 = 0$, $v_2 = 1$, $w_2 = -1$. Therefore, λ is equal to

$$\lambda = \cos^{-1}\left[\frac{(1)(0) + (2)(1) + (0)(-1)}{\sqrt{\left[(1)^2 + (2)^2 + (0)^2\right]\left[(0)^2 + (1)^2 + (-1)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{2}{\sqrt{10}}\right) = 50.8°$$

Now, the angle ϕ is equal to the angle between the normal to the (111) plane (which is the [111] direction), and the [120] direction. Again from Equation 7.6, and for $u_1 = 1$, $v_1 = 1$, $w_1 = 1$, and $u_2 = 1$, $v_2 = 2$, and $w_2 = 0$, we have

$$\phi = \cos^{-1}\left[\frac{(1)(1) + (1)(2) + (1)(0)}{\sqrt{\left[(1)^2 + (1)^2 + (1)^2\right]\left[(1)^2 + (2)^2 + (0)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{3}{\sqrt{15}}\right) = 39.2°$$

Therefore, the Schmid factor is equal to

$$\cos\phi\cos\lambda = \cos(39.2°)\cos(50.8°) = \left(\frac{3}{\sqrt{15}}\right)\left(\frac{2}{\sqrt{10}}\right) = 0.490$$

7.12 *Consider a metal single crystal oriented such that the normal to the slip plane and the slip direction are at angles of 60° and 35°, respectively, with the tensile axis. If the critical resolved shear stress is 6.2 MPa (900 psi), will an applied stress of 12 MPa (1750 psi) cause the single crystal to yield? If not, what stress will be necessary?*

Solution

This problem calls for us to determine whether or not a metal single crystal having a specific orientation and of given critical resolved shear stress will yield. We are given that ϕ = 60°, λ = 35°, and that the values of the critical resolved shear stress and applied tensile stress are 6.2 MPa (900 psi) and 12 MPa (1750 psi), respectively. From Equation 7.2

$$\tau_R = \sigma \cos\phi \cos\lambda = (12\text{ MPa})(\cos 60°)(\cos 35°) = 4.91\text{ MPa} \quad (717\text{ psi})$$

Since the resolved shear stress (4.91 MPa) is less that the critical resolved shear stress (6.2 MPa), the single crystal will not yield.

However, from Equation 7.4, the stress at which yielding occurs is

$$\sigma_y = \frac{\tau_{\text{crss}}}{\cos\phi \cos\lambda} = \frac{6.2\text{ MPa}}{(\cos 60°)(\cos 35°)} = 15.1\text{ MPa} \quad (2200\text{ psi})$$

7.13 *A single crystal of zinc is oriented for a tensile test such that its slip plane normal makes an angle of 65° with the tensile axis. Three possible slip directions make angles of 30°, 48°, and 78° with the same tensile axis.*

(a) Which of these three slip directions is most favored?

(b) If plastic deformation begins at a tensile stress of 2.5 MPa (355 psi), determine the critical resolved shear stress for zinc.

Solution

We are asked to compute the critical resolved shear stress for Zn. As stipulated in the problem, ϕ = 65°, while possible values for λ are 30°, 48°, and 78°.

(a) Slip will occur along that direction for which (cos ϕ cos λ) is a maximum, or, in this case, for the largest cos λ. Cosines for the possible λ values are given below.

$$\cos(30°) = 0.87$$

$$\cos(48°) = 0.67$$

$$\cos(78°) = 0.21$$

Thus, the slip direction is at an angle of 30° with the tensile axis.

(b) From Equation 7.4, the critical resolved shear stress is just

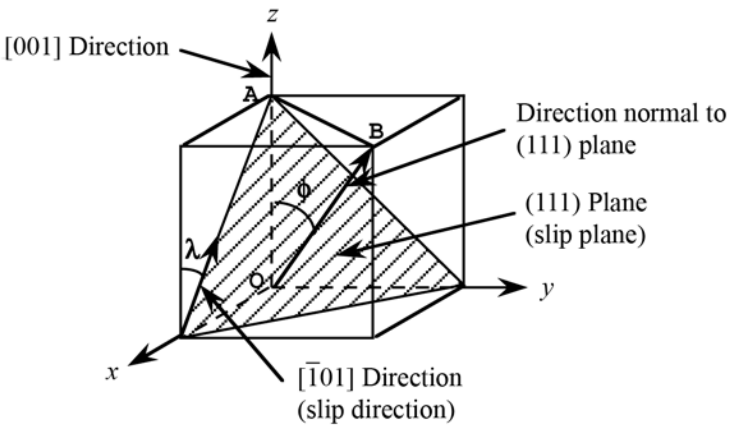
$$\tau_{\text{crss}} = \sigma_y (\cos\phi \cos\lambda)_{\text{max}}$$

$$= (2.5\ \text{MPa}) \left[\cos(65°)\cos(30°)\right] = 0.91\ \text{MPa}\ \ (130\ \text{psi})$$

7.14 *Consider a single crystal of nickel oriented such that a tensile stress is applied along a [001] direction. If slip occurs on a (111) plane and in a* $[\bar{1}01]$ *direction and is initiated at an applied tensile stress of 13.9 MPa (2020 psi), compute the critical resolved shear stress.*

Solution

This problem asks that we compute the critical resolved shear stress for nickel. In order to do this, we must employ Equation 7.4, but first it is necessary to solve for the angles λ and ϕ which are shown in the sketch below.



The angle λ is the angle between the tensile axis—i.e., along the [001] direction—and the slip direction—i.e., $[\bar{1}01]$, and may be determined using Equation 7.6 as

$$\lambda = \cos^{-1}\left[\frac{u_1u_2 + v_1v_2 + w_1w_2}{\sqrt{\left(u_1^2 + v_1^2 + w_1^2\right)\left(u_2^2 + v_2^2 + w_2^2\right)}}\right]$$

where (for [001]) $u_1 = 0$, $v_1 = 0$, $w_1 = 1$, and (for $[\bar{1}01]$) $u_2 = -1$, $v_2 = 0$, $w_2 = 1$. Therefore, λ is equal to

$$\lambda = \cos^{-1}\left[\frac{(0)(-1) + (0)(0) + (1)(1)}{\sqrt{\left[(0)^2 + (0)^2 + (1)^2\right]\left[(-1)^2 + (0)^2 + (1)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{1}{\sqrt{2}}\right) = 45°$$

Furthermore, ϕ is the angle between the tensile axis—the [001] direction—and the normal to the slip plane—i.e., the (111) plane; for this case this normal is along a [111] direction. Therefore, again using Equation 7.6

$$\phi = \cos^{-1}\left[\frac{(0)(1) + (0)(1) + (1)(1)}{\sqrt{\left[(0)^2 + (0)^2 + (1)^2\right]\left[(1)^2 + (1)^2 + (1)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{1}{\sqrt{3}}\right) = 54.7°$$

And, finally, using Equation 7.4, the critical resolved shear stress is equal to

$$\tau_{\text{crss}} = \sigma_y(\cos\phi\,\cos\lambda)$$

$$= (13.9\text{ MPa})\left[\cos(54.7°)\cos(45°)\right]$$

$$= (13.9\text{ MPa})\left(\frac{1}{\sqrt{3}}\right)\left(\frac{1}{\sqrt{2}}\right) = 5.68\text{ MPa}\quad(825\text{ psi})$$

7.15 *A single crystal of a metal that has the FCC crystal structure is oriented such that a tensile stress is applied parallel to the [100] direction. If the critical resolved shear stress for this material is 0.5 MPa, calculate the magnitude(s) of applied stress(es) necessary to cause slip to occur on the (111) plane in each of the* $[1\bar{1}0]$, $[10\bar{1}]$, *and* $[0\bar{1}1]$ *directions.*

Solution

In order to solve this problem it is necessary to employ Equation 7.4, but first we need to solve for the for λ and ϕ angles for the three slip systems.

For each of these three slip systems, the ϕ will be the same—i.e., the angle between the direction of the applied stress, [100] and the normal to the (111) plane, that is, the [111] direction. The angle ϕ may be determined using Equation 7.6 as

$$\phi = \cos^{-1}\left[\frac{u_1u_2 + v_1v_2 + w_1w_2}{\sqrt{\left(u_1^2 + v_1^2 + w_1^2\right)\left(u_2^2 + v_2^2 + w_2^2\right)}}\right]$$

where (for [100]) $u_1 = 1$, $v_1 = 0$, $w_1 = 0$, and (for [111]) $u_2 = 1$, $v_2 = 1$, $w_2 = 1$. Therefore, ϕ is equal to

$$\phi = \cos^{-1}\left[\frac{(1)(1) + (0)(1) + (0)(1)}{\sqrt{\left[(1)^2 + (0)^2 + (0)^2\right]\left[(1)^2 + (1)^2 + (1)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{1}{\sqrt{3}}\right) = 54.7°$$

Let us now determine λ for the $[1\bar{1}0]$ slip direction. Again, using Equation 7.6 where $u_1 = 1$, $v_1 = 0$, $w_1 = 0$ (for [100]), and $u_2 = 1$, $v_2 = -1$, $w_2 = 0$ (for $[1\bar{1}0]$). Therefore, λ is determined as

$$\lambda_{[100]-[1\bar{1}0]} = \cos^{-1}\left[\frac{(1)(1) + (0)(-1) + (0)(0)}{\sqrt{\left[(1)^2 + (0)^2 + (0)^2\right]\left[(1)^2 + (-1)^2 + (0)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{1}{\sqrt{2}}\right) = 45°$$

Now, we solve for the yield strength for this (111)–$[1\bar{1}0]$ slip system using Equation 7.4 as

$$\sigma_y = \frac{\tau_{\mathrm{crss}}}{(\cos\phi\cos\lambda)}$$

$$= \frac{0.5\ \mathrm{MPa}}{\cos(54.7°)\cos(45°)} = \frac{0.5\ \mathrm{MPa}}{(0.578)(0.707)} = 1.22\ \mathrm{MPa}$$

Now, we must determine the value of λ for the (111)–$[10\bar{1}]$ slip system—that is, the angle between the [100] and $[10\bar{1}]$ directions. Again using Equation 7.6

$$\lambda_{[100]-[10\bar{1}]} = \cos^{-1}\left[\frac{(1)(1) + (0)(0) + (0)(-1)}{\sqrt{\left[(1)^2 + (0)^2 + (0)^2\right]\left[(1)^2 + (0)^2 + (-1)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{1}{\sqrt{2}}\right) = 45°$$

Thus, since the values of ϕ and λ for this (111)–$[10\bar{1}]$ slip system are the same as for (111)–$[1\bar{1}0]$, so also will σ_y be the same—viz 1.22 MPa.

And, finally, for the (111)–$[0\bar{1}1]$ slip system, λ is computed using Equation 7.6 as follows:

$$\lambda_{[100]-[0\bar{1}1]} = \cos^{-1}\left[\frac{(1)(0) + (0)(-1) + (0)(1)}{\sqrt{\left[(1)^2 + (0)^2 + (0)^2\right]\left[(0)^2 + (-1)^2 + (1)^2\right]}}\right]$$

$$= \cos^{-1}(0) = 90°$$

Thus, from Equation 7.4, the yield strength for this slip system is

$$\sigma_y = \frac{\tau_{\mathrm{crss}}}{(\cos\phi\cos\lambda)}$$

$$= \frac{0.5\ \mathrm{MPa}}{\cos(54.7°)\ \cos(90°)} = \frac{0.5\ \mathrm{MPa}}{(0.578)\,(0)} = \propto$$

which means that slip will not occur on this (111)–$[0\bar{1}1]$ slip system.

7.16 *(a) A single crystal of a metal that has the BCC crystal structure is oriented such that a tensile stress is applied in the [100] direction. If the magnitude of this stress is 4.0 MPa, compute the resolved shear stress in the* $[1\bar{1}1]$ *direction on each of the (110), (011), and* $(10\bar{1})$ *planes.*

(b) On the basis of these resolved shear stress values, which slip system(s) is (are) most favorably oriented?

Solution

In order to solve this problem it is necessary to employ Equation 7.2, which means that we first need to solve for the for angles λ and ϕ for the three slip systems.

For each of these three slip systems, the λ will be the same—i.e., the angle between the direction of the applied stress, [100] and the slip direction, $[1\bar{1}1]$. This angle λ may be determined using Equation 7.6

$$\lambda = \cos^{-1}\left[\frac{u_1u_2 + v_1v_2 + w_1w_2}{\sqrt{\left(u_1^2 + v_1^2 + w_1^2\right)\left(u_2^2 + v_2^2 + w_2^2\right)}}\right]$$

where (for [100]) $u_1 = 1$, $v_1 = 0$, $w_1 = 0$, and (for $[1\bar{1}1]$) $u_2 = 1$, $v_2 = -1$, $w_2 = 1$. Therefore, λ is determined as

$$\lambda = \cos^{-1}\left[\frac{(1)(1) + (0)(-1) + (0)(1)}{\sqrt{\left[(1)^2 + (0)^2 + (0)^2\right]\left[(1)^2 + (-1)^2 + (1)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{1}{\sqrt{3}}\right) = 54.7°$$

Let us now determine ϕ for the angle between the direction of the applied tensile stress—i.e., the [100] direction—and the normal to the (110) slip plane—i.e., the [110] direction. Again, using Equation 7.6 where $u_1 = 1$, $v_1 = 0$, $w_1 = 0$ (for [100]), and $u_2 = 1$, $v_2 = 1$, $w_2 = 0$ (for [110]), ϕ is equal to

$$\phi_{[100]-[110]} = \cos^{-1}\left[\frac{(1)(1) + (0)(1) + (0)(0)}{\sqrt{\left[(1)^2 + (0)^2 + (0)^2\right]\left[(1)^2 + (1)^2 + (0)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{1}{\sqrt{2}}\right) = 45°$$

Now, using Equation 7.2

$$\tau_R = \sigma \cos\phi \cos\lambda$$

we solve for the resolved shear stress for this slip system as

$$\tau_R(110) - [1\bar{1}1] = (4.0 \text{ MPa})\left[\cos(45°)\cos(54.7°)\right] = (4.0 \text{ MPa})(0.707)(0.578) = 1.63 \text{ MPa}$$

Now, we must determine the value of ϕ for the (011)–$[1\bar{1}1]$ slip system—that is, the angle between the direction of the applied stress, [100], and the normal to the (011) plane—i.e., the [011] direction. Again using Equation 7.6

$$\lambda_{[100]-[011]} = \cos^{-1}\left[\frac{(1)(0) + (0)(1) + (0)(1)}{\sqrt{\left[(1)^2 + (0)^2 + (0)^2\right]\left[(0)^2 + (1)^2 + (1)^2\right]}}\right]$$

$$= \cos^{-1}(0) = 90°$$

Thus, the resolved shear stress for this (011)–$[1\bar{1}1]$ slip system is

$$\tau_R(011) - [111] = = (4.0 \text{ MPa})\left[\cos(90°)\cos(54.7°)\right] = (4.0 \text{ MPa})(0)(0.578) = 0 \text{ MPa}$$

And, finally, it is necessary to determine the value of ϕ for the $(10\bar{1})$–$[1\bar{1}1]$ slip system—that is, the angle between the direction of the applied stress, [100], and the normal to the $(10\bar{1})$ plane—i.e., the $[10\bar{1}]$ direction. Again using Equation 7.6

$$\lambda_{[100]-[10\bar{1}]} = \cos^{-1}\left[\frac{(1)(1) + (0)(0) + (0)(-1)}{\sqrt{\left[(1)^2 + (0)^2 + (0)^2\right]\left[(1)^2 + (0)^2 + (-1)^2\right]}}\right]$$

$$= \cos^{-1}\left(\frac{1}{\sqrt{2}}\right) = 45°$$

Here, as with the (110)–$[1\bar{1}1]$ slip system above, the value of ϕ is 45°, which again leads to

$$\tau_R(101) - [111] = (4.0 \text{ MPa})\left[\cos(45°)\cos(54.7°)\right] = (4.0 \text{ MPa})(0.707)(0.578) = 1.63 \text{ MPa}$$

(b) The most favored slip system(s) is (are) the one(s) that has (have) the largest τ_R value. Both (110)–$[1\bar{1}1]$ and $(10\bar{1}) - [1\bar{1}1]$ slip systems are most favored since they have the same τ_R (1.63 MPa), which is greater than the τ_R value for $(011) - [1\bar{1}1]$ (viz., 0 MPa)

7.17 *Consider a single crystal of some hypothetical metal that has the BCC crystal structure and is oriented such that a tensile stress is applied along a [121] direction. If slip occurs on a (101) plane and in a* $[\bar{1}11]$ *direction, compute the stress at which the crystal yields if its critical resolved shear stress is 2.4 MPa.*

Solution

To solve this problem we use Equation 7.4; however it is first necessary to determine the values of ϕ and λ. These determinations are possible using Equation 7.6. Now, λ is the angle between [121] and $[\bar{1}11]$ directions. Therefore, relative to Equation 7.6 let us take $u_1 = 1$, $v_1 = 2$, and $w_1 = 1$, as well as $u_2 = -1$, $v_2 = 1$, and $w_2 = 1$. This leads to

$$\lambda = \cos^{-1}\left[\frac{u_1u_2 + v_1v_2 + w_1w_2}{\sqrt{\left(u_1^2 + v_1^2 + w_1^2\right)\left(u_2^2 + v_2^2 + w_2^2\right)}}\right]$$

$$= \cos^{-1}\left\{\frac{(1)(-1) + (2)(1) + (1)(1)}{\sqrt{\left[(1)^2 + (2)^2 + (1)^2\right]\left[(-1)^2 + (1)^2 + (1)^2\right]}}\right\}$$

$$= \cos^{-1}\left(\frac{2}{\sqrt{18}}\right) = 61.9°$$

Now for the determination of ϕ, the normal to the (101) slip plane is the [101] direction. Again using Equation 7.6, where we now take $u_1 = 1$, $v_1 = 2$, $w_1 = 1$ (for [121]), and $u_2 = 1$, $v_2 = 0$, $w_2 = 1$ (for [101]). Thus,

$$\phi = \cos^{-1}\left\{\frac{(1)(1) + (2)(0) + (1)(1)}{\sqrt{\left[(1)^2 + (2)^2 + (1)^2\right]\left[(1)^2 + (0)^2 + (1)^2\right]}}\right\}$$

$$= \cos^{-1}\left(\frac{2}{\sqrt{12}}\right) = 54.7°$$

It is now possible to compute the yield stress (using Equation 7.4) as

$$\sigma_y = \frac{\tau_{\text{crss}}}{\cos\phi \cos\lambda} = \frac{2.4 \text{ MPa}}{\left(\frac{2}{\sqrt{12}}\right)\left(\frac{2}{\sqrt{18}}\right)} = 8.82 \text{ MPa}$$

7.18 *Consider a single crystal of some hypothetical metal that has the FCC crystal structure and is oriented such that a tensile stress is applied along a [112] direction. If slip occurs on a (111) plane and in a [011] direction, and the crystal yields at a stress of 5.12 MPa compute the critical resolved shear stress.*

Solution

To solve this problem we use Equation 7.4; however it is first necessary to determine the values of ϕ and λ. These determinations are possible using Equation 7.6. Now, λ is the angle between [112] and [011] directions. Therefore, relative to Equation 7.6 let us take $u_1 = 1$, $v_1 = 1$, and $w_1 = 2$, as well as $u_2 = 0$, $v_2 = 1$, and $w_2 = 1$. This leads to

$$\lambda = \cos^{-1}\left[\frac{u_1u_2 + v_1v_2 + w_1w_2}{\sqrt{\left(u_1^2 + v_1^2 + w_1^2\right)\left(u_2^2 + v_2^2 + w_2^2\right)}}\right]$$

$$= \cos^{-1}\left\{\frac{(1)(0) + (1)(1) + (2)(1)}{\sqrt{\left[(1)^2 + (1)^2 + (2)^2\right]\left[(0)^2 + (1)^2 + (1)^2\right]}}\right\}$$

$$= \cos^{-1}\left(\frac{3}{\sqrt{12}}\right) = 30°$$

Now for the determination of ϕ, the normal to the (111) slip plane is the [111] direction. Again using Equation 7.6, where we now take $u_1 = 1$, $v_1 = 1$, $w_1 = 2$ (for [112]), and $u_2 = 1$, $v_2 = 1$, $w_2 = 1$ (for [111]). Thus,

$$\phi = \cos^{-1}\left\{\frac{(1)(1) + (1)(1) + (2)(1)}{\sqrt{\left[(1)^2 + (1)^2 + (2)^2\right]\left[(1)^2 + (1)^2 + (1)^2\right]}}\right\}$$

$$= \cos^{-1}\left(\frac{4}{\sqrt{18}}\right) = 19.5°$$

It is now possible to compute the critical resolved shear stress (using Equation 7.4) as

$$\tau_{\text{crss}} = \sigma_y(\cos\phi \cos\lambda)$$

$$= (5.12\ \text{MPa})\left(\frac{4}{\sqrt{18}}\right)\left(\frac{3}{\sqrt{12}}\right) = 4.18\ \text{MPa}$$

7.19 *The critical resolved shear stress for copper (Cu) is 0.48 MPa (70 psi). Determine the maximum possible yield strength for a single crystal of Cu pulled in tension.*

Solution

In order to determine the maximum possible yield strength for a single crystal of Cu pulled in tension, we simply employ Equation 7.5 as

$$\sigma_y = 2\tau_{\text{crss}} = (2)(0.48\ \text{MPa}) = 0.96\ \text{MPa} \quad (140\ \text{psi})$$

Deformation by Twinning

7.20 *List four major differences between deformation by twinning and deformation by slip relative to mechanism, conditions of occurrence, and final result.*

Solution

Four major differences between deformation by twinning and deformation by slip are as follows: (1) with slip deformation there is no crystallographic reorientation, whereas with twinning there is a reorientation; (2) for slip, the atomic displacements occur in atomic spacing multiples, whereas for twinning, these displacements may be other than by atomic spacing multiples; (3) slip occurs in metals having many slip systems, whereas twinning occurs in metals having relatively few slip systems; and (4) normally slip results in relatively large deformations, whereas only small deformations result for twinning.

Strengthening by Grain Size Reduction

7.21 *Briefly explain why small-angle grain boundaries are not as effective in interfering with the slip process as are high-angle grain boundaries.*

Solution

Small-angle grain boundaries are not as effective in interfering with the slip process as are high-angle grain boundaries because there is not as much crystallographic misalignment in the grain boundary region for small-angle, and therefore not as much change in slip direction.

7.22 *Briefly explain why HCP metals are typically more brittle than FCC and BCC metals.*

Solution

Hexagonal close packed metals are typically more brittle than FCC and BCC metals because there are fewer slip systems in HCP.

7.23 *Describe in your own words the three strengthening mechanisms discussed in this chapter (i.e., grain size reduction, solid-solution strengthening, and strain hardening). Explain how dislocations are involved in each of the strengthening techniques.*

Solution

These three strengthening mechanisms are described in Sections 7.8, 7.9, and 7.10.

7.24 *(a) From the plot of yield strength versus (grain diameter)*$^{-1/2}$ *for a 70 Cu–30 Zn cartridge brass in Figure 7.15, determine values for the constants* σ_0 *and* k_y *in Equation 7.7.*

(b) Now predict the yield strength of this alloy when the average grain diameter is 2.0×10^{-3} *mm.*

Solution

(a) Perhaps the easiest way to solve for σ_0 and k_y in Equation 7.7 is to pick two values each of σ_y and $d^{-1/2}$ from Figure 7.15, and then solve two simultaneous equations, which may be set up. For example

$d^{-1/2}$ (mm)$^{-1/2}$	σ_y (MPa)
4	75
12	175

The two equations are thus

$$75 = \sigma_0 + 4k_y$$

$$175 = \sigma_0 + 12k_y$$

Simultaneous solution of these equations yield the values of

$$k_y = 12.5\ \text{MPa(mm)}^{1/2}\ \left[1810\ \text{psi(mm)}^{1/2}\right]$$

$$\sigma_0 = 25\ \text{MPa}\ \ (3630\ \text{psi})$$

(b) When $d = 2.0 \times 10^{-3}$ mm, $d^{-1/2} = 22.4$ mm$^{-1/2}$, and, using Equation 7.7,

$$\sigma_y = \sigma_0 + k_y d^{-1/2}$$

$$= (25\ \text{MPa}) + \left[12.5\ \text{MPa(mm)}^{1/2}\right]\left(22.4\ \text{mm}^{-1/2}\right) = 305\ \text{MPa}\ \ (44{,}200\ \text{psi})$$

7.25 *The lower yield point for an iron that has an average grain diameter of* 1×10^{-2} *mm is 230 MPa (33,000 psi). At a grain diameter of* 6×10^{-3} *mm, the yield point increases to 275 MPa (40,000 psi). At what grain diameter will the lower yield point be 310 MPa (45,000 psi)?*

Solution

The best way to solve this problem is to first establish two simultaneous expressions of Equation 7.7, solve for σ_0 and k_y, and finally determine the value of d when σ_y = 310 MPa. The data pertaining to this problem may be tabulated as follows:

σ_y	d (mm)	$d^{-1/2}$ (mm)$^{-1/2}$
230 MPa	1×10^{-2}	10.0
275 MPa	6×10^{-3}	12.91

The two equations thus become

$$230 \text{ MPa} = \sigma_0 + (10.0)\, k_y$$

$$275 \text{ MPa} = \sigma_0 + (12.91)\, k_y$$

Solving these two simultaneous equations leads to σ_0 = 75.4 MPa and k_y = 15.46 MPa(mm)$^{1/2}$. At a yield strength of 310 MPa

$$310 \text{ MPa} = 75.4 \text{ MPa} + \left[15.46 \text{ MPa(mm)}^{1/2}\right] d^{-1/2}$$

Or

$$d^{-1/2} = \frac{310 \text{ MPa} - 75.4 \text{ MPa}}{15.46 \text{ MPa(mm)}^{1/2}} = 15.17 \text{ mm}^{-1/2}$$

Thus,

$$d = \left[\frac{15.46 \text{ MPa(mm)}^{1/2}}{310 \text{ MPa} - 75.4 \text{ MPa}}\right]^2 = 4.34 \times 10^{-3} \text{ mm}$$

7.26 *If it is assumed that the plot in Figure 7.15 is for non-cold-worked brass, determine the grain size of the alloy in Figure 7.19; assume its composition is the same as the alloy in Figure 7.15.*

Solution

From Figure 7.19*a*, the yield strength of brass at 0%CW is approximately 175 MPa (26,000 psi). This yield strength from Figure 7.15 corresponds to a $d^{-1/2}$ value of approximately 12.0 (mm) $^{-1/2}$. Thus,

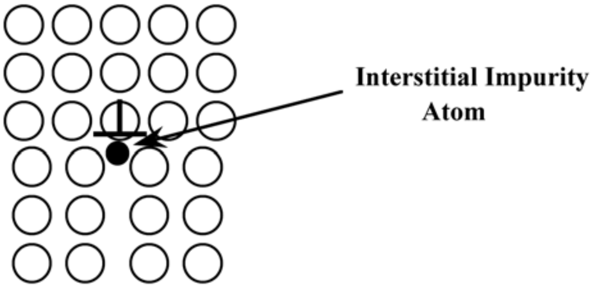
$$d = \frac{1}{\left[12.0 \text{ (mm)}^{-1/2}\right]^2} = 6.94 \times 10^{-3} \text{ mm}$$

Solid-Solution Strengthening

7.27 *In the manner of Figures 7.17b and 7.18b, indicate the location in the vicinity of an edge dislocation at which an interstitial impurity atom would be expected to be situated. Now briefly explain in terms of lattice strains why it would be situated at this position.*

<u>Solution</u>

Below is shown an edge dislocation and where an interstitial impurity atom would be located. Compressive lattice strains are introduced by the impurity atom. There will be a net reduction in lattice strain energy when these lattice strains partially cancel tensile strains associated with the edge dislocation; such tensile strains exist just below the bottom of the extra half-plane of atoms (Figure 7.4).



Strain Hardening

7.28 *(a) Show, for a tensile test, that*

$$\%\mathrm{CW} = \left(\frac{\varepsilon}{\varepsilon + 1}\right) \times 100$$

if there is no change in specimen volume during the deformation process (i.e., $A_0 l_0 = A_d l_d$).

(b) Using the result of part (a), compute the percent cold work experienced by naval brass (for which the stress–strain behavior is shown in Figure 6.12) when a stress of 415 MPa (60,000 psi) is applied.

Solution

(a) We are asked to show, for a tensile test, that

$$\%\mathrm{CW} = \left(\frac{\varepsilon}{\varepsilon + 1}\right) \times 100$$

From Equation 7.8

$$\%\mathrm{CW} = \left(\frac{A_0 - A_d}{A_0}\right) \times 100 = \left(1 - \frac{A_d}{A_0}\right) \times 100$$

The following relationship

$$A_0 l_0 = A_d l_d$$

may be rearranged to read as follows:

$$\frac{A_d}{A_0} = \frac{l_0}{l_d}$$

Substitution of the right-hand-side of this expression into the above equation for %CW leads to

$$\%\mathrm{CW} = \left(1 - \frac{l_0}{l_d}\right) \times 100$$

Now, from the definition of engineering strain (Equation 6.2)

$$\varepsilon = \frac{l_d - l_0}{l_0} = \frac{l_d}{l_0} - 1$$

Or, upon rearrangement

$$\frac{l_0}{l_d} = \frac{1}{\varepsilon + 1}$$

Substitution of this expression for l_0/l_d into the %CW expression above gives

$$\%\text{CW} = \left(1 - \frac{l_0}{l_d}\right) \times 100 = \left(1 - \frac{1}{\varepsilon + 1}\right) \times 100 = \left(\frac{\varepsilon}{\varepsilon + 1}\right) \times 100$$

the desired equation

(b) From Figure 6.12, a stress of 415 MPa (60,000 psi) corresponds to a strain of 0.15. Using the above expression

$$\%\text{CW} = \left(\frac{\varepsilon}{\varepsilon + 1}\right) \times 100 = \left(\frac{0.15}{0.15 + 1.00}\right) \times 100 = 13.0\%\text{CW}$$

7.29 *Two previously undeformed cylindrical specimens of an alloy are to be strain hardened by reducing their cross-sectional areas (while maintaining their circular cross sections). For one specimen, the initial and deformed radii are 15 and 12 mm, respectively. The second specimen, with an initial radius of 11 mm, must have the same deformed hardness as the first specimen; compute the second specimen's radius after deformation.*

Solution

In order for these two cylindrical specimens to have the same deformed hardness, they must be deformed to the same percent cold work. For the first specimen

$$\%\mathrm{CW} = \left(\frac{A_0 - A_d}{A_0}\right) \times 100 = \left(\frac{\pi r_0^2 - \pi r_d^2}{\pi r_0^2}\right) \times 100$$

in which r_0 and r_d denote the original and deformed specimen radii, respectively. Substitution of the values for these two parameters provided in the problem statement leads to the following:

$$\%\mathrm{CW} = \left(\frac{\pi r_0^2 - \pi r_d^2}{\pi r_0^2}\right) \times 100 = = \frac{\pi(15\text{ mm})^2 - \pi(12\text{ mm})^2}{\pi(15\text{ mm})^2} \times 100 = 36\%\mathrm{CW}$$

For the second specimen, the deformed radius is computed using the above equation for %CW and solving for r_d as

$$r_d = r_0\sqrt{1 - \frac{\%\mathrm{CW}}{100}}$$

And insertion of the value of %CW determined above (i.e., 36%CW) and the r_0 (11 mm) for the second specimen leads to

$$r_d = (11\text{ mm})\sqrt{1 - \frac{36\%\mathrm{CW}}{100}} = 8.80\text{ mm}$$

7.30 *Two previously undeformed specimens of the same metal are to be plastically deformed by reducing their cross-sectional areas. One has a circular cross section, and the other is rectangular; during deformation the circular cross section is to remain circular, and the rectangular is to remain as rectangular. Their original and deformed dimensions are as follows:*

	Circular (diameter, mm)	***Rectangular (mm)***
Original dimensions	*18.0*	*20 × 50*
Deformed dimensions	*15.9*	*13.7 × 55.1*

Which of these specimens will be the hardest after plastic deformation, and why?

Solution

The hardest specimen will be the one that has experienced the greatest degree of cold work. Therefore, all we need do is to compute the %CW for each specimen using Equation 7.8. For the circular one

$$\%\mathrm{CW} = \left(\frac{A_0 - A_d}{A_0}\right) \times 100$$

$$= \left(\frac{\pi r_0^2 - \pi r_d^2}{\pi r_0^2}\right) \times 100$$

$$= \left[\frac{\pi\left(\dfrac{18.0\ \mathrm{mm}}{2}\right)^2 - \pi\left(\dfrac{15.9\ \mathrm{mm}}{2}\right)^2}{\pi\left(\dfrac{18.0\ \mathrm{mm}}{2}\right)^2}\right] \times 100 = 22.0\%\mathrm{CW}$$

While, for the rectangular one (using *l* and *w* to designate specimen length and width, respectively:

$$\%\mathrm{CW} = \left(\frac{w_0 l_0 - w_d l_d}{w_0 l_0}\right) \times 100$$

$$= \left[\frac{(20\ \mathrm{mm})(50\ \mathrm{mm}) - (13.7\ \mathrm{mm})(55.1\ \mathrm{mm})}{(20\ \mathrm{mm})(50\ \mathrm{mm})}\right] \times 100 = 24.5\%\mathrm{CW}$$

Therefore, the deformed rectangular specimen will be harder since it has the greater %CW.

7.31 *A cylindrical specimen of cold-worked copper has a ductility (%EL) of 15%. If its cold-worked radius is 6.4 mm (0.25 in.), what was its radius before deformation?*

Solution

This problem calls for us to calculate the precold-worked radius of a cylindrical specimen of copper that has a cold-worked ductility of 15%EL. From Figure 7.19*c*, copper that has a ductility of 15%EL will have experienced a deformation of about 20%CW. For a cylindrical specimen, Equation 7.8 becomes

$$\%\mathrm{CW} = \left(\frac{\pi r_0^2 - \pi r_d^2}{\pi r_0^2}\right) \times 100$$

Since r_d = 6.4 mm (0.25 in.), solving for r_0 yields

$$r_0 = \frac{r_d}{\sqrt{1 - \dfrac{\%\mathrm{CW}}{100}}} = \frac{6.4\ \mathrm{mm}}{\sqrt{1 - \dfrac{20.0}{100}}} = 7.2\ \mathrm{mm}\quad (0.280\ \mathrm{in.})$$

7.32 *(a) What is the approximate ductility (%EL) of a brass that has a yield strength of 345 MPa (50,000 psi)?*

(b) What is the approximate Brinell hardness of a 1040 steel having a yield strength of 620 MPa (90,000 psi)?

Solution

In order to solve this part of the problem, it is necessary to consult Figures 7.19*a* and 7.19*c*. From Figure 7.19*a*, a yield strength of 345 MPa for brass corresponds to 20%CW. A brass that has been cold-worked 20% will have a ductility of about 24%EL (Figure 7.19*c*).

(b) This portion of the problem asks for the Brinell hardness of a 1040 steel having a yield strength of 620 MPa (90,000 psi). From Figure 7.19*a*, a yield strength of 620 MPa for a 1040 steel corresponds to about 5%CW. A 1040 steel that has been cold worked 5% will have a tensile strength of about 750 MPa (Figure 7.19*b*). Finally, using Equation 6.20a

$$\mathrm{HB} = \frac{TS(\mathrm{MPa})}{3.45} = \frac{750\ \mathrm{MPa}}{3.45} = 217$$

7.33 *Experimentally, it has been observed for single crystals of a number of metals that the critical resolved shear stress* τ_{crss} *is a function of the dislocation density* ρ_D *as*

$$\tau_{\mathrm{crss}} = \tau_0 + A\sqrt{\rho_{\mathrm{D}}}$$

where τ_0 *and A are constants. For copper, the critical resolved shear stress is 0.69 MPa (100 psi) at a dislocation density of* 10^4 mm^{-2}*. If it is known that the value of* τ_0 *for copper is 0.069 MPa (10 psi), compute* τ_{crss} *at a dislocation density of* 10^6 mm^{-2}*.*

Solution

We are asked in this problem to compute the critical resolved shear stress at a dislocation density of 10^6 mm^{-2}. It is first necessary to compute the value of the constant *A* (in the equation provided in the problem statement) from the one set of data as

$$A = \frac{\tau_{\mathrm{crss}} - \tau_0}{\sqrt{\rho_D}} = \frac{0.69\ \mathrm{MPa} - 0.069\ \mathrm{MPa}}{\sqrt{10^4\ \mathrm{mm}^{-2}}} = 6.21 \times 10^{-3}\ \mathrm{MPa\text{-}mm}\ \ (0.90\ \mathrm{psi\text{-}mm})$$

Now, since we know the values for *A* and τ_0, it is possible to compute the critical resolved shear stress at a dislocation density of 10^6 mm^{-2} as follows:

$$\tau_{\mathrm{crss}} = \tau_0 + A\sqrt{\rho_D}$$

$$= (0.069\ \mathrm{MPa}) + (6.21 \times 10^{-3}\ \mathrm{MPa\text{-}mm})\sqrt{10^6\,\mathrm{mm}^{-2}} = 6.28\ \mathrm{MPa}\ \ (910\ \mathrm{psi})$$

Recovery

Recrystallization

Grain Growth

7.34 *Briefly cite the differences between the recovery and recrystallization processes.*

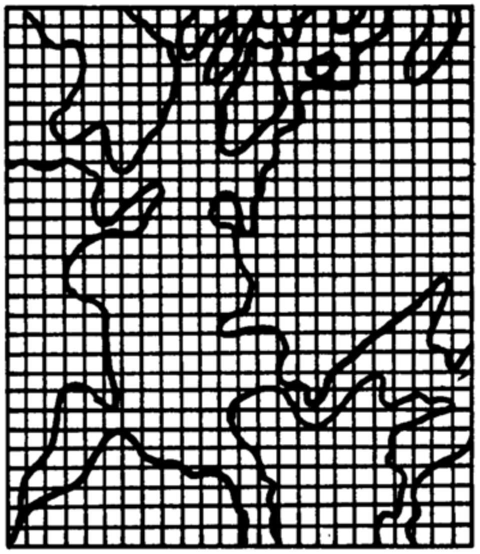
Solution

For recovery, there is some relief of internal strain energy by dislocation motion; however, there are virtually no changes in either the grain structure or mechanical characteristics. During recrystallization, on the other hand, a new set of strain-free grains forms, and the material becomes softer and more ductile.

7.35 *Estimate the fraction of recrystallization from the photomicrograph in Figure 7.21c.*

Solution

We are asked to estimate the fraction of recrystallization from the photomicrograph in Figure 7.21*c*. Below is shown a square grid onto which is superimposed the recrystallized regions from the micrograph. Approximately 400 squares lie within the recrystallized areas, and since there are 672 total squares, the specimen is about 60% recrystallized.



7.36 *Explain the differences in grain structure for a metal that has been cold worked and one that has been cold worked and then recrystallized.*

Solution

During cold-working, the grain structure of the metal has been distorted to accommodate the deformation. Recrystallization produces grains that are equiaxed and smaller than the parent grains.

7.37 *(a) What is the driving force for recrystallization?*

(b) What is the driving force for grain growth?

Solution

(a) The driving force for recrystallization is the difference in internal energy between the strained and unstrained material.

(b) The driving force for grain growth is the reduction in grain boundary energy as the total grain boundary area decreases.

7.38 *(a) From Figure 7.25, compute the length of time required for the average grain diameter to increase from 0.03 to 0.3 mm at 600°C for this brass material.*

(b) Repeat the calculation, this time using 700° C.

Solution

(a) From Figure 7.25, (and realizing that both axes are scaled logarithmly) at 600°C, the time necessary for the average grain diameter to grow to 0.03 is about 6 min; and the total time to grow to 0.3 mm is approximately 3000 min. Therefore, the time to grow from 0.03 to 0.3 mm is 3000 min – 6 min, or approximately 3000 min.

(b) At 700°C the time required for this same grain size increase is approximately 80 min.

7.39 *Consider a hypothetical material that has a grain diameter of 2.1 × 10^{-2} mm. After a heat treatment at 600°C for 3 h, the grain diameter has increased to 7.2 × 10^{-2} mm. Compute the grain diameter when a specimen of this same original material (i.e., d_0 = 2.1 × 10^{-2} mm) is heated for 1.7 h at 600°C. Assume the n grain diameter exponent has a value of 2.*

Solution

To solve this problem requires that we use Equation 7.9 with $n = 2$. It is first necessary to solve for the parameter K in this equation, using values given in the problem statement of d_0 (2.1 × 10^{-2} mm) and the grain diameter after the 3-h heat treatment (7.2 × 10^{-2} mm). The computation for K using a rearranged form of Equation 7.9 in which K becomes the dependent parameter is as follows:

$$K = \frac{d^2 - d_0^2}{t}$$

$$= \frac{(7.2 \times 10^{-2}\ \text{mm})^2 - (2.1 \times 10^{-2}\ \text{mm})^2}{3\ \text{h}}$$

$$= 1.58 \times 10^{-3}\ \text{mm}^2/\text{h}$$

It is now possible to solve for the value of d after a heat treatment of 1.7 h using a rearranged form of Equation 7.9:

$$d = \sqrt{d_0^2 + Kt}$$

$$= \sqrt{(2.1 \times 10^{-2}\ \text{mm})^2 + (1.58 \times 10^{-3}\ \text{mm}^2/\text{h})(1.7\ \text{h})}$$

$$= 5.59 \times 10^{-2}\ \text{mm}$$

7.40 *A hypothetical metal alloy has a grain diameter of 1.7 × 10^{-2} mm. After a heat treatment at 450°C for 250 min the grain diameter has increased to 4.5 × 10^{-2} mm. Compute the time required for a specimen of this same material (i.e., d_0 = 1.7 × 10^{-2} mm) to achieve a grain diameter of 8.7 × 10^{-2} mm while being heated at 450°C. Assume the n grain diameter exponent has a value of 2.1.*

Solution

To solve this problem requires that we use Equation 7.9 with n = 2.1. It is first necessary to solve for the parameter K in this equation, using values given in the problem statement of d_0 (1.7 × 10^{-2} mm) and the grain diameter after the 250-min heat treatment (4.5 × 10^{-2} mm). The computation for K using a rearranged form of Equation 7.9 in which K becomes the dependent parameter is as follows:

$$K = \frac{d^{2.1} - d_0^{2.1}}{t}$$

$$= \frac{(4.5 \times 10^{-2}\ \text{mm})^{2.1} - (1.7 \times 10^{-2}\ \text{mm})^{2.1}}{250\ \text{min}}$$

$$= 5.17 \times 10^{-6}\ \text{mm}^{2.1}/\text{min}$$

It is now possible to solve for the time required to yield a value of 8.7 × 10^{-2} mm for d using a rearranged form of Equation 7.9:

$$t = \frac{d^{2.1} - d_0^{2.1}}{K}$$

$$= \frac{(8.7 \times 10^{-2}\ \text{mm})^{2.1} - (1.7 \times 10^{-2}\ \text{mm})^{2.1}}{5.17 \times 10^{-6}\ \text{mm}^{2.1}/\text{min}}$$

$$= 1110\ \text{min}$$

7.41 *The average grain diameter for a brass material was measured as a function of time at 650°C, which is shown in the following table at two different times:*

Time (min)	*Grain Diameter (mm)*
40	*5.6×10^{-2}*
100	*8.0×10^{-2}*

(a) What was the original grain diameter?

(b) What grain diameter would you predict after 200 min at 650°C?

Solution

(a) Using the data given and Equation 7.9 (taking $n = 2$)—that is

$$d^2 - d_0^2 = Kt$$

we may set up two simultaneous equations with d_0 and K as unknowns, as follows:

$$(5.6 \times 10^{-2} \text{ mm})^2 - d_0^2 = (40 \text{ min})K$$

$$(8.0 \times 10^{-2} \text{ mm})^2 - d_0^2 = (100 \text{ min})K$$

Solution of these expressions yields a value for d_0, the original grain diameter, of

$$d_0 = 0.031 \text{ mm},$$

and a value for K of

$$K = 5.44 \times 10^{-5} \text{ mm}^2/\text{min}$$

(b) At 200 min, the diameter d is computed using a rearranged form of Equation 7.9 (incorporating values of d_0 and K that were just determined) as follows:

$$d = \sqrt{d_0^2 + Kt}$$

$$= \sqrt{(0.031 \text{ mm})^2 + (5.44 \times 10^{-5} \text{ mm}^2/\text{min})(200 \text{ min})}$$

$$= 0.109 \text{ mm}$$

7.42 *An undeformed specimen of some alloy has an average grain diameter of 0.050 mm. You are asked to reduce its average grain diameter to 0.020 mm. Is this possible? If so, explain the procedures you would use and name the processes involved. If it is not possible, explain why.*

Solution

Yes, it is possible to reduce the average grain diameter of an undeformed alloy specimen from 0.050 mm to 0.020 mm. In order to do this, plastically deform the material at room temperature (i.e., cold work it), and then anneal at an elevated temperature in order to allow recrystallization and some grain growth to occur until the average grain diameter is 0.020 mm.

7.43 *Grain growth is strongly dependent on temperature (i.e., rate of grain growth increases with increasing temperature), yet temperature is not explicitly included in Equation 7.9.*

(a) Into which of the parameters in this expression would you expect temperature to be included?

(b) On the basis of your intuition, cite an explicit expression for this temperature dependence.

Solution

(a) The temperature dependence of grain growth is incorporated into the constant K in Equation 7.9.

(b) The explicit expression for this temperature dependence is of the form

$$K = K_0 \exp\left(-\frac{Q}{RT}\right)$$

in which K_0 is a temperature-independent constant, the parameter Q is an activation energy, and R and T are the gas constant and absolute temperature, respectively.

7.44 *A non-cold-worked brass specimen of average grain size 0.01 mm has a yield strength of 150 MPa (21,750 psi). Estimate the yield strength of this alloy after it has been heated to 500°C for 1000 s, if it is known that the value of σ_0 is 25 MPa (3625 psi).*

Solution

This problem calls for us to calculate the yield strength of a brass specimen after it has been heated to an elevated temperature at which grain growth was allowed to occur; the yield strength (150 MPa) was given at a grain size of 0.01 mm. It is first necessary to calculate the constant k_y in Equation 7.7, using values for σ_y (150 MPa), σ_0 (25 MPa), and d (0.01 mm), and as follows:

$$k_y = \frac{\sigma_y - \sigma_0}{d^{-1/2}}$$

$$= \frac{150 \text{ MPa} - 25 \text{ MPa}}{(0.01 \text{ mm})^{-1/2}}$$

$$= 12.5 \text{ MPa-mm}^{1/2}$$

Next, we must determine the average grain size after the heat treatment. From Figure 7.25 at 500°C after 1000 s (16.7 min) the average grain size of a brass material is about 0.016 mm. Therefore, calculating σ_y at this new grain size using Equation 7.7 we get

$$\sigma_y = \sigma_0 + k_y d^{-1/2}$$

$$= 25 \text{ MPa} + \left(12.5 \text{ MPa-mm}^{1/2}\right)(0.016 \text{ mm})^{-1/2}$$

$$= 124 \text{ MPa } (18{,}000 \text{ psi})$$

7.45 *The following yield strength, grain diameter, and heat treatment time (for grain growth) data were gathered for an iron specimen that was heat treated at 800°C. Using these data compute the yield strength of a specimen that was heated at 800°C for 3 h. Assume a value of 2 for n, the grain diameter exponent.*

Grain diameter (mm)	***Yield Strength (MPa)***	***Heat Treating Time (h)***
0.028	300	10
0.010	385	1

Solution

This problem is solved using the following steps:

1. From data given in the problem statement, determine values of d_0 and K in Equation 7.9.
2. Using these data, compute the value of d after the heat treatment (800°C for 3 h).
3. From data provided in the problem statement, determine values of σ_0 and k_y in Equation 7.7.
4. Calculate the value of σ_y using Equation 7.7 incorporating the d value determined in step 2.

Step 1

Using grain diameter-heat treating time data provided in the problem statement, we set up two simultaneous expressions of Equation 7.9—i.e.,

$$d^2 - d_0^2 = Kt$$

as follows:

$$(0.028 \text{ mm})^2 - d_0^2 = K(10 \text{ h})$$

$$(0.010 \text{ mm})^2 - d_0^2 = K(1 \text{ h})$$

From these expressions it is possible to solve for values of d_0 and K:

d_0 = 0.0049 mm

$K = 7.60 \times 10^{-5}$ mm^2/h

Step 2

We now compute the grain size d after the three-hour heat treatment using a rearranged form of Equation 7.9 and the above values for d_0 and K as follows:

$$d = \sqrt{Kt + d_0^2}$$

$$= \sqrt{(7.60 \times 10^{-5}\ \mathrm{mm}^2/\mathrm{h})(3\ \mathrm{h}) + (0.0049\ \mathrm{mm})^2}$$

$$= 0.0159\ \mathrm{mm}$$

Step 3

Using grain diameter-yield strength data provided in the problem statement, we set up two simultaneous expressions of Equation 7.7—i.e.,

$$\sigma_y = \sigma_0 + k_y d^{-1/2}$$

as follows:

$$300\ \mathrm{MPa} = \sigma_0 + k_y (0.028\ \mathrm{mm})^{-1/2}$$

$$385\ \mathrm{MPa} = \sigma_0 + k_y (0.010\ \mathrm{mm})^{-1/2}$$

from which we determine values for k_y and σ_0; these values are as follows:

$k_y = 21.25$ MPa-mm$^{1/2}$

$\sigma_0 = 172.5$ MPa

Step 4

Finally, it is possible to calculate the value of σ_y using Equation 7.7 incorporating the d value determined in step 2. Thus,

$$\sigma_y = \sigma_0 + k_y d^{-1/2}$$

$$= 172.5\ \mathrm{MPa} + (21.25\ \mathrm{MPa} \cdot \mathrm{mm}^{1/2})(0.0159\ \mathrm{mm})^{-1/2}$$

$$= 341\ \mathrm{MPa}$$

DESIGN PROBLEMS

Strain Hardening

Recrystallization

7.D1 *Determine whether it is possible to cold work steel so as to give a minimum Brinell hardness of 240 and at the same time have a ductility of at least 15%EL. Justify your answer.*

Solution

This problem calls for us to determine whether it is possible to cold work steel so as to give a minimum Brinell hardness of 240 and a ductility of at least 15%EL. According to Figure 6.19, a Brinell hardness of 240 corresponds to a tensile strength of 800 MPa (116,000 psi). Furthermore, from Figure 7.19*b*, in order to achieve a tensile strength of 800 MPa, deformation of at least 13%CW is necessary. Finally, if we cold work the steel to 13%CW, then the ductility is 15%EL from Figure 7.19*c*. Therefore, it *is possible* to meet both of these criteria by plastically deforming the steel.

7.D2 *Determine whether it is possible to cold work brass so as to give a minimum Brinell hardness of 150 and at the same time have a ductility of at least 20%EL. Justify your answer.*

Solution

We are asked to determine whether it is possible to cold work brass so as to give a minimum Brinell hardness of 150 and at the same time have a ductility of at least 20%EL. According to Figure 6.19, for brass, a Brinell hardness of 150 corresponds to a tensile strength of 500 MPa (72,000 psi.) Furthermore, from Figure 7.19*b*, in order to achieve a tensile strength of 500 MPa for brass, deformation of at least 36%CW is necessary. Finally, if we are to achieve a ductility of at least 20%EL, then a maximum deformation of 23%CW is possible from Figure 7.19*c*. Therefore, it is *not possible* to meet both of these criteria by plastically deforming brass.

7.D3 *A cylindrical specimen of cold-worked steel has a Brinell hardness of 240.*

(a) Estimate its ductility in percent elongation.

(b) If the specimen remained cylindrical during deformation and its original radius was 10 mm (0.40 in.), determine its radius after deformation.

Solution

(a) For this portion of the problem we are to determine the ductility of cold-worked steel that has a Brinell hardness of 240. From Figure 6.19, for steel, a Brinell hardness of 240 corresponds to a tensile strength of 820 MPa (120,000 psi), which, from Figure 7.19*b*, requires a deformation of 17%CW. Furthermore, 17%CW yields a ductility of about 13%EL for steel, Figure 7.19*c*.

(b) We are now asked to determine the radius after deformation if the un-cold-worked radius is 10 mm (0.40 in.). From Equation 7.8 and for a cylindrical specimen

$$\%\mathrm{CW} = \left(\frac{A_0 - A_d}{A_0}\right) \times 100$$

$$= \left[\frac{\pi r_0^2 - \pi r_d^2}{\pi r_0^2}\right] \times 100$$

Now, solving for r_d from this expression, we get

$$r_d = r_0 \sqrt{1 - \frac{\%\mathrm{CW}}{100}}$$

And, finally, for 17%CW

$$r_d = (10\ \mathrm{mm})\sqrt{1 - \frac{17\%\mathrm{CW}}{100}} = 9.11\ \mathrm{mm} \quad (0.364\ \mathrm{in.})$$

7.D4 *It is necessary to select a metal alloy for an application that requires a yield strength of at least 310 MPa (45,000 psi) while maintaining a minimum ductility (%EL) of 27%. If the metal may be cold worked, decide which of the following are candidates: copper, brass, or a 1040 steel. Why?*

Solution

This problem asks us to determine which of copper, brass, and a 1040 steel may be cold-worked so as to achieve a minimum yield strength of 310 MPa (45,000 psi) and a minimum ductility of 27%EL. For each of these alloys, the minimum cold work necessary to achieve the yield strength may be determined from Figure 7.19*a*, while the maximum possible cold work for the ductility is found in Figure 7.19*c*. These data are tabulated below.

	Yield Strength (> 310 MPa)	Ductility (> 27%EL)
Steel	Any %CW	Not possible
Brass	> 15%CW	< 17%CW
Copper	> 38%CW	< 10%CW

Thus, only brass is a possible candidate, since for this alloy only there is an overlap of %CW's to give the required minimum yield strength and ductility values.

7.D5 *A cylindrical rod of 1040 steel originally 11.4 mm (0.45 in.) in diameter is to be cold worked by drawing; the circular cross section will be maintained during deformation. A cold-worked tensile strength in excess of 825 MPa (120,000 psi) and a ductility of at least 12%EL are desired. Furthermore, the final diameter must be 8.9 mm (0.35 in.). Explain how this may be accomplished.*

Solution

This problem calls for us to explain the procedure by which a cylindrical rod of 1040 steel may be deformed so as to produce a given final diameter (8.9 mm), as well as a specific minimum tensile strength (825 MPa) and minimum ductility (12%EL). First let us calculate the percent cold work and attendant tensile strength and ductility if the drawing is carried out without interruption. From Equation 7.8, for a cylindrical specimen having original and deformed diameters of 11.4 mm and 8.9 mm, respectively,

$$\%\mathrm{CW} = \left(\frac{A_0 - A_d}{A_0}\right) \times 100$$

$$= \frac{\pi\left(\frac{d_0}{2}\right)^2 - \pi\left(\frac{d_d}{2}\right)^2}{\pi\left(\frac{d_0}{2}\right)^2} \times 100$$

$$= \frac{\pi\left(\frac{11.4\ \mathrm{mm}}{2}\right)^2 - \pi\left(\frac{8.9\ \mathrm{mm}}{2}\right)^2}{\pi\left(\frac{11.4\ \mathrm{mm}}{2}\right)^2} \times 100 = 40\%\mathrm{CW}$$

At 40%CW, the steel will have a tensile strength on the order of 900 MPa (130,000 psi) (Figure 7.19*b*), which is adequate; however, the ductility will be less than 9%EL (Figure 7.19*c*), which is insufficient.

Instead of performing the drawing in a single operation, let us initially draw some fraction of the total deformation, then anneal to recrystallize, and, finally, cold-work the material a second time in order to achieve the final diameter, tensile strength, and ductility.

Reference to Figure 7.19*b* indicates that 17%CW is necessary to yield a tensile strength of 825 MPa (122,000 psi). Similarly, a maximum of 20%CW is possible for 12%EL (Figure 7.19*c*). The average of these extremes is 18.5%CW. If the final diameter after the first drawing is d_0', then, from Equation 7.8

$$18.5\%\text{CW} = \frac{\pi\left(\dfrac{d_0'}{2}\right)^2 - \pi\left(\dfrac{8.9\ \text{mm}}{2}\right)^2}{\pi\left(\dfrac{d_0'}{2}\right)^2} \times 100$$

And, solving for d_0', yields

$$d_0' = \frac{8.9\ \text{mm}}{\sqrt{1 - \dfrac{18.5\%\text{CW}}{100}}}$$

$$= 9.86\ \text{mm}\ \ (0.388\ \text{in.})$$

7.D6 *A cylindrical rod of brass originally 10.2 mm (0.40 in.) in diameter is to be cold worked by drawing; the circular cross section will be maintained during deformation. A cold-worked yield strength in excess of 380 MPa (55,000 psi) and a ductility of at least 15%EL are desired. Furthermore, the final diameter must be 7.6 mm (0.30 in.). Explain how this may be accomplished.*

Solution

Let us first calculate the percent cold work and attendant yield strength and ductility if the drawing is carried out without interruption. From Equation 7.8

$$\%\mathrm{CW} = \left(\frac{A_0 - A_d}{A_0}\right) \times 100$$

$$= \frac{\pi\left(\frac{d_0}{2}\right)^2 - \pi\left(\frac{d_d}{2}\right)^2}{\pi\left(\frac{d_0}{2}\right)^2} \times 100$$

$$= \frac{\pi\left(\frac{10.2\ \mathrm{mm}}{2}\right)^2 - \pi\left(\frac{7.6\ \mathrm{mm}}{2}\right)^2}{\pi\left(\frac{10.2\ \mathrm{mm}}{2}\right)^2} \times 100 = 44.5\%\mathrm{CW}$$

At 44.5%CW, the brass will have a yield strength on the order of 420 MPa (61,000 psi), Figure 7.19*a*, which is adequate; however, the ductility will be about 5%EL, Figure 7.19*c*, which is insufficient.

Instead of performing the drawing in a single operation, let us initially draw some fraction of the total deformation, then anneal to recrystallize, and, finally, cold work the material a second time in order to achieve the final diameter, yield strength, and ductility.

Reference to Figure 7.19*a* indicates that 27%CW is necessary to give a yield strength of 380 MPa. Similarly, a maximum of 27%CW is possible for 15%EL (Figure 7.19*c*). Thus, to achieve both the specified yield strength and ductility, the brass must be deformed to 27 %CW. If the final diameter after the first drawing is d'_0, then, using Equation 7.8

$$27\%\mathrm{CW} = \frac{\pi\left(\frac{d'_0}{2}\right)^2 - \pi\left(\frac{7.6\ \mathrm{mm}}{2}\right)^2}{\pi\left(\frac{d'_0}{2}\right)^2} \times 100$$

And, solving for d'_0 yields

$$d'_0 = \frac{7.6\text{ mm}}{\sqrt{1 - \dfrac{27\%\text{CW}}{100}}} = 8.90\text{ mm} \ \ (0.351\text{ in.})$$

7.D7 *A cylindrical brass rod having a minimum tensile strength of 450 MPa (65,000 psi), a ductility of at least 13%EL, and a final diameter of 12.7 mm (0.50 in.) is desired. Some brass stock of diameter 19.0 mm (0.75 in.) that has been cold worked 35% is available. Describe the procedure you would follow to obtain this material. Assume that brass experiences cracking at 65%CW.*

Solution

This problem calls for us to cold work some brass stock that has been previously cold worked in order to achieve minimum tensile strength and ductility values of 450 MPa (65,000 psi) and 13%EL, respectively, while the final diameter must be 12.7 mm (0.50 in.). Furthermore, the material may not be deformed beyond 65%CW. Let us start by deciding what percent coldwork is necessary for the minimum tensile strength and ductility values, assuming that a recrystallization heat treatment is possible. From Figure 7.19*b*, at least 27%CW is required for a tensile strength of 450 MPa. Furthermore, according to Figure 7.19*c*, 13%EL corresponds a maximum of 30%CW. Let us take the average of these two values (i.e., 28.5%CW), and determine what previous specimen diameter is required to yield a final diameter of 12.7 mm. For cylindrical specimens, Equation 7.8 takes the form

$$\%\mathrm{CW} = \left(\frac{A_0 - A_d}{A_0}\right) \times 100$$

$$= \frac{\pi\left(\frac{d_0}{2}\right)^2 - \pi\left(\frac{d_d}{2}\right)^2}{\pi\left(\frac{d_0}{2}\right)^2} \times 100$$

Solving for the original diameter d_0 when d_d = 12.7 mm and for 28.5%CW yields

$$d_0 = \frac{d_d}{\sqrt{1 - \frac{\%\mathrm{CW}}{100}}}$$

$$= \frac{12.7\ \mathrm{mm}}{\sqrt{1 - \frac{28.5\%\mathrm{CW}}{100}}} = 15.0\ \mathrm{mm}\quad (0.591\ \mathrm{in.})$$

Now, let us determine its undeformed diameter realizing that a diameter of 19.0 mm corresponds to 35%CW. Again solving for d_0 using the above equation and assuming d_d = 19.0 mm yields

$$d_0 = \frac{d_d}{\sqrt{1 - \frac{\%\text{CW}}{100}}}$$

$$= \frac{19.0\ \text{mm}}{\sqrt{1 - \frac{35\%\text{CW}}{100}}} = 23.6\ \text{mm} \quad (0.930\ \text{in.})$$

At this point let us see if it is possible to deform the material from 23.6 mm to 15.0 mm without exceeding the 65%CW limit. Again employing Equation 7.8

$$\%\text{CW} = \frac{\pi\left(\frac{23.6\ \text{mm}}{2}\right)^2 - \pi\left(\frac{15.0\ \text{mm}}{2}\right)^2}{\pi\left(\frac{23.6\ \text{mm}}{2}\right)^2} \times 100 = 59.6\%\text{CW}$$

which is less that 65%CW.

In summary, the procedure which can be used to produce the desired material would be as follows: cold work the as-received stock to 15.0 mm (0.591 in.), heat treat it to achieve complete recrystallization, and then cold work the material again to 12.7 mm (0.50 in.), which will give the desired tensile strength and ductility.

7.D8 *Consider the brass alloy discussed in Problem 7.41. Given the following yield strengths for the two specimens, compute the heat treatment time required at 650°C to give a yield strength of 90 MPa. Assume a value of 2 for n, the grain diameter exponent.*

Time **(*min*)**	***Yield Strength*** **(*MPa*)**
40	80
100	70

Solution

This problem is solved using the following steps:

1. From data provided in the problem statement and Problem 7.41, determine values of σ_0 and k_y in Equation 7.7.
2. Calculate the value of *d* that is required for to give a yield strength of 90 MPa using these values and Equation 7.7.
3. From data given in Problem 7.41, determine values of d_0 and *K* in Equation 7.9.
4. Calculate the heat-treating time required to give the *d* value determined in step 2, using Equation 7.9.

Step 1

Using grain diameter-yield strength data provided in the problem statement and Problem 7.41, we set up two simultaneous expressions of Equation 7.7—i.e.,

$$\sigma_y = \sigma_0 + k_y d^{-1/2}$$

as follows:

$$80 \text{ MPa} = \sigma_0 + k_y (0.056 \text{ mm})^{-1/2}$$

$$70 \text{ MPa} = \sigma_0 + k_y (0.080 \text{ mm})^{-1/2}$$

From these expressions it is possible to solve for values of σ_0 and k_y:

k_y = 14.49 MPa-mm$^{1/2}$

σ_0 = 18.75 MPa

Step 2

We now compute the grain size *d* required to give a yield strength of 90 MPa using a rearranged from of Equation 7.7 and the above values of σ_0 and k_y as follows:

$$d = \left(\frac{k_y}{\sigma_y - \sigma_0}\right)^2$$

$$= \left(\frac{14.49\ \text{MPa-mm}^{1/2}}{90\ \text{MPa} - 18.75\ \text{MPa}}\right)^2$$

$$= 0.041\ \text{mm}$$

Step 3

Using grain diameter-heat treating time data provided in Problem 7.41, we set up two simultaneous expressions of Equation 7.9—i.e.,

$$d^2 - d_0^2 = Kt$$

as follows:

$$(0.056\ \text{mm})^2 - d_0^2 = K(40\ \text{min})$$

$$(0.080\ \text{mm})^2 - d_0^2 = K(100\ \text{min})$$

From which we determine values for d_0 and K as follows:

$d_0 = 0.031$ mm

$K = 5.44 \times 10^{-5}$ mm^2/min

Step 4

And finally, we calculate the heat-treating time t required to give the d value determined in step 2 (0.041 mm), using a rearranged form of Equation 7.9:

$$t = \frac{d^2 - d_0^2}{K}$$

$$= \frac{(0.041\ \text{mm})^2 - (0.031\ \text{mm})^2}{5.44 \times 10^{-5}\ \text{mm}^2/\text{min}}$$

$$= 13.2\ \text{min}$$

Fundamentals of Engineering Questions and Problems

7.1FE *Plastically deforming a metal specimen near room temperature generally leads to which of the following property changes?*

(A) An increased tensile strength and a decreased ductility
(B) A decreased tensile strength and an increased ductility
(C) An increased tensile strength and an increased ductility
(D) A decreased tensile strength and a decreased ductility

Solution

The correct answer is A. Plastically deforming (or strain hardening) a metal increases the dislocation density; this produces an increase in tensile strength and a decrease in ductility.

7.2FE *A dislocation formed by adding an extra half-plane of atoms to a crystal is referred to as a (an)*

(A) screw dislocation

(B) vacancy dislocation

(C) interstitial dislocation

(D) edge dislocation

Solution

The correct answer is D. A dislocation formed by adding an extra half plane of atoms to a crystal is referred to as an edge dislocation.

7.3FE *The atoms surrounding a screw dislocation experience which kinds of strains?*

(A) Tensile strains

(B) Shear strains

(C) Compressive strains

(D) Both B and C

Solution

The correct answer is B. The atoms surrounding a screw dislocation experience only *shear* strains.

CHAPTER 8

FAILURE

PROBLEM SOLUTIONS

Principles of Fracture Mechanics

8.1 *What is the magnitude of the maximum stress that exists at the tip of an internal crack having a radius of curvature of 1.9 × 10^{-4} mm (7.5 × 10^{-6} in.) and a crack length of 3.8 × 10^{-2} mm (1.5 × 10^{-3} in.) when a tensile stress of 140 MPa (20,000 psi) is applied?*

Solution

Equation 8.1 is employed to solve this problem—i.e.,

$$\sigma_m = 2\sigma_0 \left(\frac{a}{\rho_t}\right)^{1/2}$$

Values for σ_0 (140 MPa), 2a (3.8 × 10^{-2} mm), and ρ_t (1.9 × 10^{-4} mm) are provided in the problem statement. Therefore, we solve for σ_m as follows:

$$\sigma_m = (2)(140\ \text{MPa})\left(\frac{\dfrac{3.8 \times 10^{-2}\ \text{mm}}{2}}{1.9 \times 10^{-4}\ \text{mm}}\right)^{1/2} = 2800\ \text{MPa}\quad (400{,}000\ \text{psi})$$

8.2 *Estimate the theoretical fracture strength of a brittle material if it is known that fracture occurs by the propagation of an elliptically shaped surface crack of length 0.5 mm (0.02 in.) and a tip radius of curvature of 5 ×* 10^{-3} *mm (2 ×* 10^{-4} *in.), when a stress of 1035 MPa (150,000 psi) is applied.*

Solution

In order to estimate the theoretical fracture strength of this material it is necessary to calculate σ_m using Equation 8.1 given that σ_0 = 1035 MPa, a = 0.5 mm, and ρ_t = 5 × 10^{-3} mm. Thus,

$$\sigma_m = 2\sigma_0 \left(\frac{a}{\rho_t}\right)^{1/2}$$

$$= (2)(1035\ \text{MPa})\left(\frac{0.5\ \text{mm}}{5 \times 10^{-3}\ \text{mm}}\right)^{1/2}$$

$$= 2.07 \times 10^4\ \text{MPa} = 20.7\ \text{GPa} \quad (3 \times 10^6\ \text{psi})$$

8.3 *If the specific surface energy for aluminum oxide is 0.90 J/m^2, then using data in Table 12.5, compute the critical stress required for the propagation of an internal crack of length 0.40 mm.*

Solution

We may determine the critical stress required for the propagation of an internal crack in aluminum oxide using Equation 8.3. Taking the value of 393 GPa (Table 12.5) as the modulus of elasticity, and realizing that values for γ_s (0.90 J/m^2) and $2a$ (0.40 mm) are given in the problem statement, leads to

$$\sigma_c = \left(\frac{2E\gamma_s}{\pi a}\right)^{1/2}$$

$$= \left[\frac{(2)(393 \times 10^9 \text{ N/m}^2)(0.90 \text{ N/m})}{(\pi)\left(\dfrac{0.4 \times 10^{-3} \text{ m}}{2}\right)}\right]^{1/2}$$

$$= 33.6 \times 10^6 \text{ N/m}^2 = 33.6 \text{ MPa}$$

8.4 *An MgO component must not fail when a tensile stress of 13.5 MPa (1960 psi) is applied. Determine the maximum allowable surface crack length if the surface energy of MgO is 1.0 J/m^2. Data found in Table 12.5 may prove helpful.*

Solution

The maximum allowable surface crack length for MgO may be determined using a rearranged form of Equation 8.3. Taking 225 GPa as the modulus of elasticity (Table 12.5), and realizing that values of σ_c (13.5 MPa) and γ_s (1.0 J/m^2) are given in the problem statement, we solve for *a*, as follows:

$$a = \frac{2E\gamma_s}{\pi\sigma_c^2}$$

$$= \frac{(2)(225 \times 10^9 \text{ N/m}^2)(1.0 \text{ N/m})}{(\pi)(13.5 \times 10^6 \text{ N/m}^2)^2}$$

$$= 7.9 \times 10^{-4} \text{ m} = 0.79 \text{ mm} \ (0.031 \text{ in.})$$

8.5 *A specimen of a 4340 steel alloy with a plane strain fracture toughness of 54.8 MPa* $\sqrt{m}$ *(50 ksi* $\sqrt{in.}$*) is exposed to a stress of 1030 MPa (150,000 psi). Will this specimen experience fracture if the largest surface crack is 0.5 mm (0.02 in.) long? Why or why not? Assume that the parameter Y has a value of 1.0.*

Solution

This problem asks us to determine whether or not the 4340 steel alloy specimen will fracture when exposed to a stress of 1030 MPa. This requires that we solve for σ_c from Equation 8.6, given the values of K_{Ic} $(54.8\ \mathrm{MPa}\sqrt{\mathrm{m}})$, the largest value of *a* (0.5 mm), and *Y* (1.0). Thus, the critical stress for fracture is equal to

$$\sigma_c = \frac{K_{Ic}}{Y\sqrt{\pi a}}$$

$$= \frac{54.8\ \mathrm{MPa}\sqrt{\mathrm{m}}}{(1.0)\sqrt{(\pi)(0.5 \times 10^{-3}\ \mathrm{m})}}$$

$$= 1380\ \mathrm{MPa} \quad (200{,}000\ \mathrm{psi})$$

Therefore, fracture will *not* occur because this specimen will tolerate a stress of 1380 MPa (200,000 psi) before fracture, which is greater than the applied stress of 1030 MPa (150,000 psi).

8.6 *An aircraft component is fabricated from an aluminum alloy that has a plane strain fracture toughness of 40 MPa* $\sqrt{m}$ *(36.4 ksi* $\sqrt{in.}$*). It has been determined that fracture results at a stress of 300 MPa (43,500 psi) when the maximum (or critical) internal crack length is 4.0 mm (0.16 in.). For this same component and alloy, will fracture occur at a stress level of 260 MPa (38,000 psi) when the maximum internal crack length is 6.0 mm (0.24 in.)? Why or why not?*

Solution

We are asked to determine if an aircraft component will fracture for a given fracture toughness ($40\ \mathrm{MPa}\sqrt{\mathrm{m}}$), stress level (260 MPa), and maximum internal crack length (6.0 mm), given that fracture occurs for the same component using the same alloy for another stress level and internal crack length. (*Note:* Because the cracks are internal, their lengths are equal to 2*a*.) It first becomes necessary to solve for the parameter *Y*, using Equation 8.5, for the conditions under which fracture occurred (i.e., σ = 300 MPa and 2*a* = 4.0 mm). Therefore,

$$Y = \frac{K_{Ic}}{\sigma\sqrt{\pi a}} = \frac{40\ \mathrm{MPa}\sqrt{\mathrm{m}}}{(300\ \mathrm{MPa})\sqrt{(\pi)\left(\dfrac{4 \times 10^{-3}\ \mathrm{m}}{2}\right)}} = 1.68$$

Now we will solve for the product $Y\sigma\sqrt{\pi a}$ for the other set of conditions, so as to ascertain whether or not this value is greater than the K_{Ic} for the alloy. Thus,

$$Y\sigma\sqrt{\pi a} = (1.68)(260\ \ \mathrm{MPa})\sqrt{(\pi)\left(\frac{6 \times 10^{-3}\ \mathrm{m}}{2}\right)}$$

$$= 42.4\ \ \mathrm{MPa}\sqrt{\mathrm{m}}\quad (39\ \ \mathrm{ksi}\sqrt{\mathrm{in.}})$$

Therefore, fracture *will* occur since this value ($42.4\ \mathrm{MPa}\sqrt{\mathrm{m}}$) is greater than the K_{Ic} of the material, $40\ \mathrm{MPa}\sqrt{\mathrm{m}}$.

8.7 *Suppose that a wing component on an aircraft is fabricated from an aluminum alloy that has a plane-strain fracture toughness of 26.0 MPa* $\sqrt{m}$ *(23.7 ksi* $\sqrt{in.}$*). It has been determined that fracture results at a stress of 112 MPa (16,240 psi) when the maximum internal crack length is 8.6 mm (0.34 in.). For this same component and alloy, compute the stress level at which fracture will occur for a critical internal crack length of 6.0 mm (0.24 in.).*

Solution

This problem asks us to determine the stress level at which an a wing component on an aircraft will fracture for a given fracture toughness $\left(26\ \text{MPa}\sqrt{\text{m}}\right)$ and maximum internal crack length (6.0 mm), given that fracture occurs for the same component using the same alloy at one stress level (112 MPa) and another internal crack length (8.6 mm). (*Note:* Because the cracks are internal, their lengths are equal to 2*a*.) It first becomes necessary to solve for the parameter *Y* for the conditions under which fracture occurred using Equation 8.5. Therefore,

$$Y = \frac{K_{Ic}}{\sigma\sqrt{\pi a}} = \frac{26\ \text{MPa}\sqrt{\text{m}}}{(112\ \text{MPa})\sqrt{(\pi)\left(\dfrac{8.6\times 10^{-3}\ \text{m}}{2}\right)}} = 2.0$$

Now we will solve for σ_c (for a crack length of 6 mm) using Equation 8.6 as

$$\sigma_c = \frac{K_{Ic}}{Y\sqrt{\pi a}} = \frac{26\ \text{MPa}\sqrt{\text{m}}}{(2.0)\sqrt{(\pi)\left(\dfrac{6\times 10^{-3}\ \text{m}}{2}\right)}} = 134\ \text{MPa}\quad (19{,}300\ \text{psi})$$

8.8 *A structural component is fabricated from an alloy that has a plane-strain fracture toughness of* $62\ MPa\sqrt{m}$. *It has been determined that this component fails at a stress of 250 MPa when the maximum length of a surface crack is 1.6 mm. What is the maximum allowable surface crack length (in mm) without fracture for this same component exposed to a stress of 250 MPa and made from another alloy that has a plane strain fracture toughness of* $51\ MPa\sqrt{m}$?

Solution

This problem asks us to determine the maximum allowable surface crack length without fracture for a structural component for a specified fracture toughness $(51\ \mathrm{MPa}\sqrt{\mathrm{m}})$, given that fracture occurs for the same component using the same stress level (250 MPa) and another fracture toughness $(62\ \mathrm{MPa}\sqrt{\mathrm{m}})$. (*Note:* Because the cracks surface cracks, their lengths are equal to *a*.) The maximum crack length without fracture a_c may be calculated using Equation 8.7—i.e.,

$$a_c = \frac{1}{\pi}\left(\frac{K_{Ic}}{\sigma Y}\right)^2$$

where K_{Ic} is the plane strain fracture toughness, σ is the applied stress, and Y is a design parameter. Using data for the first alloy [$K_{Ic} = 62\ \mathrm{MPa}\sqrt{\mathrm{m}}$, a_c = 1.6 mm (1.6×10^{-3} m), σ = 250 MPa], it is possible to calculate the value of Y using a rearranged form of the above equation as follows:

$$Y = \frac{K_{Ic}}{\sigma\sqrt{\pi a_c}}$$

$$= \frac{62\ \mathrm{MPa}\sqrt{\mathrm{m}}}{(250\ \mathrm{MPa})\sqrt{(\pi)(1.6\ \times\ 10^{-3}\ \mathrm{m})}}$$

$$= 3.50$$

Using this value of Y, the maximum crack length for the second alloy is determined, again using Equation 8.7 as

$$a_c = \frac{1}{\pi}\left(\frac{K_{Ic}}{\sigma Y}\right)^2$$

$$= \frac{1}{\pi}\left[\frac{51\ \text{MPa}\sqrt{\text{m}}}{(250\ \text{MPa})(3.50)}\right]^2$$

= 0.00108 m = 1.08 mm

8.9 *A large plate is fabricated from a steel alloy that has a plane strain fracture toughness of* $82.4\ MPa\sqrt{m}$ *(*$75.0\ ksi\sqrt{in.}$*). If the plate is exposed to a tensile stress of 345 MPa (50,000 psi) during service use, determine the minimum length of a surface crack that will lead to fracture. Assume a value of 1.0 for Y.*

Solution

For this problem, we are given values of K_{Ic} $\left(82.4\ \mathrm{MPa}\sqrt{\mathrm{m}}\right)$, σ (345 MPa), and Y (1.0) for a large plate and are asked to determine the minimum length of a surface crack that will lead to fracture. All we need do is to solve for a_c using Equation 8.7; therefore

$$a_c = \frac{1}{\pi}\left(\frac{K_{Ic}}{Y\sigma}\right)^2$$

$$= \frac{1}{\pi}\left[\frac{82.4\ \mathrm{MPa}\sqrt{\mathrm{m}}}{(1.0)(345\ \mathrm{MPa})}\right]^2$$

$$= 0.0182\ \mathrm{m} = 18.2\ \mathrm{mm}\quad (0.72\ \mathrm{in.})$$

8.10 *Calculate the maximum internal crack length allowable for a Ti-6Al-4V titanium alloy (Table 8.1) component that is loaded to a stress one-half its yield strength. Assume that the value of Y is 1.50.*

Solution

This problem asks us to calculate the maximum internal crack length allowable for the Ti-6Al-4V titanium alloy in Table 8.1 given that it is loaded to a stress level equal to one-half of its yield strength. For this alloy, $K_{Ic} = 55 \text{ MPa}\sqrt{\text{m}}$; also, $\sigma = \sigma_y/2$ = (910 MPa)/2 = 455 MPa. Now solving for $2a_c$ (since this crack is an internal one) using Equation 8.7 yields

$$2a_c = \frac{2}{\pi}\left(\frac{K_{Ic}}{Y\sigma}\right)^2$$

$$= \frac{2}{\pi}\left[\frac{55 \text{ MPa}\sqrt{\text{m}}}{(1.5)(455 \text{ MPa})}\right]^2$$

$$= \mathbf{0.0041 \ m = 4.1 \ mm \quad (0.16 \ in.)}$$

8.11 *A structural component in the form of a wide plate is to be fabricated from a steel alloy that has a plane-strain fracture toughness of* $98.9\ \text{MPa}\sqrt{\text{m}}$ *(*$90\ \text{ksi}\sqrt{\text{in.}}$*) and a yield strength of 860 MPa (125,000 psi). The flaw size resolution limit of the flaw detection apparatus is 3.0 mm (0.12 in.). If the design stress is one-half the yield strength and the value of Y is 1.0, determine whether a critical flaw for this plate is subject to detection.*

Solution

This problem asks that we determine whether or not a critical flaw in a wide plate is subject to detection given the limit of the flaw detection apparatus (3.0 mm), the value of K_{Ic} $\left(98.9\ \text{MPa}\sqrt{\text{m}}\right)$, the design stress ($\sigma_y/2$ in which σ_y = 860 MPa), and Y = 1.0. We first need to compute the value of a_c using Equation 8.7; thus

$$a_c = \frac{1}{\pi}\left(\frac{K_{Ic}}{Y\sigma}\right)^2$$

$$= \frac{1}{\pi}\left[\frac{98.9\ \text{MPa}\sqrt{\text{m}}}{(1.0)\left(\dfrac{860\ \text{MPa}}{2}\right)}\right]^2$$

$$= 0.0168\ \text{m} = 16.8\ \text{mm}\quad (0.66\ \text{in.})$$

Therefore, the critical flaw *is subject to detection* since this value of a_c (16.8 mm) is greater than the 3.0 mm resolution limit.

8.12 *After consultation of other references, write a brief report on one or two nondestructive test techniques that are used to detect and measure internal and/or surface flaws in metal alloys.*

The student should answer this question on his/her own.

Fracture Toughness Testing

8.13 *The following tabulated data were gathered from a series of Charpy impact tests on a tempered 4340 steel alloy.*

Temperature (°C)	***Impact Energy (J)***
0	*105*
–25	*104*
–50	*103*
–75	*97*
–100	*63*
–113	*40*
–125	*34*
–150	*28*
–175	*25*
–200	*24*

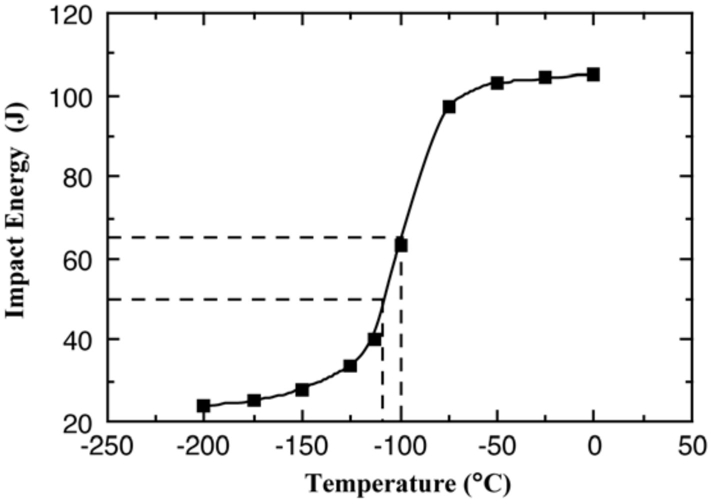
(a) Plot the data as impact energy versus temperature.

(b) Determine a ductile-to-brittle transition temperature as the temperature corresponding to the average of the maximum and minimum impact energies.

(c) Determine a ductile-to-brittle transition temperature as the temperature at which the impact energy is 50 J.

<u>Solution</u>

(a) The plot of impact energy versus temperature is shown below.



(b) The average of the maximum and minimum impact energies from the data is

$$\text{Average} = \frac{105 \text{ J} + 24 \text{ J}}{2} = 64.5 \text{ J}$$

As indicated on the plot by the one set of dashed lines, the ductile-to-brittle transition temperature according to this criterion is about –100°C.

(c) Also, as noted on the plot by the other set of dashed lines, the ductile-to-brittle transition temperature for an impact energy of 50 J is about –110°C.

8.14 *The following tabulated data were gathered from a series of Charpy impact tests on a commercial low-carbon steel alloy.*

Temperature (°C)	***Impact Energy (J)***
50	*76*
40	*76*
30	*71*
20	*58*
10	*38*
0	*23*
–10	*14*
–20	*9*
–30	*5*
–40	*1.5*

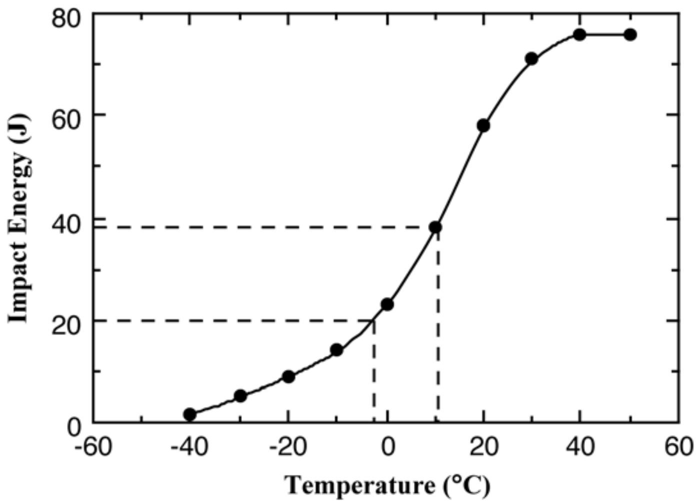
(a) Plot the data as impact energy versus temperature.

(b) Determine a ductile-to-brittle transition temperature as the temperature corresponding to the average of the maximum and minimum impact energies.

(c) Determine a ductile-to-brittle transition temperature as the temperature at which the impact energy is 20 J.

Solution

(a) The plot of impact energy versus temperature is shown below.



(b) The average of the maximum and minimum impact energies from the data is

$$\text{Average} = \frac{76\ \text{J} + 1.5\ \text{J}}{2} = 38.8\ \text{J}$$

As indicated on the plot by the one set of dashed lines, the ductile-to-brittle transition temperature according to this criterion is about 10°C.

(c) Also, as noted on the plot by the other set of dashed lines, the ductile-to-brittle transition temperature for an impact energy of 20 J is about –2°C.

8.15 *What is the maximum carbon content possible for a plain carbon steel that must have an impact energy of at least 200 J at –50°C?*

Solution

From the curves in Figure 8.16, for only the 0.11 wt%C and 0.01 wt% C steels are impact energies (and therefore, ductile-to-brittle temperatures) greater than 200 J. Therefore, 0.11 wt% is the maximum carbon concentration.

Cyclic Stresses
The S–N *Curve*

8.16 *A fatigue test was conducted in which the mean stress was 70 MPa (10,000 psi), and the stress amplitude was 210 MPa (30,000 psi).*

(a) Compute the maximum and minimum stress levels.

(b) Compute the stress ratio.

(c) Compute the magnitude of the stress range.

Solution

(a) Given the values of σ_m (70 MPa) and σ_a (210 MPa) we are asked to compute σ_{max} and σ_{min}. From Equation 8.14

$$\sigma_m = \frac{\sigma_{\max} + \sigma_{\min}}{2} = 70 \text{ MPa}$$

Or,

$$\sigma_{\max} + \sigma_{\min} = 140 \text{ MPa} \tag{8.14a}$$

Furthermore, utilization of Equation 8.16 yields

$$\sigma_a = \frac{\sigma_{\max} - \sigma_{\min}}{2} = 210 \text{ MPa}$$

Or,

$$\sigma_{\max} - \sigma_{\min} = 420 \text{ MPa} \tag{8.16a}$$

Simultaneously solving Equations 8.14a and 8.16a leads to

$$\sigma_{\max} = 280 \text{ MPa} \ \ (40{,}000 \text{ psi})$$

$$\sigma_{\min} = -140 \text{ MPa} \ \ (-20{,}000 \text{ psi})$$

(b) Using Equation 8.17 the stress ratio *R* is determined as follows:

$$R = \frac{\sigma_{\min}}{\sigma_{\max}} = \frac{-140 \text{ MPa}}{280 \text{ MPa}} = -0.50$$

(c) The magnitude of the stress range σ_r is determined using Equation 8.15 as

$$\sigma_r = \sigma_{\max} - \sigma_{\min} = 280 \text{ MPa} - (-140 \text{ MPa})$$

$$= 420 \text{ MPa} \ \ (60{,}000 \text{ psi})$$

8.17 *A cylindrical bar of ductile cast iron is subjected to reversed and rotating-bending tests; test results (i.e., S-N behavior) are shown in Figure 8.20. If the bar diameter is 9.5 mm, determine the maximum cyclic load that may be applied to ensure that fatigue failure will not occur. Assume a factor of safety of 2.25 and that the distance between load-bearing points is 55.5 mm.*

Solution

From Figure 8.20, the ductile cast iron has a fatigue limit (maximum stress) of magnitude 220 MPa. For rotating-bending tests and a cylindrical bar of diameter d_0 (Figure 8.18*b*), maximum stress may be determined using Equation 8.18—i.e.,

$$\sigma = \frac{16FL}{\pi d_0^3}$$

Here L is equal to the distance between the two load-bearing points (Figure 8.18*b*), σ is the maximum stress (in our case the fatigue limit), and F is the maximum applied load. When σ is divided by the factor of safety (N) Equation 8.18 takes the form of Equation 8.19—that is

$$\frac{\sigma}{N} = \frac{16FL}{\pi d_0^3}$$

and solving this expression for F leads to

$$F = \frac{\sigma \pi d_0^3}{16NL}$$

Incorporating into this expression values for d_0 (9.5 mm = 9.5×10^{-3} m) L (55.5 mm = 55.5×10^{-3} m), and N (2.25) provided in the problem statement as well as the fatigue limit taken from Figure 8.20 (220 MPa or 220×10^6 N/m^2) yields the following

$$F = \frac{(220 \times 10^6 \text{ N/m}^2)(\pi)(9.5 \times 10^{-3} \text{ m})^3}{(16)(2.25)(55.5 \times 10^{-3} \text{ m})}$$

$$= 297 \text{ N}$$

Therefore, for cyclic reversed and rotating-bending, a maximum load of 297 N may be applied without causing the ductile cast iron bar to fail by fatigue.

8.18 *A cylindrical 4340 steel bar is subjected to reversed rotating-bending stress cycling, which yielded the test results presented in Figure 8.20. If the maximum applied load is 5,000 N, compute the minimum allowable bar diameter to ensure that fatigue failure will not occur. Assume a factor of safety of 2.25 and that the distance between load-bearing points is 55.0 mm.*

Solution

From Figure 8.20, the fatigue limit for this steel is 480 MPa. For rotating-bending tests on a cylindrical specimen of diameter d_0, stress is defined in Equation 8.18 as

$$\sigma = \frac{16FL}{\pi d_0^3}$$

When we divide stress by the factor of safety (N), the above equation becomes Equation 8.19—that is

$$\frac{\sigma}{N} = \frac{16FL}{\pi d_0^3}$$

And solving for d_0 realizing that σ is the fatigue limit (480 MPa or 480 × 10^6 N/m^2) and incorporating values for F (5,000 N), L (55.0 mm = 55 × 10^{-3} m), and N (2.25) provided in the problem statement, leads to

$$d_0 = \left(\frac{16FLN}{\sigma\pi}\right)^{1/3}$$

$$\left[\frac{(16)(5{,}000\text{ N})(55.0 \times 10^{-3}\text{ m})(2.25)}{(480 \times 10^6\text{ N/m}^2)(\pi)}\right]^{1/3}$$

$$0.0187\text{ m} = 18.7\text{ mm}$$

8.19 *A cylindrical 2014-T6 aluminum alloy bar is subjected to compression-tension stress cycling along its axis; results of these tests are shown in Figure 8.20. If the bar diameter is 12.0 mm, calculate the maximum allowable load amplitude (in N) to ensure that fatigue failure will not occur at* 10^7 *cycles. Assume a factor of safety of 3.0, data in Figure 8.20 were taken for reversed axial tension-compression tests, and that S is stress amplitude.*

Solution

From Figure 8.20, the fatigue strength at 10^7 cycles for this aluminum alloy is 170 MPa. For a cylindrical specimen having an original diameter of d_0, the stress may be computed using Equation 6.1, which is equal to

$$\sigma = \frac{F}{A_0} = \frac{F}{\pi\left(\frac{d_0}{2}\right)^2}$$

$$= \frac{4F}{\pi d_0^2}$$

When we divide σ by the factor of safety, the above equation takes the form

$$\frac{\sigma}{N} = \frac{4F}{\pi d_0^2}$$

Solving the above equation for F leads to

$$F = \frac{\sigma \pi d_0^2}{4N}$$

Now taking σ to be the fatigue strength (i.e., 170 MPa = 170×10^6 N/m^2) and incorporating values for d_0 and N provided in the problem statement [i.e., 12.0 mm (12.0×10^{-3} m) and 3.0, respectively], we calculate the maximum load as follows:

$$F = \frac{(170 \times 10^6 \text{ N/m}^2)(\pi)(12.0 \times 10^{-3} \text{ m})^2}{(4)(3.0)}$$

6,400 N

8.20 *A cylindrical rod of diameter 6.7 mm fabricated from a 70Cu-30Zn brass alloy is subjected to rotating-bending load cycling; test results (as S-N behavior) are shown in Figure 8.20. If the maximum and minimum loads are +120 N and –120 N, respectively, determine its fatigue life. Assume that the separation between loadbearing points is 67.5 mm.*

Solution

In order to solve this problem we compute the maximum stress using Equation 8.18, and then determine the fatigue life from the curve in Figure 8.20 for the brass material. In Equation 8.18, F is the maximum applied load, which for this problem is +120 N. Values for L and d_0 are provided in the problem statement—viz. 67.5 mm (67.5×10^{-3} m) and 6.7 mm (6.7×10^{-3} m), respectively. Therefore the maximum stress σ is equal to

$$\sigma = \frac{16FL}{\pi d_0^3}$$

$$= \frac{(16)(120\text{ N})(67.5 \times 10^{-3}\text{ m})}{(\pi)(6.7 \times 10^{-3}\text{ m})^3}$$

$$= 137 \times 10^6\text{ N/m}^2 = 137\text{ MPa}$$

From Figure 8.20 and the curve for brass, the logarithm of the fatigue life (log N_f) at 137 MPa is about 6.5, which means that the fatigue life is equal to

$$N_f = 10^{6.5}\text{ cycles} = 3 \times 10^6\text{ cycles}$$

8.21 *A cylindrical rod of diameter 14.7 mm fabricated from a Ti-5Al-2.5Sn titanium alloy (Figure 8.20) is subjected to a repeated tension-compression load cycling along its axis. Compute the maximum and minimum loads that will be applied to yield a fatigue life of 1.0 × 10^6 cycles. Assume that data in Figure 8.20 were taken for repeated axial tension-compression tests, that stress plotted on the vertical axis is stress amplitude, and data were taken for a mean stress of 50 MPa.*

Solution

This problem asks that we compute the maximum and minimum loads to which a 14.7 mm diameter Ti-5Al-2.5Sn titanium alloy specimen may be subjected in order to yield a fatigue life of 1.0 × 10^6 cycles; Figure 8.20 is to be used assuming that data were taken for repeated axial tension-compression tests and a mean stress of 50 MPa. Upon consultation of Figure 8.20, for this titanium alloy, a fatigue life of 1.0 × 10^6 cycles corresponds to a stress amplitude of 510 MPa. Or, from Equation 8.16

$$\sigma_{\max} - \sigma_{\min} = 2\sigma_a = (2)(510 \text{ MPa}) = 1020 \text{ MPa}$$

Since σ_m = 50 MPa, then from Equation 8.14

$$\sigma_{\max} + \sigma_{\min} = 2\sigma_m = (2)(50 \text{ MPa}) = 100 \text{ MPa}$$

Simultaneous solution of these two expressions for $\sigma_{\max}$ and $\sigma_{\min}$ yields

$$\sigma_{\max} = +560 \text{ MPa}$$
$$\sigma_{\min} = -460 \text{ MPa}$$

Now, inasmuch as from Equation 6.1 and for a cylindrical rod

$$\sigma = \frac{F}{A_0} = \frac{F}{\pi\left(\frac{d_0}{2}\right)^2} = \frac{4F}{\pi d_0^2}$$

then the load, *F*, is equal to

$$F = \frac{\sigma \pi d_0^2}{4}$$

It is now possible to compute maximum and minimum loads from the $\sigma_{\max}$ and $\sigma_{\min}$ values determined above:

$$F_{\max} = \frac{\sigma_{\max}\pi d_0^2}{4} = \frac{(560 \times 10^6 \text{ N/m}^2)(\pi)(14.7 \times 10^{-3} \text{ m})^2}{4} = 95{,}000 \text{ N}$$

$$F_{\min} = \frac{\sigma_{\min} \pi d_0^2}{4} = \frac{\left(-460 \times 10^6 \text{ N/m}^2\right)(\pi)\left(14.7 \times 10^{-3} \text{ m}\right)^2}{4} = -78{,}000 \text{ N}$$

8.22 *The fatigue data for a brass alloy are given as follows:*

Stress Amplitude (MPa)	***Cycles to Failure***
170	3.7×10^4
148	1.0×10^5
130	3.0×10^5
114	1.0×10^6
92	1.0×10^7
80	1.0×10^8
74	1.0×10^9

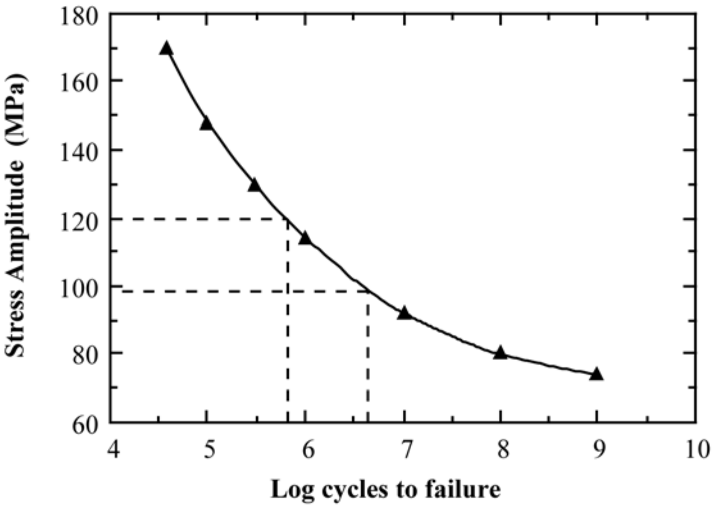
(a) Make an S–N plot (stress amplitude versus logarithm of cycles to failure) using these data.

(b) Determine the fatigue strength at 4×10^6 cycles.

(c) Determine the fatigue life for 120 MPa.

Solution

(a) The fatigue data for this alloy are plotted below.



(b) As indicated by one set of dashed lines on the plot, the fatigue strength at 4×10^6 cycles [log (4×10^6) = 6.6] is about 100 MPa.

(c) As noted by the other set of dashed lines, the fatigue life for 120 MPa is about 6×10^5 cycles (i.e., the log of the lifetime is about 5.8).

8.23 *Suppose that the fatigue data for the brass alloy in Problem 8.22 were taken from bending-rotating tests and that a rod of this alloy is to be used for an automobile axle that rotates at an average rotational velocity of 1800 revolutions per minute. Give the maximum bending stress amplitude possible for each of the following lifetimes of the rod: (a) 1 year, (b) 1 month, (c) 1 day, and (d) 1 hour.*

Solution

We are asked to compute the maximum torsional stress amplitude possible at each of several fatigue lifetimes for the brass alloy the fatigue behavior of which is given in Problem 8.22. For each lifetime, first compute the number of cycles, and then read the corresponding fatigue strength from the above plot.

(a) Fatigue lifetime = (1 yr)(365 days/yr)(24 h/day)(60 min/h)(1800 cycles/min) = 9.5×10^8 cycles. The stress amplitude corresponding to this lifetime is about 74 MPa.

(b) Fatigue lifetime = (30 days)(24 h/day)(60 min/h)(1800 cycles/min) = 7.8×10^7 cycles. The stress amplitude corresponding to this lifetime is about 80 MPa.

(c) Fatigue lifetime = (24 h)(60 min/h)(1800 cycles/min) = 2.6×10^6 cycles. The stress amplitude corresponding to this lifetime is about 115 MPa.

(d) Fatigue lifetime = (60 min/h)(1800 cycles/min) = 108,000 cycles. The stress amplitude corresponding to this lifetime is about 145 MPa.

8.24 *The fatigue data for a steel alloy are given as follows:*

Stress Amplitude [MPa (ksi)]	***Cycles to Failure***
470 (68.0)	10^4
440 (63.4)	3×10^4
390 (56.2)	10^5
350 (51.0)	3×10^5
310 (45.3)	10^6
290 (42.2)	3×10^6
290 (42.2)	10^7
290 (42.2)	10^8

(a) Make an S–N plot (stress amplitude versus logarithm of cycles to failure) using these data.

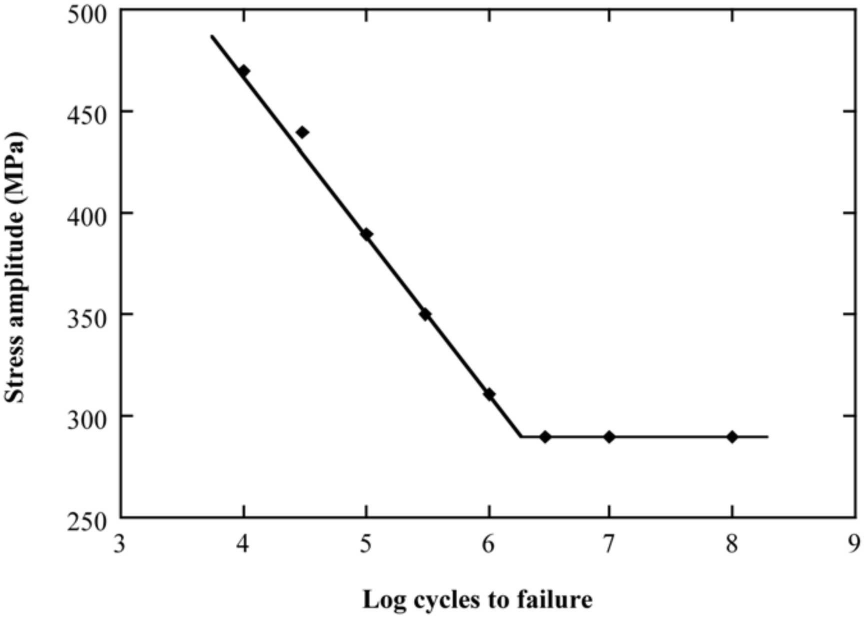
(b) What is the fatigue limit for this alloy?

(c) Determine fatigue lifetimes at stress amplitudes of 415 MPa (60,000 psi) and 275 MPa (40,000 psi).

(d) Estimate fatigue strengths at 2×10^4 *and* 6×10^5 *cycles.*

Solution

(a) The fatigue data for this alloy are plotted below.



(b) The fatigue limit is the stress level at which the curve becomes horizontal, which is 290 MPa (42,200 psi).

(c) From the plot, the fatigue lifetimes at a stress amplitude of 415 MPa (60,000 psi) is about 50,000 cycles (log N = 4.7). At 275 MPa (40,000 psi) the fatigue lifetime is essentially an infinite number of cycles since this stress amplitude is below the fatigue limit.

(d) Also from the plot, the fatigue strengths at 2×10^4 cycles (log N = 4.30) and 6×10^5 cycles (log N = 5.78) are 440 MPa (64,000 psi) and 325 MPa (47,500 psi), respectively.

8.25 *Suppose that the fatigue data for the steel alloy in Problem 8.24 were taken for bending-rotating tests and that a rod of this alloy is to be used for an automobile axle that rotates at an average rotational velocity of 600 revolutions per minute. Give the maximum lifetimes of continuous driving that are allowable for the following stress levels: (a) 450 MPa (65,000 psi), (b) 380 MPa (55,000 psi), (c) 310 MPa (45,000 psi), and (d) 275 MPa (40,000 psi).*

Solution

This problem asks that we determine the maximum lifetimes of continuous driving that are possible at an average rotational velocity of 600 rpm for the alloy the fatigue data of which is provided in Problem 8.24 and at a variety of stress levels.

(a) For a stress level of 450 MPa (65,000 psi), the fatigue lifetime is approximately 18,000 cycles (i.e., log $N_f = 4.25$). This translates into (1.8×10^4 cycles)(1 min/600 cycles) = 30 min.

(b) For a stress level of 380 MPa (55,000 psi), the fatigue lifetime is approximately 1.5×10^5 cycles (i.e., log $N_f = 5.15$). This translates into (1.5×10^5 cycles)(1 min/600 cycles) = 250 min = 4.2 h.

(c) For a stress level of 310 MPa (45,000 psi), the fatigue lifetime is approximately 1×10^6 cycles (i.e., log $N_f = 6.0$). This translates into (1×10^6 cycles)(1 min/600 cycles) = 1667 min = 27.8 h.

(d) For a stress level of 275 MPa (40,000 psi), the fatigue lifetime is essentially infinite since we are below the fatigue limit (290 MPa).

8.26 *Three identical fatigue specimens (denoted A, B, and C) are fabricated from a nonferrous alloy. Each is subjected to one of the maximum-minimum stress cycles listed in the following table; the frequency is the same for all three tests.*

Specimen	***σ_{max} (MPa)***	***σ_{min} (MPa)***
A	*+450*	*–150*
B	*+300*	*–300*
C	*+500*	*–200*

(a) Rank the fatigue lifetimes of these three specimens from the longest to the shortest.

(b) Now justify this ranking using a schematic S–N plot.

Solution

For this problem we are given, for three identical fatigue specimens of the same material, σ_{max} and σ_{min} data, and are asked to rank the lifetimes from the longest to the shortest. In order to do this it is necessary to compute both the mean stress and stress amplitude for each specimen. From Equation 8.14, mean stresses are calculated as follows:

$$\sigma_m = \frac{\sigma_{max} + \sigma_{min}}{2}$$

$$\sigma_m(\mathrm{A}) = \frac{450\ \mathrm{MPa} + (-150\ \mathrm{MPa})}{2} = 150\ \mathrm{MPa}$$

$$\sigma_m(\mathrm{B}) = \frac{300\ \mathrm{MPa} + (-300\ \mathrm{MPa})}{2} = 0\ \mathrm{MPa}$$

$$\sigma_m(\mathrm{C}) = \frac{500\ \mathrm{MPa} + (-200\ \mathrm{MPa})}{2} = 150\ \mathrm{MPa}$$

Furthermore, using Equation 8.16, stress amplitudes are determined:

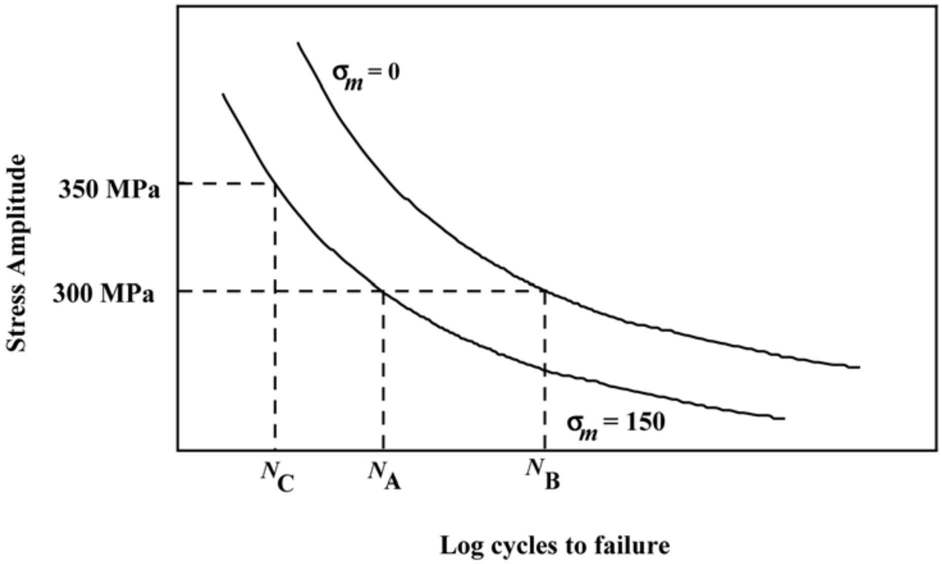
$$\sigma_a = \frac{\sigma_{max} - \sigma_{min}}{2}$$

$$\sigma_a(\mathrm{A}) = \frac{450\ \mathrm{MPa} - (-150\ \mathrm{MPa})}{2} = 300\ \mathrm{MPa}$$

$$\sigma_a(\mathrm{B}) = \frac{300\ \mathrm{MPa} - (-300\ \mathrm{MPa})}{2} = 300\ \mathrm{MPa}$$

$$\sigma_a(\mathrm{C}) = \frac{500\ \mathrm{MPa} - (-200\ \mathrm{MPa})}{2} = 350\ \mathrm{MPa}$$

On the basis of these results, the fatigue lifetime for specimen B will be greater than specimen A which in turn will be greater than specimen C. This conclusion is based upon the following *S-N* plot on which curves are plotted for two σ_m values.



8.27 *Cite five factors that may lead to scatter in fatigue life data.*

Answer

Five factors that lead to scatter in fatigue life data are (1) specimen fabrication and surface preparation, (2) metallurgical variables, (3) specimen alignment in the test apparatus, (4) variation in mean stress, and (5) variation in test cycle frequency.

Crack Initiation and Propagation

Factors That Affect Fatigue Life

8.28 *Briefly explain the difference between fatigue striations and beachmarks in terms of (a) size and (b) origin.*

Solution

(a) With regard to size, beachmarks are normally of macroscopic dimensions and may be observed with the naked eye; fatigue striations are of microscopic size and it is necessary to observe them using electron microscopy.

(b) With regard to origin, beachmarks result from interruptions in the stress cycles; each fatigue striation is corresponds to the advance of a fatigue crack during a single load cycle.

8.29 *List four measures that may be taken to increase the resistance to fatigue of a metal alloy.*

Answer

Four measures that may be taken to increase the fatigue resistance of a metal alloy are as follows:

(1) Polish the surface to remove stress amplification sites.

(2) Reduce the number of internal defects (pores, etc.) by means of altering processing and fabrication techniques.

(3) Modify the design to eliminate notches and sudden contour changes.

(4) Harden the outer surface of the structure by case hardening (carburizing, nitriding) or shot peening.

Generalized Creep Behavior

8.30 *Give the approximate temperature at which creep deformation becomes an important consideration for each of the following metals: tin, molybdenum, iron, gold, zinc, and chromium.*

Solution

Creep becomes important at about $0.4T_m$, T_m being the absolute melting temperature of the metal. (The melting temperatures in degrees Celsius are found inside the front cover of the book.)

For Sn, $0.4T_m$ = (0.4)(232 + 273) = 202 K or –71°C (–96°F)

For Mo, $0.4T_m$ = (0.4)(2617 + 273) = 1049 K or 776°C (1429°F)

For Fe, $0.4T_m$ = (0.4)(1538 + 273) = 724 K or 451°C (845°F)

For Au, $0.4T_m$ = (0.4)(1064 + 273) = 535 K or 262°C (504°F)

For Zn, $0.4T_m$ = (0.4)(420 + 273) = 277 K or 4°C (39°F)

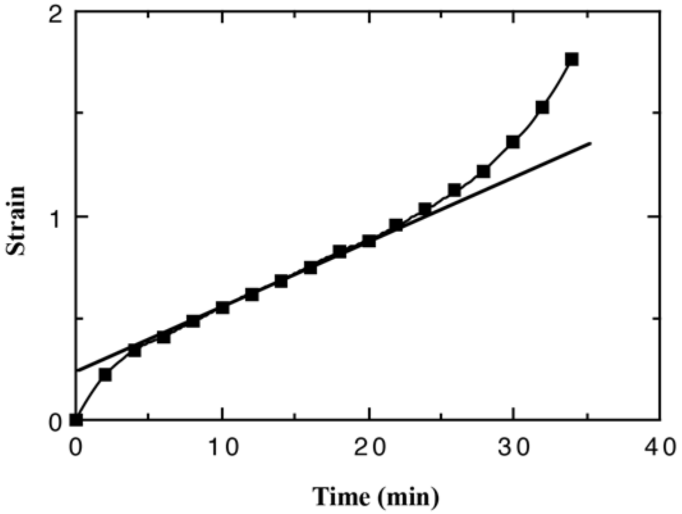
For Cr, $0.4T_m$ = (0.4)(1875 + 273) = 859 K or 586°C (1087°F)

8.31 *The following creep data were taken on an aluminum alloy at 480°C (900°F) and a constant stress of 2.75 MPa (400 psi). Plot the data as strain versus time, then determine the steady-state or minimum creep rate. Note: The initial and instantaneous strain is not included.*

Time (min)	***Strain***	***Time (min)***	***Strain***
0	*0.00*	*18*	*0.82*
2	*0.22*	*20*	*0.88*
4	*0.34*	*22*	*0.95*
6	*0.41*	*24*	*1.03*
8	*0.48*	*26*	*1.12*
10	*0.55*	*28*	*1.22*
12	*0.62*	*30*	*1.36*
14	*0.68*	*32*	*1.53*
16	*0.75*	*34*	*1.77*

Solution

These creep data are plotted below



The steady-state creep rate ($\Delta\varepsilon/\Delta t$) is the slope of the linear region (i.e., the straight line that has been superimposed on the curve). Taking strain values at 0 min and 30 min, leads to the following:

$$\frac{\Delta\varepsilon}{\Delta t} = \frac{1.20 - 0.25}{30\,\text{min} - 0\,\text{min}} = 3.2 \times 10^{-2}\ \text{min}^{-1}$$

Stress and Temperature Effects

8.32 *A specimen 975 mm (38.4 in.) long of an S-590 alloy (Figure 8.32) is to be exposed to a tensile stress of 300 MPa (43,500 psi) at 730°C (1350°F). Determine its elongation after 4.0 h. Assume that the total of both instantaneous and primary creep elongations is 2.5 mm (0.10 in.).*

Solution

From the 730°C line in Figure 8.32, the steady state creep rate $\dot{\varepsilon}_s$ is about 1.0×10^{-2} h^{-1} at 300 MPa. The steady state creep strain, ε_s, therefore, is just the product of $\dot{\varepsilon}_s$ and time as

$$\varepsilon_s = \dot{\varepsilon}_s \times \text{(time)}$$

$$= (1.0 \times 10^{-2}\ \text{h}^{-1})(4.0\ \text{h}) = 0.040$$

Strain and elongation are related as in Equation 6.2—viz.

$$\varepsilon = \frac{\Delta l}{l_0}$$

Now, using the steady-state elongation, l_0, provided in the problem statement (975 mm) and the value of ε_s, determined above (0.040), the steady-state elongation, Δl_s, is determined as follows:

$$\Delta l_s = l_0 \varepsilon_s$$

$$= (975\ \text{mm})(0.040) = 39.0\ \text{mm}\ \ (1.54\ \text{in.})$$

Finally, the total elongation is just the sum of this Δl_s and the total of both instantaneous and primary creep elongations [i.e., 2.5 mm (0.10 in.)]. Therefore, the total elongation is 39.0 mm + 2.5 mm = 41.5 mm (1.64 in.).

8.33 *For a cylindrical S-590 alloy specimen (Figure 8.31) originally 14.5 mm (0.57 in.) in diameter and 400 mm (15.7 in.) long, what tensile load is necessary to produce a total elongation of 52.7 mm (2.07 in.) after 1150 h at 650°C (1200°F)? Assume that the sum of instantaneous and primary creep elongations is 4.3 mm (0.17 in.).*

Solution

It is first necessary to calculate the steady state creep rate so that we may utilize Figure 8.32 in order to determine the tensile stress. The steady state elongation, Δl_s, is just the difference between the total elongation and the sum of the instantaneous and primary creep elongations; that is,

$$\Delta l_s = 52.7 \text{ mm} - 4.3 \text{ mm} = 48.4 \text{ mm} \quad (1.90 \text{ in.})$$

Now the steady state creep rate, $\dot{\varepsilon}_s$, is just

$$\dot{\varepsilon}_s = \frac{\Delta \varepsilon}{\Delta t}$$

$$= \frac{\dfrac{\Delta l_s}{l_0}}{\Delta t} = \frac{\dfrac{48.4 \text{ mm}}{400 \text{ mm}}}{1150 \text{ h}}$$

$$= 1.05 \times 10^{-4} \text{ h}^{-1}$$

Employing the 650°C line in Figure 8.32, a steady state creep rate of 1.05×10^{-4} h^{-1} corresponds to a stress σ of about 300 MPa (or 43,500 psi). From this we may compute the tensile load (for this cylindrical specimen) using Equation 6.1 as follows:

$$F = \sigma A_0 = \sigma \pi \left(\frac{d_0}{2}\right)^2$$

Here d_0 is the original cross-sectional diameter (14.5 mm = 14.5×10^{-3} m). Solving this equation for tensile load, incorporating the value of stress determined from Figure 8.32 above (300 MPa = 300×10^6 N/m^2) leads to

$$F = \sigma \pi \left(\frac{d_0}{2}\right)^2$$

$$= (300 \times 10^6 \text{ N/m}^2)(\pi)\left(\frac{14.5 \times 10^{-3} \text{ m}}{2}\right)^2$$

$$= 49{,}500 \text{ N} \quad (11{,}100 \text{ lb}_\text{f})$$

8.34 *A cylindrical component 50 mm long constructed from an S-590 alloy (Figure 8.32) is to be exposed to a tensile load of 70,000 N. What minimum diameter is required for it to experience an elongation of no more than 8.2 mm after an exposure for 1,500 h at 650°C? Assume that the sum of instantaneous and primary creep elongations is 0.6 mm.*

Solution

It is first necessary to calculate the steady state creep rate so that we may utilize Figure 8.31 in order to determine the tensile stress. The steady state elongation, Δl_s, is just the difference between the total elongation and the sum of the instantaneous and primary creep elongations; that is,

$$\Delta l_s = 8.2 \text{ mm} - 0.6 \text{ mm} = 7.6 \text{ mm}$$

Now the steady state creep rate, $\dot{\varepsilon}_s$ is just

$$\dot{\varepsilon}_s = \frac{\Delta \varepsilon}{\Delta t}$$

$$= \frac{\dfrac{\Delta l_s}{l_0}}{\Delta t} = \frac{\dfrac{7.6 \text{ mm}}{50 \text{ mm}}}{1500 \text{ h}}$$

$$= 1.01 \times 10^{-4} \text{ h}^{-1}$$

From the 650°C line in Figure 8.32, a steady state creep rate of 1.01×10^{-4} h^{-1} corresponds to a stress σ of about 300 MPa. Now from Equation 6.1 and for a cylindrical specimen having a diameter of d_0

$$\sigma = \frac{F}{A_0} = \frac{F}{\pi \left(\dfrac{d_0}{2}\right)^2}$$

Solving for d_0 and realizing that σ = 300 MPa (300×10^6 N/m^2) and F = 70,000 N leads to

$$d_0 = \sqrt{\frac{4F}{\pi \sigma}}$$

$$= \sqrt{\frac{(4)(70{,}000\ \text{N})}{(\pi)(300\ \times\ 10^6\ \text{N/m}^2)}}$$

$$= 0.0172\ \text{m} = 17.2\ \text{mm}$$

8.35 *A cylindrical specimen 13.2 mm in diameter of an S-590 alloy is to be exposed to a tensile load of 27,000 N. At approximately what temperature will the steady-state creep be* 10^{-3} h^{-1}*?*

Solution

Let us first determine the stress imposed on this specimen using values of cross-section diameter and applied load; this is possible using Equation 6.1 as

$$\sigma = \frac{F}{A_0} = \frac{F}{\pi\left(\frac{d_0}{2}\right)^2}$$

Inasmuch as d_0 = 13.2 mm (13.2 × 10^{-3} m) and F = 27,000 N, the stress is equal to

$$\sigma = \frac{27{,}000\ \text{N}}{\pi\left(\frac{13.2 \times 10^{-3}\ \text{m}}{2}\right)^2}$$

$$= 197 \times 10^6\ \text{N/m}^2 = 197\ \text{MPa}$$

Or approximately 200 MPa. From Figure 8.32 the point corresponding 10^{-3} h^{-1} and 200 MPa lies approximately midway between 730°C and 815°C lines; therefore, the temperature would be approximately 775°C.

8.36 *If a component fabricated from an S-590 alloy (Figure 8.31) is to be exposed to a tensile stress of 100 MPa (14,500 psi) at 815°C (1500°F), estimate its rupture lifetime.*

Solution

This problem asks us to calculate the rupture lifetime of a component fabricated from an S-590 alloy exposed to a tensile stress of 100 MPa at 815°C. All that we need do is read from the 815°C line in Figure 8.30 the rupture lifetime at 100 MPa; this value is about 2000 h.

8.37 *A cylindrical component constructed from an S-590 alloy (Figure 8.31) has a diameter of 14.5 mm (0.57 in.). Determine the maximum load that may be applied for it to survive 10 h at 925°C (1700°F).*

Solution

We are asked in this problem to determine the maximum load that may be applied to a cylindrical S-590 alloy component that must survive 10 h at 925°C. From Figure 8.31, the stress corresponding to 10 h is about 100 MPa (14,500 psi). In order to determine the applied load, we use the expression used to compute stress, as given in Equation 6.1, which for a cylindrical specimen takes the form:

$$\sigma = \frac{F}{A_0} = \frac{F}{\pi\left(\frac{d_0}{2}\right)^2}$$

From which the force *F* (or load) is equal to

$$F = \sigma\pi\left(\frac{d_0}{2}\right)^2$$

For a stress of 100 MPa (100×10^6 N/m^2) and a cross-sectional diameter of 14.5 mm (14.5×10^{-3} m) the load is equal to

$$F = (100 \times 10^6 \text{ N/m}^2)(\pi)\left(\frac{14.5 \times 10^{-3} \text{ m}}{2}\right)^2$$

$$= 16{,}500 \text{ N} \quad (3700 \text{ lb}_\text{f})$$

8.38 *A cylindrical component constructed from an S-590 alloy (Figure 8.31) is to be exposed to a tensile load of 20,000 N. What minimum diameter is required for it to have a rupture lifetime of at least 100 h at 925°C?*

Solution

From Figure 8.31 on the 925°C, the stress corresponding to a rupture lifetime of 100 h is approximately 70 MPa.). In order to determine the minimum diameter, we use the expression used to compute stress, as given in Equation 6.1, which for a cylindrical specimen takes the form:

$$\sigma = \frac{F}{A_0} = \frac{F}{\pi\left(\frac{d_0}{2}\right)^2}$$

Solving for d_0 and realizing that σ = 70 MPa (70 × 10^6 N/m^2) and F = 20,000 N leads to

$$d_0 = \sqrt{\frac{4F}{\pi\sigma}}$$

$$= \sqrt{\frac{(4)(20{,}000\text{ N})}{(\pi)(70 \times 10^6\text{ N/m}^2)}}$$

$$= 0.0191\text{ m} = 19.1\text{ mm}$$

8.39 *From Equation 8.24, if the logarithm of* $\dot{\varepsilon}_s$ *is plotted versus the logarithm of σ, then a straight line should result, the slope of which is the stress exponent n. Using Figure 8.32, determine the value of n for the S-590 alloy at 925°C, and for the initial (lower-temperature) straight line segments at each of 650°C, 730°C, and 815°C.*

Solution

The slope of the line from a log $\dot{\varepsilon}_s$ versus log σ plot yields the value of *n* in Equation 8.24; that is

$$n = \frac{\Delta \log \dot{\varepsilon}_s}{\Delta \log \sigma}$$

We are asked to determine the values of *n* for the creep data at the four temperatures in Figure 8.32. This is accomplished by taking ratios of the differences between two log $\dot{\varepsilon}_s$ and log σ values. (Note: Figure 8.32 plots log σ versus log $\dot{\varepsilon}_s$; therefore, values of *n* are equal to the reciprocals of the slopes of the straight-line segments.)

Thus for the line segment for 925°C

$$n_{925} = \frac{\Delta \log \dot{\varepsilon}_s}{\Delta \log \sigma} = \frac{\log (1) - \log (10^{-4})}{\log (200\text{ MPa}) - \log (60\text{ MPa})}$$

$$= \frac{0 - (-4)}{2.301 - 1.778} = 7.65$$

While for 815°C

$$n_{815} = \frac{\Delta \log \dot{\varepsilon}_s}{\Delta \log \sigma} = \frac{\log (1) - \log (10^{-6})}{\log (350\text{ MPa}) - \log (65\text{ MPa})} = 8.2$$

And at 730°C

$$n_{730} = \frac{\Delta \log \dot{\varepsilon}_s}{\Delta \log \sigma} = \frac{\log (1) - \log (10^{-6})}{\log (450\text{ MPa}) - \log (130\text{ MPa})} = 11.1$$

And at 650°C

$$n_{650} = \frac{\Delta \log \dot{\varepsilon}_s}{\Delta \log \sigma} = \frac{\log \left(2 \times 10^{-1}\right) - \log (7 \times 10^{-6})}{\log (600\text{ MPa}) - \log (220\text{ MPa})} = 10.2$$

8.40 *(a) Estimate the activation energy for creep (i.e., Q_c in Equation 8.25) for the S-590 alloy having the steady-state creep behavior shown in Figure 8.32. Use data taken at a stress level of 300 MPa (43,500 psi) and temperatures of 650°C and 730°C. Assume that the stress exponent n is independent of temperature.*

(b) Estimate $\dot{\epsilon}_s$ at 600°C (873 K) and 300 MPa.

Solution

(a) We are asked to estimate the activation energy for creep for the S-590 alloy having the steady-state creep behavior shown in Figure 8.32, using data taken at σ = 300 MPa (43,500 psi) and temperatures of 650°C and 730°C. Since σ is a constant, Equation 8.25 takes the form

$$\dot{\epsilon}_s = K_2 \sigma^n \exp\left(-\frac{Q_c}{RT}\right) = K_2' \exp\left(-\frac{Q_c}{RT}\right) \tag{8.25a}$$

where K_2' is now a constant (since σ and n are now constants) . (Note: the exponent n has about the same value at these two temperatures per Problem 8.39.) Taking natural logarithms of the above expression

$$\ln \dot{\epsilon}_s = \ln K_2' - \frac{Q_c}{RT}$$

For the case in which we have creep data at two temperatures (denoted as T_1 and T_2) and their corresponding steady-state creep rates ($\dot{\epsilon}_{s_1}$ and $\dot{\epsilon}_{s_2}$), it is possible to set up two simultaneous equations of the form as above, with two unknowns, namely K_2' and Q_c. Solving for the above equation for Q_c yields

$$Q_c = -\frac{R\left(\ln \dot{\epsilon}_{s_1} - \ln \dot{\epsilon}_{s_2}\right)}{\left[\frac{1}{T_1} - \frac{1}{T_2}\right]}$$

Let us choose T_1 as 650°C (923 K) and T_2 as 730°C (1003 K); then from Figure 8.32, at σ = 300 MPa, $\dot{\epsilon}_{s_1} = 10^{-4}$ h^{-1} and $\dot{\epsilon}_{s_2} = 10^{-2}$ h^{-1}. Substitution of these values into the above equation leads to

$$Q_c = -\frac{(8.31 \text{ J/mol-K})\left[\ln\left(10^{-4}\right) - \ln\left(10^{-2}\right)\right]}{\left[\frac{1}{923 \text{ K}} - \frac{1}{1003 \text{ K}}\right]}$$

$$= 442{,}800 \text{ J/mol}$$

(b) We are now asked to estimate $\dot{\varepsilon}_s$ at 600°C (873 K). It is first necessary to determine the value of K_2', which is accomplished Equation 8.25a, the value of Q_c, and one of the two $\dot{\varepsilon}_s$ values and its temperature T (say $\dot{\varepsilon}_{s_1}$ and T_1). Thus,

$$K_2' = \dot{\varepsilon}_{s_1} \exp\left(\frac{Q_c}{RT_1}\right)$$

$$= \left(10^{-4}\ \text{h}^{-1}\right)\exp\left[\frac{442{,}800\ \text{J/mol}}{(8.31\ \text{J/mol-K})(923\ \text{K})}\right] = 1.18 \times 10^{21}\ \text{h}^{-1}$$

Now it is possible to calculate $\dot{\varepsilon}_s$ at 600°C (873 K) as follows:

$$\dot{\varepsilon}_s = K_2' \exp\left(-\frac{Q_c}{RT}\right)$$

$$= \left(1.18 \times 10^{21}\ \text{h}^{-1}\right)\exp\left[-\frac{442{,}800\ \text{J/mol}}{(8.31\ \text{J/mol-K})(873\ \text{K})}\right]$$

$$= 3.7 \times 10^{-6}\ \text{h}^{-1}$$

8.41 *Steady-state creep rate data are given in the following table for a nickel alloy at 538°C (811 K):*

$\dot{\varepsilon}_s$ (h^{-1})	σ *(MPa)*
10^{-7}	*22.0*
10^{-6}	*36.1*

Compute the stress at which the steady-state creep is 10^{-5} h^{-1} *(also at 538°C).*

Solution

This problem gives $\dot{\varepsilon}_s$ values at two different stress levels and 538°C, and asks that we determine the stress at which the steady-state creep rate is 10^{-5} h^{-1} (also at 538°C). It is possible to solve this problem using Equation 8.24. First of all, it is necessary to determine values of K_1 and n. Taking the logarithms of both sides of Equation 8.24 leads to the following expression:

$$\log \dot{\varepsilon}_s = \log K_1 + n \log \sigma \qquad (8.24a)$$

We can now generate two simultaneous equations from the data given in the problem statement in which the two unknowns are K_1 and n. These two equations are as follows:

$$\log(10^{-7}) = \log K_1 + n\log(22.0 \text{ MPa})$$

$$\log(10^{-6}) = \log K_1 + n\log(36.1 \text{ MPa})$$

Simultaneous solution to these expressions leads to the following:

$K_1 = 6.12 \times 10^{-14}$

$n = 4.63$

Using these values we may determine the stress at which $\dot{\varepsilon}_s = 10^{-5}$ h^{-1}. Let us rearrange Equation 8.24a above such that $\log \sigma$ is the dependent variable:

$$\log \sigma = \frac{\log \dot{\varepsilon}_s - \log K_1}{n}$$

Incorporation of values of $\dot{\varepsilon}_s$, K_1, and n yields the following:

$$\log \sigma = \frac{\log(10^{-5}) - \log(6.12 \times 10^{-14})}{4.63}$$

$$= 1.774$$

From which we determine σ as follows:

$$\boldsymbol{\sigma} = \mathbf{10^{1.774} = 59.4\ MPa}$$

8.42 *Steady-state creep rate data are given in the following table for some alloy taken at 200°C (473 K):*

$\dot{\varepsilon}_s$ *(h^{-1})*	σ *[MPa (psi)]*
2.5 × 10^{-3}	*55 (8000)*
2.4 × 10^{-2}	*69 (10,000)*

If it is known that the activation energy for creep is 140,000 J/mol, compute the steady-state creep rate at a temperature of 250°C (523 K) and a stress level of 48 MPa (7000 psi).

Solution

This problem gives $\dot{\varepsilon}_s$ values at two different stress levels and 200°C, and the activation energy for creep, and asks that we determine the steady-state creep rate at 250°C and 48 MPa (7000 psi).

Taking natural logarithms of both sides of Equation 8.25 yields

$$\ln \dot{\varepsilon}_s = \ln K_2 + n \ln \sigma - \frac{Q_c}{RT}$$

With the given data there are two unknowns in this equation--namely K_2 and n. Using the data provided in the problem statement we can set up two independent equations as follows:

$$\ln(2.5 \times 10^{-3}\ \mathrm{h}^{-1}) = \ln K_2 + n \ln(55\ \mathrm{MPa}) - \frac{140{,}000\ \mathrm{J/mol}}{(8.31\ \mathrm{J/mol\text{-}K})(473\ \mathrm{K})}$$

$$\ln(2.4 \times 10^{-2}\ \mathrm{h}^{-1}) = \ln K_2 + n \ln(69\ \mathrm{MPa}) - \frac{140{,}000\ \mathrm{J/mol}}{(8.31\ \mathrm{J/mol\text{-}K})(473\ \mathrm{K})}$$

Now, solving simultaneously for n and K_2 leads to $n = 9.97$ and $K_2 = 3.27 \times 10^{-5}\ \mathrm{h}^{-1}$. Thus it is now possible to solve for $\dot{\varepsilon}_s$ at 48 MPa and 523 K using Equation 8.25 as

$$\dot{\varepsilon}_s = K_2 \sigma^n \exp\left(-\frac{Q_c}{RT}\right)$$

$$= (3.27 \times 10^{-5}\ \mathrm{h}^{-1})(48\ \mathrm{MPa})^{9.97} \exp\left[-\frac{140{,}000\ \mathrm{J/mol}}{(8.31\ \mathrm{J/mol\text{-}K})(523\ \mathrm{K})}\right]$$

$$= 1.94 \times 10^{-2}\ \mathrm{h}^{-1}$$

8.43 *Steady-state creep data taken for an iron at a stress level of 140 MPa (20,000 psi) are given here:*

$\dot{\varepsilon}_s$ *(*h^{-1}*)*	*T (K)*
6.6 × 10^{-4}	*1090*
8.8 × 10^{-2}	*1200*

If it is known that the value of the stress exponent n for this alloy is 8.5, compute the steady-state creep rate at 1300 K and a stress level of 83 MPa (12,000 psi).

Solution

This problem gives $\dot{\varepsilon}_s$ values at two different temperatures and 140 MPa (20,000 psi), and the value of the stress exponent n = 8.5, and asks that we determine the steady-state creep rate at a stress of 83 MPa (12,000 psi) and 1300 K.

Taking natural logarithms of both sides of Equation 8.25 yields

$$\ln \dot{\varepsilon}_s = \ln K_2 + n \ln \sigma - \frac{Q_c}{RT}$$

With the given data there are two unknowns in this equation--namely K_2 and Q_c. Using the data provided in the problem statement we can set up two independent equations as follows:

$$\ln(6.6 \times 10^{-4}\ \mathrm{h}^{-1}) = \ln K_2 + (8.5)\ln(140\ \mathrm{MPa}) - \frac{Q_c}{(8.31\ \mathrm{J/mol\text{-}K})(1090\ \mathrm{K})}$$

$$\ln(8.8 \times 10^{-2}\ \mathrm{h}^{-1}) = \ln K_2 + (8.5)\ln(140\ \mathrm{MPa}) - \frac{Q_c}{(8.31\ \mathrm{J/mol\text{-}K})(1200\ \mathrm{K})}$$

Now, solving simultaneously for K_2 and Q_c leads to K_2 = 57.5 h^{-1} and Q_c = 483,500 J/mol. Thus, it is now possible to solve for $\dot{\varepsilon}_s$ at 83 MPa and 1300 K using Equation 8.25 as

$$\dot{\varepsilon}_s = K_2 \sigma^n \exp\left(-\frac{Q_c}{RT}\right)$$

$$= (57.5\ \mathrm{h}^{-1})(83\ \mathrm{MPa})^{8.5} \exp\left[-\frac{483{,}500\ \mathrm{J/mol}}{(8.31\ \mathrm{J/mol\text{-}K})(1300\ \mathrm{K})}\right]$$

$$= 4.31 \times 10^{-2}\ \mathrm{h}^{-1}$$

8.44 *(a) Using Figure 8.31 compute the rupture lifetime for an S-590 alloy that is exposed to a tensile stress of 400 MPa at 815°C.*

(b) Compare this value to the one determined from the Larson-Miller plot of Figure 8.33, which is for this same S-590 alloy.

Solution

(a) From Figure 8.31 using the 815°C the rupture lifetime at 400 MPa is about 10^{-2} h.

(b) Using Figure 8.33, at a stress of 400 MPa, the value of the Larson-Miller parameter is about m = 19.7, which is equal to $10^3\ T(20 + \log t_r)$ for T in K and t_r in h. We take the temperature to be 815°C + 273 = 1088 K. Therefore, we may write the following:

$$19.7 = \left(\frac{1}{10^3}\right)(1088\ \text{K})(20 + \log t_r) = 1.088(20 + \log t_r)$$

Or

$$\frac{19.7}{1.088} = 18.11 = 20 + \log t_r$$

Which leads to

$$\log t_r = 18.11 - 20 = -1.89$$

And, solving for t_r we obtain

$$t_r = 10^{-1.89}\ \text{h} = 1.3 \times 10^{-2}\ \text{h}$$

Which value is very close to the 10^{-2} h that was obtained using Figure 8.31.

Alloys for High-Temperature Use

8.45 *Cite three metallurgical/processing techniques that are employed to enhance the creep resistance of metal alloys.*

Answer

Three metallurgical/processing techniques that are employed to enhance the creep resistance of metal alloys are (1) solid solution alloying, (2) dispersion strengthening by using an insoluble second phase, and (3) increasing the grain size or producing a grain structure with a preferred orientation.

DESIGN PROBLEMS

8.D1 *Each student (or group of students) is to obtain an object/structure/component that has failed. It may come from the home, an automobile repair shop, a machine shop, and so on. Conduct an investigation to determine the cause and type of failure (i.e., simple fracture, fatigue, creep). In addition, propose measures that can be taken to prevent future incidents of this type of failure. Finally, submit a report that addresses these issues.*

Each student or group of students is to submit their own report on a failure analysis investigation that was conducted.

Principles of Fracture Mechanics

8.D2 *(a) For the thin-walled spherical tank discussed in Design Example 8.1, on the basis of the critical-crack size-criterion [as addressed in part (a)], rank the following polymers from longest to shortest critical crack length: nylon 6,6 (50% relative humidity), polycarbonate, poly(ethylene terephthalate), and poly(methyl methacrylate). Comment on the magnitude range of the computed values used in the ranking relative to those tabulated for metal alloys as provided in Table 8.3. For these computations, use data contained in Tables B.4 and B.5 in Appendix B.*

(b) Now rank these same four polymers relative to maximum allowable pressure according to the leak-before-break criterion, as described in part (b) of Design Example 8.1. As before, comment on these values in relation to those for the metal alloys tabulated in Table 8.4.

Solution

(a) This portion of the problem calls for us to rank four polymers relative to critical crack length in the wall of a spherical pressure vessel. In the development of Design Example 8.1, it was noted that critical crack length is proportional to the square of the K_{Ic}–σ_y ratio. Values of K_{Ic} and σ_y as taken from Tables B.4 and B.5 are tabulated below. (Note: when a range of σ_y or K_{Ic} values is given, the average value is used.)

Material	K_{Ic} $(\mathrm{MPa}\sqrt{\mathrm{m}})$	σ_y (MPa)
Nylon 6,6	2.75	51.7
Polycarbonate	2.2	62.1
Poly(ethylene terephthlate)	5.0	59.3
Poly(methyl methacrylate)	1.2	63.5

On the basis of these values, the five polymers are ranked per the squares of the K_{Ic}–σ_y ratios as follows:

Material	$\left(\frac{K_{Ic}}{\sigma_y}\right)^2$ (mm)
PET	7.11
Nylon 6,6	2.83
PC	1.26
PMMA	0.36

These values are smaller than those for the metal alloys given in Table 8.3, which range from 0.93 to 43.1 mm.

(b) Relative to the leak-before-break criterion, the $K_{Ic}^2 - \sigma_y$ ratio is used. The five polymers are ranked according to values of this ratio as follows:

Material	$\frac{K_{Ic}^2}{\sigma_y}$ (MPa-m)
PET	0.422
Nylon 6,6	0.146
PC	0.078
PMMA	0.023

These values are all smaller than those for the metal alloys given in Table 8.4, which values range from 1.2 to 11.2 MPa-m.

The Fatigue S-N *Curve*

8.D3 *A cylindrical metal bar is to be subjected to reversed and rotating-bending stress cycling. Fatigue failure is not to occur for at least* 10^7 *cycles when the maximum load is 250 N. Possible materials for this application are the seven alloys having S-N behaviors displayed in Figure 8.20. Rank these alloys from least to most costly for this application. Assume a factor of safety of 2.0 and that the distance between load-bearing points is 80.0 mm (0.0800 m). Use cost data found in Appendix C for these alloys as follows:*

Alloy designation (Figure 8.20)	*Alloy designation (Cost data to use—Appendix C)*
EQ21A-T6 Mg	*AZ31B (extruded) Mg*
70Cu-30Zn brass	*Alloy C26000*
2014-T6 Al	*Alloy 2024-T3*
Ductile cast iron	*Ductile irons (all grades)*
1045 steel	*Steel alloy 1040 Plate, cold rolled*
4340 steel	*Steel alloy 4340 Bar, normalized*
Ti-5Al-2.5Sn titanium	*Alloy Ti-5Al-2.5Sn*

You may also find useful data that appears in Appendix B.

Solution

The following steps will be used to solve this problem:

1. Determine the fatigue strength or endurance limit at 10^7cycles for each alloy.
2. Using these data, compute the original cross-sectional diameter for each alloy.
3. Calculate the volume of material required using these d_0 values.
4. Using density values from Table B.1, determine the mass of material required for each alloy.
5. Compute the cost using mass data and cost per unit mass data found in Appendix C

Step 1

Below are tabulated the fatigue limits or fatigue strengths at 10^7cycles as taken from Figure 8.20:

Alloy	σ (Fatigue limit or fatigue strength) (MPa)
EQ21A-T6 Mg	100
70Cu-30Zn brass	115
2014-T6 Al	170
Ductile cast iron	220
1045 steel	310
4340 steel	485
Ti-5Al-2.5Sn titanium	490

Step 2

In order to compute the cross-sectional diameter d_0 for each alloy it is necessary to use Equation 8.19—viz.,

$$\frac{\sigma}{N} = \frac{16FL}{\pi d_0^3}$$

which incorporates the following values for the parameters in this expression:

σ = the fatigue strength at 10^7 cycles or endurance limit (Figure 8.20)

N = the factor of safety (2.0)

F = maximum applied load (250 N)

L = distance between load-bearing points (80.0 mm)

Solving for d_0 from Equation 8.19 leads to

$$d_0 = \left(\frac{16FLN}{\pi\sigma}\right)^{1/3}$$

The following table lists values of d_0 that were calculated using the above equation:

Alloy	d_0 (mm)
EQ21A-T6 Mg	12.7
70Cu-30Zn brass	12.1
2014-T6 Al	10.6
Ductile cast iron	9.75
1045 steel	8.69
4340 steel	7.50
Ti-5Al-2.5Sn titanium	7.46

Step 3

Using these d_0 values we may compute the cylinder volume V for each alloy using the following equation:

$$V = \pi l \left(\frac{d_0}{2}\right)^2$$

Here, l is the cylinder length. For the sake of convenience, let us arbitrarily assume that this length is L, the distance between load-bearing points from above—i.e., 80.0 mm. (*Note:* inasmuch as densities are expressed in units of grams per centimeters cubed, we now choose to express lengths and diameters in centimeters—i.e., l = 8.0 cm and d_0 values in the above table divided by a factor of 10.) The table below presents cylindrical specimen volumes for these seven alloys.

Alloy	d_0 (cm)	V (cm^3)
EQ21A-T6 Mg	1.27	10.1
70Cu-30Zn brass	1.21	9.20
2014-T6 Al	1.06	7.06
Ductile cast iron	0.975	5.97
1045 steel	0.869	4.74
4340 steel	0.750	3.53
Ti-5Al-2.5Sn titanium	0.746	3.50

Step 4

The next step is to determine the mass of each alloy in its cylinder. This is possible by multiplying the cylinder volume (V)by the alloy density (ρ). Density values are tabulated in Table B.1 of Appendix B. The following table lists volumes, densities, and cylinder masses for the seven alloys. (*Note:* Table B.1 does not present densities for all of the seven alloys. Therefore, in some cases it has been necessary to use approximate density values.)

Alloy	V (cm^3)	ρ (g/cm^3)	Alloy mass (g)
EQ21A-T6 Mg	10.1	1.80	18.2
70Cu-30Zn brass	9.20	8.50	78.2
2014-T6 Al	7.06	2.70	19.1
Ductile cast iron	5.97	7.10	42.4
1045 steel	4.74	7.85	37.2
4340 steel	3.53	7.85	27.7
Ti-5Al-2.5Sn titanium	3.50	4.50	15.8

Step 5

Now, to calculate the cost of each alloy it is necessary to multiply alloy mass (from above converted into kilograms) by cost data found in Appendix C. (*Notes:* the problem statement lists alloy cost data that is to be used in these computations. Also, in Appendix C when cost ranges are cited, average values are used.) These mass and cost data are tabulated below.

Alloy	Alloy mass (kg)	Cost per unit mass ($US/kg)	Cost ($US)
EQ21A-T6 Mg [AZ31B (extruded) Mg]	0.0182	12.10	0.22
70Cu-30Zn brass (Alloy C26000)	0.0782	9.95	0.78
2014-T6 Al (Alloy 2024-T3)	0.0191	16.00	0.31
Ductile cast iron [Ductile irons (all grades)]	0.0424	2.60	0.11
1045 steel (Steel alloy 1040 Plate, cold rolled)	0.0372	2.20	0.08
4340 steel (Steel alloy 4340 Bar, normalized)	0.0277	3.60	0.10
Ti-5Al-2.5Sn titanium (Alloy Ti-5Al-2.5Sn)	0.0158	115.00	1.82

And, finally, the following lists the ranking of these alloys from least to most costly.

1045 steel
4340 steel
Ductile cast iron
EQ21A-T6 Mg
2014-T6 Al
70Cu-30Zn brass
Ti-5Al-2.5Sn titanium

Data Extrapolation Methods

8.D4 *An S-590 iron component (Figure 8.33) must have a creep rupture lifetime of at least 20 days at 650°C (923 K). Compute the maximum allowable stress level.*

Solution

This problem asks that we compute the maximum allowable stress level to give a rupture lifetime of 20 days for an S-590 iron component at 923 K. It is first necessary to compute the value of the Larson-Miller parameter as follows:

$$m = T\left(20 + \log t_r\right) = (923\ \mathrm{K})\left\{20 + \log\left[(20\ \mathrm{days})(24\ \mathrm{h/day})\right]\right\}$$

$$= 20.9 \times 10^3$$

From the curve in Figure 8.33, this value of the Larson-Miller parameter corresponds to a stress level of about 280 MPa (40,000 psi).

8.D5 *Consider an S-590 iron component (Figure 8.33) that is subjected to a stress of 55 MPa (8000 psi). At what temperature will the rupture lifetime be 200 h?*

Solution

We are asked in this problem to calculate the temperature at which the rupture lifetime is 200 h when an S-590 iron component is subjected to a stress of 55 MPa (8000 psi). From the curve shown in Figure 8.33, at 55 MPa, the value of the Larson-Miller parameter is 27 × 10^3 (K-h). Thus,

$$27 \times 10^3 \text{ (K-h)} = T(20 + \log t_r)$$

$$= T[20 + \log(200 \text{ h})]$$

And, solving for T yields T = 1210 K (937°C).

8.D6 *For an 18-8 Mo stainless steel (Figure 8.35), predict the time to rupture for a component that is subjected to a stress of 100 MPa (14,500 psi) at 600°C (873 K).*

Solution

This problem asks that we determine, for an 18-8 Mo stainless steel, the time to rupture for a component that is subjected to a stress of 100 MPa (14,500 psi) at 600°C (873 K). From Figure 8.35, the value of the Larson-Miller parameter at 100 MPa is about 22.6×10^3, for T in K and t_r in h. Therefore,

$$22.6 \times 10^3 = T(20 + \log t_r)$$

$$= 873(20 + \log t_r)$$

Which leads to the following:

$$25.89 = 20 + \log t_r$$

And upon rearrangement

$$\log t_r = 5.89$$

Solving for leads to t_r

$$t_r = 10^{5.89} = 7.8 \times 10^5 \text{ h} = 89 \text{ yr}$$

8.D7 *Consider an 18-8 Mo stainless steel component (Figure 8.35) that is exposed to a temperature of 650°C (923 K). What is the maximum allowable stress level for a rupture lifetime of 1 year? 15 years?*

Solution

We are asked in this problem to calculate the stress levels at which the rupture lifetime will be 1 year and 15 years when an 18-8 Mo stainless steel component is subjected to a temperature of 650°C (923 K). It first becomes necessary to calculate the value of the Larson-Miller parameter for each time. The values of t_r corresponding to 1 and 15 years are 8.76×10^3 h and 1.31×10^5 h, respectively. Hence, for a lifetime of 1 year

$$T(20 + \log t_r) = 923\left[20 + \log\left(8.76 \times 10^3\right)\right] = 22.10 \times 10^3$$

And for t_r = 15 years

$$T(20 + \log t_r) = 923\left[20 + \log\left(1.31 \times 10^5\right)\right] = 23.18 \times 10^3$$

Using the curve shown in Figure 8.35, the stress values corresponding to the one- and fifteen-year lifetimes are approximately 150 MPa (21,750 psi) and 90 MPa (13,000 psi), respectively.

8.1FE *The following metal specimen was tensile tested until failure.*

Which type of metal would experience this type of failure?

(A) Very ductile

(B) Indeterminate

(C) Brittle

(D) Moderately ductile

Solution

The correct answer is C. A brittle metal fails with little or no plastic deformation, and with flat fracture surfaces (due to rapid crack propagation).

8.2FE *Which type of fracture is associated with intergranular crack propagation?*

(A) Ductile

(B) Brittle

(C) Either ductile or brittle

(D) Neither ductile nor brittle

Solution

The correct answer is B. Intergranular fractures are *brittle* in nature, and crack propagation is along grain boundaries.

8.3FE *Estimate the theoretical fracture strength (in MPa) of a brittle material if it is known that fracture occurs by the propagation of an elliptically shaped surface crack of length 0.25 mm that has a tip radius of curvature of 0.004 mm when a stress of 1060 MPa is applied.*

(A) 16,760 MPa

(B) 8,380 MPa

(C) 132,500 MPa

(D) 364 MPa

Solution

For an elliptically shaped crack, the maximum stress at the crack tip (or in this case the theoretical strength) σ_m when a tensile stress of σ_0 is applied, may be determined using Equation 8.1:

$$\sigma_m = 2\sigma_0\left(\frac{a}{\rho_t}\right)^{1/2}$$

Here, a is the length of a surface crack or half of the length of an internal crack, and ρ_t is the radius of curvature of the crack tip. Using values provided in the problem statement, σ_m is determined as follows:

$$\sigma_m = (2)(1060\ \text{MPa})\left(\frac{0.25\ \text{mm}}{0.004\ \text{mm}}\right)^{1/2}$$

$$= 16{,}760\ \text{MPa}$$

which is answer A.

8.4FE *A cylindrical 1045 steel bar (Figure 8.20) is subjected to repeated compression–tension stress cycling along its axis. If the load amplitude is 23,000 N, calculate the minimum allowable bar diameter (in mm) to ensure that fatigue failure will not occur. Assume a factor of safety of 2.0.*

(A) 19.4 mm

(B) 9.72 mm

(C) 17.4 mm

(D) 13.7 mm

Solution

From Figure 8.20, the fatigue limit stress amplitude for this steel alloy (i.e., the maximum stress for fatigue failure) is about 310 MPa. For a cylindrical specimen having an original diameter of d_0 the cross sectional $A_0 = \pi(d_0/2)^2$. Therefore, using Equation 6.1 the stress is calculated as

$$\sigma = \frac{F}{A_0} = \frac{F}{\pi\left(\frac{d_0}{2}\right)^2} = \frac{4F}{\pi d_0^2}$$

And when we incorporate the factor of safety, N, the above equation takes the form:

$$\frac{\sigma}{N} = \frac{4F}{\pi d_0^2}$$

Now, we solve for d_0, taking stress as the fatigue limit (310 MPa = 310×10^6 N/m^2), a value of 2.0 for the factor of safety, and for the load amplitude, F, a value of 23,000 N as follows:

$$d_0 = 2\sqrt{\frac{FN}{\pi\sigma}}$$

$$= 2\sqrt{\frac{(23{,}000 \text{ N})(2.0)}{(\pi)(310 \times 10^6 \text{ N/m}^2)}} = 0.0137 \text{ m} = 13.7 \text{ mm}$$

which is answer D.

CHAPTER 9~~10~~

PHASE DIAGRAMS

PROBLEM SOLUTIONS

Solubility Limit

9.1 *Consider the sugar–water phase diagram of Figure 9.1.*

(a) How much sugar will dissolve in 1000 g of water at 80°C (176°F)?

(b) If the saturated liquid solution in part (a) is cooled to 20°C (68°F), some of the sugar will precipitate out as a solid. What will be the composition of the saturated liquid solution (in wt% sugar) at 20°C?

(c) How much of the solid sugar will come out of solution upon cooling to 20°C?

Solution

(a) We are asked to determine how much sugar will dissolve in 1000 g of water at 80°C. From the solubility limit curve in Figure 9.1, at 80°C the maximum concentration of sugar in the syrup is about 74 wt%. It is now possible to calculate the mass of sugar using Equation 4.3a as

$$C_{\text{sugar}}(\text{wt\%}) = \frac{m_{\text{sugar}}}{m_{\text{sugar}} + m_{\text{water}}} \times 100$$

$$74 \text{ wt\%} = \frac{m_{\text{sugar}}}{m_{\text{sugar}} + 1000 \text{ g}} \times 100$$

Solving for m_{sugar} yields $m_{\text{sugar}} = 2846$ g

(b) Again using this same plot, at 20°C the solubility limit (or the concentration of the saturated solution) is about 64 wt% sugar.

(c) The mass of sugar in this saturated solution at 20°C (m'_{sugar}) may also be calculated using Equation 4.3a as follows:

$$64 \text{ wt\%} = \frac{m'_{\text{sugar}}}{m'_{\text{sugar}} + 1000 \text{ g}} \times 100$$

which yields a value for m'_{sugar} of 1778 g. Subtracting the latter from the former of these sugar concentrations yields the amount of sugar that precipitated out of the solution upon cooling m''_{sugar}; that is

$$m''_{\text{sugar}} = m_{\text{sugar}} - m'_{\text{sugar}} = 2846 \text{ g} - 1778 \text{ g} = 1068 \text{ g}$$

9.2 *At 100°C, what is the maximum solubility of the following:*

(a) Pb in Sn

(b) Sn in Pb

Solution

(a) From Figure 9.8, the maximum solubility of Pb in Sn at 100°C corresponds to the position of the β–(α + β) phase boundary at this temperature, or to about 2 wt% Pb.

(b) From this same figure, the maximum solubility of Sn in Pb corresponds to the position of the α–(α + β) phase boundary at this temperature, or about 5 wt% Sn.

Microstructure

9.3 *Cite three variables that determine the microstructure of an alloy.*

Solution

Three variables that determine the microstructure of an alloy are (1) the alloying elements present, (2) the concentrations of these alloying elements, and (3) the heat treatment of the alloy.

Phase Equilibria

9.4 *What thermodynamic condition must be met for a state of equilibrium to exist?*

Solution

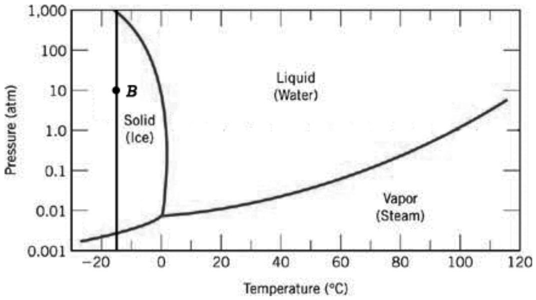
In order for a system to exist in a state of equilibrium the free energy must be a minimum for some specified combination of temperature, pressure, and composition.

One-Component (or Unary) Phase Diagrams

9.5 *Consider a specimen of ice that is at –15°C and 10 atm pressure. Using Figure 9.2, the pressure–temperature phase diagram for H_2O, determine the pressure to which the specimen must be raised or lowered to cause it (a) to melt and (b) to sublime.*

Solution

The figure below shows the pressure-temperature phase diagram for H_2O, Figure 10.2; a vertical line has been constructed at –15°C, and the location on this line at 10 atm pressure (point *B*) is also noted.



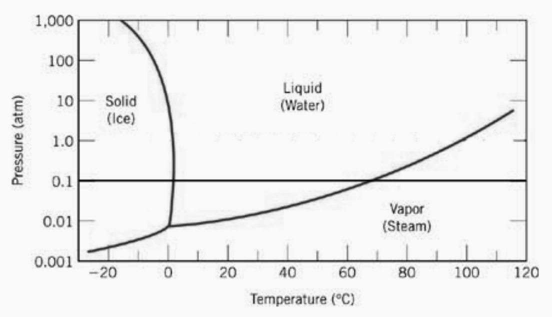
(a) Melting occurs, (by changing pressure) as, moving vertically (upward) along this line, we cross the Solid-Liquid phase boundary. This occurs at approximately 1,000 atm; thus, the pressure of the specimen must be raised from 10 to 1,000 atm.

(b) In order to determine the pressure at which sublimation occurs at this temperature, we move vertically downward along this line from 10 atm until we cross the Solid-Vapor phase boundary. This intersection occurs at approximately 0.003 atm.

9.6 *At a pressure of 0.1 atm, determine (a) the melting temperature for ice and (b) the boiling temperature for water.*

Solution

The melting temperature for ice and the boiling temperature for water at a pressure of 0.1 atm may be determined from the pressure-temperature diagram for this system, Figure 9.2, which is shown below; a horizontal line has been constructed across this diagram at a pressure of 0.1 atm.



The temperature corresponding to the intersection of this line with the Solid-Liquid phase boundary is the melting temperature, which is approximately 2°C. On the other hand, the boiling temperature is at the intersection of the horizontal line with the Liquid-Vapor phase boundary--approximately 70°C.

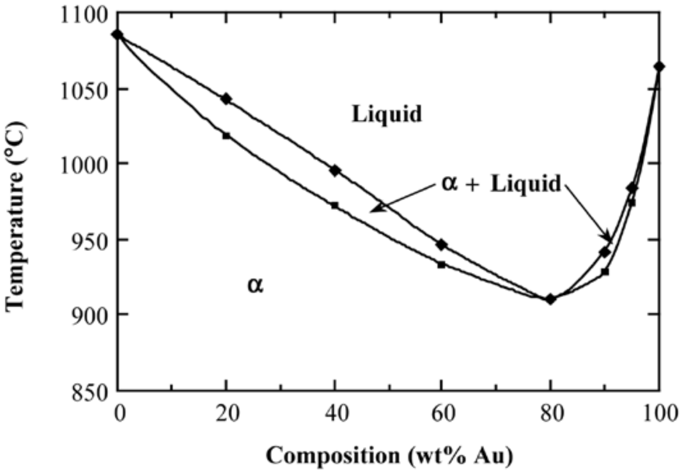
Binary Isomorphous Systems

9.7 *Given here are the solidus and liquidus temperatures for the copper–gold system. Construct the phase diagram for this system and label each region.*

Composition (wt% Au)	***Solidus Temperature (°C)***	***Liquidus Temperature (°C)***
0	*1085*	*1085*
20	*1019*	*1042*
40	*972*	*996*
60	*934*	*946*
80	*911*	*911*
90	*928*	*942*
95	*974*	*984*
100	*1064*	*1064*

Solution

The copper-gold phase diagram is constructed below.



9.8 *How many kilograms of nickel must be added to 1.75 kg of copper to yield a liquidus temperature of 1300°C?*

Solution

According to the copper-nickel phase diagram, the composition at the 1300°C liquidus temperature is about 43 wt% Ni. In order to determine the amount of nickel that must be added to 1.75 kg Ni, it is necessary to use Equation 4.3a. If we let m_{Ni} represent the mass of nickel required, then Equation 4.3a takes the form

$$\mathbf{43\ wt\%\ Ni} = \frac{\boldsymbol{m}_{\mathbf{Ni}}}{\mathbf{1.75\ kg} + \boldsymbol{m}_{\mathbf{Ni}}} \times \mathbf{100}$$

And solving this expression for m_{Ni} leads to m_{Ni} = 1.32 kg.

9.9 *How many kilograms of nickel must be added to 5.43 kg of copper to yield a solidus temperature of 1200°C?*

Solution

According to the copper-nickel phase diagram, the composition at the 1200°C solidus temperature is about 30 wt% Ni, which is equivalent to 70 wt% Cu. In order to determine the amount of copper that must be added to 5.43 kg Cu, it is necessary to use Equation 4.3a. If we let m_{Cu} represent the mass of copper required, then Equation 4.3a takes the form

$$\mathbf{70\ wt\%\ Cu} = \frac{\boldsymbol{m}_{\mathbf{Cu}}}{\mathbf{5.43\ kg} + \boldsymbol{m}_{\mathbf{Cu}}} \times \mathbf{100}$$

And solving this expression for m_{Cu} leads to m_{Cu} = 12.7 kg.

Interpretation of Phase Diagrams

9.10 *Cite the phases that are present and the phase compositions for the following alloys:*

(a) 15 wt% Sn–85 wt% Pb at 100°C (212°F)
(b) 25 wt% Pb–75 wt% Mg at 425°C (800°F)
(c) 85 wt% Ag–15 wt% Cu at 800°C (1470°F)
(d) 55 wt% Zn–45 wt% Cu at 600°C (1110°F)
(e) 1.25 kg Sn and 14 kg Pb at 200°C (390°F)
(f) 7.6 lb$_m$ Cu and 144.4 lb$_m$ Zn at 600°C (1110°F)
(g) 21.7 mol Mg and 35.4 mol Pb at 350°C (660°F)
(h) 4.2 mol Cu and 1.1 mol Ag at 900°C (1650°F)

Solution

(a) For an alloy composed of 15 wt% Sn-85 wt% Pb and at 100°C, from Figure 9.8, α and β phases are present, and using a tie line constructed at this temperature, the compositions of these phases are determined as follows:

C_α = 5 wt% Sn-95 wt% Pb
C_β = 98 wt% Sn-2 wt% Pb

(b) For an alloy composed of 25 wt% Pb-75 wt% Mg and at 425°C, from Figure 9.20, only the α phase is present; ~~-~~its composition is 25 wt% Pb-75 wt% Mg.

(c) For an alloy composed of 85 wt% Ag-15 wt% Cu and at 800°C, from Figure 9.7, β and liquid phases are present, and using a tie line constructed at this temperature the compositions of these phases are determined as follows:~~and~~

C_β = 92 wt% Ag-8 wt% Cu
C_L = 77 wt% Ag-23 wt% Cu

(d) For an alloy composed of 55 wt% Zn-45 wt% Cu and at 600°C, from Figure 9.19, β and γ phases are present, and using a tie line constructed at this temperature, the compositions of these phases are determined as follows:~~and~~

C_β = 51 wt% Zn-49 wt% Cu
C_γ = 58 wt% Zn-42 wt% Cu

(e) For an alloy composed of 1.25 kg Sn and 14 kg Pb and at 200°C, we must first determine the Sn and Pb concentrations in weight percent (using Equation 4.3a), as

$$C_{\text{Sn}} = \frac{1.25\text{ kg}}{1.25\text{ kg} + 14\text{ kg}} \times 100 = 8.2\text{ wt\%}$$

$$C_{\text{Pb}} = \frac{14\text{ kg}}{1.25\text{ kg} + 14\text{ kg}} \times 100 = 91.8\text{ wt\%}$$

From Figure 9.8, only the α phase is present; its composition is 8.2 wt% Sn-91.8 wt% Pb.

(f) For an alloy composed of 7.6 lb_m Cu and 144.4 lb_m Zn and at 600°C, we must first determine the Cu and Zn concentrations (using Equation 4.3a), as

$$C_{\text{Cu}} = \frac{7.6\text{ lb}_\text{m}}{7.6\text{ lb}_\text{m} + 144.4\text{ lb}_\text{m}} \times 100 = 5.0\text{ wt\%}$$

$$C_{\text{Zn}} = \frac{144.4\text{ lb}_\text{m}}{7.6\text{ lb}_\text{m} + 144.4\text{ lb}_\text{m}} \times 100 = 95.0\text{ wt\%}$$

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From Figure 9.19, only the *L* phase is present; its composition is 95.0 wt% Zn-5.0 wt% Cu

(g) For an alloy composed of 21.7 mol Mg and 35.4 mol Pb and at 350°C, it is necessary to determine the Mg and Pb concentrations in weight percent. However, we must first compute the masses of Mg and Pb (in grams) using a rearranged form of Equation 4.4 (and the atomic weights of Pb and Mg—207.2 g/mol and 24.31 g/mol) as follows:

$$m'_{\text{Pb}} = n_{m_{\text{Pb}}} A_{\text{Pb}} = (35.4\text{ mol})(207.2\text{ g/mol}) = 7335\text{ g}$$

$$m'_{\text{Mg}} = n_{m_{\text{Mg}}} A_{\text{Mg}} = (21.7\text{ mol})(24.31\text{ g/mol}) = 527\text{ g}$$

Now, using Equation 4.3a, concentrations of Pb and Mg are determined as follows:

$$C_{\text{Pb}} = \frac{7335\text{ g}}{7335\text{ g} + 527\text{ g}} \times 100 = 93.3\text{ wt\%}$$

$$C_{\text{Mg}} = \frac{527\text{ g}}{7335\text{ g} + 527\text{ g}} \times 100 = 6.7\text{ wt\%}$$

From Figure 9.20, *L* and Mg_2Pb phases are present, and using a tie line constructed at this temperature, the compositions of these phases are determined as follows:~~and~~

$$C_L = 94\ \text{wt\% Pb} - 6\ \text{wt\% Mg}$$

$$C_{\text{Mg}_2\text{Pb}} = 81\ \text{wt\% Pb} - 19\ \text{wt\% Mg}$$

(h) For an alloy composed of 4.2 mol Cu and 1.1 mol Ag and at 900°C, it is necessary to determine the Cu and Ag concentrations in weight percent. However, we must first compute the masses of Cu and Ag (in grams) using a rearranged form of Equation 4.4 (and the atomic weights of Cu and Ag—63.55 g/mol and 107.87 g/mol) as follows:

$$m'_{\text{Cu}} = n_{m_{\text{Cu}}} A_{\text{Cu}} = (4.2\ \text{mol})(63.55\ \text{g/mol}) = 266.9\ \text{g}$$

$$m_{\text{Ag}} = n_{m_{\text{Ag}}} A_{\text{Ag}} = (1.1\ \text{mol})(107.87\ \text{g/mol}) = 118.7\ \text{g}$$

Now, using Equation 4.3a, concentrations of Cu and Ag are determined as follows:

$$C_{\text{Cu}} = \frac{266.9\ \text{g}}{266.9\ \text{g} + 118.7\ \text{g}} \times 100 = 69.2\ \text{wt\%}$$

$$C_{\text{Ag}} = \frac{118.7\ \text{g}}{266.9\ \text{g} + 118.7\ \text{g}} \times 100 = 30.8\ \text{wt\%}$$

From Figure 9.7, α and liquid phases are present; and using a tie line constructed at this temperature, the compositions of these phases are determined as follows:~~and~~

C_α = 8 wt% Ag-92 w% Cu
C_L = 45 wt% Ag-55 wt% Cu

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9.11 *Is it possible to have a copper–silver alloy that, at equilibrium, consists of a* β *phase of composition 92 wt% Ag–8 wt% Cu and also a liquid phase of composition 76 wt% Ag–24 wt% Cu? If so, what will be the approximate temperature of the alloy? If this is not possible, explain why.*

Solution

It *is possible* to have a Cu-Ag alloy, which at equilibrium consists of a β phase of composition 92 wt% Ag-8 wt% Cu and a liquid phase of composition 77 wt% Ag-23 wt% Cu. From Figure 9.7 a horizontal tie line can be constructed across the $\beta + L$ phase region at about 800°C which intersects the L–($\beta + L$) phase boundary at 76 wt% Ag, and also the ($\beta + L$)–β phase boundary at 92 wt% Ag.

9.12 *Is it possible to have a copper–silver alloy that, at equilibrium, consists of an α phase of composition 4 wt% Ag–96 wt% Cu and also a β phase of composition 95 wt% Ag–5 wt% Cu? If so, what will be the approximate temperature of the alloy? If this is not possible, explain why.*

Solution

It *is possible* to have a Cu-Ag alloy, which at equilibrium consists of an α phase of composition 4 wt% Ag-96 wt% Cu and a β phase of composition 95 wt% Ag-5 wt% Cu. From Figure 9.7 a horizontal tie can be constructed across the $\alpha + \beta$ region at 690°C which intersects the α–($\alpha + \beta$) phase boundary at 4 wt% Ag, and also the ($\alpha + \beta$)–β phase boundary at 95 wt% Ag.

9.13 *A lead–tin alloy of composition 30 wt% Sn–70 wt% Pb is slowly heated from a temperature of 150°C (300°F).*

(a) At what temperature does the first liquid phase form?

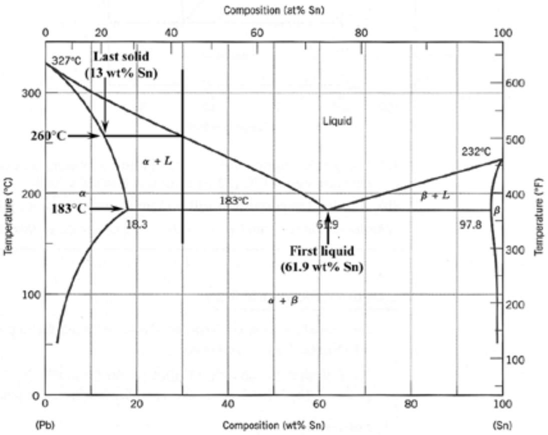
(b) What is the composition of this liquid phase?

(c) At what temperature does complete melting of the alloy occur?

(d) What is the composition of the last solid remaining prior to complete melting?

Solution

Upon heating a lead-tin alloy of composition 30 wt% Sn-70 wt% Pb from 150°C and utilizing Figure 10.8 as shown below:



(a) The first liquid forms at the temperature at which a vertical line at this composition intersects the eutectic isotherm--i.e., at 183°C.

(b) The composition of this liquid phase corresponds to the intersection with the (α + L)–L phase boundary, of a tie line constructed across the $\alpha + L$ phase region just above this eutectic isotherm--i.e., C_L = 61.9 wt% Sn.

(c) Complete melting of the alloy occurs at the intersection of this same vertical line at 30 wt% Sn with the ($\alpha + L$)–L phase boundary--i.e., at about 260°C.

(d) The composition of the last solid remaining prior to complete melting corresponds to the intersection with α–(α + L) phase boundary, of the tie line constructed across the $\alpha + L$ phase region at 260°C--i.e., C_α is about 13 wt% Sn.

9.14 *A 50 wt% Ni–50 wt% Cu alloy is slowly cooled from 1400°C (2550°F) to 1200°C (2190°F).*

(a) At what temperature does the first solid phase form?

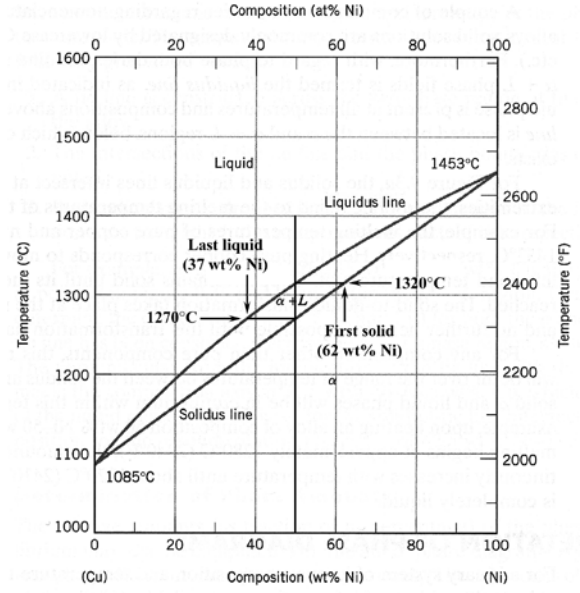
(b) What is the composition of this solid phase?

(c) At what temperature does the liquid solidify?

(d) What is the composition of this last remaining liquid phase?

Solution

Shown below is the Cu-Ni phase diagram (Figure 10.3a) and a vertical line constructed at a composition of 50 wt% Ni-50 wt% Cu.



(a)

(a) The first solid phase forms at the temperature at which a vertical line at this composition intersects the L–($\alpha + L$) phase boundary--i.e., at about 1320°C.

(b) The composition of this solid phase corresponds to the intersection with the L–($\alpha + L$) phase boundary, of a tie line constructed across the $\alpha + L$ phase region at 1320°C--i.e., C_α = 62 wt% Ni-38 wt% Cu.

(c) Complete solidification of the alloy occurs at the intersection of this same vertical line at 50 wt% Ni with the ($\alpha + L$)–α phase boundary--i.e., at about 1270°C.

(d) The composition of the last liquid phase remaining prior to complete solidification corresponds to the intersection with the L–($\alpha + L$) boundary, of the tie line constructed across the $\alpha + L$ phase region at 1270°C--i.e., C_L is about 37 wt% Ni-63 wt% Cu.

9.15 *A copper-zinc alloy of composition 75 wt% Zn-25 wt% Cu is slowly heated from room temperature.*

(a) At what temperature does the first liquid phase form?

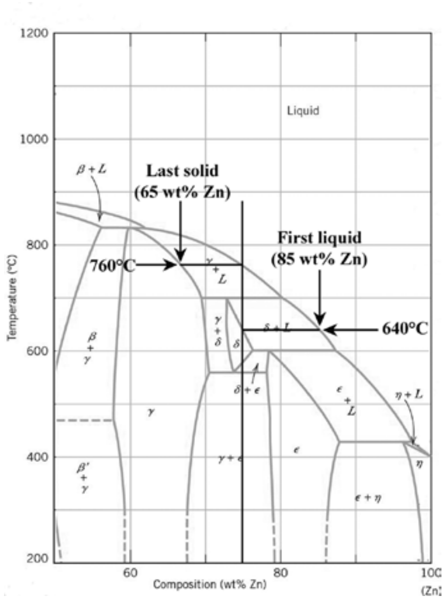
(b) What is the composition of this liquid phase?

(c) At what temperature does complete melting of the alloy occur?

(d) What is the composition of the last solid remaining prior to complete melting?

Solution

Shown below is a portion of the Cu-Zn phase diagram (Figure 9.19) and a vertical line constructed at a composition of 75 wt% Zn-25 wt% Cu.



Upon heating a copper-zinc alloy of composition 75 wt% Zn-25 wt% Cu from room temperature and utilizing Figure 9.19 the following occur:

(a) The first liquid forms at the temperature at which a vertical line at this composition intersects the δ–(δ + L) phase boundary—i.e., at about 640°C.

(b) The composition of this liquid phase corresponds to the intersection with the δ–($\delta + L$) phase boundary, of a tie line constructed across the $\delta + L$ phase region boundary i.e., C_L = 85 wt% Zn.

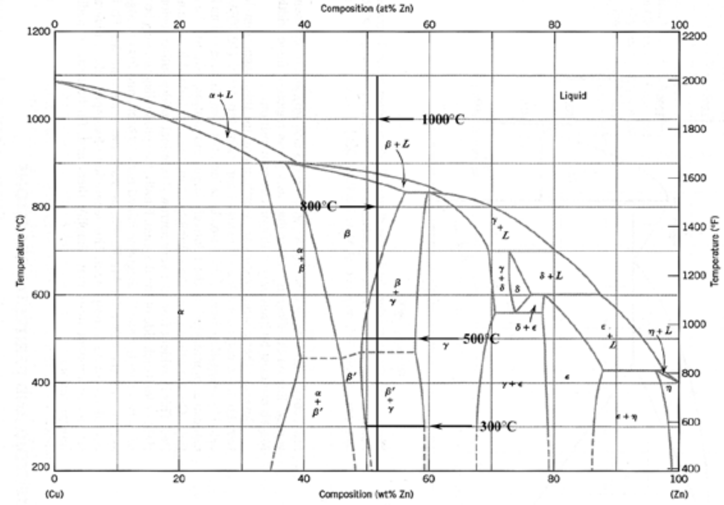
(c) Complete melting of the alloy occurs at the intersection of this same vertical line at 75 wt% Zn with the $(\gamma + L)$ –L phase boundary--i.e., at about 760°C.

(d) The composition of the last solid remaining prior to complete melting corresponds to the intersection with γ–$(\gamma + L)$ phase boundary, of the tie line constructed across the $\gamma + L$ phase region at 760°C--i.e., C_{γ} is about 65 wt% Zn.

9.16 *For an alloy of composition 52 wt% Zn–48 wt% Cu, cite the phases present and their mass fractions at the following temperatures: 1000°C, 800°C, 500°C, and 300°C.*

Solution

This problem asks us to determine the phases present and their concentrations at several temperatures, as an alloy of composition 52 wt% Zn-48 wt% Cu is cooled. From Figure 9.19 (the Cu-Zn phase diagram), which is shown below with a vertical line constructed at the specified composition:



At 1000°C, a liquid phase is present; $W_L = 1.0$
At 800°C, the β phase is present, and $W_\beta = 1.0$

At 500°C, β and γ phases are present, and from the tie lie constructed on the above diagram

$$W_\gamma = \frac{C_0 - C_\beta}{C_\gamma - C_\beta} = \frac{52 - 49}{58 - 49} = 0.33$$

$$W_\beta = 1.00 - 0.33 = 0.67$$

At 300°C, the β' and γ phases are present, and from the tie line constructed above

$$W_{\beta'} = \frac{C_\gamma - C_0}{C_\gamma - C_{\beta'}} = \frac{59 - 52}{59 - 50} = 0.78$$

$W_\gamma = 1.00 - 0.78 = 0.22$

9.17 *Determine the relative amounts (in terms of mass fractions) of the phases for the alloys and temperatures given in Problem 9.10.*

Solution

(a) For an alloy composed of 15 wt% Sn-85 wt% Pb and at 100°C, compositions of the α and β phases are

C_α = 5 wt% Sn-95 wt% Pb
C_β = 98 wt% Sn-2 wt% Pb

And, since the composition of the alloy, C_0 = 15 wt% Sn-85 wt% Pb, then, using the appropriate lever rule expressions and taking compositions in weight percent tin

$$\boldsymbol{W_\alpha = \frac{C_\beta - C_0}{C_\beta - C_\alpha} = \frac{98 - 15}{98 - 5} = 0.89}$$

$$\boldsymbol{W_\beta = \frac{C_0 - C_\alpha}{C_\beta - C_\alpha} = \frac{15 - 5}{98 - 5} = 0.11}$$

(b) For an alloy composed of 25 wt% Pb-75 wt% Mg and at 425°C, only the α phase is present; therefore W_α = 1.0.

(c) For an alloy composed of 85 wt% Ag-15 wt% Cu and at 800°C, compositions of the β and liquid phases are

C_β = 92 wt% Ag-8 wt% Cu
C_L = 77 wt% Ag-23 wt% Cu

And, since the composition of the alloy, C_0 = 85 wt% Ag-15 wt% Cu, then, using the appropriate lever rule expressions and taking compositions in weight percent silver

$$\boldsymbol{W_\beta = \frac{C_0 - C_L}{C_\beta - C_L} = \frac{85 - 77}{92 - 77} = 0.53}$$

$$\boldsymbol{W_L = \frac{C_\beta - C_0}{C_\beta - C_L} = \frac{92 - 85}{92 - 77} = 0.47}$$

(d) For an alloy composed of 55 wt% Zn-45 wt% Cu and at 600°C, compositions of the β and γ phases are

C_β = 51 wt% Zn-49 wt% Cu

C_γ = 58 wt% Zn-42 wt% Cu

And, since the composition of the alloy, C_0 = 55 wt% Zn-45 wt% Cu, then, using the appropriate lever rule expressions and taking compositions in weight percent zinc

$$W_\beta = \frac{C_\gamma - C_0}{C_\gamma - C_\beta} = \frac{58 - 55}{58 - 51} = 0.43$$

$$W_\gamma = \frac{C_0 - C_\beta}{C_\gamma - C_\beta} = \frac{55 - 51}{58 - 51} = 0.57$$

(e) For an alloy composed of 1.25 kg Sn and 14 kg Pb (8.2 wt% Sn-91.8 wt% Pb) and at 200°C, only the α phase is present; therefore W_α = 1.0.

(f) For an alloy composed of 7.6 $\mathrm{lb_m}$ Cu and 144.4 $\mathrm{lb_m}$ Zn (95.0 wt% Zn-5.0 wt% Cu) and at 600°C, only the liquid phase is present; therefore, W_L = 1.0

(g) For an alloy composed of 21.7 mol Mg and 35.4 mol Pb (94 wt% Pb-6 wt% Mg) and at 350°C, *L* and Mg_2Pb phases are present, with

$$C_L = 94\text{ wt\% Pb} - 6\text{ wt\% Mg}$$

$$C_{\mathrm{Mg_2Pb}} = 81\text{ wt\% Pb} - 19\text{ wt\% Mg}$$

And, since the composition of the alloy, C_0 = 93 wt% Pb-7 wt% Mg, then, using the appropriate lever rule expressions and taking compositions in weight percent lead

$$W_{\mathrm{Mg_2Pb}} = \frac{C_L - C_0}{C_L - C_{\mathrm{Mg_2Pb}}} = \frac{94 - 93}{94 - 81} = 0.08$$

$$W_L = \frac{C_0 - C_{\mathrm{Mg_2Pb}}}{C_L - C_{\mathrm{Mg_2Pb}}} = \frac{93 - 81}{94 - 81} = 0.92$$

(h) For an alloy composed of 4.2 mol Cu and 1.1 mol Ag (30.8 wt% Ag-69.2 wt% Cu) and at 900°C, compositions of the α and liquid phases are

C_α = 8 wt% Ag-92 w% Cu
C_L = 45 wt% Ag-55 wt% Cu

And, since the composition of the alloy, C_0 = 30.8 wt% Ag-69.2 wt% Cu, then, using the appropriate lever rule expressions and taking compositions in weight percent silver

$$W_\alpha = \frac{C_L - C_0}{C_L - C_\alpha} = \frac{45 - 30.8}{45 - 8} = 0.38$$

$$W_L = \frac{C_0 - C_\alpha}{C_L - C_\alpha} = \frac{30.8 - 8}{45 - 8} = 0.62$$

9.18 *A 2.0-kg specimen of an 85 wt% Pb–15 wt% Sn alloy is heated to 200°C (390°F); at this temperature it is entirely an α-phase solid solution (Figure 9.8). The alloy is to be melted to the extent that 50% of the specimen is liquid, the remainder being the α phase. This may be accomplished by heating the alloy or changing its composition while holding the temperature constant.*

(a) To what temperature must the specimen be heated?

(b) How much tin must be added to the 2.0-kg specimen at 200°C to achieve this state?

Solution

(a) This part of the problem calls for us to cite the temperature to which a 85 wt% Pb-15 wt% Sn alloy must be heated in order to have 50% liquid. Probably the easiest way to solve this problem is by trial and error—that is, on the Pb-Sn phase diagram (Figure 9.8), moving vertically at the given composition, through the $\alpha + L$ region until the tie-line lengths on both sides of the given composition are the same. This occurs at approximately 280°C (535°F).

(b) We can also produce a 50% liquid solution at 200°C, by adding Sn to the alloy. At 200°C and within the $\alpha + L$ phase region, compositions of α and liquid phases are determined using a tie line constructed at this temperature, as follows

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$$C_\alpha = 17 \text{ wt\% Sn-83 wt\% Pb}$$
$$C_L = 57 \text{ wt\% Sn-43 wt\% Pb}$$

Let C_0 be the new alloy composition to give $W_\alpha = W_L = 0.5$. Then,

$$W_\alpha = 0.5 = \frac{C_L - C_0}{C_L - C_\alpha} = \frac{57 - C_0}{57 - 17}$$

And solving for C_0 gives 37 wt% Sn. Now, let m_{Sn} be the mass of Sn added to the alloy to achieve this new composition. The amount of Sn in the original alloy is

$$(0.15)(2.0 \text{ kg}) = 0.30 \text{ kg}$$

Then, using a modified form of Equation 4.3a

$$\left(\frac{0.30 \text{ kg} + m_{\text{Sn}}}{2.0 \text{ kg} + m_{\text{Sn}}}\right) \times 100 = 37$$

And, solving for m_{Sn} (the mass of tin to be added), yields $m_{\text{Sn}} = 0.698$ kg.

9.19 *A magnesium–lead alloy of mass 7.5 kg consists of a solid α phase that has a composition just slightly below the solubility limit at 300°C (570°F).*

(a) What mass of lead is in the alloy?

(b) If the alloy is heated to 400°C (750°F), how much more lead may be dissolved in the α phase without exceeding the solubility limit of this phase?

Solution

(a) This portion of the problem asks that we calculate, for a Pb-Mg alloy, the mass of lead in 7.5 kg of the solid α phase at 300°C just below the solubility limit. From Figure 9.20, the solubility limit for the α phase at 300°C corresponds to the position (composition) of the α–(α + Mg_2Pb) phase boundary at this temperature, which is about 17 wt% Pb. Therefore, the mass of Pb in the alloy is just (0.17)(7.5 kg) = 1.28 kg.

(b) At 400°C, the solubility limit of the α phase increases to approximately 32 wt% Pb. In order to determine the additional amount of Pb that may be added $(m_{\mathrm{Pb}'})$, we utilize a modified form of Equation 4.3a as

$$C_{\mathrm{Pb}} = 32\ \mathrm{wt\%} = \frac{1.28\ \mathrm{kg} + m_{\mathrm{Pb}'}}{7.5\ \mathrm{kg} + m_{\mathrm{Pb}'}} \times 100$$

Solving for $m_{\mathrm{Pb}'}$ yields $m_{\mathrm{Pb}'}$ = 1.69 kg.

9.20 *Consider 2.5 kg of a 80 wt% Cu-20 wt% Ag copper-silver alloy at 800°C. How much copper must be added to this alloy to cause it to completely solidify 800°C?*

Solution

From the Cu-Ag phase diagram, Figure 9.7, for a composition of 80 wt% Cu, the α and liquid phases are present and at 800°C. In order for this alloy to completely solidify at 800°C copper must be added such that a new composition is achieved that lies just within the single-phase α region; from Figure 9.7 this composition is approximately 92 wt% Cu-8 wt% Ag (at 800°C). In order to determine the additional amount of Cu that may be added (m_{Cu}), we utilize a modified form of Equation 4.3. However it is first necessary to determine how much copper is in the original alloy; this amount is just 80% of 2.5 kg, which is (0.80)(2.5 kg) = 2.0 kg. For employment of Equation 4.3a, the total amount of copper is equal to 2.0 kg + m_{Cu} whereas the total mass of alloy is 2.5 kg + m_{Cu}. Therefore

$$C_{Cu} = 92 \text{ wt\%} = \frac{2.0 \text{ kg} + m_{Cu}}{2.5 \text{ kg} + m_{Cu}} \times 100$$

Solving for m_{Cu} yields m_{Cu} = 3.75 kg.

9.21 *A 65 wt% Ni–35 wt% Cu alloy is heated to a temperature within the α + liquid-phase region. If the composition of the α phase is 70 wt% Ni, determine:*

(a) The temperature of the alloy

(b) The composition of the liquid phase

(c) The mass fractions of both phases

Solution

(a) In order to determine the temperature of a 65 wt% Ni-35 wt% Cu alloy for which α and liquid phases are present with the α phase of composition 70 wt% Ni, we need to construct a tie line across the $\alpha + L$ phase region of Figure 10.3a that intersects the solidus line at 70 wt% Ni; this is possible at about 1345°C.

(b) The composition of the liquid phase at this temperature is determined from the intersection of this same tie line with liquidus line, which corresponds to about 59 wt% Ni.

(c) The mass fractions of the two phases are determined using the lever rule, Equations 9.1 and 9.2 with C_0 = 65 wt% Ni, C_L = 59 wt% Ni, and C_α = 70 wt% Ni, as

$$\boldsymbol{W_\alpha = \frac{C_0 - C_L}{C_\alpha - C_L} = \frac{65 - 59}{70 - 59} = 0.55}$$

$$\boldsymbol{W_L = \frac{C_\alpha - C_0}{C_\alpha - C_L} = \frac{70 - 65}{70 - 59} = 0.45}$$

9.22 *A 40 wt% Pb–60 wt% Mg alloy is heated to a temperature within the α + liquid-phase region. If the mass fraction of each phase is 0.5, then estimate:*

(a) the temperature of the alloy

(b) the compositions of the two phases in weight percent

(c) the compositions of the two phases in atom percent

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Solution

(a) We are given that the mass fractions of α and liquid phases are both 0.5 for a 40 wt% Pb-60 wt% Mg alloy and are asked to estimate the temperature of the alloy. Using the appropriate phase diagram, Figure 9.20, by trial and error with a ruler, a tie line within the α + L phase region that is divided in half for an alloy of this composition exists at about 540°C.

(b) We are now asked to determine the compositions (in weight percent) of the two phases. This is accomplished by noting the intersections of this tie line with both the solidus and liquidus lines. From these intersections, C_α = 26 wt% Pb-74 wt% Mg and C_L = 54 wt% Pb-46 wt% Mg.

(c) In order to convert these compositions to atom percent it is necessary to use Equations 4.6a and 4.6b, which include the atomic weights of lead and magnesium (as taken from inside the front cover):

A_{Pb} = 207.2 g/mol

A_{Mg} = 24.31 g/mol

Therefore, these concentration conversions are as follows:

For the concentration of lead in the α phase, $C'_{\mathrm{Pb}}(\alpha)$, in atom percent

$$C'_{\mathrm{Pb}}(\alpha) = \frac{C_{\mathrm{Pb}}(\alpha)A_{\mathrm{Mg}}}{C_{\mathrm{Pb}}(\alpha)A_{\mathrm{Mg}} + C_{\mathrm{Mg}}(\alpha)A_{\mathrm{Pb}}} \times 100$$

$$= \frac{(26\text{ wt\% Pb})(24.31\text{ g/mol})}{(26\text{ wt\% Pb})(24.31\text{ g/mol}) + (74\text{ wt\% Mg})(207.2\text{ g/mol})} \times 100$$

= 4.0 at%

The concentration of magnesium (in atom percent) in the α phase, is determined as follows:

$$C'_{\mathrm{Mg}}(\alpha) = \frac{C_{\mathrm{Mg}}(\alpha)A_{\mathrm{Pb}}}{C_{\mathrm{Pb}}(\alpha)A_{\mathrm{Mg}} + C_{\mathrm{Mg}}(\alpha)A_{\mathrm{Pb}}} \times 100$$

$$= \frac{(74 \text{ wt\% Mg})(207.2 \text{ g/mol})}{(26 \text{ wt\% Pb})(24.31 \text{ g/mol}) + (74 \text{ wt\% Mg})(207.2 \text{ g/mol})} \times 100$$

= 96.0 at%

We now conduct liquid-phase computations ion a similar manner. The concentration of lead in the liquid phase, $C'_{\text{Pb}}(L)$, in atom percent, is determined as follows:

$$C'_{\text{Pb}}(L) = \frac{C_{\text{Pb}}(L)A_{\text{Mg}}}{C_{\text{Pb}}(L)A_{\text{Mg}} + C_{\text{Mg}}(L)A_{\text{Pb}}} \times 100$$

$$= \frac{(54 \text{ wt\% Pb})(24.31 \text{ g/mol})}{(54 \text{ wt\% Pb})(24.31 \text{ g/mol}) + (46 \text{ wt\% Mg})(207.2 \text{ g/mol})} \times 100$$

$$= \frac{(54 \text{ wt\%}}{(54 \text{ wt\% Pb})(24.31 \text{ g/mol}) + (46 \text{ wt\% Mg})(207.2 \text{ g/mol})}$$

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= 12.1 at%

And, finally, the concentration (in atom percent) of magnesium in the liquid is

$$C'_{\text{Mg}}(L) = \frac{C_{\text{Mg}}(L)A_{\text{Pb}}}{C_{\text{Pb}}(L)A_{\text{Mg}} + C_{\text{Mg}}(L)A_{\text{Pb}}} \times 100$$

$$= \frac{(46 \text{ wt\% Mg})(207.2 \text{ g/mol})}{(54 \text{ wt\% Pb})(24.31 \text{ g/mol}) + (46 \text{ wt\% Mg})(207.2 \text{ g/mol})} \times 100$$

= 87.9 at%

9.23 *A copper-silver alloy is heated to 900°C and is found to consist of α and liquid phases. If the mass fraction of the liquid phase is 0.68 determine*

(a) the composition of both phases, in both weight percent and atom percent, and

(b) the composition of the alloy, in both weight percent and atom percent

Solution

(a) To determine the compositions of the α and liquid phases it is necessary to construct a tie-line at 900°C in the α + liquid phase region. The composition of the α phase corresponds to the tie-line intersection with the α–(α + liquid) phase boundary—that is, C_α = 8 wt% Ag-92 wt% Cu). Likewise, the composition of the liquid (L) phase is determined by the tie-line intersection with the (α + liquid)–L phase boundary—i.e., C_L = 43 wt% Ag-57 wt% Cu.

Atom percent computations require the use of Equations 4.6a and 4.6b as well as the atomic weights for silver and copper, which are found inside the front cover, and are as follows:

A_{Ag} = 107.87 g/mol

A_{Cu} = 63.55 g/mol

Therefore, for the concentration of silver (in at%) in the α phase, $C'_{\text{Ag}}(\alpha)$

$$C'_{\text{Ag}}(\alpha) = \frac{C_{\text{Ag}}(\alpha)A_{\text{Cu}}}{C_{\text{Ag}}(\alpha)A_{\text{Cu}} + C_{\text{Cu}}(\alpha)A_{\text{Ag}}} \times 100$$

$$= \frac{(8 \text{ wt\% Ag})(63.55 \text{ g/mol})}{(8 \text{ wt\% Ag})(63.55 \text{ g/mol}) + (92 \text{ wt\% Cu})(107.87 \text{ g/mol})} \times 100$$

4.9 at%

And the concentration of copper (in at%) in the α phase, $C'_{\text{Cu}}(\alpha)$

$$C'_{\text{Cu}}(\alpha) = \frac{C_{\text{Cu}}(\alpha)A_{\text{Ag}}}{C_{\text{Ag}}(\alpha)A_{\text{Cu}} + C_{\text{Cu}}(\alpha)A_{\text{Ag}}} \times 100$$

$$= \frac{(92 \text{ wt\% Cu})(107.87 \text{ g/mol})}{(8 \text{ wt\% Ag})(63.55 \text{ g/mol}) + (92 \text{ wt\% Cu})(107.87 \text{ g/mol})} \times 100$$

95.1 at%

For concentrations of silver and copper (in atom percent) in the liquid phase—for silver, $C'_{\mathrm{Ag}}(L)$

$$C'_{\mathrm{Ag}}(L) = \frac{C_{\mathrm{Ag}}(L)A_{\mathrm{Cu}}}{C_{\mathrm{Ag}}(L)A_{\mathrm{Cu}} + C_{\mathrm{Cu}}(L)A_{\mathrm{Ag}}} \times 100$$

$$= \frac{(43 \text{ wt\% Ag})(63.55 \text{ g/mol})}{(43 \text{ wt\% Ag})(63.55 \text{ g/mol}) + (57 \text{ wt\% Cu})(107.87 \text{ g/mol})} \times 100$$

30.8 at%

Also, for the concentration of copper in the liquid phase, $C'_{\mathrm{Cu}}(L)$

$$C'_{\mathrm{Cu}}(L) = \frac{C_{\mathrm{Cu}}(L)A_{\mathrm{Ag}}}{C_{\mathrm{Ag}}(L)A_{\mathrm{Cu}} + C_{\mathrm{Cu}}(L)A_{\mathrm{Ag}}} \times 100$$

$$= \frac{(57 \text{ wt\% Cu})(107.87 \text{ g/mol})}{(43 \text{ wt\% Ag})(63.55 \text{ g/mol}) + (57 \text{ wt\% Cu})(107.87 \text{ g/mol})} \times 100$$

= 69.2 at%

(b) For this part of the problem, we are to determine the composition of the alloy, in both weight percent and atom percent. First of all, the composition in weight percent will be computed. Because we know the mass fraction of the liquid phase (W_L = 0.68), and compositions of both α and liquid phases, it is possible to determine the alloy composition (C_0) using the lever rule (at 900°C). In this case, the lever-rule expression~~it~~ is as follows:

$$W_L = \frac{C_0 - C_\alpha}{C_L - C_\alpha}$$

For compositions, in weight percent silver

C_α = 8 wt% Ag

C_L = 43 wt% Ag

Thus, the above lever-rule expression takes the form

$$0.68 = \frac{C_0 - 8 \text{ wt\% Ag}}{43 \text{ wt\% Ag} - 8 \text{ wt\% Ag}}$$

And solving this expression for C_0 the alloy composition leads to

$$C_0 = 31.8 \text{ wt\% Ag}$$

Or, in terms of both silver and copper

$$C_0 = 31.8 \text{ wt\% Ag} - 68.2 \text{ wt\% Cu}$$

Now, it is possible to compute the composition of the alloy in terms of atom percent, again using Equations 4.6a and 4.6b (and the atomic weights noted above). Thus, the concentration of silver $C_0'(\text{Ag})$ is equal to

$$C_0'(\text{Ag}) = \frac{C_0(\text{Ag})A_{\text{Cu}}}{C_0(\text{Ag})A_{\text{Cu}} + C_0(\text{Cu})A_{\text{Ag}}} \times 100$$

$$= \frac{(31.8 \text{ wt\% Ag})(63.55 \text{ g/mol})}{(31.8 \text{ wt\% Ag})(63.55 \text{ g/mol}) + (68.2 \text{ wt\% Cu})(107.87 \text{ g/mol})} \times 100$$

=21.6 at% Ag

And, for the concentration of copper $C_0'(\text{Cu})$ we have

$$C_0'(\text{Cu}) = \frac{C_0(\text{Cu})A_{\text{Ag}}}{C_0(\text{Ag})A_{\text{Cu}} + C_0(\text{Cu})A_{\text{Ag}}} \times 100$$

$$= \frac{(68.2 \text{ wt\% Cu})(107.87 \text{ g/mol})}{(31.8 \text{ wt\% Ag})(63.55 \text{ g/mol}) + (68.2 \text{ wt\% Cu})(107.87 \text{ g/mol})} \times 100$$

= 78.4 at% Cu

9.24 *For alloys of two hypothetical metals A and B, there exist an α, A-rich phase and a β, B-rich phase. From the mass fractions of both phases for two different alloys provided in the following table (which are at the same temperature), determine the composition of the phase boundary (or solubility limit) for both α and β phases at this temperature.*

Alloy Composition	***Fraction α Phase***	***Fraction β Phase***
70 wt% A–30 wt% B	*0.78*	*0.22*
35 wt% A–65 wt% B	*0.36*	*0.64*

Solution

The problem is to solve for compositions at the phase boundaries for both α and β phases (i.e., C_α and C_β). We may set up two independent lever-~~–~~rule expressions, one for each composition, in terms of C_α and C_β ;~~as~~ these lever-rule equations may be for either W_α or W_β; we have chosen to use expressions in terms of W_α, which are as follows:

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$$W_{\alpha 1} = 0.78 = \frac{C_\beta - C_{01}}{C_\beta - C_\alpha} = \frac{C_\beta - 70}{C_\beta - C_\alpha}$$

$$W_{\alpha 2} = 0.36 = \frac{C_\beta - C_{02}}{C_\beta - C_\alpha} = \frac{C_\beta - 35}{C_\beta - C_\alpha}$$

In these expressions, compositions are given in wt% of A. Solving for C_α and C_β from these equations, yield

C_α = 88.3 (or 88.3 wt% A-11.7 wt% B)

C_β = 5.0 (or 5.0 wt% A-95.0 wt% B)

9.25 *A hypothetical A–B alloy of composition 40 wt% B–60 wt% A at some temperature is found to consist of mass fractions of 0.66 and 0.34 for the α and β phases, respectively. If the composition of the α phase is 13 wt% B–87 wt% A, what is the composition of the β phase?*

Solution

For this problem, we are asked to determine the composition of the β phase given that

$$C_0 = 40 \text{ (or 40 wt\% B-60 wt\% A)}$$

$$C_\alpha = 13 \text{ (or 13 wt\% B-87 wt\% A)}$$

$$W_\alpha = 0.66$$

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$$W_\beta = 0.34$$

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When~~If~~ we set up the lever rule for W_α in terms of the composition of component B, the following equation results:

$$W_\alpha = 0.66 = \frac{C_\beta - C_0}{C_\beta - C_\alpha} = \frac{C_\beta - 40}{C_\beta - 13}$$

And solving for C_β

$$C_\beta = 92.4 \text{ (or 92.4 wt\% B-7.6 wt\% A)}$$

9.26 *Is it possible to have a copper–silver alloy of composition 20 wt% Ag–80 wt% Cu that, at equilibrium, consists of α and liquid phases having mass fractions* W_α *= 0.80 and* W_L *= 0.20? If so, what will be the approximate temperature of the alloy? If such an alloy is not possible, explain why.*

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Solution

Yes, it is possible to have a Cu-Ag alloy of composition 20 wt% Ag-80 wt% Cu which consists of mass fractions $W_\alpha = 0.80$ and $W_L = 0.20$. Using the appropriate phase diagram, Figure 9.7, by trial and error with a ruler, the tie-line segments within the $\alpha + L$ phase region are proportioned such that

$$W_\alpha = 0.8 = \frac{C_L - C_0}{C_L - C_\alpha}$$

for C_0 = 20 wt% Ag. This occurs at about 800°C. Also, at this temperature compositions of the α and liquid phases (corresponding to the intersection of the tie line with the α–($\alpha + L$) and ($\alpha + L$)–L phase boundaries) are as follows:

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C_α = 7 wt% Ag-93 wt% Cu

C_L = 67 wt% Ag-33 wt% C

To check this answer, we will apply the lever rule at 800°C and calculate the value of W_α~~.~~ (taking compositions in terms of wt% Ag). Thus,
~~where~~

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~~C_α = 7 wt% Ag~~

~~C_L = 67 wt% Ag~~

~~C_0 = 20 wt% Ag~~

~~Thus,~~

$$W_\alpha = \frac{C_L - C_0}{C_L - C_\alpha} = \frac{67 - 20}{67 - 7} = 0.783$$

which is reasonably close to 0.8.

9.27 *For 5.7 kg of a magnesium–lead alloy of composition 50 wt% Pb–50 wt% Mg, is it possible, at equilibrium, to have α and* Mg_2Pb *phases with respective masses of 5.13 and 0.57 kg? If so, what will be the approximate temperature of the alloy? If such an alloy is not possible, then explain why.*

Solution

It is *not possible* to have a 50 wt% Pb-50 wt% Mg alloy that has masses of 5.13 kg and 0.57 kg for the α and Mg_2Pb phases, respectively. In order to demonstrate this, it is first necessary to determine the mass fraction of each phase as:

$$W_\alpha = \frac{m_\alpha}{m_\alpha + m_{Mg_2Pb}} = \frac{5.13\ \text{kg}}{5.13\ \text{kg} + 0.57\ \text{kg}} = 0.90$$

$$W_{Mg_2Pb} = 1.00 - 0.90 = 0.10$$

Now, if we apply the lever rule expression for W_α

$$W_\alpha = \frac{C_{Mg_2Pb} - C_0}{C_{Mg_2Pb} - C_\alpha}$$

Since the Mg_2Pb phase exists only at 81 wt% Pb, and C_0 = 50 wt% Pb

$$W_\alpha = 0.90 = \frac{81 - 50}{81 - C_\alpha}$$

Solving for C_α from this expression yields C_α = 46.6 wt% Pb. From Figure 9.20, the maximum concentration of Pb in the α phase in the $\alpha + Mg_2Pb$ phase field is about 42 wt% Pb. Therefore, this alloy is *not possible*.

9.28 *Derive Equations 9.6a and 9.7a, which may be used to convert mass fraction to volume fraction, and vice versa.*

Solution

This portion of the problem asks that we derive Equation 9.6a, which is used to convert from phase weight fraction to phase volume fraction. Volume fraction of phase α, V_α, is defined by Equation 9.5 as

$$V_\alpha = \frac{v_\alpha}{v_\alpha + v_\beta} \tag{9.S1}$$

where v_α and v_β are the volumes of the respective phases in the alloy. Furthermore, the density of each phase is equal to the ratio of its mass and volume, or upon rearrangement

$$v_\alpha = \frac{m_\alpha}{\rho_\alpha} \tag{9.S2a}$$

$$v_\beta = \frac{m_\beta}{\rho_\beta} \tag{9.S2b}$$

Substitution of these expressions into Equation 9.S1 leads to

$$V_\alpha = \frac{\dfrac{m_\alpha}{\rho_\alpha}}{\dfrac{m_\alpha}{\rho_\alpha} + \dfrac{m_\beta}{\rho_\beta}} \tag{9.S3}$$

in which *m*'s and ρ's denote masses and densities, respectively. Now, the mass fractions of the α and β phases (i.e., W_α and W_β) are defined in terms of the phase masses as

$$W_\alpha = \frac{m_\alpha}{m_\alpha + m_\beta} \tag{9.S4a}$$

$$W_\beta = \frac{m_\beta}{m_\alpha + m_\beta} \tag{9.S4b}$$

Which, upon rearrangement yield

$$m_\alpha = W_\alpha \left(m_\alpha + m_\beta\right) \tag{9.S5a}$$

$$m_\beta = W_\beta \left(m_\alpha + m_\beta\right) \tag{9.S5b}$$

Incorporation of these relationships into Equation 9.S3 leads to

$$V_\alpha = \frac{\dfrac{W_\alpha (m_\alpha + m_\beta)}{\rho_\alpha}}{\dfrac{W_\alpha (m_\alpha + m_\beta)}{\rho_\alpha} + \dfrac{W_\beta (m_\alpha + m_\beta)}{\rho_\beta}}$$

$$V_\alpha = \frac{\dfrac{W_\alpha}{\rho_\alpha}}{\dfrac{W_\alpha}{\rho_\alpha} + \dfrac{W_\beta}{\rho_\beta}} \qquad (9.S6)$$

which is the desired equation.

For this portion of the problem we are asked to derive Equation 9.7a, which is used to convert from phase volume fraction to mass fraction. Mass fraction of the α phase is defined as

$$W_\alpha = \frac{m_\alpha}{m_\alpha + m_\beta} \qquad (9.S7)$$

From Equations 9.S2a and 9.S2b

$$m_\alpha = v_\alpha \rho_\alpha \qquad (9.S8a)$$

$$m_\beta = v_\beta \rho_\beta \qquad (9.S8b)$$

Substitution of these expressions into Equation 9.S7 yields

$$W_\alpha = \frac{v_\alpha \rho_\alpha}{v_\alpha \rho_\alpha + v_\beta \rho_\beta} \qquad (9.S9)$$

From Equation 9.5 and its equivalent for V_β the following may be written as:

$$v_\alpha = V_\alpha (v_\alpha + v_\beta) \qquad (9.S10a)$$

$$v_\beta = V_\beta (v_\alpha + v_\beta) \qquad (9.S10b)$$

Substitution of Equations 9.S10a and 9.S10b into Equation 9.S9 yields

$$W_{\alpha} = \frac{V_{\alpha}\left(v_{\alpha} + v_{\beta}\right)\rho_{\alpha}}{V_{\alpha}\left(v_{\alpha} + v_{\beta}\right)\rho_{\alpha} + V_{\beta}\left(v_{\alpha} + v_{\beta}\right)\rho_{\beta}}$$

$$W_{\alpha} = \frac{V_{\alpha}\rho_{\alpha}}{V_{\alpha}\rho_{\alpha} + V_{\beta}\rho_{\beta}} \tag{9.S11}$$

the desired expression.

9.29 *Determine the relative amounts (in terms of volume fractions) of the phases for the alloys and temperatures given in Problems 9.10a, b, and d. The following table gives the approximate densities of the various metals at the alloy temperatures:*

Metal	***Temperature* (°*C*)**	***Density* (*g/cm*^{3})**
Cu	600	8.68
Mg	425	1.68
Pb	100	11.27
Pb	425	10.96
Sn	100	7.29
Zn	600	6.67

Solution

This problem asks that we determine the phase volume fractions for the alloys and temperatures in Problems 9.10a, b, and d. This is accomplished by using the technique illustrated in Example Problem 9.3, and also the results of Problems 9.10 and 9.17.

(a) This is a Sn-Pb alloy at 100°C, wherein

C_α = 5 wt% Sn-95 wt% Pb
C_β = 98 wt% Sn-2 wt% Pb
W_α = 0.89
W_β = 0.11
ρ_{Sn} = 7.29 g/cm^3
ρ_{Pb} = 11.27 g/cm^3

Using these data it is first necessary to compute the densities of the α and β phases using Equation 4.10a. Thus

$$\rho_\alpha = \frac{100}{\dfrac{C_{\text{Sn}(\alpha)}}{\rho_{\text{Sn}}} + \dfrac{C_{\text{Pb}(\alpha)}}{\rho_{\text{Pb}}}}$$

$$= \frac{100}{\dfrac{5}{7.29 \text{ g/cm}^3} + \dfrac{95}{11.27 \text{ g/cm}^3}} = 10.97 \text{ g/cm}^3$$

$$\rho_\beta = \frac{100}{\dfrac{C_{\text{Sn}(\beta)}}{\rho_{\text{Sn}}} + \dfrac{C_{\text{Pb}(\beta)}}{\rho_{\text{Pb}}}}$$

$$= \frac{100}{\dfrac{98}{7.29 \text{ g/cm}^3} + \dfrac{2}{11.27 \text{ g/cm}^3}} = 7.34 \text{ g/cm}^3$$

Now we may determine the V_α and V_β values using Equation 9.6. Thus,

$$V_\alpha = \frac{\dfrac{W_\alpha}{\rho_\alpha}}{\dfrac{W_\alpha}{\rho_\alpha} + \dfrac{W_\beta}{\rho_\beta}}$$

$$= \frac{\dfrac{0.89}{10.97 \text{ g/cm}^3}}{\dfrac{0.89}{10.97 \text{ g/cm}^3} + \dfrac{0.11}{7.34 \text{ g/cm}^3}} = 0.84$$

$$V_\beta = \frac{\dfrac{W_\beta}{\rho_\beta}}{\dfrac{W_\alpha}{\rho_\alpha} + \dfrac{W_\beta}{\rho_\beta}}$$

$$= \frac{\dfrac{0.11}{7.34 \text{ g/cm}^3}}{\dfrac{0.89}{10.97 \text{ g/cm}^3} + \dfrac{0.11}{7.34 \text{ g/cm}^3}} = 0.16$$

(b) This is a Pb-Mg alloy at 425°C, wherein only the α phase is present. Therefore, $V_{\square}$ = 1.0.

(d) This is a Zn-Cu alloy at 600°C, wherein

$C_{\square}$ = 51 wt% Zn-49 wt% Cu

$C_{\square}$ = 58 wt% Zn-42 wt% Cu

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$W_\beta = 0.43$

$W_\gamma = 0.57$

$\rho_{\text{Zn}} = 6.67\ \text{g/cm}^3$

$\rho_{\text{Cu}} = 8.68\ \text{g/cm}^3$

Using these data it is first necessary to compute the densities of the β and γ phases using Equation 4.10a. Thus

$$\rho_\beta = \frac{100}{\dfrac{C_{\text{Zn}(\beta)}}{\rho_{\text{Zn}}} + \dfrac{C_{\text{Cu}(\beta)}}{\rho_{\text{Cu}}}}$$

$$= \frac{100}{\dfrac{51}{6.67\ \text{g/cm}^3} + \dfrac{49}{8.68\ \text{g/cm}^3}} = 7.52\ \text{g/cm}^3$$

$$\rho_\gamma = \frac{100}{\dfrac{C_{\text{Zn}(\gamma)}}{\rho_{\text{Zn}}} + \dfrac{C_{\text{Cu}(\gamma)}}{\rho_{\text{Cu}}}}$$

$$= \frac{100}{\dfrac{58}{6.67\ \text{g/cm}^3} + \dfrac{42}{8.68\ \text{g/cm}^3}} = 7.39\ \text{g/cm}^3$$

Now we may determine the V_β and V_γ values using Equation 9.6. Thus,

$$V_\beta = \frac{\dfrac{W_\beta}{\rho_\beta}}{\dfrac{W_\beta}{\rho_\beta} + \dfrac{W_\gamma}{\rho_\gamma}}$$

$$= \frac{\dfrac{0.43}{7.52\ \text{g/cm}^3}}{\dfrac{0.43}{7.52\ \text{g/cm}^3} + \dfrac{0.57}{7.39\ \text{g/cm}^3}} = 0.43$$

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$$V_\gamma = \frac{\dfrac{W_\gamma}{\rho_\gamma}}{\dfrac{W_\beta}{\rho_\beta} + \dfrac{W_\gamma}{\rho_\gamma}}$$

$$= \frac{\dfrac{0.57}{7.39\ \text{g/cm}^3}}{\dfrac{0.43}{7.52\ \text{g/cm}^3} + \dfrac{0.57}{7.39\ \text{g/cm}^3}} = 0.57$$

Development of Microstructure in Isomorphous Alloys

9.30 *(a) Briefly describe the phenomenon of coring and why it occurs.*

(b) Cite one undesirable consequence of coring.

Answer

(a) Coring is the phenomenon whereby concentration gradients exist across grains in polycrystalline alloys, with higher concentrations of the component having the lower melting temperature at the grain boundaries. It occurs, during solidification, as a consequence of cooling rates that are too rapid to allow for the maintenance of the equilibrium composition of the solid phase.

(b) One undesirable consequence of a cored structure is that, upon heating, the grain boundary regions will melt first and at a temperature below the equilibrium phase boundary from the phase diagram; this melting results in a loss in mechanical integrity of the alloy.

Mechanical Properties of Isomorphous Alloys

9.31 *It is desirable to produce a copper–nickel alloy that has a minimum non-cold-worked tensile strength of 380 MPa (55,000 psi) and a ductility of at least 45%EL. Is such an alloy possible? If so, what must be its composition? If this is not possible, then explain why.*

Solution

From Figure 9.6*a*, a tensile strength greater than 380 MPa is possible for compositions between about 32 and 90 wt% Ni. On the other hand, according to Figure 9.6*b*, ductilities greater than 45%EL exist for compositions less than about 12 wt% and greater than about 94 wt% Ni. Therefore, such an alloy is *not possible* inasmuch, that in order to meet the stipulated criteria:

For a TS > 380 MPa $\qquad$ $32 \text{ wt\%} < C_{\text{Ni}} < 90 \text{ wt\%}$

For %EL > 45% $\qquad$ $C_{\text{Ni}} < 13 \text{ wt\%}$ or $C_{\text{Ni}} > 94 \text{ wt\%}$

That is, there is no range of composition overlap to satisfy both tensile strength and ductility criteria.

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Binary Eutectic Systems

9.32 *A 60 wt% Pb–40 wt% Mg alloy is rapidly quenched to room temperature from an elevated temperature in such a way that the high-temperature microstructure is preserved. This microstructure is found to consist of the α phase and Mg_2Pb, having respective mass fractions of 0.42 and 0.58. Determine the approximate temperature from which the alloy was quenched.*

Solution

We are asked to determine the approximate temperature from which a 60 wt% Pb-40 wt% Mg alloy was quenched, given the mass fractions of *α* and Mg_2Pb phases. Using Figure 9.20, we can write a lever-rule expression for the mass fraction of the *α* phase as

$$W_{\alpha} = 0.42 = \frac{C_{\mathrm{Mg_2Pb}} - C_0}{C_{\mathrm{Mg_2Pb}} - C_{\alpha}}$$

The value of C_0 is stated as 60 wt% Pb-40 wt% Mg, and $C_{\mathrm{Mg_2Pb}}$ is 81 wt% Pb-19 wt% Mg, which is independent of temperature (Figure 9.20); thus, incorporation of these values for C_0 and $C_{\mathrm{Mg_2Pb}}$ into the above equation yields

$$0.42 = \frac{81 - 60}{81 - C_{\alpha}}$$

and solving for C_{α} leads to the following:

$$C_{\alpha} = 31.0 \text{ wt\% Pb}$$

From Figure 9.20, the temperature at which the *α*–(*α* + Mg_2Pb) phase boundary has a value of 31.0 wt% Pb is about 400°C (750°F).

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Development of Microstructure in Eutectic Alloys

9.33 *Briefly explain why, upon solidification, an alloy of eutectic composition forms a microstructure consisting of alternating layers of the two solid phases.*

Answer

Upon solidification, an alloy of eutectic composition forms a microstructure consisting of alternating layers of the two solid phases because during the solidification atomic diffusion must occur, and with this layered configuration the diffusion path length for the atoms is a minimum.

9.34 *What is the difference between a phase and a microconstituent?*

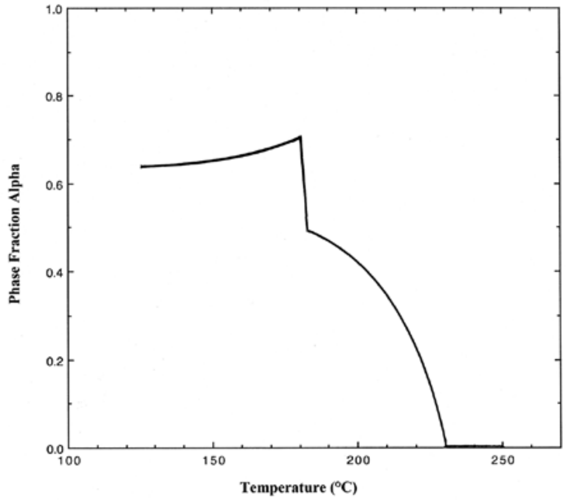
Answer

A “phase” is a homogeneous portion of the system having uniform physical and chemical characteristics, whereas a “microconstituent” is an identifiable element of the microstructure (that may consist of more than one phase).

9.35 *Plot the mass fraction of phases present versus temperature for a 40 wt% Sn-60 wt% Pb alloy as it is slowly cooled from 250°C to 150°C.*

Solution

Using the Pb-Sn phase diagram shown in Figure 9.8, as we move vertically downward at the 40 wt% Sn-60 wt% Pb composition, and using the lever rule at various temperatures, the following phase-fraction vs temperature plots result:



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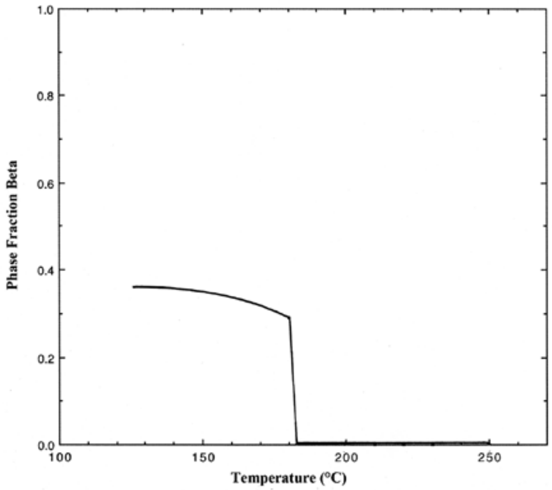
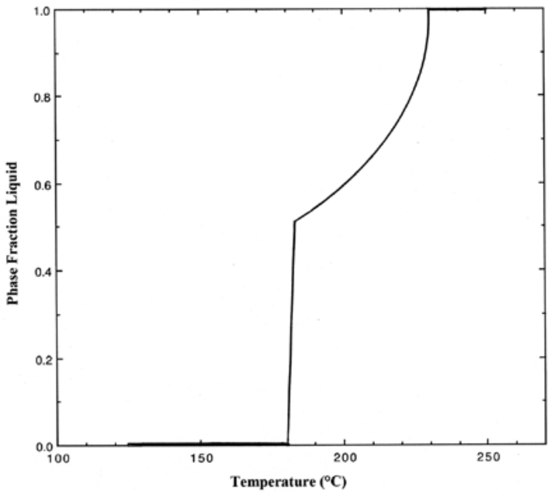

Phase Fraction Beta
0.0
0.2
0.4
0.6
0.8
1.0
100
150
200
250
Temperature (°C)


Phase Fraction Liquid
0.0
0.2
0.4
0.6
0.8
1.0
100
150
200
250
Temperature (°C)

9.36 *Is it possible to have a magnesium–lead alloy in which the mass fractions of primary α and total α are 0.60 and 0.85, respectively, at 460°C (860°F)? Why or why not?*

Solution

In order to decide we need to set up the appropriate lever rule expression for the determination of each of primary α and total α and then solve for the alloy composition C_0. If the value of C_0 is the same for both mass fractions, then the alloy is possible.

From Figure 9.20 and at 460°C, $C_{\square}$ = 41 wt% Pb, $C_{\mathrm{Mg_2Pb}}$ = 81 wt% Pb, and C_{eutectic} = 67 wt% Pb.

For primary α

$$W_{\alpha'} = \frac{C_{\mathrm{eutectic}} - C_0}{C_{\mathrm{eutectic}} - C_\alpha} = \frac{67 - C_0}{67 - 41} = 0.60$$

Solving for C_0 gives C_0 = 51.4 wt% Pb.

Now the analogous expression for total α

$$W_\alpha = \frac{C_{\mathrm{Mg_2Pb}} - C_0}{C_{\mathrm{Mg_2Pb}} - C_\alpha} = \frac{81 - C_0}{81 - 41} = 0.85$$

which yields a value of 47 wt% Pb for C_0. Therefore, since these two C_0 values are different, this alloy is *not* possible.

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9.37 *For 2.8 kg of a lead–tin alloy, is it possible to have the masses of primary β and total β of 2.21 and 2.53 kg, respectively, at 180°C (355°F)? Why or why not?*

Solution

In order to decide we first need to compute the mass fraction of each of primary *β* and total *β*. It is then necessary to set up the appropriate lever rule expression for the determination of each of these two microconstituents and then solve for the alloy composition C_0. If the value of C_0 is the same for both primary *β* and total *β*, then the alloy is possible.

Mass fractions of primary *β* and total *β* (designed by $W_{\beta'}$ and W_{β}, respectively) are computed as follows:

$$W_{\beta'} = \frac{2.21\ \text{kg}}{2.8\ \text{kg}} = 0.789$$

$$W_{\beta} = \frac{2.53\ \text{kg}}{2.8\ \text{kg}} = 0.904$$

Next it is necessary to set up the appropriate lever rule expression for each of these quantities. From Figure 9.8 and at 180°C, $C_{\square}$ = 18.3 wt% Sn, $C_{\square}$ = 97.8 wt% Sn, and C_{eutectic} = 61.9 wt% Sn.

The lever-rule expression for primary *β* is as follows:

$$W_{\beta'} = \frac{C_0 - C_{\text{eutectic}}}{C_{\beta} - C_{\text{eutectic}}} = \frac{C_0 - 61.9}{97.8 - 61.9} = 0.789$$

And solving for C_0 gives C_0 = 90.2 wt% Sn.

The analogous expression for total *β* is

$$W_{\beta} = \frac{C_0 - C_{\alpha}}{C_{\beta} - C_{\alpha}} = \frac{C_0 - 18.3}{97.8 - 18.3} = 0.904$$

which also yields a value for C_0 of 90.2 wt% Sn. Therefore, since these two C_0 values are identical, this alloy *is possible*.

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9.38 *For a lead–tin alloy of composition 80 wt% Sn–20 wt% Pb and at 180°C (355°F) do the following:*

(a) Determine the mass fractions of the α and β phases.

(b) Determine the mass fractions of primary β and eutectic microconstituents.

(c) Determine the mass fraction of eutectic β.

Solution

(a) This portion of the problem asks that we determine the mass fractions of *α* and *β* phases for an 80 wt% Sn-20 wt% Pb alloy (at 180°C). In order to do this it is necessary to employ the lever rule using a tie line that extends entirely across the *α* + *β* phase field. From Figure 9.8 and at 180°C, $C_{□}$ = 18.3 wt% Sn, $C_{□}$ = 97.8 wt% Sn, and C_{eutectic} = 61.9 wt% Sn. Therefore, the two lever-rule expressions are as follows:

$$W_{\alpha} = \frac{C_{\beta} - C_0}{C_{\beta} - C_{\alpha}} = \frac{97.8 - 80}{97.8 - 18.3} = 0.224$$

$$W_{\beta} = \frac{C_0 - C_{\alpha}}{C_{\beta} - C_{\alpha}} = \frac{80 - 18.3}{97.8 - 18.3} = 0.776$$

(b) Now it is necessary to determine the mass fractions of primary *β* and eutectic microconstituents for this same alloy. This requires that we utilize the lever rule and a tie line that extends from the maximum solubility of Pb in the *β* phase at 180°C (i.e., 97.8 wt% Sn) to the eutectic composition (61.9 wt% Sn). Thus, mass fractions of primary *β* and eutectic microconstituents (denoted by $W_{\beta'}$ and W_e, respectively) are determined using the following lever-rule expressions:

$$W_{\beta'} = \frac{C_0 - C_{\text{eutectic}}}{C_{\beta} - C_{\text{eutectic}}} = \frac{80.0 - 61.9}{97.8 - 61.9} = 0.504$$

$$W_e = \frac{C_{\beta} - C_0}{C_{\beta} - C_{\text{eutectic}}} = \frac{97.8 - 80.0}{97.8 - 61.9} = 0.496$$

(c) And, finally, we are asked to compute the mass fraction of eutectic *β*, $W_{e□}$. This quantity is simply the difference between the mass fractions of total *β* and primary *β* as follows:

$$W_{e\beta} = W_{\beta} - W_{\beta'}$$

$$= 0.776 - 0.504 = 0.272$$

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9.39 *The microstructure of a copper–silver alloy at 775°C (1425°F) consists of primary α and eutectic structures. If the mass fractions of these two microconstituents are 0.73 and 0.27, respectively, determine the composition of the alloy.*

Solution

This problem asks that we determine the composition of a Cu-Ag alloy at 775°C given that $W_{\alpha'}$ = 0.73 and W_{eutectic} = 0.27. Since there is a primary α microconstituent present, we know that the alloy composition, C_0 is between 8.0 and 71.9 wt% Ag (Figure 9.7). Furthermore, this figure also indicates that $C_{\square}$ = 8.0 wt% Ag and C_{eutectic} = 71.9 wt% Ag. Applying the appropriate lever rule expression for $W_{\alpha'}$ (which includes C_0 the alloy composition)

$$W_{\alpha'} = \frac{C_{\text{eutectic}} - C_0}{C_{\text{eutectic}} - C_{\alpha}} = \frac{71.9 - C_0}{71.9 - 8.0} = 0.73$$

and solving for C_0 yields C_0 = 25.2 wt% Ag.

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9.40 *A magnesium-lead alloy is cooled from 600°C to 450°C and is found to consist of primary* Mg_2Pb *and eutectic microconstituents. If the mass fraction of the eutectic microconstituent is 0.28, determine the alloy composition.*

Solution

Because primary Mg_2Pb and the eutectic structure are the microconstituents, we know that the alloy composition must lie between the eutectic composition (67 wt% Pb-33 wt% Mg, Figure 9.20). The lever rule expression for the mass fraction of the eutectic microconstituent is as follows:

$$W_{\text{eutectic}} = \frac{C_{\text{Mg}_2\text{Pb}} - C_0}{C_{\text{Mg}_2\text{Pb}} - C_{\text{eutectic}}}$$

Here C_0 = the alloy composition. Inasmuch as

$W_{\text{eutectic}} = 0.28$

$C_{\text{Mg}_2\text{Pb}} = 81$ wt% Pb

$C_{\text{eutectic}} = 67$ wt% Pb

We solve for the value of C_0 by rearrangement of the above equation as follows:

$$C_0 = C_{\text{Mg}_2\text{Pb}} - W_{\text{eutectic}}(C_{\text{Mg}_2\text{Pb}} - C_{\text{eutectic}})$$

$$= 81 \text{ wt\% Pb} - (0.28)(81 \text{ wt\% Pb} - 67 \text{ wt\% Pb})$$

$$= 77.1 \text{ wt\% Pb}$$

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9.41 *Consider a hypothetical eutectic phase diagram for metals A and B that is similar to that for the lead–tin system (Figure 9.8). Assume that: (1~~l~~) α and β phases exist at the A and B extremes of the phase diagram, respectively; (2) the eutectic composition is 36 wt% A–64 wt% B; and (3) the composition of the α phase at the eutectic temperature is 88 wt% A–12 wt% B. Determine the composition of an alloy that will yield primary β and total β mass fractions of 0.367 and 0.768, respectively.*

Solution

We are given a hypothetical eutectic phase diagram for which C_{eutectic} = 64 wt% B, C_{α} = 12 wt% B at the eutectic temperature, and also that $W_{\beta'}$ = 0.367 and W_{β} = 0.768; from this we are asked to determine the composition of the alloy. Let us write lever rule expressions for $W_{\beta'}$ and W_{β} as follows (using C_0 to denote the alloy composition):

$$W_{\beta} = \frac{C_0 - C_{\alpha}}{C_{\beta} - C_{\alpha}} = \frac{C_0 - 12\text{ wt\% B}}{C_{\beta} - 12\text{ wt\% B}} = 0.768$$

$$W_{\beta'} = \frac{C_0 - C_{\text{eutectic}}}{C_{\beta} - C_{\text{eutectic}}} = \frac{C_0 - 64\text{ wt\% B}}{C_{\beta} - 64\text{ wt\% B}} = 0.367$$

Thus, we have two simultaneous equations with C_0 and C_{β} as unknowns. Solving them for C_0 gives C_0 = 75 wt% B.

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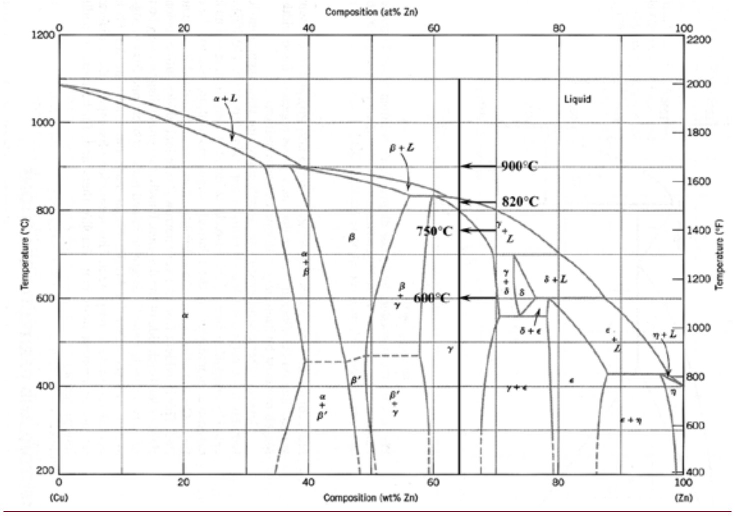
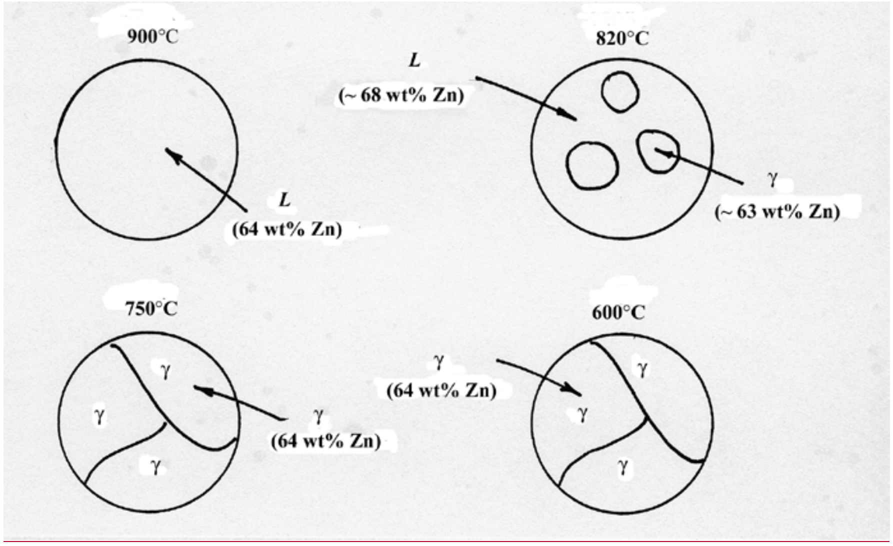
9.42 *For a 64 wt% Zn–36 wt% Cu alloy, make schematic sketches of the microstructure that would be observed for conditions of very slow cooling at the following temperatures: 900°C (1650°F), 820°C (1510°F), 750°C (1380°F), and 600°C (1100°F). Label all phases and indicate their approximate compositions.*

Solution

The illustration below is of the Cu-Zn phase diagram (Figure 9.19). A vertical line at a composition of 64 wt% Zn-36 wt% Cu has been drawn, and, in addition, horizontal arrows at the four temperatures called for in the problem statement (i.e., 900°C, 820°C, 750°C, and 600°C).



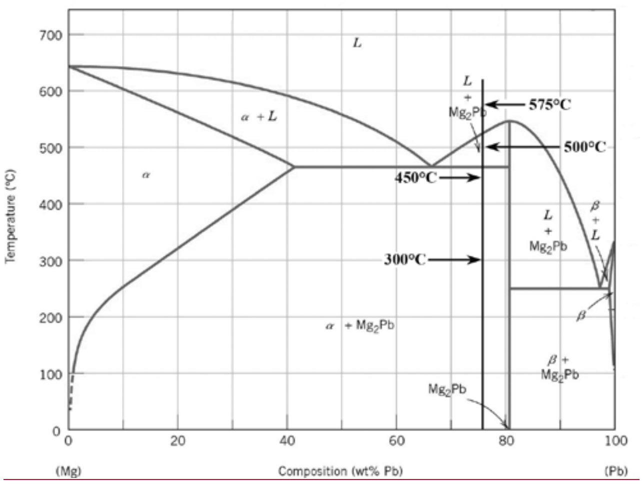
On the basis of the locations of the four temperature-composition points, schematic sketches of the four respective microstructures along with phase compositions are represented as follows:


900°C
L
(64 wt% Zn)
820°C
L
(~ 68 wt% Zn)
γ
(~ 63 wt% Zn)
750°C
γ
γ
γ
γ
(64 wt% Zn)
600°C
γ
(64 wt% Zn)
γ
γ
γ

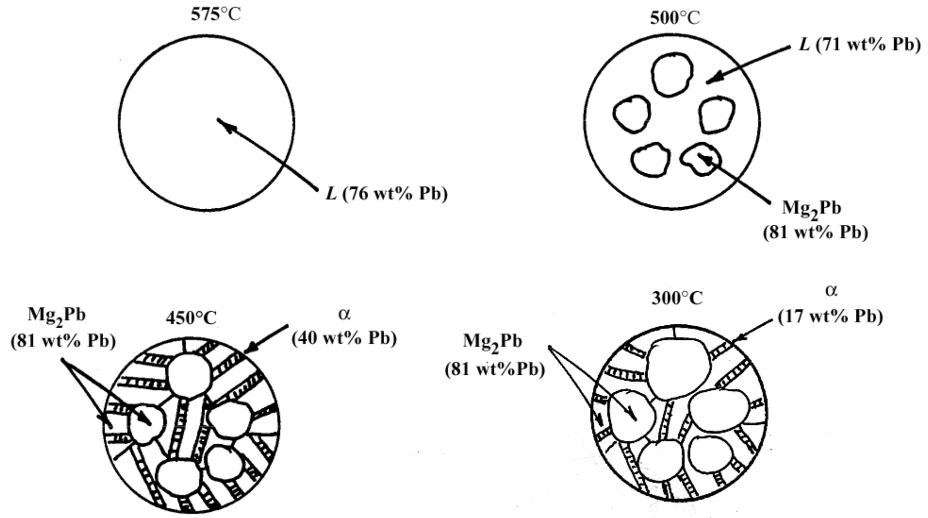
9.43 *For a 76 wt% Pb–24 wt% Mg alloy, make schematic sketches of the microstructure that would be observed for conditions of very slow cooling at the following temperatures: 575°C (1070°F), 500°C (930°F), 450°C (840°F), and 300°C (570°F). Label all phases and indicate their approximate compositions.*

Solution

The illustration below is the Mg-Pb phase diagram (Figure 9.20). A vertical line at a composition of 76 wt% Pb-24 wt% Mg has been drawn, and, in addition, horizontal arrows at the four temperatures called for in the problem statement (i.e., 575°C, 500°C, 450°C, and 300°C).



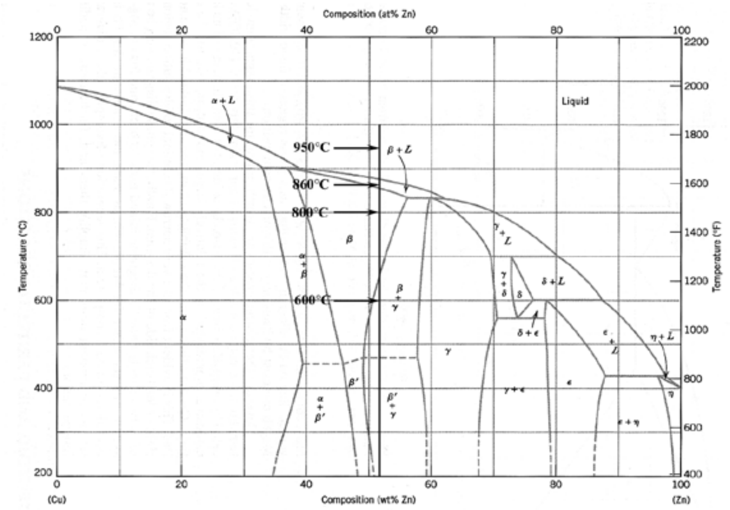
On the basis of the locations of the four temperature-composition points, schematic sketches of the four respective microstructures along with phase compositions are epresented as follows:


575°C
L (76 wt% Pb)
500°C
L (71 wt% Pb)
Mg_2Pb
(81 wt% Pb)
Mg_2Pb
(81 wt% Pb)
450°C
α
(40 wt% Pb)
300°C
α
(17 wt% Pb)
Mg_2Pb
(81 wt%Pb)

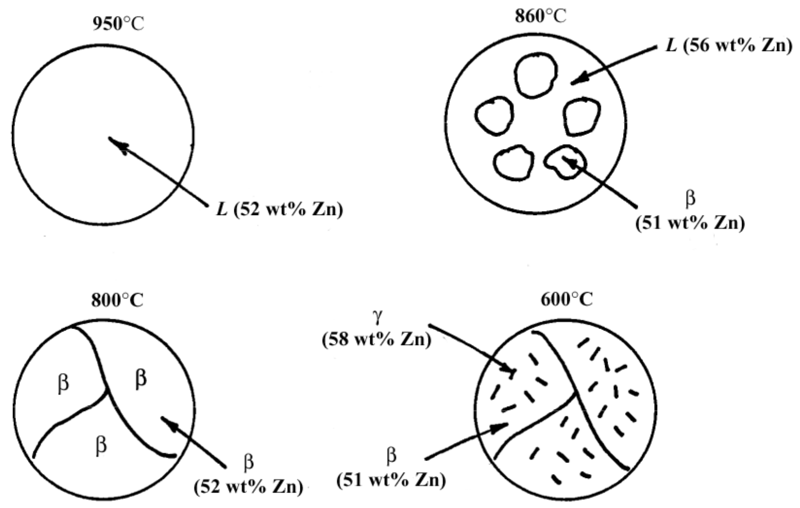
9.44 *For a 52 wt% Zn–48 wt% Cu alloy, make schematic sketches of the microstructure that would be observed for conditions of very slow cooling at the following temperatures: 950°C (1740°F), 860°C (1580°F), 800°C (1470°F), and 600°C (1100°F). Label all phases and indicate their approximate compositions.*

Solution

The illustration below is the Cu-Zn phase diagram (Figure 9.19). A vertical line at a composition of 52 wt% Zn-48 wt% Cu has been drawn, and, in addition, horizontal arrows at the four temperatures called for in the problem statement (i.e., 950°C, 860°C, 800°C, and 600°C).



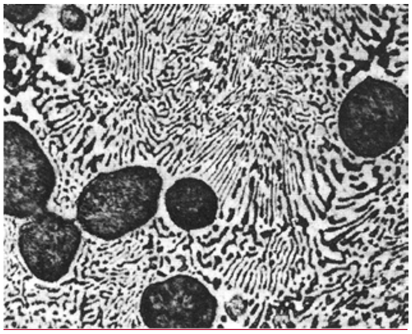
On the basis of the locations of the four temperature-composition points, schematic sketches of the four respective microstructures along with phase compositions are represented as follows:


950°C
L (52 wt% Zn)
860°C
L (56 wt% Zn)
β
(51 wt% Zn)
800°C
β
β
β
β
(52 wt% Zn)
600°C
γ
(58 wt% Zn)
β
(51 wt% Zn)

9.45 *On the basis of the photomicrograph (i.e., the relative amounts of the microconstituents) for the lead–tin alloy shown in Figure 9.17 and the Pb–Sn phase diagram (Figure 9.8), estimate the composition of the alloy, and then compare this estimate with the composition given in the legend of Figure 9.17. Make the following assumptions: (1) The area fraction of each phase and microconstituent in the photomicrograph is equal to its volume fraction; (2) the densities of the α and β phases and the eutectic structure are 11.2, 7.3, and 8.7 g/cm^3, respectively; and (3) this photomicrograph represents the equilibrium microstructure at 180°C (355°F).*

Solution

Below is shown the micrograph of the Pb-Sn alloy, Figure 9.17:



Primary *α* and eutectic microconstituents are present in the photomicrograph, and it is given that their densities are 11.2 and 8.7 g/cm^3, respectively. Below is shown a square grid network onto which is superimposed outlines of the primary α phase areas.

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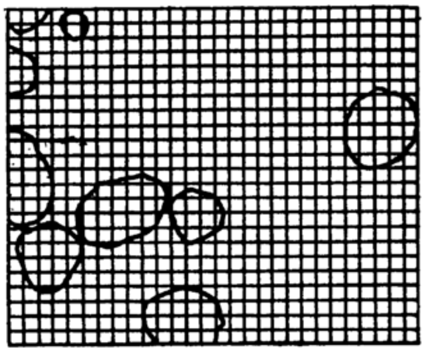

The area fraction of this primary α phase may be determined by counting squares. There are a total of 644 squares, and of these, approximately 104 lie within the primary α phase particles. Thus, the area fraction of primary α is 104/644 = 0.16, which is also assumed to be the volume fraction $(V_{\alpha'})$; furthermore, the volume fraction of the eutectic microconstituent (V_{eutectic}) is equal to 1.00 – 0.16 = 0.84.

We now want to convert the volume fractions into mass fractions in order to employ the lever rule to the Pb-Sn phase diagram. To do this, it is necessary to utilize Equations 9.7a and 9.7b as follows:

$$W_{\alpha'} = \frac{V_{\alpha'}\rho_{\alpha'}}{V_{\alpha'}\rho_{\alpha'} + V_{\text{eutectic}}\,\rho_{\text{eutectic}}}$$

$$= \frac{(0.16)(11.2\ \text{g/cm}^3)}{(0.16)(11.2\ \text{g/cm}^3) + (0.84)(8.7\ \text{g/cm}^3)} = 0.197$$

$$W_{\text{eutectic}} = \frac{V_{\text{eutectic}}\,\rho_{\text{eutectic}}}{V_{\alpha'}\rho_{\alpha'} + V_{\text{eutectic}}\,\rho_{\text{eutectic}}}$$

$$= \frac{(0.84)(8.7\ \text{g/cm}^3)}{(0.16)(11.2\ \text{g/cm}^3) + (0.84)(8.7\ \text{g/cm}^3)} = 0.803$$

From Figure 9.8, we want to use the lever rule and a tie-line that extends from the eutectic composition (61.9 wt% Sn) to the α–(α + β) phase boundary at 180°C (about 18.3 wt% Sn). Accordingly, the weight fraction of the primary α phase is equal to

$$W_{\alpha'} = 0.197 = \frac{61.9 - C_0}{61.9 - 18.3}$$

wherein C_0 is the alloy composition (in wt% Sn). Solving for C_0 yields C_0 = 53.3 wt% Sn. This value is in good agreement with the composition noted in the legend for Figure 9.17—viz. 50 wt% Sn.

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9.46 *The room-temperature tensile strengths of pure copper and pure silver are 209 and 125 MPa, respectively.*

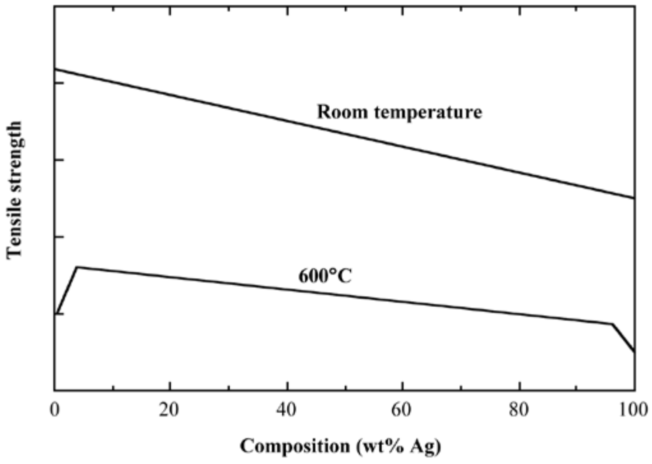
(a) Make a schematic graph of the room-temperature tensile strength versus composition for all compositions between pure copper and pure silver. (Hint: You may want to consult Sections 9.10 and 9.11, as well as Equation 9.24 in Problem 9.79.)

(b) On this same graph schematically plot tensile strength versus composition at 600°C.

(c) Explain the shapes of these two curves, as well as any differences between them.

Solution

The (a) and (b) portions of the problem ask that we make schematic plots on the same graph for the tensile strength versus composition for copper-silver alloys at both room temperature and 600°C; such a graph is shown below.



(c) Upon consultation of the Cu-Ag phase diagram (Figure 9.7) we note that, at room temperature, silver is virtually insoluble in copper (i.e., there is no *α*-phase region at the left extremity of the phase diagram); the same may be said the solubility of copper in silver and for the *β* phase. Thus, only the *α* and *β* phase will exist for all compositions at room temperature; in other words, there will be no solid-solution strengthening effects at room temperature. All other things being equal, the tensile strength will depend (approximately) on the tensile strengths of each of the *α* and *β* phases as well as their phase fractions in a manner described by Equation 9.24 for the elastic modulus (Problem 9.79). That is, for this problem

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$$(TS)_{\text{alloy}} \cong (TS)_\alpha V_\alpha + (TS)_\beta V_\beta$$

in which *TS* and *V* denote tensile strength and volume fraction, respectively, and the subscripts represent the alloy/phases. Also, mass fractions of the α and β phases change linearly with changing composition (according to the lever rule). Furthermore, inasmuch as the densities of both Cu and Ag are similar, weight and volume fractions of the α and β phases will also be similar (see Equation 9.6). In summary, the previous discussion explains the linear dependence of the room temperature tensile strength on composition as represented in the above plot given that the *TS* of pure copper is greater than for pure silver (as stipulated in the problem statement).

At 600°C, the curve will be shifted to significantly lower tensile strengths inasmuch as tensile strength diminishes with increasing temperature (Section 6.6, Figure 6.14). In addition, according to Figure 9.7, about 4 wt% of silver will dissolve in copper (i.e., in the α phase), and about 4 wt% of copper will dissolve in silver (i.e., in the β phase). Therefore, solid-solution strengthening will occur over these compositions ranges, as noted in the graph shown above. Furthermore, between 4% Ag and 96% Ag, the curve will be approximately linear for the same reasons noted in the previous paragraph.

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Equilibrium Diagrams Having Intermediate Phases or Compounds

9.47 *Two intermetallic compounds, A_3B and AB_3, exist for elements A and B. If the compositions for A_3B and AB_3 are 91.0 wt% A–9.0 wt% B and 53.0 wt% A–47.0 wt% B, respectively, and element A is zirconium, identify element B.*

Solution

Probably the easiest way to solve this problem is to first compute the ratio of the atomic weights of these two elements using Equation 4.6a; then, since we know the atomic weight of zirconium (91.22 g/mol), it is possible to determine the atomic weight of element B, from which an identification may be made.

First of all, consider the A_3B intermetallic compound; inasmuch as it contains three times the number of A atoms than and B atoms, its composition in atomic percent is 75 at% A-25 at% B. Equation 4.6a may be written in the form:

$$C'_B = 25 \text{ at\%} = \frac{C_B A_A}{C_A A_B + C_B A_A} \times 100$$

where A_A and A_B are the atomic weights for elements A and B, and C_A and C_B are their compositions in weight percent. For this A_3B compound, and making the appropriate substitutions in the above equation leads to

$$25 \text{ at\% B} = \frac{(9.0 \text{ wt\% B})(A_A)}{(91.0 \text{ wt\% A})(A_B) + (9.0 \text{ wt\% B})(A_A)} \times 100$$

Now, solving for A_B from this expression yields,

$$A_B = 0.297\, A_A$$

Since zirconium is element A and it has an atomic weight of 91.22 g/mol, the atomic weight of element B is just

$$A_B = (0.297)(91.22 \text{ g/mol}) = 27.09 \text{ g/mol}$$

Upon consultation of the period table of the elements (Figure 2.8) we note the element that has an atomic weight closest to this value is aluminum (26.98 g/mol). Therefore, element B is aluminum, and the two intermetallic compounds are Zr_3Al and $ZrAl_3$.

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9.48 *An intermetallic compound is found in the aluminum-zirconium system that has a composition of 22.8 wt% Al-77.2 wt% Zr. Specify the formula for this compound.*

Solution

Probably the easiest way to solve this problem is to begin by computing concentrations of Al and Zr in terms of atom percents; from these values, it is possible to determine the ratio of Al to Zr in this compound. Atom percent $(C'_{\rm Al} \text{ and } C'_{Zr})$ are computed using Equation 4.6 as follows (incorporating atomic weight values of 26.98 g/mol and 91.22 g/mol, respectively for Al and Zr):

$$C'_{\rm Al} = \frac{C_{\rm Al}A_{\rm Zr}}{C_{\rm Al}A_{\rm Zr} + C_{\rm Zr}A_{\rm Al}} \times 100$$

$$= \frac{(22.8 \text{ wt\%})(91.22 \text{ g/mol})}{(22.8 \text{ wt\%})(91.22 \text{ g/mol}) + (77.2 \text{ wt\%})(26.98 \text{ g/mol})} \times 100$$

50.0 at%

Because this intermetallic compound is composed of only Al and Zr, C'_{Zr} will also be equal to 50.0 at%. Finally, the formula for this intermetallic compound is ZrAl, since the aluminum-to-zirconium atom percent ratio is 1:1.

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9.49 *An intermetallic compound is found in the gold-titanium system that has a composition of 58.0 wt% Au-42.0 wt% Ti. Specify the formula for this compound.*

Solution

Probably the easiest way to solve this problem is to begin by computing concentrations of Au and Ti in terms of atom percents; from these values, it is possible to determine the ratio of Au to Ti in this compound. Atom percent $(C'_{Au} \text{ and } C'_{Ti})$ are computed using Equation 4.6 as follows (incorporating atomic weight values of 196.97 g/mol and 47.87 g/mol, respectively for Au and Ti):

$$C'_{Au} = \frac{C_{Au}A_{Ti}}{C_{Au}A_{Ti} + C_{Ti}A_{Au}} \times 100$$

$$= \frac{(58.0 \text{ wt\%})(47.87 \text{ g/mol})}{(58.0 \text{ wt\%})(47.87 \text{ g/mol}) + (42.0 \text{ wt\%})(196.97 \text{ g/mol})} \times 100$$

25.1 at%

Because this intermetallic compound is composed of only Au and Ti, C'_{Ti} will be equal to

$$C'_{Ti} = 100 \text{ at\%} - 25.1 \text{ at\%} = 74.9 \text{ at\%}$$

Since the titanium-to-gold atom percent ratio is very nearly 3:1, the formula for this intermetallic compound is Ti_3Au.

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9.50 *Specify the liquidus, solidus, and solvus temperatures for the following alloys:*

(a) 30 wt% Ni-70 wt% Cu

(b) 5 wt% Ag-95 wt% Cu

(c) 20 wt% Zn-80 wt% Cu

(d) 30 wt% Pb-70 wt% Mg

(e) 3 wt% C-97 wt% Fe

Solution

Definitions of liquidus, solidus, and solvus lines are as follows:

Liquidus—boundary between liquid and (liquid + solid) phase regions

Solidus—boundary between solid and (liquid + solid) phase regions

Solvus—boundary between a single solid phase region and a two solid phase region.

For this problem, a liquidus, solidus, or solvus temperature corresponds to the intersection between a vertical line (constructed at a specific composition) with the respective liquidus, solidus, or solvus line.

(a) The liquidus and solidus temperatures for a 30 wt% Ni-70 wt% Cu alloy (1195°C and 1240°C, respectively) are noted on the Cu-Ni phase diagram shown below. For this alloy, there is no solvus line inasmuch as no two-solid-phase region exists for this system.

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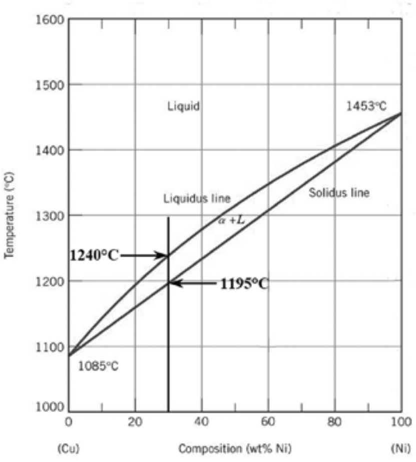

(b) The solvus, solidus, and liquidus temperatures for a 5 wt% Ag-95 wt% Cu alloy are 700°C, 1015°C, and 1070°C, respectively, as noted on the Cu-Ag phase diagram shown below.

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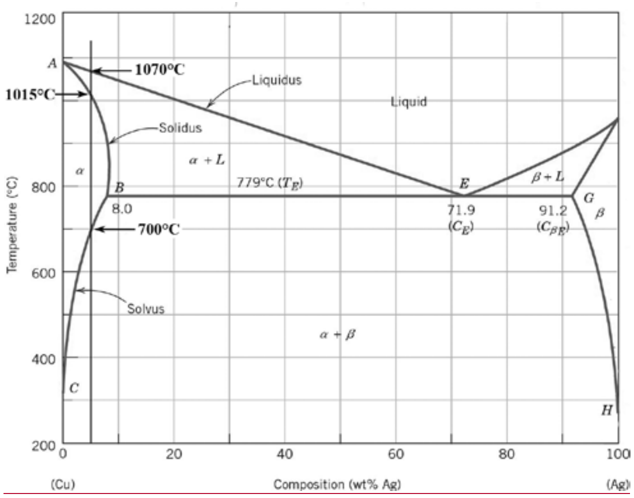

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(c) The solidus and liquidus temperatures for a 20 wt% Zn-80 wt% Cu alloy are 990°C and 1025°C, respectively, as noted on the Cu-Zn phase diagram shown below. For this alloy, there is no solvus line inasmuch as the vertical line at 20 wt% Zn does not pass through a two-solid-phase region.

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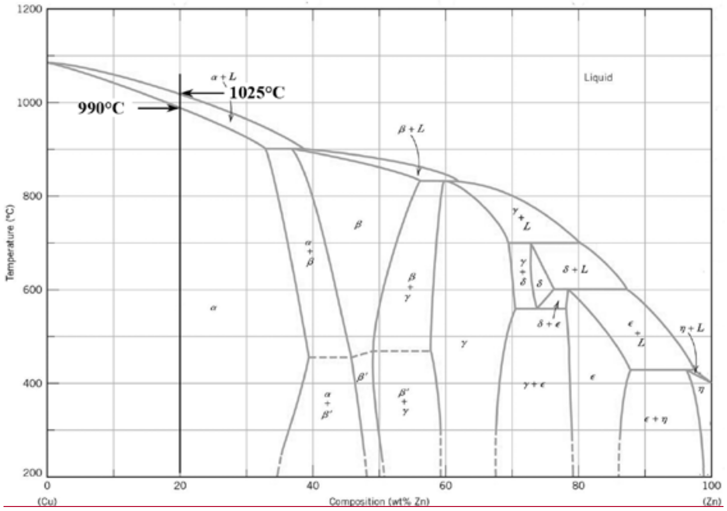

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(d) The solvus, solidus, and liquidus temperatures for a 30 wt% Pb-70 wt% Mg alloy are 390°C, 520°C, and 615°C, respectively, as noted on the Mg-Pb phase diagram shown below.

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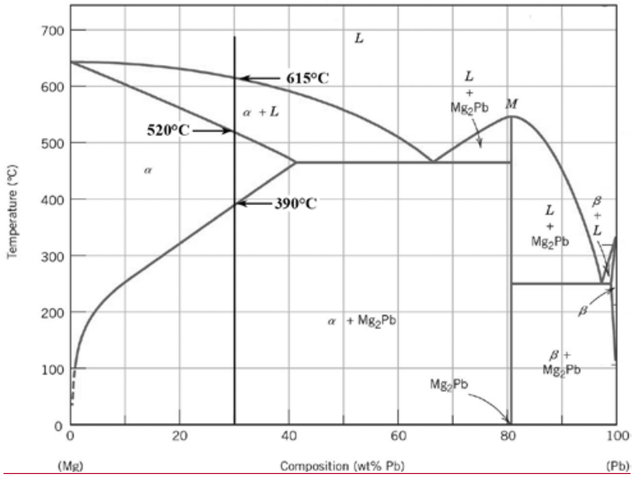

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(e) The liquidus temperature for 3 wt% C-97 wt% Fe is 1290°C as noted on the Fe-Fe_3C phase diagram shown below. For this alloy, there is neither a solidus line or a solvus line.

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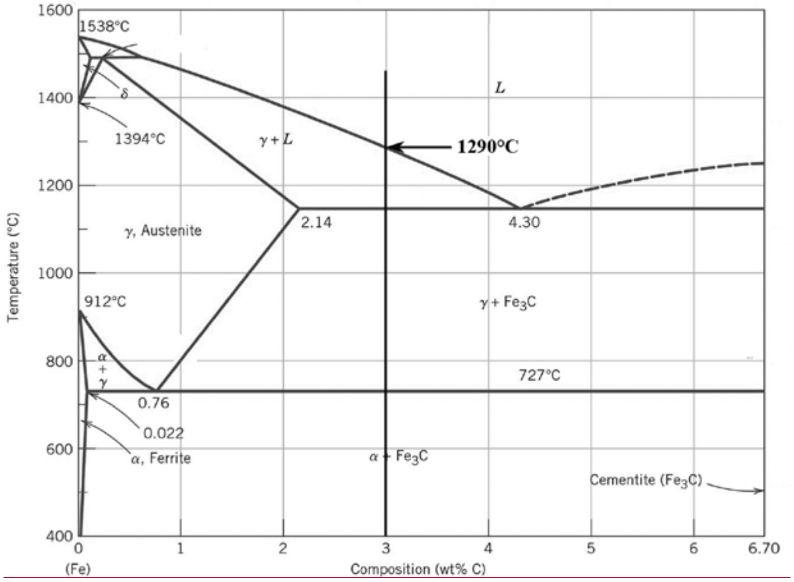

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Congruent Phase Transformations

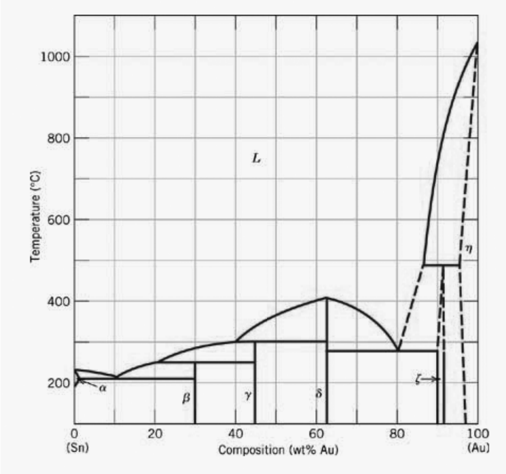
Eutectoid and Peritectic Reactions

9.51 *What is the principal difference between congruent and incongruent phase transformations?*

Answer

The principal difference between congruent and incongruent phase transformations is that for congruent no compositional changes occur with any of the phases that are involved in the transformation. For incongruent there will be compositional alterations of the phases.

9.52 *Figure 9.36 is the tin–gold phase diagram, for which only single-phase regions are labeled. Specify temperature–composition points at which all eutectics, eutectoids, peritectics, and congruent phase transformations occur. Also, for each, write the reaction upon cooling.*



Solution

In this problem we are asked to specify temperature-composition points for all eutectics, eutectoids, peritectics, and congruent phase transformations for the tin-gold system (Figure 9.36).

There are two eutectics on this phase diagram. One exists at 10 wt% Au-90 wt% Sn and 217°C. The reaction upon cooling is

$$L \rightarrow \alpha + \beta$$

The other eutectic exists at 80 wt% Au-20 wt% Sn and 280°C. This reaction upon cooling is

$$L \rightarrow \delta + \zeta$$

There are three peritectics. One exists at 30 wt% Au-70 wt% Sn and 252°C. Its reaction upon cooling is as follows:

$$L + \gamma \rightarrow \beta$$

The second peritectic exists at 45 wt% Au-55 wt% Sn and 309°C. This reaction upon cooling is

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$$L + \delta \rightarrow \gamma$$

The third peritectic exists at 92 wt% Au-8 wt% Sn and 490°C. This reaction upon cooling is

$$L + \eta \rightarrow \zeta$$

There is one congruent melting point at 62.5 wt% Au-37.5 wt% Sn and 418°C. Its reaction upon cooling is

$$L \rightarrow \delta$$

No eutectoids are present.

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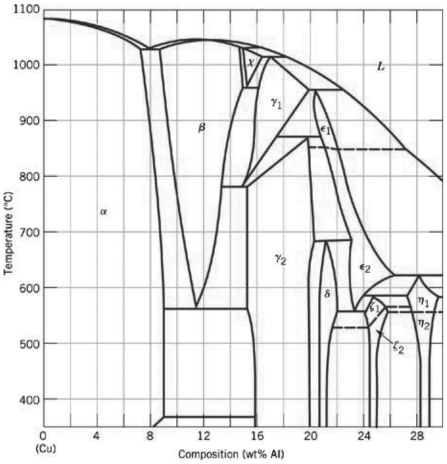
9.53 *Figure 9.37 is a portion of the copper–aluminum phase diagram for which only single-phase regions are labeled. Specify temperature–composition points at which all eutectics, eutectoids, peritectics, and congruent phase transformations occur. Also, for each, write the reaction upon cooling.*



Solution

In this problem we are asked to specify temperature-composition points for all eutectics, eutectoids, peritectics, and congruent phase transformations for a portion of the aluminum-copper phase diagram (Figure 9.37).

There is one eutectic on this phase diagram, which exists at 8.3 wt% Al-91.7 wt% Cu and 1036°C. Its reaction upon cooling is

$$L \rightarrow \alpha + \beta$$

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There are four eutectoids for this system. One exists at 11.8 wt% Al-88.2 wt% Cu and 565°C. This reaction upon cooling is

$$\beta \rightarrow \alpha + \gamma_2$$

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Another eutectoid exists at 15.4 wt% Al-84.6 wt% Cu and 964°C. For cooling the reaction is

$$\chi \rightarrow \beta + \gamma_1$$

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A third eutectoid exists at 15.5 wt% Al-84.5 wt% Cu and 786°C. For cooling the reaction is

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$$\gamma_1 \rightarrow \beta + \gamma_2$$

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The other eutectoid exists at 23.5 wt% Al-76.5 wt% Cu and 560°C. For cooling the reaction is

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$$\varepsilon_2 \rightarrow \delta + \zeta_1$$

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There are four peritectics on this phase diagram. One exists at 15.3 wt% Al-84.7 wt% Cu and 1037°C. The reaction upon cooling is

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$$\beta + L \rightarrow \chi$$

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Another peritectic exists at 17 wt% Al-83 wt% Cu and 1021°C. It's cooling reaction is

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$$\chi + L \rightarrow \gamma_1$$

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Another peritectic exists at 20.5 wt% Al-79.5 wt% Cu and 961°C. The reaction upon cooling is

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$$\gamma_1 + L \rightarrow \varepsilon_1$$

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Another peritectic exists at 28.4 wt% Al-71.6 wt% Cu and 626°C. The reaction upon cooling is

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$$\varepsilon_2 + L \rightarrow \eta_1$$

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There is a single congruent melting point that exists at 12.5 wt% Al-87.5 wt% Cu and 1049°C. The reaction upon cooling is

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$$L \rightarrow \beta$$

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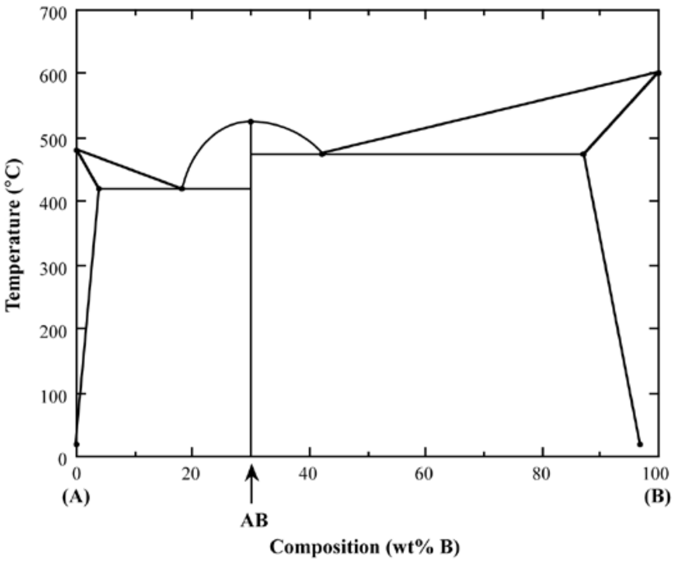
9.54 *Construct the hypothetical phase diagram for metals A and B between room temperature (20°C) and 700°C, given the following information:*

- *The melting temperature of metal A is 480°C.*
- *The maximum solubility of B in A is 4 wt% B, which occurs at 420°C.*
- *The solubility of B in A at room temperature is 0 wt% B.*
- *One eutectic occurs at 420°C and 18 wt% B–82 wt% A.*
- *A second eutectic occurs at 475°C and 42 wt% B–58 wt% A.*
- *The intermetallic compound AB exists at a composition of 30 wt% B–70 wt% A, and melts congruently at 525°C.*
- *The melting temperature of metal B is 600°C.*
- *The maximum solubility of A in B is 13 wt% A, which occurs at 475°C.*
- *The solubility of A in B at room temperature is 3 wt% A.*

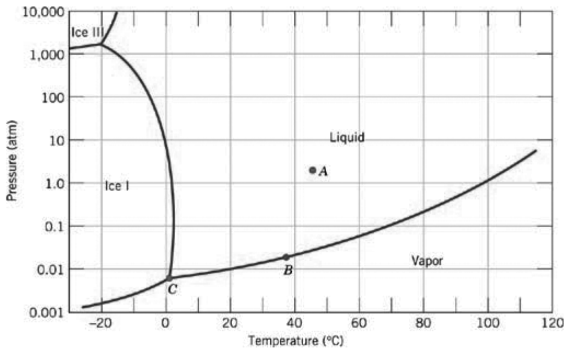
Solution

Below is shown the phase diagram for these two A and B metals.



The Gibbs Phase Rule

9.55 *Figure 9.38 shows the pressure–temperature phase diagram for* H_2O*. Apply the Gibbs phase rule at points A, B, and C, and specify the number of degrees of freedom at each of the points—that is, the number of externally controllable variables that must be specified to define the system completely.*



Solution

We are asked to specify the value of F for Gibbs phase rule at points A, B, and C on the pressure-temperature diagram for H_2O (Figure 9.38). Gibbs phase rule in general form is

$$P + F = C + N$$

For this system, the number of components, C, is 1, whereas N, the number of noncompositional variables, is 2—viz. temperature and pressure. Thus, the phase rule now becomes

$$P + F = 1 + 2 = 3$$

Or

$$F = 3 - P$$

where P is the number of phases present at equilibrium.

At point A, only a single (liquid) phase is present (i.e., $P = 1$), or

$$F = 3 - P = 3 - 1 = 2$$

which means that both temperature and pressure are necessary to define the system.

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At point B which is on the phase boundary between liquid and vapor phases, two phases are in equilibrium ($P = 2$); hence

$$F = 3 - P = 3 - 2 = 1$$

Or that we need to specify the value of either temperature or pressure, which determines the value of the other (pressure or temperature).

And, finally, at point C, three phases are present—viz. ice I, vapor, and liquid—and the number of degrees of freedom is zero since

$$F = 3 - P = 3 - 3 = 0$$

Thus, point C is a triple point, and we have no choice in the selection of externally controllable variables in order to define the system.

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9.56 *Specify the number of degrees of freedom for the following alloys:*

(a) 20 wt% Ni-80 wt% Cu at 1300°C

(b) 71.9 wt% Ag-28.1 wt% Cu at 779°C

(c) 52.7 wt% Zn-47.3 wt% Cu at 525°C

(d) 81 wt% Pb-19 wt% Mg at 545°C

(e) 1 wt% C-99wt% Fe at 1000°C

Solution

We are asked to specify the value of F for Gibbs phase rule for several alloys and, for each, at a specified temperature. Gibbs phase rule in general form is

$$P + F = C + N$$

For this system, the number of components, C, is 2, whereas N, the number of noncompositional variables, is 1—viz. temperature. Thus, the phase rule now becomes

$$P + F = 2 + 1 = 3$$

Or

$$F = 3 - P \qquad (9.17a)$$

where P is the number of phases present at equilibrium.

Therefore, for each of these alloys we need to ascertain the number of phases present at equilibrium at the specified temperature. This gives us the value of P in the preceding equation, from which it is possible to determine the value of F, the number of degrees of freedom.

(a) A 20 wt% Ni-80 wt% Cu alloy at 1300°C is entirely liquid, which means that only a single phase is present—i.e., P = 1; insertion of this value into Equation 9.17a yields

$$F = 3 - P = 3 - 1 = 2$$

(b) The location of a 71.9 wt% Ag-28.1 wt% Cu alloy at 779°C on the Cu-Ag phase diagram is at the eutectic, which means that three phases (α, β, and liquid) are in equilibrium and that the value of P = 3; or that, from Equation 9.17a

$$F = 3 - P = 3 - 3 = 0$$

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(c) The location of a 52.7 wt% Zn-47.3 wt% Cu alloy at 525°C on the Cu-Zn phase diagram is in the $\beta + \gamma$ region, which means that two phases (β and γ) are in equilibrium and the value of P = 2; or that, from Equation 9.17a

$$F = 3 - P = 3 - 2 = 1$$

(d) The location of a 81 wt% Pb-19 wt% Mg alloy at 545°C on the Mg-Pb phase diagram is at the congruent melting point of Mg_2Pb, which means that both the liquid phase and Mg_2Pb coexist—i.e., the number of phases, P is equal to 2. Thus, Equation 9.17a becomes

$$F = 3 - P = 3 - 2 = 1$$

(e) The location of a 1 wt% C-99 wt% Fe alloy at 1000°C on the Fe-Fe_3C phase diagram is in the γ phase region, or that a single phase is present—i.e., P = 1. This means that Equation 9.17a is of the form

$$F = 3 - P = 3 - 1 = 2$$

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The Iron–Iron Carbide (Fe–Fe$_3$C) Phase Diagram

Development of Microstructure in Iron–Carbon Alloys

9.57 *Compute the mass fractions of α-ferrite and cementite in pearlite.*

Solution

This problem asks that we compute the mass fractions of *α*-ferrite and cementite in pearlite. The lever-rule expression for ferrite in this situation is the following:

$$W_{\alpha} = \frac{C_{\mathrm{Fe_3C}} - C_0}{C_{\mathrm{Fe_3C}} - C_{\alpha}}$$

and, since $C_{\mathrm{Fe_3C}}$ = 6.70 wt% C, C_0 = 0.76 wt% C, and C_{α} = 0.022 wt% C, the above equation takes the form

$$W_{\alpha} = \frac{6.70 - 0.76}{6.70 - 0.022} = 0.89$$

Similarly, for cementite the lever-rule expression is

$$W_{\mathrm{Fe_3C}} = \frac{C_0 - C_{\alpha}}{C_{\mathrm{Fe_3C}} - C_{\alpha}}$$

which leads to the following when appropriate phase composition values are included:

$$W_{\mathrm{Fe_3C}} = \frac{0.76 - 0.022}{6.70 - 0.022} = 0.11$$

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9.58 *(a) What is the distinction between hypoeutectoid and hypereutectoid steels?*

(b) In a hypoeutectoid steel, both eutectoid and proeutectoid ferrite exist. Explain the difference between them. What will be the carbon concentration in each?

Answer

(a) A “hypoeutectoid” steel has a carbon concentration less than the eutectoid; on the other hand, a “hypereutectoid” steel has a carbon content greater than the eutectoid.

(b) For a hypoeutectoid steel, the proeutectoid ferrite is a microconstituent that formed above the eutectoid temperature. The eutectoid ferrite is one of the constituents of pearlite that formed at a temperature below the eutectoid. The carbon concentration for both ferrites is 0.022 wt% C.

9.59 *What is the carbon concentration of an iron–carbon alloy for which the fraction of total cementite is 0.10?*

Solution

This problem asks that we compute the carbon concentration of an iron-carbon alloy for which the fraction of total cementite is 0.10. Application of the lever rule (of the form of Equation 9.12) yields

$$W_{\alpha} = 0.10 = \frac{C_0' - C_{\alpha}}{C_{\mathrm{Fe_3C}} - C_{\alpha}} = \frac{C_0' - 0.022}{6.70 - 0.022}$$

and solving for C_0', the concentration of carbon in the alloy leads to

$$C_0' = 0.69 \text{ wt\% C}$$

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9.60 *What is the proeutectoid phase for an iron–carbon alloy in which the mass fractions of total ferrite and total cementite are 0.86 and 0.14, respectively? Why?*

Solution

In this problem we are given values of W_{α} and W_{Fe_3C} (0.86 and 0.14, respectively) for an iron-carbon alloy and then are asked to specify the proeutectoid phase. Employment of the lever rule for the mass fraction of total α leads to the following expression:

$$W_{\alpha} = 0.86 = \frac{C_{Fe_3C} - C_0}{C_{Fe_3C} - C_{\alpha}} = \frac{6.70 - C_0}{6.70 - 0.022}$$

Now, solving for C_0, the alloy composition, leads to C_0 = 0.96 wt% C. Therefore, the proeutectoid phase is Fe_3C since C_0 is greater than 0.76 wt% C.

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9.61 *Consider 3.5 kg of austenite containing 0.95 wt% C and cooled to below 727°C (1341°F).*

(a) What is the proeutectoid phase?

(b) How many kilograms each of total ferrite and cementite form?

(c) How many kilograms each of pearlite and the proeutectoid phase form?

(d) Schematically sketch and label the resulting microstructure.

Solution

(a) The proeutectoid phase will be Fe_3C since 0.95 wt% C is greater than the eutectoid composition (0.76 wt% C).

(b) For this portion of the problem, we are asked to determine how much total ferrite and cementite form. Application of the appropriate lever rule expression for the mass fraction of total α yields

$$W_\alpha = \frac{C_{Fe_3C} - C_0}{C_{Fe_3C} - C_\alpha} = \frac{6.70 - 0.95}{6.70 - 0.022} = 0.86$$

which, when multiplied by the total mass of the alloy, gives (0.86)(3.5 kg) = 3.01 kg of total ferrite.

Similarly, for the mass fraction of total cementite,

$$W_{Fe_3C} = \frac{C_0 - C_\alpha}{C_{Fe_3C} - C_\alpha} = \frac{0.95 - 0.022}{6.70 - 0.022} = 0.14$$

And the mass of total cementite that forms is (0.14)(3.5 kg) = 0.49 kg.

(c) Now we are asked to calculate how much pearlite and the proeutectoid phase (cementite) form. To determine the mass fraction of pearlite that forms (W_p), we apply Equation 9.22, in which $C_1' = 0.95 \text{ wt\% C}$:

$$W_p = \frac{6.70 - C_1'}{6.70 - 0.76} = \frac{6.70 - 0.95}{6.70 - 0.76} = 0.97$$

which corresponds to a mass of (0.97)(3.5 kg) = 3.4 kg. Likewise, from Equation 9.23, we calculate the mass fraction of proeutectoid cementite as follows:

$$W_{Fe_3C'} = \frac{C_1' - 0.76}{5.94} = \frac{0.95 - 0.76}{5.94} = 0.03$$

which is equivalent to (0.03)(3.5 kg) = 0.11 kg of the total 3.5 kg mass.

(d) Schematically, the microstructure would appear as follows:

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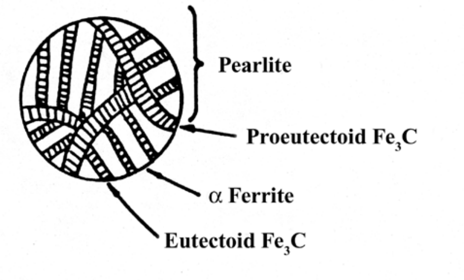
Pearlite
Proeutectoid Fe_3C
α Ferrite
Eutectoid Fe_3C

9.62 Consider 6.0 kg of austenite containing 0.45 wt% C and cooled to less than 727°C (1341°F).

(a) What is the proeutectoid phase?

(b) How many kilograms each of total ferrite and cementite form?

(c) How many kilograms each of pearlite and the proeutectoid phase form?

(d) Schematically sketch and label the resulting microstructure.

Solution

(a) Ferrite is the proeutectoid phase since 0.45 wt% C is less than 0.76 wt% C.

(b) For this portion of the problem, we are asked to determine how much total ferrite and cementite form. For the mass fraction of ferrite, application of the appropriate lever rule expression yields

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$$W_\alpha = \frac{C_{\mathrm{Fe_3C}} - C_0}{C_{\mathrm{Fe_3C}} - C_\alpha} = \frac{6.70 - 0.45}{6.70 - 0.022} = 0.936$$

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which corresponds to (0.936)(6.0 kg) = 5.62 kg of total ferrite.

Similarly, for mass fraction of total cementite,

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$$W_{\mathrm{Fe_3C}} = \frac{C_0 - C_\alpha}{C_{\mathrm{Fe_3C}} - C_\alpha} = \frac{0.45 - 0.022}{6.70 - 0.022} = 0.064$$

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Or (0.064)(6.0 kg) = 0.38 kg of total cementite form.

(c) Now consider the amounts of pearlite and proeutectoid ferrite. For pearlite we use Equation 9.20, as follows:

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$$W_p = \frac{C_0' - 0.022}{0.74} = \frac{0.45 - 0.022}{0.74} = 0.578$$

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This corresponds to (0.578)(6.0 kg) = 3.47 kg of pearlite.

Also, from Equation 9.21, we compute the mass fraction of proeutectoid ferrite as follows:

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$$W_{\alpha'} = \frac{0.76 - 0.45}{0.74} = 0.420$$

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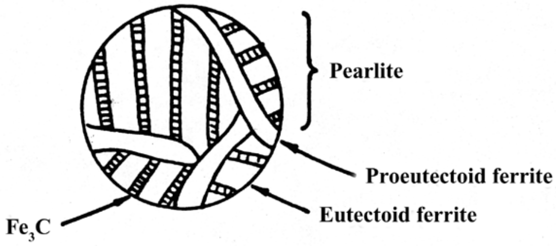
Or, there are (0.420)(6.0 kg) = 2.52 kg of proeutectoid ferrite.

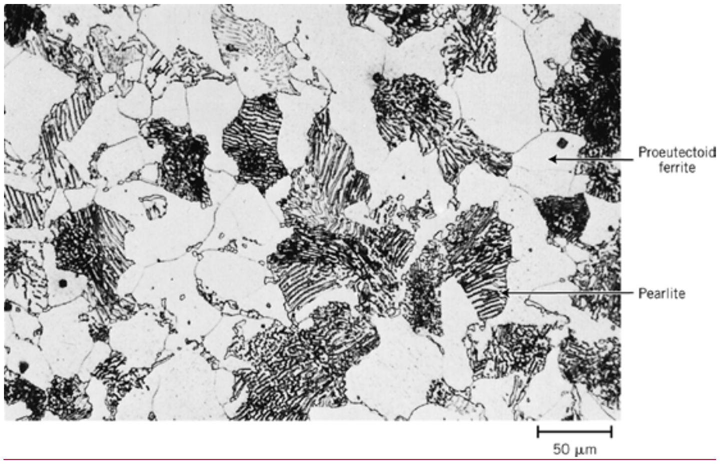
(d) Schematically, the microstructure would appear as follows:


Pearlite
Proeutectoid ferrite
Eutectoid ferrite
Fe$_3$C

9.63 *On the basis of the photomicrograph (i.e., the relative amounts of the microconstituents) for the iron-carbon alloy shown in Figure 9.30 and the Fe-Fe$_3$C phase diagram (Figure 9.24), estimate the composition of the alloy, and then compare this estimate with the composition given in the figure legend of Figure 9.30. Make the following assumptions: (1) The area fraction of each phase and microconstituent in the photomicrograph is equal to its volume fraction; (2) the densities of proeutectoid ferrite and pearlite are 7.87 and 7.84 g/cm^3, respectively; and (3) this photomicrograph represents the equilibrium microstructure at 725°C.*

Solution

Below is shown the micrograph of the iron-carbon alloy, Figure 9.30:



Proeutectoid ferrite and pearlite microconstituents are present in the photomicrograph, and it is given that their densities are 7.87 and 7.84 g/cm^3, respectively. Below is shown a square grid network onto which are superimposed outlines of the proeutectoid ferrite-pearlite phase boundaries.

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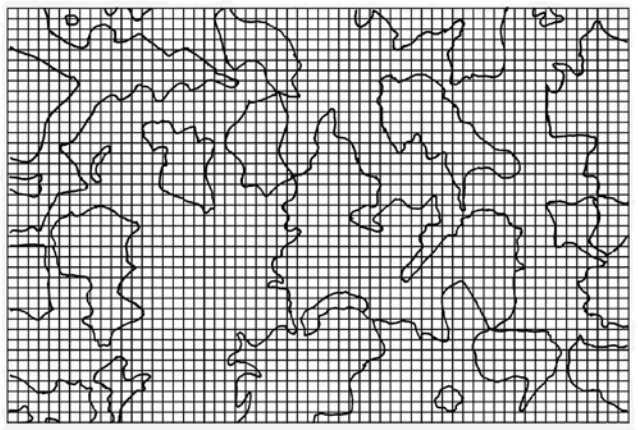

The area fraction of the pearlite may be determined by counting squares. There are a total of 2400 squares, and of these, approximately 1020 lie within the pearlite particles. Thus, the area fraction of pearlite is 1020/2400 = 0.425, which is also assumed to be the volume fraction (V_p).

We now want to convert this volume fraction of pearlite into mass fraction (of pearlite, W_p), and then use the appropriate lever rule on the Fe-Fe_3C phase diagram to determine the composition of the alloy. Conversion from V_p to W_p is accomplished using Equation 9.7 as follows:

$$W_p = \frac{V_p \rho_p}{V_p \rho_p + V_{\alpha'} \rho_{\alpha'}}$$

$$= \frac{(0.425)(7.84\ \text{g/cm}^3)}{(0.425)(7.84\ \text{g/cm}^3) + (1.000 - 0.425)(7.87\ \text{g/cm}^3)} = 0.424$$

Computation of the alloy composition, C_0', is possible using the lever-rule expression of Equation 9.20 as follows:

$$W_p = \frac{C_0' - 0.022}{0.74} = 0.424$$

And solving for C_0' from this expression leads to $C_0' = 0.336$ wt% C.

This value is in reasonable agreement with the 0.38 wt% C cited in the legend of Figure 9.30.

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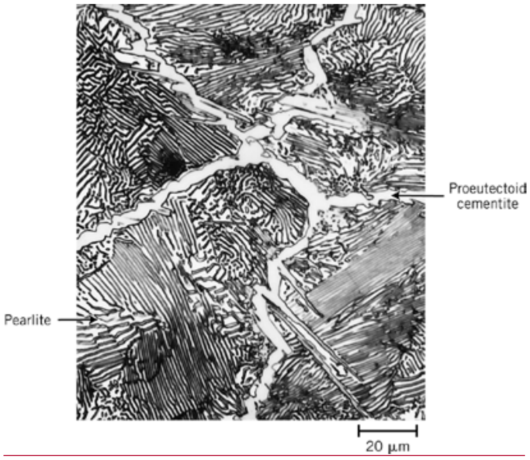
9.64 On the basis of the photomicrograph (i.e., the relative amounts of the microconstituents) for the iron-carbon alloy shown in Figure 9.33 and the Fe-Fe$_3$*C phase diagram (Figure 9.24), estimate the composition of the alloy, and then compare this estimate with the composition given in the figure legend of Figure 9.33. Make the following assumptions: (1) The area fraction of each phase and microconstituent in the photomicrograph is equal to its volume fraction; (2) the densities of proeutectoid cementite and pearlite are 7.64 and 7.84 g/cm*^{3}*, respectively; and (3) this photomicrograph represents the equilibrium microstructure at 725°C.*

Solution

Below is shown the micrograph of the iron-carbon alloy, Figure 9.33:



Proeutectoid cementite and pearlite microconstituents are present in the photomicrograph, and it is given that their densities are 7.64 and 7.84 g/cm^3, respectively. Below is shown a square grid network onto which is superimposed outlines of the proeutectoid cementite-pearlite phase boundaries.

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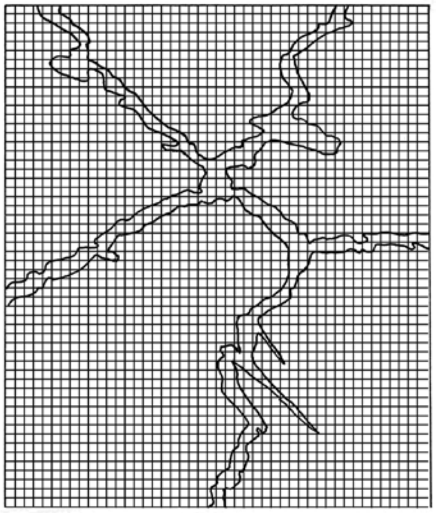

The area fraction of the proeutectoid cementite may be determined by counting squares. There are a total of 2530 squares, and of these, approximately 230 lie within the proeutectoid cementite phase particles. Thus, the area fraction of proeutectoid cementite is 230/2530 = 0.091, which is also assumed to be the volume fraction $(V_{\mathrm{Fe_3C'}})$.

We now want to convert this volume fraction of proeutectoid cementite into mass fraction (of proeutectoid cementite, $W_{\mathrm{Fe_3C'}}$), and then use the appropriate lever rule on the Fe-Fe$_3$C phase diagram to determine the composition of the alloy. Conversion from $V_{\mathrm{Fe_3C'}}$ to $W_{\mathrm{Fe_3C'}}$ is accomplished using Equation 9.7 as follows:

$$W_{\mathrm{Fe_3C'}} = \frac{V_{\mathrm{Fe_3C'}}\,\rho_{\mathrm{Fe_3C'}}}{V_{\mathrm{Fe_3C'}} + V_p\,\rho_p}$$

Here V_p and ρ_p represent, respectively, the volume fraction and density of pearlite. Insertion of values of the parameters in the above equation, leads to computation of the mass fraction of proeutectoid cementite:

$$W_{\mathrm{Fe_3C}} = \frac{(0.091)(7.64\ \mathrm{g/cm^3})}{(0.091)(7.64\ \mathrm{g/cm^3}) + (1.000\ -\ 0.091)(7.84\ \mathrm{g/cm^3})} = 0.089$$

Computation of the alloy composition, C_1', is possible using the lever-rule expression of Equation 9.23 as follows:

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$$W_{\mathrm{Fe_3C'}} = \frac{C_1' - 0.76}{5.94} = 0.089$$

And solving for C_1' from this expression leads to $C_1' = 1.29\ \text{wt\% C}$.

This value is in reasonable agreement with the 1.4 wt% C cited in the legend of Figure 9.33.

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9.65 *Compute the mass fractions of proeutectoid ferrite and pearlite that form in an iron–carbon alloy containing 0.35 wt% C.*

Solution

The mass fractions of proeutectoid ferrite and pearlite that form in a 0.35 wt% C iron-carbon alloy are considered in this problem. To solve this problem we use Equation 9.20, which is the lever-rule expression for computation of the mass fraction of pearlite in a hypoeutectoid alloy. This computation is as follows:

$$W_P = \frac{C_0' - 0.022}{0.74} = \frac{0.35 - 0.022}{0.74} = 0.44$$

Likewise, the mass fraction of proeutectoid ferrite is determined using Equation 9.21:

$$W_{\alpha'} = \frac{0.76 - C_0'}{0.74} = \frac{0.76 - 0.35}{0.74} = 0.56$$

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9.66 For a series of Fe-Fe$_3$C alloys that have compositions ranging between 0.022 and 0.76 wt% C that have been cooled slowly from 1000°C, plot the following:

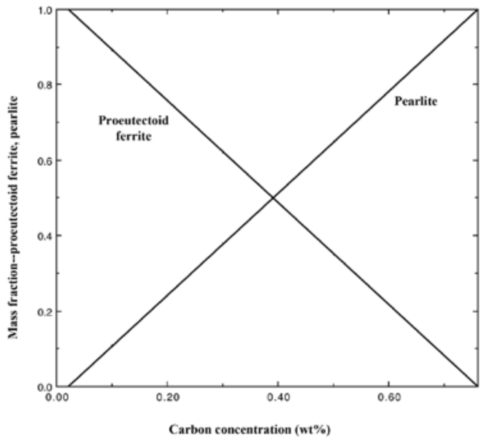
(a) mass fractions of proeutectoid ferrite and pearlite versus carbon concentration at 725°C

(b) mass fractions of ferrite and cementite versus carbon concentration at 725°C

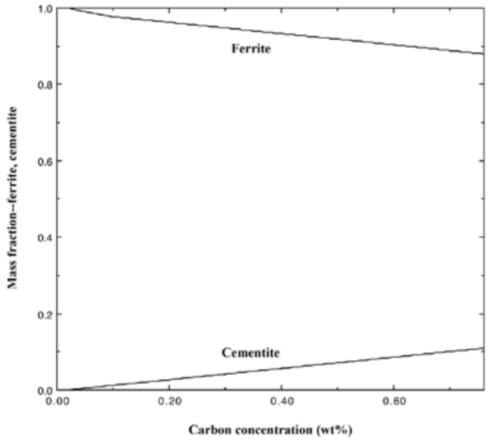
Solution

These plots are shown below.

(a)



(b)



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9.67 *The microstructure of an iron–carbon alloy consists of proeutectoid ferrite and pearlite; the mass fractions of these two microconstituents are 0.174 and 0.826, respectively. Determine the concentration of carbon in this alloy.*

Solution

To solve this problem we use Equation 9.20, which is the lever-rule expression for computation of the mass fraction of pearlite in a hypoeutectoid alloy. We are given the mass fraction of pearlite (W_p), 0.826, which allows us to determine the concentration of carbon in the alloy, C_0'. For this problem, Equation 9.20 is expressed as follows:

$$W_p = \frac{C_0' - 0.022}{0.74} = 0.826$$

And solving for C_0' leads to $C_0' = 0.63\ \text{wt\% C}$.

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9.68 *The mass fractions of total ferrite and total cementite in an iron–carbon alloy are 0.91 and 0.09, respectively. Is this a hypoeutectoid or hypereutectoid alloy? Why?*

Solution

In this problem we are given values of $W_{\square}$ and W_{Fe_3C} for an iron-carbon alloy (0.91 and 0.09, respectively), and then are asked to specify whether the alloy is hypoeutectoid or hypereutectoid. To solve the problem it is necessary to employ the appropriate lever-rule expression for the computation of either W_α or W_{Fe_3C} and from this expression solve for the composition of the alloy, C_0. The following is the lever rule for determining the mass fraction of total α:

$$W_\alpha = 0.91 = \frac{C_{Fe_3C} - C_0}{C_{Fe_3C} - C_\alpha} = \frac{6.70 - C_0}{6.70 - 0.022}$$

Now, solving for the alloy composition, leads to C_0 = 0.62 wt% C. Therefore, the alloy is hypoeutectoid since C_0 is less than 0.76 wt% C.

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9.69 *The microstructure of an iron–carbon alloy consists of proeutectoid cementite and pearlite; the mass fractions of these microconstituents are 0.11 and 0.89, respectively. Determine the concentration of carbon in this alloy.*

Solution

In this problem we are given values of $W_{Fe_3C'}$ (0.11) and W_p (0.89) for an iron-carbon alloy and are asked to determine the concentration of carbon present. To solve the problem it is necessary to employ the appropriate lever-rule expression for the computation of either $W_{Fe_3C'}$ or W_p, from which it is possible to solve for the composition of the alloy, C_1'. We will use Equation 9.22, from which the value of W_p may be computed. Hence,

$$W_p = \frac{6.7 - C_1'}{6.7 - 0.76} = 0.89$$

And solving for C_1' yields $C_1' = 1.41 \text{ wt\% C}$.

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9.70 *Consider 1.5 kg of a 99.7 wt% Fe–0.3 wt% C alloy that is cooled to a temperature just below the eutectoid.*

(a) How many kilograms of proeutectoid ferrite form?

(b) How many kilograms of eutectoid ferrite form?

(c) How many kilograms of cementite form?

Solution

In this problem we are asked to consider 1.5 kg of a 99.7 wt% Fe-0.3 wt% C alloy that is cooled to a temperature below the eutectoid.

(a) We first determine the mass fraction of proeutectoid ferrite that forms using Equation 9.21 as follows:

$$W_{\alpha'} = \frac{0.76 - C_0'}{0.74} = \frac{0.76 - 0.30}{0.74} = 0.622$$

The corresponding mass of proeutectoid ferrite is the product of this mass fraction and the mass of the alloy (1.5 kg)—that is (0.622)(1.5 kg) = 0.933 kg.

(b) In order to determine the amount of eutectoid ferrite, it first becomes necessary to compute the mass fraction of total ferrite using the lever rule applied entirely across the α + Fe_3C phase field, as

$$W_{\alpha} = \frac{C_{Fe_3C} - C_0'}{C_{Fe_3C} - C_{\alpha}} = \frac{6.70 - 0.30}{6.70 - 0.022} = 0.958$$

Which means that the mass of total ferrite is equal to (0.958)(1.5 kg) = 1.437 kg. Now, the amount of eutectoid ferrite is just the difference between the masses of total and proeutectoid ferrites, or

1.437 kg – 0.933 kg = 0.504 kg

(c) With regard to the amount of cementite that forms, again application of the lever rule across the entirety of the α + Fe_3C phase field to determine the mass fraction, which leads to

$$W_{Fe_3C} = \frac{C_0' - C_{\alpha}}{C_{Fe_3C} - C_{\alpha}} = \frac{0.30 - 0.022}{6.70 - 0.022} = 0.042$$

which amounts to (0.042)(1.5 kg) = 0.063 kg of cementite in the alloy.

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9.71 *Compute the maximum mass fraction of proeutectoid cementite possible for a hypereutectoid iron-carbon alloy.*

Solution

This problem asks that we compute the maximum mass fraction of proeutectoid cementite possible for a hypereutectoid iron-carbon alloy. This requires that we utilize Equation 9.23 with C_1' = 2.14 wt% C, the maximum solubility of carbon in austenite. Thus,

$$W_{\mathrm{Fe_3C'}} = \frac{C_1' - 0.76}{5.94} = \frac{2.14 - 0.76}{5.94} = 0.232$$

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9.72 *Is it possible to have an iron–carbon alloy for which the mass fractions of total cementite and proeutectoid ferrite are 0.057 and 0.36, respectively? Why or why not?*

Solution

This problem asks if it is possible to have an iron-carbon alloy for which W_{Fe_3C} = 0.057 and $W_{\alpha'}$ = 0.36. In order to make this determination, it is necessary to set up lever rule expressions for these two mass fractions in terms of the alloy composition, then to solve for the alloy composition of each; if both alloy composition values are equal, then such an alloy is possible. The lever-rule expression for the mass fraction of total cementite is

$$W_{Fe_3C} = \frac{C_0 - C_\alpha}{C_{Fe_3C} - C_\alpha} = \frac{C_0 - 0.022}{6.70 - 0.022} = 0.057$$

Solving for this C_0 yields C_0 = 0.40 wt% C. Now for $W_{\alpha'}$ we utilize Equation 9.21 as

$$W_{\alpha'} = \frac{0.76 - C_0'}{0.74} = 0.36$$

This expression leads to $C_0' = 0.49 \text{ wt\% C}$. Since C_0 and C_0' are different, this alloy is *not* possible.

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9.73 *Is it possible to have an iron–carbon alloy for which the mass fractions of total ferrite and pearlite are 0.860 and 0.969, respectively? Why or why not?*

Solution

This problem asks if it is possible to have an iron-carbon alloy for which W_{α} = 0.860 and W_p = 0.969. In order to make this determination, it is necessary to set up lever rule expressions for these two mass fractions in terms of the alloy composition, then to solve for the alloy composition of each; if both alloy composition values are equal, then such an alloy is possible. The lever-rule expression for the mass fraction of total ferrite is

$$W_{\alpha} = \frac{C_{\mathrm{Fe_3C}} - C_0}{C_{\mathrm{Fe_3C}} - C_{\alpha}} = \frac{6.70 - C_0}{6.70 - 0.022} = 0.860$$

Solving for this C_0 yields C_0 = 0.95 wt% C. Therefore, this alloy is hypereutectoid since C_0 is greater than the eutectoid composition (0.76 wt%). Thus, it is necessary to use Equation 9.22 for W_p as

$$W_p = \frac{6.70 - C_1'}{5.94} = 0.969$$

This expression leads to $C_1' = 0.95$ wt% C. Since C_0 = C_1', this alloy *is possible.*

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9.74 *Compute the mass fraction of eutectoid cementite in an iron–carbon alloy that contains 1.00 wt% C.*

Solution

This problem asks that we compute the mass fraction of eutectoid cementite in an iron-carbon alloy that contains 1.00 wt% C. In order to solve this problem it is necessary to compute mass fractions of total and proeutectoid cementites, and then to subtract the latter from the former. To calculate the mass fraction of total cementite, it is necessary to use the lever rule and a tie line that extends across the entire $\alpha + Fe_3C$ phase field as

$$W_{Fe_3C} = \frac{C_0 - C_\alpha}{C_{Fe_3C} - C_\alpha} = \frac{1.00 - 0.022}{6.70 - 0.022} = 0.146$$

Now, for the mass fraction of proeutectoid cementite we use Equation 9.23

$$W_{Fe_3C} = \frac{C_1' - 0.76}{5.94} = \frac{1.00 - 0.76}{5.94} = 0.040$$

And, finally, the mass fraction of eutectoid cementite $W_{Fe_3C''}$ is just

$$W_{Fe_3C''} = W_{Fe_3C} - W_{Fe_3C'}$$

$$= 0.146 - 0.04 = 0.106$$

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9.75 *Compute the mass fraction of eutectoid cementite in an iron-carbon alloy that contains 0.87 wt% C.*

Solution

This problem asks that we compute the mass fraction of eutectoid cementite in an iron-carbon alloy that contains 0.87 wt% C. In order to solve this problem it is necessary to compute mass fractions of total and proeutectoid cementites, and then to subtract the latter from the former. To calculate the mass fraction of total cementite, it is necessary to use the lever rule and a tie line that extends across the entire $\alpha + Fe_3C$ phase field as

$$W_{Fe_3C} = \frac{C_0 - C_\alpha}{C_{Fe_3C} - C_\alpha} = \frac{0.87 - 0.022}{6.70 - 0.022} = 0.127$$

Now, for the mass fraction of proeutectoid cementite we use Equation 9.23:

$$W_{Fe_3C'} = \frac{C_1' - 0.76}{5.94} = \frac{0.87 - 0.76}{5.94} = 0.019$$

And, finally, the mass fraction of eutectoid cementite $W_{Fe_3C''}$ is just

$$W_{Fe_3C''} = W_{Fe_3C} - W_{Fe_3C'}$$

$$= 0.127 - 0.019 = 0.108$$

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9.76 *The mass fraction of eutectoid cementite in an iron–carbon alloy is 0.109. On the basis of this information, is it possible to determine the composition of the alloy? If so, what is its composition? If this is not possible, explain why.*

Solution

Yes, it is possible to determine the alloy composition; and, in fact, there are two possible answers. For the first, the eutectoid cementite exists in addition to proeutectoid cementite. For this case the mass fraction of eutectoid cementite ($W_{Fe_3C''}$) is just the difference between total cementite and proeutectoid cementite mass fractions; that is

$$W_{Fe_3C''} = W_{Fe_3C} - W_{Fe_3C'}$$

Now, it is possible to write expressions for W_{Fe_3C} (of the form of Equation 9.12) and $W_{Fe_3C'}$ (Equation 9.23) in terms of C_0, the alloy composition. Thus,

$$W_{Fe_3C''} = \frac{C_0 - C_\alpha}{C_{Fe_3C} - C_\alpha} - \frac{C_0 - 0.76}{5.94}$$

$$= \frac{C_0 - 0.022}{6.70 - 0.022} - \frac{C_0 - 0.76}{5.94} = 0.109$$

And, solving for C_0 yields C_0 = 0.84 wt% C.

For the second possibility, we have a hypoeutectoid alloy wherein all of the cementite is eutectoid cementite. Thus, it is necessary to set up a lever rule expression wherein the mass fraction of total cementite is 0.109. Therefore,

$$W_{Fe_3C} = \frac{C_0 - C_\alpha}{C_{Fe_3C} - C_\alpha} = \frac{C_0 - 0.022}{6.70 - 0.022} = 0.109$$

And, solving for C_0 yields C_0 = 0.75 wt% C.

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9.77 *The mass fraction of eutectoid ferrite in an iron–carbon alloy is 0.71. On the basis of this information, is it possible to determine the composition of the alloy? If so, what is its composition? If this is not possible, explain why.*

Solution

Yes, it is possible to determine the alloy composition; and, in fact, there are two possible answers. For the first, the eutectoid ferrite exists in addition to proeutectoid ferrite (for a hypoeutectoid alloy). For this case the mass fraction of eutectoid ferrite $(W_{\alpha''})$ is just the difference between total ferrite and proeutectoid ferrite mass fractions; that is

$$W_{\alpha''} = W_{\alpha} - W_{\alpha'}$$

Now, it is possible to write expressions for $W_{\square}$ (of the form of Equation 9.12) and $W_{\alpha'}$ (Equation 9.21) in terms of C_0, the alloy composition. Thus,

$$W_{\alpha''} = \frac{C_{\mathrm{Fe_3C}} - C_0}{C_{\mathrm{Fe_3C}} - C_{\alpha}} - \frac{0.76 - C_0}{0.74}$$

$$= \frac{6.70 - C_0}{6.70 - 0.022} - \frac{0.76 - C_0}{0.74} = 0.71$$

And, solving for C_0 yields C_0 = 0.61 wt% C.

For the second possibility, we have a hypereutectoid alloy wherein all of the ferrite is eutectoid ferrite. Thus, it is necessary to set up a lever rule expression wherein the mass fraction of total ferrite is 0.71. Therefore,

$$W_{\alpha} = \frac{C_{\mathrm{Fe_3C}} - C_0}{C_{\mathrm{Fe_3C}} - C_{\alpha}} = \frac{6.70 - C_0}{6.70 - 0.022} = 0.71$$

And, solving for C_0 yields C_0 = 1.96 wt% C.

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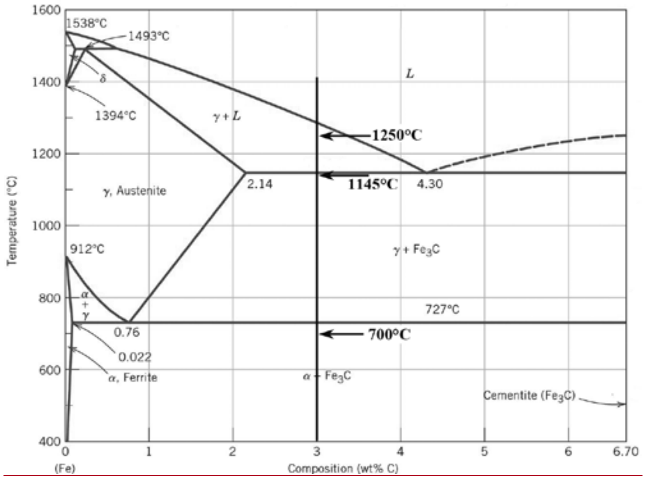
9.78 *For an iron–carbon alloy of composition 3 wt% C–97 wt% Fe, make schematic sketches of the microstructure that would be observed for conditions of very slow cooling at the following temperatures: 1250°C (2280°F), 1145°C (2095°F), and 700°C (1290°F). Label the phases and indicate their compositions (approximate).*

Solution

Below is shown the Fe-Fe_3C phase diagram with a vertical line constructed at 3 wt% C; also along this line noted temperatures of 1250°C, 1145°C, and 700°C.



Schematic microstructures for this iron-carbon alloy at the three temperatures are shown below; approximate phase compositions are also indicated.

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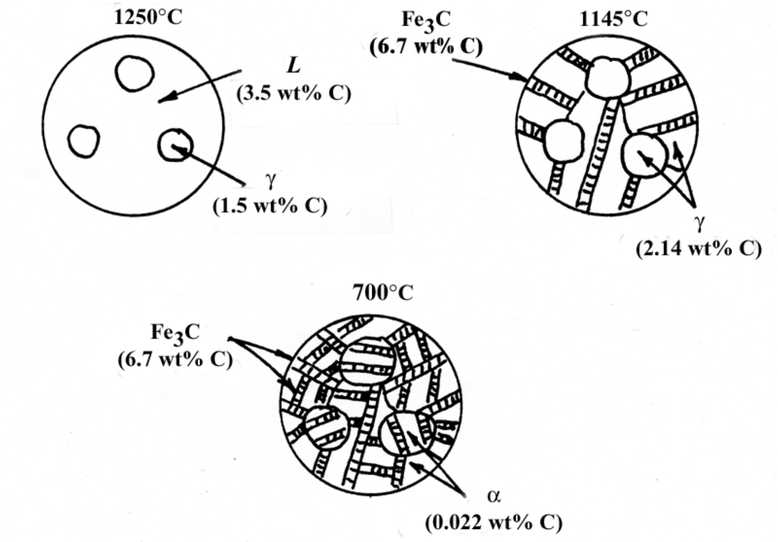
1250°C
L
(3.5 wt% C)
γ
(1.5 wt% C)
Fe$_3$C
(6.7 wt% C)
1145°C
γ
(2.14 wt% C)
700°C
Fe$_3$C
(6.7 wt% C)
α
(0.022 wt% C)

9.79 *Often, the properties of multiphase alloys may be approximated by the relationship*

$$E\ (\text{alloy}) = E_\alpha V_\alpha + E_\beta V_\beta \qquad (9.24)$$

where E represents a specific property (modulus of elasticity, hardness, etc.), and V is the volume fraction. The subscripts α and β denote the existing phases or microconstituents. Use this relationship to determine the approximate Brinell hardness of a 99.75 wt% Fe–0.25 wt% C alloy. Assume Brinell hardnesses of 80 and 280 for ferrite and pearlite, respectively, and that volume fractions may be approximated by mass fractions.

Solution

To solve this problem, we first note that this alloy is a hypoeutectoid one since the concentration of carbon is 0.25 wt%--is less that 0.76 wt% C. Therefore, it is necessary to compute mass fractions of pearlite and proeutectoid ferrite (denoted as W_p and $W_{\alpha'}$, respectively) using Equations 9.20 and 9.21, as follows

$$W_p = \frac{C'_0 - 0.022}{0.74} = \frac{0.25 - 0.022}{0.74} = 0.308$$

$$W_{\alpha'} = \frac{0.76 - C_0}{0.74} = \frac{0.76 - 0.25}{0.74} = 0.689$$

Now, we compute the Brinell hardness of the alloy using a modified form of Equation 9.24 as follows:

$$\text{HB}_{\text{alloy}} = \text{HB}_{\alpha'} W_{\alpha'} + \text{HB}_p W_p$$

$$= (80)(0.689) + (280)(0.308) = 141$$

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The Influence of Other Alloying Elements

9.80 *A steel alloy contains 95.7 wt% Fe, 4.0 wt% W, and 0.3 wt% C.*

(a) What is the eutectoid temperature of this alloy?

(b) What is the eutectoid composition?

(c) What is the proeutectoid phase?

Assume that there are no changes in the positions of other phase boundaries with the addition of W.

Solution

(a) From Figure 9.34, the eutectoid temperature for 4.0 wt% W is approximately 900°C.

(b) From Figure 9.35, the eutectoid composition is approximately 0.21 wt% C.

(c) Since the carbon concentration of the alloy (0.3 wt%) is greater than the eutectoid (0.21 wt% C), cementite is the proeutectoid phase.

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9.81 *A steel alloy is known to contain 93.65 wt% Fe, 6.0 wt% Mn, and 0.35 wt% C.*

(a) What is the approximate eutectoid temperature of this alloy?

(b) What is the proeutectoid phase when this alloy is cooled to a temperature just below the eutectoid?

(c) Compute the relative amounts of the proeutectoid phase and pearlite. Assume that there are no alterations in the positions of other phase boundaries with the addition of Mn.

Solution

(a) From Figure 9.34, the eutectoid temperature for 6.0 wt% Mn is approximately 700°C (1290°F).

(b) From Figure 9.35, the eutectoid composition is approximately 0.44 wt% C. Since the carbon concentration in the alloy (0.35 wt%) is less than the eutectoid (0.44 wt% C), the proeutectoid phase is ferrite.

(c) Assume that the α–(α + Fe_3C) phase boundary is at a negligible carbon concentration. Modifying Equation 9.21 leads to

$$W_{\alpha'} = \frac{0.44 - C_0'}{0.44 - 0} = \frac{0.44 - 0.35}{0.44} = 0.20$$

Likewise, using a modified Equation 9.20

$$W_p = \frac{C_0' - 0}{0.44 - 0} = \frac{0.35}{0.44} = 0.80$$

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FUNDAMENTALS OF ENGINEERING QUESTIONS AND PROBLEMS

9.1FE *Once a system is at a state of equilibrium, a shift from equilibrium may result by alteration of which of the following?*

(A) Pressure *(C) Temperature*

(B) Composition *(D) All of the above*

Answer

The correct answer is D. A shift from equilibrium may result from alteration of *temperature*, *pressure*, and/or *composition*.

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9.2FE *A binary composition–temperature phase diagram for an isomorphous system will be composed of regions that contain which of the following phases and/or combinations of phases?*

(A) Liquid

(B) Liquid □□α

(C) α

(D) α, liquid, and liquid □ α

Answer

The correct answer is D. For an isomorphous system the two components are completely miscible in both the liquid and solid phases; thus, the phase regions are as follows: *α*, liquid, and liquid + *α*.

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9.3FE *From the lead–tin phase diagram (Figure 9.8), which of the following phases/phase combinations is present for an alloy of composition 46 wt% Sn–54 wt% Pb that is at equilibrium at 44℃?*

(A) α

(B) α + β

(C) β □ liquid

(D) α + β □ liquid

Answer

The correct answer is B. Locate this temperature-composition point on the phase diagram. Inasmuch as it is within the *α* + *β* region, both *alpha* + *beta* phases will be present.

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9.4FE *For a lead–tin alloy of composition 25 wt% Sn—75 wt% Pb, select from the following list the phase(s) present and their composition(s) at 200 ℃. (The Pb–Sn phase diagram appears in Figure 9.8.)*

(A) α □ 17 wt% Sn–83 wt% Pb; L □□ 55.7 wt% Sn–44.3 wt% Pb

(B) α □ 25 wt% Sn–75 wt% Pb; L □ 25 wt% Sn–75 wt% Pb

(C) α □ 17 wt% Sn–83 wt% Pb; β □ 55.7 wt% Sn–44.3 wt% Pb

(D) α □ 18.3 wt% Sn–81.7 wt% Pb; β □ 97.8 wt% Sn–2.2 wt% Pb

Answer

The correct answer is A. Locate this temperature-composition point on the phase diagram. Inasmuch as it is within the *α* + *L* region, at 200°C both *α* and liquid phases are present. A tie line drawn across the *α* + *L* phase field intersects the *α*–*α* + *L* phase boundary at about 17 wt% Sn-83 wt% Pb (which is the composition of the *α* phase) and the *α* + *L*–*L* phase boundary at about 55.7 wt% Sn-44.3 wt% Pb (which is the composition of the liquid phase).

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CHAPTER 10

PHASE TRANSFORMATIONS

PROBLEM SOLUTIONS

The Kinetics of Phase Transformations

10.1 *Name the two stages involved in the formation of particles of a new phase. Briefly describe each.*

Answer

The two stages involved in the formation of particles of a new phase are *nucleation* and *growth*. The nucleation process involves the formation of normally very small particles of the new phase(s), which are stable and capable of continued growth. The growth stage is simply the increase in size of the new phase particles.

10.2 *(a) Rewrite the expression for the total free energy change for nucleation (Equation 10.1) for the case of a cubic nucleus of edge length a (instead of a sphere of radius r). Now differentiate this expression with respect to a (per Equation 10.2) and solve for both the critical cube edge length, a*, and ΔG*.*

(b) Is ΔG greater for a cube or a sphere? Why?*

Solution

(a) This problem first asks that we rewrite the expression for the total free energy change for nucleation (analogous to Equation 10.1) for the case of a cubic nucleus of edge length a. The volume of such a cubic radius is a^3, whereas the total surface area is $6a^2$ (since there are six faces each of which has an area of a^2). Thus, the expression for ΔG is as follows:

$$\Delta G = a^3 \Delta G_v + 6a^2\gamma$$

Differentiation of this expression with respect to a is as

$$\frac{d\Delta G}{da} = \frac{d(a^3\Delta G_v)}{da} + \frac{d(6a^2\gamma)}{da}$$

$$= 3a^2\Delta G_v + 12a\gamma$$

If we set this expression equal to zero as

$$3a^2\Delta G_v + 12a\gamma = 0$$

and then solve for a (= a*), which gives

$$a^* = -\frac{4\gamma}{\Delta G_v}$$

Substitution of this expression for a in the above expression for ΔG yields an equation for ΔG^* as

$$\Delta G^* = (a^*)^3\Delta G_v + 6(a^*)^2\gamma$$

$$= \left(-\frac{4\gamma}{\Delta G_v}\right)^3 \Delta G_v + 6\gamma\left(-\frac{4\gamma}{\Delta G_v}\right)^2$$

$$= \frac{32\gamma^3}{(\Delta G_v)^2}$$

(b) ΔG_v for a cube—i.e., $(32)\left[\frac{\gamma^3}{(\Delta G_v)^2}\right]$—is greater that for a sphere—i.e., $\left(\frac{16\pi}{3}\right)\left[\frac{\gamma^3}{(\Delta G_v)^2}\right]$ = $(16.8)\left[\frac{\gamma^3}{(\Delta G_v)^2}\right]$. The reason for this is that surface-to-volume ratio of a cube is greater than for a sphere.

10.3 *If ice homogeneously nucleates at –40°C, calculate the critical radius given values of* -3.1×10^8 *J/m*^{3} *and 25 ×* 10^{-3} *J/m*^{2}*, respectively, for the latent heat of fusion and the surface free energy.*

Solution

This problem states that ice homogeneously nucleates at –40°C, and that we are to calculate the critical radius given the latent heat of fusion (-3.1×10^8 J/m^3) and the surface free energy (25×10^{-3} J/m^2). Solution to this problem requires the utilization of Equation 10.6 as

$$r^* = \left(-\frac{2\gamma T_m}{\Delta H_f}\right)\left(\frac{1}{T_m - T}\right)$$

$$= \left[-\frac{(2)(25 \times 10^{-3}\ \mathrm{J/m^2})(273\ \mathrm{K})}{-3.1 \times 10^8\ \mathrm{J/m^3}}\right]\left(\frac{1}{40\ \mathrm{K}}\right)$$

$$= \mathbf{1.10 \times 10^{-9}\ m = 1.10\ nm}$$

10.4 *(a) For the solidification of nickel, calculate the critical radius r* and the activation free energy ΔG* if nucleation is homogeneous. Values for the latent heat of fusion and surface free energy are* -2.53×10^9 *J/m*^{3} *and 0.255 J/m*^{2}*, respectively. Use the supercooling value found in Table 10.1.*

(b) Now calculate the number of atoms found in a nucleus of critical size. Assume a lattice parameter of 0.360 nm for solid nickel at its melting temperature.

Solution

(a) This portion of the problem asks that we compute r^* and ΔG^* for the homogeneous nucleation of the solidification of Ni. First of all, Equation 10.6 is used to compute the critical radius. The melting temperature for nickel, found inside the front cover is 1455°C; also values of ΔH_f (-2.53×10^9 J/m^3) and γ (0.255 J/m^2) are given in the problem statement, and the supercooling value found in Table 10.1 is 319°C (which is also 319 K because this value is really $T_m - T$, which is the same for Celsius and Kelvin). Thus, from Equation 10.6 we have

$$r^* = \left(-\frac{2\gamma T_m}{\Delta H_f}\right)\left(\frac{1}{T_m - T}\right)$$

$$= \left[-\frac{(2)(0.255 \text{ J/m}^2)(1455 + 273 \text{ K})}{-2.53 \times 10^9 \text{ J/m}^3}\right]\left(\frac{1}{319 \text{ K}}\right)$$

$$= 1.09 \times 10^{-9} \text{ m} = 1.09 \text{ nm}$$

For computation of the activation free energy, Equation 10.7 is employed. Thus

$$\Delta G^* = \left(\frac{16\pi\gamma^3 T_m^2}{3\Delta H_f^2}\right)\frac{1}{(T_m - T)^2}$$

$$= \left[\frac{(16)(\pi)(0.255 \text{ J/m}^2)^3 (1455 + 273 \text{ K})^2}{(3)(-2.53 \times 10^9 \text{ J/m}^3)^2}\right]\left[\frac{1}{(319 \text{ K})^2}\right]$$

$$= 1.27 \times 10^{-18} \text{ J}$$

(b) In order to compute the number of atoms in a nucleus of critical size (assuming a spherical nucleus of radius r^*), it is first necessary to determine the number of unit cells, which we then multiply by the number of atoms per unit cell. The number of unit cells found in this critical nucleus is just the ratio of critical nucleus and unit cell volumes. Inasmuch as nickel has the FCC crystal structure, its unit cell volume is just a^3 where a is the unit cell length (i.e., the lattice parameter); this value is 0.360 nm, as cited in the problem statement. Therefore, the number of unit cells found in a radius of critical size is just

$$\text{\# unit cells/particle} = \frac{\frac{4}{3}\pi r^{*3}}{a^3}$$

$$= \frac{\left(\frac{4}{3}\right)(\pi)(1.09 \text{ nm})^3}{(0.360 \text{ nm})^3} = 116 \text{ unit cells}$$

Inasmuch as 4 atoms are associated with each FCC unit cell, the total number of atoms per critical nucleus is just

$$(116 \text{ unit cells/critical nucleus})(4 \text{ atoms/unit cell})$$

$$= 464 \text{ atoms/critical nucleus}$$

10.5 *(a) Assume for the solidification of nickel (Problem 10.4) that nucleation is homogeneous and that the number of stable nuclei is* 10^6 *nuclei per cubic meter. Calculate the critical radius and the number of stable nuclei that exist at the following degrees of supercooling: 200 and 300 K.*

(b) What is significant about the magnitudes of these critical radii and the numbers of stable nuclei?

Solution

(a) For this part of the problem we are asked to calculate the critical radius for the solidification of nickel (per Problem 10.4), for 200 K and 300 K degrees of supercooling, and assuming that the there are 10^6 nuclei per meter cubed for homogeneous nucleation. In order to calculate the critical radii, we replace the $T_m - T$ term in Equation 10.6 by the degree of supercooling (denoted as ΔT) cited in the problem.

For 200 K supercooling,

$$r^*_{200} = \left(-\frac{2\gamma T_m}{\Delta H_f}\right)\left(\frac{1}{\Delta T}\right)$$

$$= \left[-\frac{(2)(0.255\ \text{J/m}^2)(1455 + 273\ \text{K})}{-2.53 \times 10^9\ \text{J/m}^3}\right]\left(\frac{1}{200\ \text{K}}\right)$$

$$= 1.74 \times 10^{-9}\ \text{m} = 1.74\ \text{nm}$$

For 300 K supercooling,

$$r^*_{300} = \left[-\frac{(2)(0.255\ \text{J/m}^2)(1455 + 273\ \text{K})}{-2.53 \times 10^9\ \text{J/m}^3}\right]\left(\frac{1}{300\ \text{K}}\right)$$

$$= 1.16 \times 10^{-9}\ \text{m} = 1.16\ \text{nm}$$

In order to compute the number of stable nuclei that exist at 200 K and 300 K degrees of supercooling, it is necessary to use Equation 10.8. However, we must first determine the value of K_1 in Equation 10.8, which in turn requires that we calculate ΔG^* at the homogeneous nucleation temperature using Equation 10.7; this was done in Problem 10.4, and yielded a value of $\Delta G^* = 1.27 \times 10^{-18}$ J. Now for the computation of K_1, using the value of n^* for at the homogenous nucleation temperature (10^6 nuclei/m^3):

$$K_1 = \frac{n^*}{\exp\left(-\frac{\Delta G^*}{kT}\right)}$$

$$= \frac{10^6 \text{ nuclei/m}^3}{\exp\left[-\dfrac{1.27 \times 10^{-18}\text{ J}}{(1.38 \times 10^{-23}\text{ J/atom-K})(1455\text{ K} - 319\text{ K})}\right]}$$

$$= 1.52 \times 10^{41} \text{ nuclei/m}^3$$

Now for 200 K supercooling, it is first necessary to recalculate the value ΔG^* of using Equation 10.7, where, again, the $T_m - T$ term is replaced by the number of degrees of supercooling, denoted as ΔT, which in this case is 200 K. Thus

$$\Delta G^*_{200} = \left(\frac{16\pi\gamma^3 T_m^2}{3\Delta H_f^2}\right)\frac{1}{(\Delta T)^2}$$

$$= \left[\frac{(16)(\pi)(0.255\text{ J/m}^2)^3(1455 + 273\text{ K})^2}{(3)(-2.53 \times 10^9\text{ J/m}^3)^2}\right]\left[\frac{1}{(200\text{ K})^2}\right]$$

$$= 3.24 \times 10^{-18}\text{ J}$$

And, from Equation 10.8, the value of n^* is

$$n^*_{200} = K_1 \exp\left(-\frac{\Delta G^*_{200}}{kT}\right)$$

$$= (1.52 \times 10^{41}\text{ nuclei/m}^3)\exp\left[-\frac{3.24 \times 10^{-18}\text{ J}}{(1.38 \times 10^{-23}\text{ J/atom-K})(1455\text{ K} - 200\text{ K})}\right]$$

$$= 8.60 \times 10^{-41} \text{ stable nuclei}$$

Now, for 300 K supercooling the value of ΔG^* is equal to

$$\Delta G^*_{300} = \left[\frac{(16)(\pi)(0.255\text{ J/m}^2)^3(1455 + 273\text{ K})^2}{(3)(-2.53 \times 10^9\text{ J/m}^3)^2}\right]\left[\frac{1}{(300\text{ K})^2}\right]$$

$$= 1.44 \times 10^{-18}\text{ J}$$

from which we compute the number of stable nuclei at 300 K of supercooling as

$$n_{300}^{*} = K_1 \exp\left(-\frac{\Delta G_{300}^{*}}{kT}\right)$$

$$= (1.52 \times 10^{41} \text{ nuclei/m}^3)\exp\left[-\frac{1.44 \times 10^{-18} \text{ J}}{(1.38 \times 10^{-23} \text{ J/atom-K})(1455 \text{ K} - 300 \text{ K})}\right]$$

= 88 stable nuclei

(b) Relative to critical radius, r^* for 300 K supercooling is slightly smaller that for 200 K (1.16 nm versus 1.74 nm). [From Problem 10.4, the value of r^* at the homogeneous nucleation temperature (319 K) was 1.09 nm.] More significant, however, are the values of n^* at these two degrees of supercooling, which are dramatically different—8.60×10^{-41} stable nuclei at $\Delta T = 200$ K, versus 88 stable nuclei at $\Delta T = 300$ K!

10.6 *For some transformation having kinetics that obey the Avrami equation (Equation 10.17), the parameter n is known to have a value of 1.5. If the reaction is 25% complete after 125 s, how long (total time) will it take the transformation to go to 90% completion?*

Solution

This problem calls for us to compute the length of time required for a reaction to go to 90% completion. It first becomes necessary to solve for the parameter k in Equation 10.17. But before this is possible, we must manipulate this equation such that k is the dependent variable. We first rearrange Equation 10.17 as

$$\exp\left(-kt^n\right) = 1 - y$$

and then take natural logarithms of both sides:

$$-kt^n = \ln(1 - y)$$

Now solving for k gives

$$k = -\frac{\ln(1 - y)}{t^n} \tag{10.17a}$$

And, from the problem statement, for $y = 0.25$ when $t = 125$ s and given that $n = 1.5$, the value of k is equal to

$$k = -\frac{\ln(1 - 0.25)}{(125\ s)^{1.5}} = 2.06 \times 10^{-4}$$

We now want to manipulate Equation 10.17 such that t is the dependent variable. The above Equation 10.17a may be written in the form:

$$t^n = -\frac{\ln(1 - y)}{k}$$

And solving this expression for t leads to

$$t = \left[-\frac{\ln(1 - y)}{k}\right]^{1/n}$$

Now, using this equation and the value of k determined above, the time to 90% transformation completion is equal to

$$t = \left[-\frac{\ln(1 - 0.90)}{2.06 \times 10^{-4}}\right]^{1/1.5} = 500\ \text{s}$$

10.7 *Compute the rate of some reaction that obeys Avrami kinetics, assuming that the constants n and k have values of 2.0 and 5 × 10^{-4}, respectively, for time expressed in seconds.*

Solution

This problem asks that we compute the rate of some reaction given the values of n and k in Equation 10.17. Since the reaction rate is defined by Equation 10.18, it is first necessary to determine $t_{0.5}$, or the time necessary for the reaction to reach y = 0.5. We must first manipulate Equation 10.17 such that t is the dependent variable. We first rearrange Equation 10.17 as

$$\exp\left(-kt^n\right) = 1 - y$$

and then take natural logarithms of both sides:

$$-kt^n = \ln(1 - y)$$

which my be rearranged so as to read

$$t^n = -\frac{\ln(1 - y)}{k}$$

Now, solving for t from this expression leads to

$$t = \left[-\frac{\ln(1 - y)}{k}\right]^{1/n}$$

For $t_{0.5}$ this equation takes the form

$$t_{0.5} = \left[-\frac{\ln(1 - 0.5)}{k}\right]^{1/n}$$

And, incorporation of values for n and k given in the problem statement (2.0 and 5 × 10^{-4}, respectively), then

$$t_{0.5} = \left[-\frac{\ln(1 - 0.5)}{5 \times 10^{-4}}\right]^{1/2} = 37.23 \text{ s}$$

Now, the rate is computed using Equation 10.18 as

$$\text{rate} = \frac{1}{t_{0.5}} = \frac{1}{37.23 \text{ s}} = 2.69 \times 10^{-2} \text{ s}^{-1}$$

10.8 *It is known that the kinetics of recrystallization for some alloy obeys the Avrami equation, and that the value of n in the exponential is 5.0. If, at some temperature, the fraction recrystallized is 0.30 after 100 min, determine the rate of recrystallization at this temperature.*

Solution

This problem gives us the value of y (0.30) at some time t (100 min), and also the value of n (5.0) for the recrystallization of an alloy at some temperature, and then asks that we determine the rate of recrystallization at this same temperature. It is first necessary to calculate the value of k. We first rearrange Equation 10.17 as

$$\exp\left(-kt^n\right) = 1 - y$$

and then take natural logarithms of both sides:

$$-kt^n = \ln(1 - y)$$

Now solving for k gives

$$k = -\frac{\ln(1 - y)}{t^n} \tag{10.17b}$$

which, using the values cited above for y, n, and t yields

$$k = -\frac{\ln(1 - 0.30)}{(100 \text{ min})^5} = 3.57 \times 10^{-11}$$

At this point we want to compute $t_{0.5}$, the value of t for $y = 0.5$, which means that it is necessary to establish a form of Equation 10.17 in which t is the dependent variable. Rearrangement of Equation 10.17b above leads to

$$t^n = -\frac{\ln(1 - y)}{k}$$

And solving this expression for t leads to

$$t = \left[-\frac{\ln(1 - y)}{k}\right]^{1/n}$$

For $t_{0.5}$, this equation takes the form

$$t_{0.5} = \left[-\frac{\ln(1 - 0.5)}{k} \right]^{1/n}$$

and incorporation of the value of k determined above, as well as the value of n cited in the problem statement (5.0), we compute the value of $t_{0.5}$ as follows:

$$t_{0.5} = \left[-\frac{\ln(1 - 0.5)}{3.57 \times 10^{-11}} \right]^{1/5} = 114.2 \text{ min}$$

Therefore, from Equation 10.18, the rate is just

$$\text{rate} = \frac{1}{t_{0.5}} = \frac{1}{114.2 \text{ min}} = 8.76 \times 10^{-3} \text{ (min)}^{-1}$$

10.9 *It is known that the kinetics of some transformation obeys the Avrami equation and that the value of k is 2.6 × 10^{-6} (for time in minutes). If the fraction recrystallized is 0.65 after 120 min, determine the rate of this transformation.*

Solution

First of all, we note that the rate of a reaction is defined by Equation 10.18 as

$$\text{rate} = \frac{1}{t_{0.5}}$$

For this problem it is necessary to compute the value of $t_{0.5}$, the time it takes for the reaction to progress to 50% completion—or for the fraction of reaction y to equal 0.50. Furthermore, we may determine $t_{0.5}$ using the Avrami equation, Equation 10.17:

$$y = 1 - \exp(-kt^n) \qquad (10.17)$$

The problem statement provides us with the value of y (0.65) at some time t (120 min), and also the value of k (2.6 × 10^{-6}) from which data it is possible to compute the value of the constant n. In order to perform this calculation some algebraic manipulation of Equation 10.17 is necessary. First of all, we rearrange this expression as follows:

$$\exp\left(-kt^n\right) = 1 - y$$

We then take natural logarithms of both sides, which leads to:

$$-kt^n = \ln(1 - y) \qquad (10.17a)$$

Now solving for n requires further algebraic manipulation. Performing another rearrangement yields

$$t^n = \frac{\ln(1 - y)}{-k}$$

And taking natural logarithms of both sides of this equation results in the following expression

$$n\ln t = \ln\left(\frac{\ln(1-y)}{-k}\right)$$

From which we solve for *n* as follows

$$n = \frac{\ln\left[\frac{\ln(1-y)}{-k}\right]}{\ln t}$$

And incorporating values cited above for *y*, *k*, and *t* yields

$$n = \frac{\ln\left[\frac{\ln(1-0.65)}{-(2.6\times 10^{-6})}\right]}{\ln(120\ \text{min})} = 2.70$$

At this point we want to compute $t_{0.5}$, the value of *t* for *y* = 0.5, which means that it is necessary to establish a form of Equation 10.17 in which *t* is the dependent variable. This is accomplished using a rearranged form of Equation 10.17a as

$$t^n = -\frac{\ln(1-y)}{k}$$

From which we solve for *t:*

$$t = \left[-\frac{\ln(1-y)}{k}\right]^{1/n}$$

And for $t = t_{0.5}$, this equation becomes

$$t_{0.5} = \left[-\frac{\ln(1-0.5)}{k}\right]^{1/n}$$

Now incorporation of the value of *n* determined above, as well as the value of *k* cited in the problem statement (2.6 × 10^{-6}), we calculate $t_{0.5}$ as follows:

$$t_{0.5} = \left[-\frac{\ln(1-0.5)}{2.6\times 10^{-6}}\right]^{1/2.70} = 102\ \text{min}$$

And, finally, from Equation 10.18, the rate is equal to

$$\text{rate} = \frac{1}{t_{0.5}} = \frac{1}{102\ \text{min}} = 9.8 \times 10^{-3}\ (\text{min})^{-1}$$

10.10 *The kinetics of the austenite-to-pearlite transformation obeys the Avrami relationship. Using the fraction transformed–time data given here, determine the total time required for 95% of the austenite to transform to pearlite:*

Fraction Transformed	***Time (s)***
0.2	280
0.6	425

Solution

The first thing necessary is to set up two expressions of the form of Equation 10.17, and then to solve simultaneously for the values of *n* and *k*. In order to expedite this process, we will rearrange and do some algebraic manipulation of Equation 10.17. First of all, we rearrange as follows:

$$1 - y = \exp\left(-kt^n\right)$$

Now taking natural logarithms

$$\ln(1 - y) = -kt^n$$

Or

$$-\ln(1 - y) = kt^n \tag{10.17c}$$

which may also be expressed as

$$\ln\left(\frac{1}{1 - y}\right) = kt^n$$

Now taking natural logarithms again of both sides of this equation, leads to

$$\ln\left[\ln\left(\frac{1}{1 - y}\right)\right] = \ln k + n \ln t$$

which is the form of the equation that we will now use. Using values cited in the problem statement, the two equations are thus

$$\ln\left\{\ln\left[\frac{1}{1 - 0.2}\right]\right\} = \ln k + n \ln(280 \text{ s})$$

$$\ln\left\{\ln\left[\frac{1}{1 - 0.6}\right]\right\} = \ln k + n \ln(425 \text{ s})$$

Solving these two expressions simultaneously for *n* and *k* yields *n* = 3.385 and *k* = 1.162 × 10^{-9} for time in seconds.

Now it becomes necessary to solve for the value of *t* at which *y* = 0.95. Equation 10.17c given above may be rewritten as follows:

$$t^n = -\frac{\ln(1 - y)}{k}$$

And solving for *t* leads to

$$t = \left[-\frac{\ln(1 - y)}{k}\right]^{1/n}$$

Now incorporating into this expression values for *n* and *k* determined above, the time required for 95% austenite transformation is equal to

$$t = \left[-\frac{\ln(1 - 0.95)}{1.162 \times 10^{-9}}\right]^{1/3.385} = 603\text{ s}$$

10.11 *The fraction recrystallized–time data for the recrystallization at 350°C of a previously deformed aluminum are tabulated here. Assuming that the kinetics of this process obey the Avrami relationship, determine the fraction recrystallized after a total time of 116.8 min.*

Fraction Recrystallized	***Time (min)***
0.30	*95.2*
0.80	*126.6*

Solution

The first thing necessary is to set up two expressions of the form of Equation 10.17, and then to solve simultaneously for the values of *n* and *k*. In order to expedite this process, we will rearrange and do some algebraic manipulation of Equation 10.17. First of all, we rearrange as follows:

$$1 - y = \exp\left(-kt^n\right)$$

Now taking natural logarithms

$$\ln(1 - y) = -kt^n$$

Or

$$-\ln(1 - y) = kt^n$$

which may also be expressed as

$$\ln\left(\frac{1}{1 - y}\right) = kt^n$$

Now taking natural logarithms again of both sides of the above equation, leads to

$$\ln\left[\ln\left(\frac{1}{1 - y}\right)\right] = \ln k + n \ln t$$

which is the form of the equation that we will now use. The two equations are as follows:

$$\ln\left\{\ln\left[\frac{1}{1 - 0.30}\right]\right\} = \ln k + n \ln(95.2 \text{ min})$$

$$\ln\left\{\ln\left[\frac{1}{1-0.80}\right]\right\} = \ln k + n\ln(126.6\ \text{min})$$

Solving these two expressions simultaneously for *n* and *k* yields $n = 5.286$ and $k = 1.239 \times 10^{-11}$ for time in minutes.

Now it becomes necessary to solve for *y* when $t = 116.8$ min. Application of Equation 10.17 leads to

$$y = 1 - \exp\left(-kt^n\right)$$

$$= 1 - \exp\left[-\left(1.239 \times 10^{-11}\right)(116.8\ \text{min})^{5.286}\right] = 0.65$$

10.12 *(a) From the curves shown in Figure 10.11 and using Equation 10.18, determine the rate of recrystallization for pure copper at the several temperatures.*

(b) Make a plot of ln(rate) versus the reciprocal of temperature (in K^{-1}*), and determine the activation energy for this recrystallization process. (See Section 5.5.)*

(c) By extrapolation, estimate the length of time required for 50% recrystallization at room temperature, 20°C (293 K).

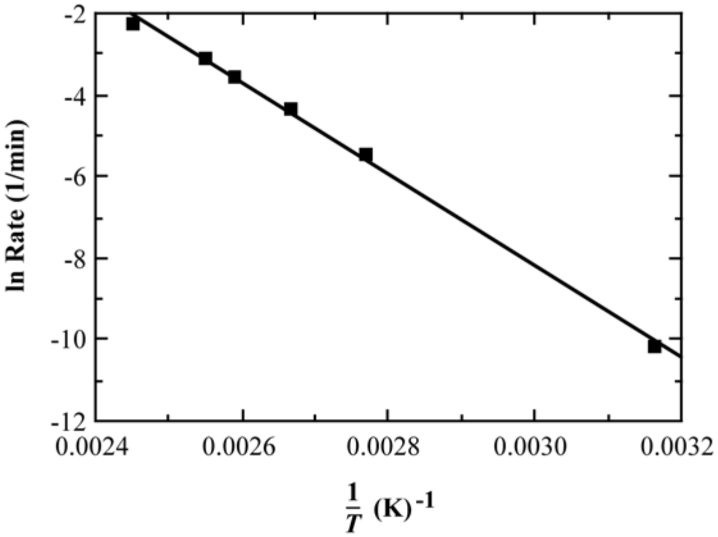
Solution

This problem asks us to consider the percent recrystallized versus logarithm of time curves for copper shown in Figure 10.11.

(a) The rates at the different temperatures are determined using Equation 10.18, which rates are tabulated below:

Temperature (°C)	Rate $(\text{min})^{-1}$
135	0.105
119	4.4×10^{-2}
113	2.9×10^{-2}
102	1.25×10^{-2}
88	4.2×10^{-3}
43	3.8×10^{-5}

(b) These data are plotted below.



The activation energy, Q, is related to the slope of the line drawn through the data points as

$$Q = -\,\mathrm{Slope}\,(R)$$

where R is the gas constant. The slope of this line is equal to

$$\mathrm{Slope} = \frac{\Delta \ln \mathrm{rate}}{\Delta\left(\dfrac{1}{T}\right)} = \frac{\ln \mathrm{rate}_1 - \ln \mathrm{rate}_2}{\dfrac{1}{T_1} - \dfrac{1}{T_2}}$$

Let us take $1/T_1$ = 0.0025 K^{-1} and $1/T_2$ = 0.0031 K^{-1}; the corresponding ln rate values are ln rate_1 = –2.6 and ln rate_2 = –9.4. Thus, using these values, the slope is equal to

$$\mathrm{Slope} = \frac{-2.6 - (-9.4)}{0.0025\ \mathrm{K}^{-1} - 0.0031\ \mathrm{K}^{-1}} = -\,1.133 \times 10^4\ \mathrm{K}$$

And, finally the activation energy is

$$Q = -\ (\mathrm{Slope})(R) = -\left(-1.133 \times 10^4\ \mathrm{K}^{-1}\right)(8.31\ \ \mathrm{J/mol\text{-}K})$$

$$= 94{,}150\ \mathrm{J/mol}$$

(c) At room temperature (20°C), $1/T = 1/(20 + 273\ \mathrm{K}) = 3.41 \times 10^{-3}\ \mathrm{K}^{-1}$. Extrapolation of the data in the plot to this $1/T$ value gives

$$\ln\,(\mathrm{rate}) \cong\ -12.8$$

which leads to

$$\mathrm{rate} \cong \exp\,(-\,12.8) = 2.76 \times\ 10^{-6}\ \ (\mathrm{min})^{-1}$$

But since

$$\mathrm{rate} = \frac{1}{t_{0.5}}$$

Then

$$t_{0.5} = \frac{1}{\mathrm{rate}} = \frac{1}{2.76\ \times 10^{-6}\ (\mathrm{min})^{-1}}$$

$$= 3.62\ \times 10^5\ \mathrm{min} = 250\ \mathrm{days}$$

10.13 *Determine values for the constants n and k (Equation 10.17) for the recrystallization of copper (Figure 10.11) at 119°C.*

Solution

One way to solve this problem is to take two values of percent recrystallization (which is just 100*y*, Equation 10.17) and their corresponding time values, then set up two simultaneous equations, from which *n* and *k* may be determined. In order to expedite this process, we will rearrange and do some algebraic manipulation of Equation 10.17. First of all, we rearrange as follows:

$$1 - y = \exp\left(-kt^n\right)$$

Now taking natural logarithms of both sides of this equation leads to

$$\ln\,(1 - y) = -kt^n$$

Or

$$-\ln\,(1 - y) = kt^n$$

which may also be expressed as

$$\ln\left(\frac{1}{1 - y}\right) = kt^n$$

Now taking natural logarithms of this expression leads to

$$\ln\left[\ln\left(\frac{1}{1 - y}\right)\right] = \ln k + n \ln t$$

which is the form of the equation that we will now use. From the 119°C curve of Figure 10.11, let us arbitrarily choose two percent recrystallized values, 20% and 80% (i.e., y_1 = 0.20 and y_2 = 0.80). Their corresponding time values are t_1 = 16 min and t_2 = 30 min (realizing that the time axis is scaled logarithmically). Thus, our two simultaneous equations become

$$\ln\left[\ln\left(\frac{1}{1 - 0.2}\right)\right] = \ln k + n \ln\,(16)$$

$$\ln\left[\ln\left(\frac{1}{1 - 0.8}\right)\right] = \ln k + n \ln\,(30)$$

from which we obtain the values $n = 3.09$ and $k = 4.24 \times 10^{-5}$.

Metastable Versus Equilibrium States

10.14 *In terms of heat treatment and the development of microstructure, what are two major limitations of the iron–iron carbide phase diagram?*

Answer

Two limitations of the iron-iron carbide phase diagram are:

(1) The nonequilibrium martensite does not appear on the diagram; and

(2) The diagram provides no indication as to the time-temperature relationships for the formation of pearlite, bainite, and spheroidite, all of which are composed of the equilibrium ferrite and cementite phases.

10.15 *(a) Briefly describe the phenomena of superheating and supercooling.*

(b) Why do these phenomena occur?

Answer

(a) Superheating and supercooling correspond, respectively, to heating or cooling above or below a phase transition temperature without the occurrence of the transformation.

(b) These phenomena occur because right at the phase transition temperature, the driving force is not sufficient to cause the transformation to occur. The driving force is enhanced during superheating or supercooling.

Isothermal Transformation Diagrams

10.16 *Suppose that a steel of eutectoid composition is cooled to 675°C (1250°F) from 760°C (1400°F) in less than 0.5 s and held at this temperature.*

(a) How long will it take for the austenite-to-pearlite reaction to go to 50% completion? To 100% completion?

(b) Estimate the hardness of the alloy that has completely transformed to pearlite.

Answer

We are called upon to consider the isothermal transformation of an iron-carbon alloy of eutectoid composition.

(a) From Figure 10.22, a horizontal line at 675°C intersects the 50% and reaction completion curves at about 100 and 300 seconds, respectively; these are the times asked for in the problem statement.

(b) The pearlite formed will be coarse pearlite. From Figure 10.30*a*, the hardness of an alloy of composition 0.76 wt% C that consists of coarse pearlite is about 200 HB (93 HRB).

10.17 *Briefly cite the differences between pearlite, bainite, and spheroidite relative to microstructure and mechanical properties.*

Answer

The microstructures of pearlite, bainite, and spheroidite all consist of α-ferrite and cementite phases. For pearlite, the two phases exist as layers which alternate with one another. Bainite consists of very fine and parallel needle-shaped particles of cementite that are surrounded an α-ferrite matrix. For spheroidite, the matrix is ferrite, and the cementite phase is in the shape of sphere-shaped particles.

Bainite is harder and stronger than pearlite, which, in turn, is harder and stronger than spheroidite.

10.18 *What is the driving force for the formation of spheroidite?*

Answer

The driving force for the formation of spheroidite is the net reduction in ferrite-cementite phase boundary area.

10.19 *Using the isothermal transformation diagram for an iron–carbon alloy of eutectoid composition (Figure 10.22), specify the nature of the final microstructure (in terms of microconstituents present and approximate percentages of each) of a small specimen that has been subjected to the following time–temperature treatments. In each case assume that the specimen begins at 760°C (1400°F) and that it has been held at this temperature long enough to have achieved a complete and homogeneous austenitic structure.*

(a) Cool rapidly to 350°C (660°F), hold for 10^3 *s, then quench to room temperature.*

(b) Rapidly cool to 625°C (1160°F), hold for 10 s, then quench to room temperature.

(c) Rapidly cool to 600°C (1110°F), hold for 4 s, rapidly cool to 450°C (840°F), hold for 10 s, then quench to room temperature.

(d) Reheat the specimen in part (c) to 700°C (1290°F) for 20 h.

(e) Rapidly cool to 300°C (570°F), hold for 20 s, then quench to room temperature in water. Reheat to 425°C (800°F) for 10^3 *s and slowly cool to room temperature.*

(f) Cool rapidly to 665°C (1230°F), hold for 10^3 *s, then quench to room temperature.*

(g) Rapidly cool to 575°C (1065°F), hold for 20 s, rapidly cool to 350°C (660°F), hold for 100 s, then quench to room temperature.

(h) Rapidly cool to 350°C (660°F), hold for 150 s, then quench to room temperature.

Solution

This problem asks us to determine the nature of the final microstructure of an iron-carbon alloy of eutectoid composition, that has been subjected to various isothermal heat treatments. Figure 10.22 is used in these determinations.

(a) 100% bainite

(b) 50% medium pearlite and 50% martensite

(c) 50% fine pearlite, 25% bainite, and 25% martensite

(d) 100% spheroidite

(e) 100% tempered martensite

(f) 100% coarse pearlite

(g) 100% fine pearlite

(h) 50% bainite and 50% martensite

10.20 *Make a copy of the isothermal transformation diagram for an iron–carbon alloy of eutectoid composition (Figure 10.22) and then sketch and label time–temperature paths on this diagram to produce the following microstructures:*

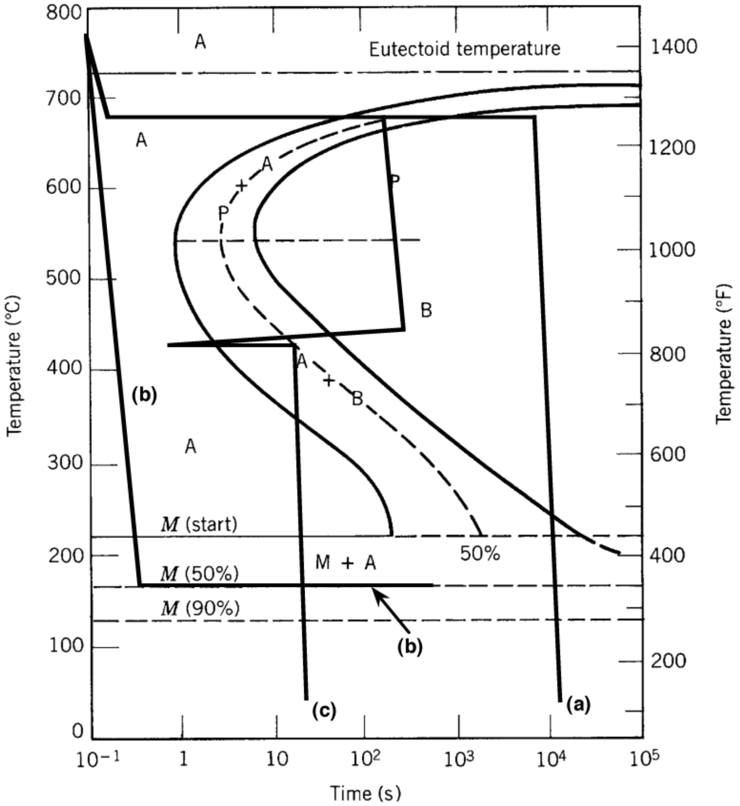
(a) 100% coarse pearlite

(b) 50% martensite and 50% austenite

(c) 50% coarse pearlite, 25% bainite, and 25% martensite

Solution

Below is shown the isothermal transformation diagram for a eutectoid iron-carbon alloy, with time-temperature paths that will yield (a) 100% coarse pearlite; (b) 50% martensite and 50% austenite; and (c) 50% coarse pearlite, 25% bainite, and 25% martensite.



10.21 *Using the isothermal transformation diagram for a 1.13 wt% C steel alloy (Figure 10.39), determine the final microstructure (in terms of just the microconstituents present) of a small specimen that has been subjected to the following time–temperature treatments. In each case assume that the specimen begins at 920°C (1690°F) and that it has been held at this temperature long enough to have achieved a complete and homogeneous austenitic structure.*

(a) Rapidly cool to 250°C (480°F), hold for 10^3 *s, then quench to room temperature.*

(b) Rapidly cool to 775°C (1430°F), hold for 500 s, then quench to room temperature.

(c) Rapidly cool to 400°C (750°F), hold for 500 s, then quench to room temperature.

(d) Rapidly cool to 700°C (1290°F), hold at this temperature for 10^5 *s, then quench to room temperature.*

(e) Rapidly cool to 650°C (1200°F), hold at this temperature for 3 s, rapidly cool to 400°C (750°F), hold for 25 s, then quench to room temperature.

(f) Rapidly cool to 350°C (660°F), hold for 300 s, then quench to room temperature.

(g) Rapidly cool to 675°C (1250°F), hold for 7 s, then quench to room temperature.

(h) Rapidly cool to 600°C (1110°F), hold at this temperature for 7 s, rapidly cool to 450°C (840°F), hold at this temperature for 4 s, then quench to room temperature.

Solution

We are asked to determine which microconstituents are present in a 1.13 wt% C iron-carbon alloy that has been subjected to various isothermal heat treatments. These microconstituents are as follows:

(a) Martensite

(b) Proeutectoid cementite and martensite

(c) Bainite

(d) Spheroidite

(e) Cementite, medium pearlite, bainite, and martensite

(f) Bainite and martensite

(g) Proeutectoid cementite, pearlite, and martensite

(h) Proeutectoid cementite and fine pearlite

10.22 *For parts a, c, d, f, and h of Problem 10.21, determine the approximate percentages of the microconstituents that form.*

Solution

This problem asks us to determine the approximate percentages of the microconstituents that form for five of the heat treatments described in Problem 10.20.

(a) 100% martensite

(c) 100% bainite

(d) 100% spheroidite

(f) 60% bainite and 40% martensite

(h) After holding for 7 s at 600°C, the specimen has completely transformed to proeutectoid cementite and fine pearlite; no further reaction will occur at 450°C. Therefore, we can calculate the mass fractions using the appropriate lever rule expressions, Equations 9.22 and 9.23, as follows:

$$W_{\mathrm{Fe_3C'}} = \frac{C_1' - 0.76}{5.94} = \frac{1.13 - 0.76}{5.94} = 0.062 \text{ or } 6.2\%$$

$$W_p = \frac{6.70 - C_1'}{5.94} = \frac{6.70 - 1.13}{5.94} = 0.938 \text{ or } 93.8\%$$

10.23 *Make a copy of the isothermal transformation diagram for a 1.13 wt% C iron–carbon alloy (Figure 10.39), and then on this diagram sketch and label time–temperature paths to produce the following microstructures:*

(a) 6.2% proeutectoid cementite and 93.8% coarse pearlite

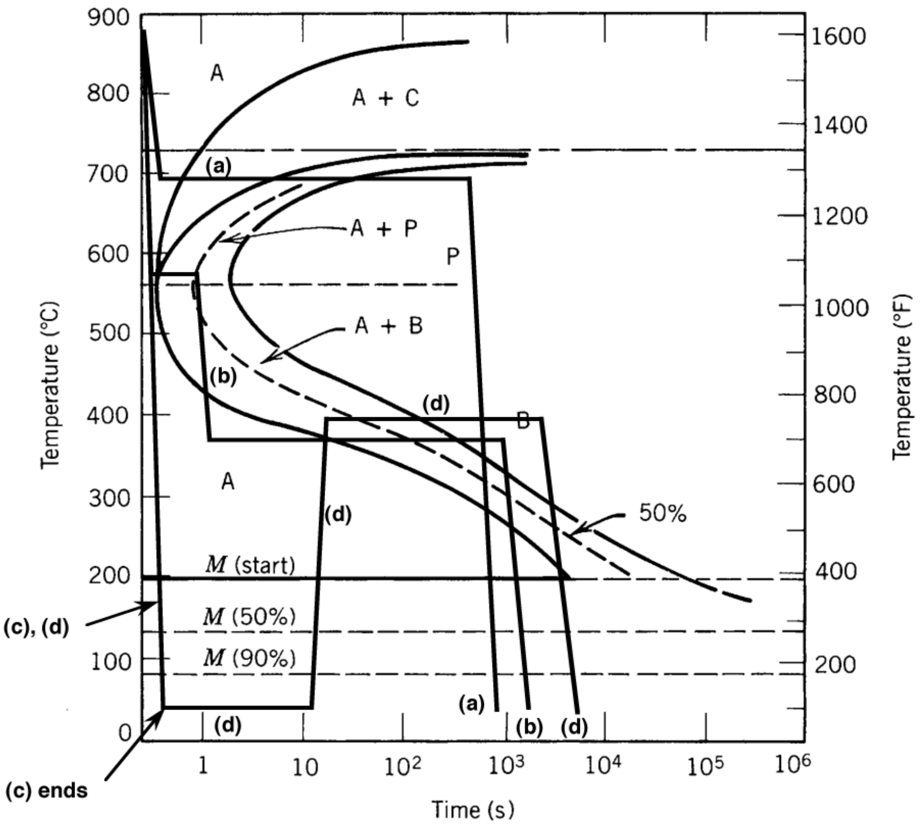
(b) 50% fine pearlite and 50% bainite

(c) 100% martensite

(d) 100% tempered martensite

Solution

Below is shown an isothermal transformation diagram for a 1.13 wt% C iron-carbon alloy, with time-temperature paths that will produce (a) 6.2% proeutectoid cementite and 93.8% coarse pearlite; (b) 50% fine pearlite and 50% bainite; (c) 100% martensite; and (d) 100% tempered martensite.



Continuous-Cooling Transformation Diagrams

10.24 *Name the microstructural products of eutectoid iron–carbon alloy (0.76 wt% C) specimens that are first completely transformed to austenite, then cooled to room temperature at the following rates:*

(a) 1°C/s

(b) 20°C/s

(c) 50°C/s

(d) 175°C/s

Solution

We are called upon to name the microstructural products that form for specimens of an iron-carbon alloy of eutectoid composition that are continuously cooled to room temperature at a variety of rates. Figure 10.27 is used in these determinations.

(a) At a rate of 1°C/s, coarse pearlite forms.

(b) At a rate of 20°C/s, fine pearlite forms.

(c) At a rate of 50°C/s, fine pearlite and martensite form.

(d) At a rate of 175ºC/s, martensite forms.

10.25 *Figure 10.40 shows the continuous-cooling transformation diagram for a 0.35 wt% C iron–carbon alloy. Make a copy of this figure, and then sketch and label continuous-cooling curves to yield the following microstructures:*

(a) Fine pearlite and proeutectoid ferrite

(b) Martensite

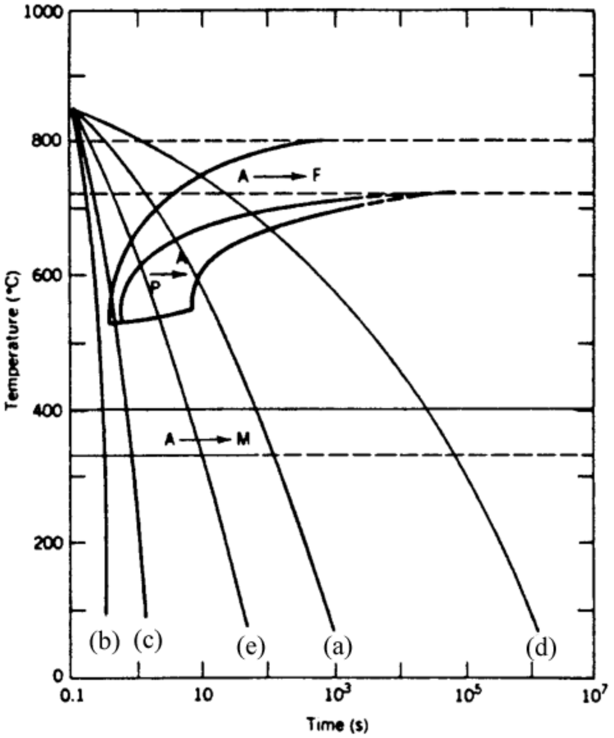
(c) Martensite and proeutectoid ferrite

(d) Coarse pearlite and proeutectoid ferrite

(e) Martensite, fine pearlite, and proeutectoid ferrite

Solution

Below is shown a continuous cooling transformation diagram for a 0.35 wt% C iron-carbon alloy, with continuous cooling paths that will produce (a) fine pearlite and proeutectoid ferrite; (b) martensite; (c) martensite and proeutectoid ferrite; (d) coarse pearlite and proeutectoid ferrite; and (e) martensite, fine pearlite, and proeutectoid ferrite.



10.26 *Cite two important differences between continuous-cooling transformation diagrams for plain carbon and alloy steels.*

Answer

Two important differences between continuous cooling transformation diagrams for plain carbon and alloy steels are: (1) for an alloy steel, a bainite nose will be present, which nose will be absent for plain carbon alloys; and (2) the pearlite-proeutectoid noses for plain carbon steel alloys are positioned at shorter times than for the alloy steels.

10.27 *Briefly explain why there is no bainite transformation region on the continuous-cooling transformation diagram for an iron–carbon alloy of eutectoid composition.*

Answer

There is no bainite transformation region on the continuous cooling transformation diagram for an iron-carbon alloy of eutectoid composition (Figure 10.25) because by the time a cooling curve has passed into the bainite region, the entirety of the alloy specimen will have transformed to pearlite.

10.28 *Name the microstructural products of 4340 alloy steel specimens that are first completely transformed to austenite, then cooled to room temperature at the following rates:*

(a) 0.005°C/s

(b) 0.05°C/s

(c) 0.5°C/s

(d) 5°C/s

Solution

This problem asks for the microstructural products that form when specimens of a 4340 steel are continuously cooled to room temperature at several rates. Figure 10.28 is used for these determinations.

(a) At a cooling rate of 0.005°C/s, proeutectoid ferrite and pearlite form.

(b) At a cooling rate of 0.05°C/s, martensite, ferrite, and bainite form.

(c) At a cooling rate of 0.5°C/s, martensite and bainite form.

(d) At a cooling rate of 5°C/s, martensite and bainite form.

10.29 *Briefly describe the simplest continuous-cooling heat treatment procedure that would be used in converting a 4340 steel from one microstructure to another.*

(a) (Martensite + ferrite + bainite) to (martensite + ferrite + pearlite + bainite)

(b) (Martensite + ferrite + bainite) to spheroidite

(c) (Martensite + bainite + ferrite) to tempered martensite

Solution

This problem asks that we briefly describe the simplest continuous cooling heat treatment procedure that would be used in converting a 4340 steel from one microstructure to another. Solutions to this problem require the use of Figure 10.28.

(a) In order to convert from (martensite + ferrite + bainite) to (martensite + ferrite + pearlite + bainite) it is necessary to heat above about 720°C, allow complete austenitization, then cool to room temperature at a rate between 0.02 and 0.006°C/s.

(b) To convert from (martensite + ferrite + bainite) to spheroidite the alloy must be heated to about 700°C for several hours.

(c) In order to convert from (martensite + bainite + ferrite) to tempered martensite it is necessary to heat to above about 720°C, allow complete austenitization, then cool to room temperature at a rate greater than 8.3°C/s, and finally isothermally heat treat the alloy at a temperature between about 400 and 550°C (Figure 10.34) for about one hour.

10.30 *On the basis of diffusion considerations, explain why fine pearlite forms for the moderate cooling of austenite through the eutectoid temperature, whereas coarse pearlite is the product for relatively slow cooling rates.*

Answer

For moderately rapid cooling, the time allowed for carbon diffusion is not as great as for slower cooling rates. Therefore, the diffusion distance is shorter, and thinner layers of ferrite and cementite form (i.e., fine pearlite forms).

Mechanical Behavior of Iron–Carbon Alloys

Tempered Martensite

10.31 *Briefly explain why fine pearlite is harder and stronger than coarse pearlite, which in turn is harder and stronger than spheroidite.*

Answer

The hardness and strength of iron-carbon alloys that have microstructures consisting of α-ferrite and cementite phases depend on the boundary area between the two phases. The greater this area, the harder and stronger the alloy inasmuch as (1) these boundaries impede the motion of dislocations, and (2) the cementite phase restricts the deformation of the ferrite phase in regions adjacent to the phase boundaries. Fine pearlite is harder and stronger than coarse pearlite because the alternating ferrite-cementite layers are thinner for fine, and therefore, there is more phase boundary area. The phase boundary area between the sphere-like cementite particles and the ferrite matrix is less in spheroidite than for the alternating layered microstructure found in coarse pearlite.

10.32 *Cite two reasons why martensite is so hard and brittle.*

Answer

Two reasons why martensite is so hard and brittle are: (1) there are relatively few operable slip systems for the body-centered tetragonal crystal structure, and (2) virtually all of the carbon is in solid solution, which produces a solid-solution hardening effect.

10.33 *Rank the following iron–carbon alloys and associated microstructures from the hardest to the softest:*

(a) 0.25 wt% C with coarse pearlite
(b) 0.80 wt% C with spheroidite
(c) 0.25 wt% C with spheroidite
(d) 0.80 wt% C with fine pearlite.
Justify this ranking.

Answer

This problem asks us to rank four iron-carbon alloys of specified composition and microstructure according to hardness. This ranking is as follows:

0.80 wt% C, fine pearlite
0.80 wt% C, spheroidite
0.25 wt% C, coarse pearlite
0.25 wt% C, spheroidite

The 0.25 wt% C, coarse pearlite is harder than the 0.25 wt% C, spheroidite since coarse pearlite is harder than spheroidite; the compositions of the alloys are the same. The 0.80 wt% C, spheroidite is harder than the 0.25 wt% C, coarse pearlite, Figure 10.30*a*. Finally, the 0.80 wt% C, fine pearlite is harder than the 0.80 wt% C, spheroidite inasmuch as the hardness of fine pearlite is greater than spheroidite because of the many more ferrite-cementite phase boundaries in fine pearlite.

10.34 *Briefly explain why the hardness of tempered martensite diminishes with tempering time (at constant temperature) and with increasing temperature (at constant tempering time).*

Answer

This question asks for an explanation as to why the hardness of tempered martensite diminishes with tempering time (at constant temperature) and with increasing temperature (at constant tempering time). The hardness of tempered martensite depends on the ferrite-cementite phase boundary area; since these phase boundaries are barriers to dislocation motion, the greater the area the harder the alloy. The microstructure of tempered martensite consists of small sphere-like particles of cementite embedded within a ferrite matrix. As the size of the cementite particles increases, the phase boundary area diminishes, and the alloy becomes softer. Therefore, with increasing tempering time, the cementite particles grow, the phase boundary area decreases, and the hardness diminishes. As the tempering temperature is increased, the rate of cementite particle growth also increases, and the alloy softens, again, because of the decrease in phase boundary area.

10.35 *Briefly describe the simplest heat treatment procedure that would be used in converting a 0.76 wt% C steel from one microstructure to the other, as follows:*

(a) Martensite to spheroidite

(b) Spheroidite to martensite

(c) Bainite to pearlite

(d) Pearlite to bainite

(e) Spheroidite to pearlite

(f) Pearlite to spheroidite

(g) Tempered martensite to martensite

(h) Bainite to spheroidite

Answer

In this problem we are asked to describe the simplest heat treatment that would be required to convert a eutectoid steel from one microstructure to another. Figure 10.27 is used to solve the several parts of this problem.

(a) For martensite to spheroidite, heat to a temperature in the vicinity of 700°C (but below the eutectoid temperature), for on the order of 24 h.

(b) For spheroiridte to martensite, austenitize at a temperature of about 760°C, then quench to room temperature at a rate greater than about 140°C/s (according to Figure 10.27).

(c) For bainite to pearlite, first austenitize at a temperature of about 760°C, then cool to room temperature at a rate less than about 35°C/s (according to Figure 10.27).

(d) For pearlite to bainite, first austenitize at a temperature of about 760°C, rapidly cool to a temperature between about 220°C and 540°C, and hold at this temperature for the time necessary to complete the bainite transformation (according to Figure 10.22).

(e) For spheroidite to pearlite, same as (c) above.

(f) For pearlite to spheroidite, heat at about 700°C for approximately 20 h.

(g) For tempered martensite to martensite, first austenitize at a temperature of about 760°C, and rapidly quench to room temperature at a rate greater than about 140°C/s (according to Figure 10.27).

(h) For bainite to spheroidite, simply heat at about 700°C for approximately 20 h.

10.36 *(a) Briefly describe the microstructural difference between spheroidite and tempered martensite. (b) Explain why tempered martensite is much harder and stronger.*

Answer

(a) Both tempered martensite and spheroidite have sphere-like cementite particles within a ferrite matrix; however, these particles are much larger for spheroidite.

(b) Tempered martensite is harder and stronger inasmuch as there is much more ferrite-cementite phase boundary area for the smaller particles; thus, there is greater reinforcement of the ferrite phase, and more phase boundary barriers to dislocation motion.

10.37 *Estimate Brinell hardnesses and ductilities (%RA) for specimens of an iron–carbon alloy of eutectoid composition that have been subjected to the heat treatments described in parts (a) through (h) of Problem 10.19.*

Solution

(a) The isothermal heat treatment at 350°C produces 100% bainite. From Figure 10.31*a* at a transformation temperature of 350°C the hardness of bainite is about 460 HB. According to Figure 10.31*b* at the same transformation temperature, the ductility is about 46 %RA.

(b) The products of this heat treatment are 50% medium pearlite (that transformed at a temperature of 625°C) and 50% martensite. Because the microstructure consists of two microconstituents, we use rule-of-mixtures expressions similar to Equation 10.21 to determine both hardness and ductility values.

For hardness, the rule-of-mixtures equation is as follows:

$$\text{HB(alloy)} = W_p \text{HB}_p + W_M \text{HB}_M$$

in which

W_p and W_M represent mass fractions of pearlite and martensite, respectively

HB_p and HB_M denote Brinell hardness values for pearlite and martensite microconstituents, respectively.

From Figure 10.31*a* for a eutectoid iron-carbon alloy that transformed to pearlite at 625°C, the HB value is about 300. According to Figure 10.32, the hardness of a eutectoid (0.76 wt% C) iron-carbon alloy having a martensitic structure is about 700 HB. For this heat treatment $W_p = W_M = 0.50$. Therefore, the Brinell hardness of this alloy is determined using the above equation as follows:

$$\text{HB(alloy)} = W_p \text{HB}_p + W_M \text{HB}_M$$

$$= (0.50)(300 \text{ HB}) + (0.50)(700 \text{ HB})$$

$$= 500 \text{ HB}$$

Likewise for the ductility: the appropriate rule-of-mixtures is expression is

$$\%\text{RA(alloy)} = W_p(\%\text{RA}_p) + W_M(\%\text{RA}_M)$$

From Figure 10.31*b* the ductility of a eutectoid iron-carbon alloy that transformed to pearlite at 625°C is 36%RA. Furthermore, the ductility of martensite is negligible, which we will take as 0%RA. Therefore, using the above equation we compute the ductility of this alloy as follows:

$$\%\text{RA(alloy)} = W_p(\%\text{RA}_p) + W_M(\%\text{RA}_M)$$

$$= (0.50)(36\%\text{RA}) + (0.50)(0\%\text{RA})$$

$$= 18\%\text{RA}$$

(c) The products of this heat treatment are 50% fine pearlite (that transformed at 600°C), 25% bainite (transformation temperature of 450°C), and 25% martensite. Because the microstructure consists of three microconstituents, we use modified forms of the rule-of-mixtures expression similar to Equation 10.21 to determine both hardness and ductility values.

For hardness, the modified rule-of-mixtures equation is as follows:

$$\text{HB(alloy)} = W_p\text{HB}_p + W_b\text{HB}_b + W_M\text{HB}_M$$

in which

W_p, W_b, and W_M represent mass fractions of pearlite, bainite, and martensite, respectively

HB_p, HB_b, and HB_M denote Brinell hardness values for pearilite, bainite, and martensite microconstituents, respectively.

From Figure 10.31*a* for a eutectoid iron-carbon alloy that transformed to pearlite at 600°C, the HB value is about 325; and bainite that formed at 450°C has a hardness of about 360 HB. According to Figure 10.32, the hardness of a eutectoid (0.76 wt% C) iron-carbon alloy having a martensitic structure is about 700 HB. For this heat treatment W_p = 0.5, W_b = 0.25, and W_M = 0.25. Therefore, the Brinell hardness of this alloy is determined using the above equation as follows:

$$\text{HB(alloy)} = W_p\text{HB}_p + W_b\text{HB}_b + W_M\text{HB}_M$$

$$= (0.50)(325\text{ HB}) + (0.25)(360\text{ HB}) + (0.25)(700\text{ HB})$$

$$= 428\text{ HB}$$

Likewise for the ductility: the appropriate rule-of-mixtures is expression is

$$\%\text{RA(alloy)} = W_p(\%\text{RA}_p) + W_b(\%\text{RA}_b) + W_M(\%\text{RA}_M)$$

From Figure 10.31*b* the ductility of a eutectoid iron-carbon alloy that transformed to pearlite at 600°C is 38%RA and bainite that transformed at 450°C is 55%RA. Furthermore, the ductility of martensite is negligible, which we will take as 0%RA. Therefore, using the above equation we compute the ductility of this alloy as follows:

$$\%\mathrm{RA(alloy)} = W_p(\%\mathrm{RA}_p) + W_b(\%\mathrm{RA}_b) + W_M(\%\mathrm{RA}_M)$$

$$= (0.50)(38\%\mathrm{RA}) + (0.25)(55\%\mathrm{RA}) + (0.25)(0\%\mathrm{RA})$$

$$= 33\%\mathrm{RA}$$

(d) The product of this heat treatment is 100% spheroidite. According to Figure 10.30*a* the hardness of an alloy of eutectoid composition (0.76 wt%C) that has a spheroiditic microstructure is about 180 HB. Determination of the ductility of this alloy is possible using the "Spheroidite" curve of Figure 10.30*b*, which, for an alloy of eutectoid composition is about 67%RA.

(f) The isothermal heat treatment at 665°C produces 100% pearlite (coarse). From Figure 10.31*a* at a transformation temperature of 665°C the hardness of pearlite is about 260 HB. According to Figure 10.31*b* at the same transformation temperature, the ductility is about 30 %RA.

(g) The isothermal heat treatment at 575°C produces 100% pearlite (fine). From Figure 10.31*a* at a transformation temperature of 575°C the hardness of pearlite is about 350 HB. According to Figure 10.31*b* at the same transformation temperature, the ductility is about 36 %RA.

(h) The products of this heat treatment are 50% bainite (that transformed at a temperature of 350°C) and 50% martensite. Because the microstructure consists of two microconstituents, we use rule-of-mixtures expressions similar to Equation 10.21 to determine both hardness and ductility values.

For hardness, the rule-of-mixtures equation is as follows:

$$\mathrm{HB(alloy)} = W_b\mathrm{HB}_b + W_M\mathrm{HB}_M$$

in which

W_b and W_M represent mass fractions of bainite and martensite, respectively

HB_b and HB_M denote Brinell hardness values for bainite and martensite microconstituents, respectively.

From Figure 10.31*a* for a eutectoid iron-carbon alloy that transformed to pearlite at 350°C, the HB value is about 460. According to Figure 10.32, the hardness of a eutectoid (0.76 wt% C) iron-carbon alloy having a martensitic structure is about 700 HB. For this heat treatment $W_b = W_M = 0.50$. Therefore, the Brinell hardness of this alloy is determined using the above equation as follows:

$$\mathrm{HB(alloy)} = W_b\mathrm{HB}_b + W_M\mathrm{HB}_M$$

$$= (0.50)(460\ \mathrm{HB}) + (0.50)(700\ \mathrm{HB})$$

$$= 580\ \mathrm{HB}$$

Likewise for the ductility: the appropriate rule-of-mixtures is expression is

$$\%\mathrm{RA(alloy)} = W_b(\%\mathrm{RA}_b) + W_M(\%\mathrm{RA}_M)$$

From Figure 10.31*b* the ductility of a eutectoid iron-carbon alloy that transformed to bainite at 350°C is 46%RA. Furthermore, the ductility of martensite is negligible, which we will take as 0%RA. Therefore, using the above equation we compute the ductility of this alloy as follows:

$$\%\mathrm{RA(alloy)} = W_b(\%\mathrm{RA}_b) + W_M(\%\mathrm{RA}_M)$$

$$= (0.50)(46\%\mathrm{RA}) + (0.50)(0\%\mathrm{RA})$$

$$= 23\%\mathrm{RA}$$

10.38 *Estimate the Brinell hardnesses for specimens of a 1.13 wt% C iron–carbon alloy that have been subjected to the heat treatments described in parts (a), (d), and (h) of Problem 10.21.*

Solution

(a) The microstructural product of this heat treatment is 100% martensite. According to Figure 10.32, the hardness of a 1.13 wt% C alloy consisting of martensite is about 700 HB (by extrapolation).

(d) The microstructural product of this heat treatment is 100% spheroidite. According to Figure 10.30*a*, the hardness of a 1.13 wt% C alloy consisting of spheroidite is about 190 HB (by extrapolation).

(h) The microstructural product of this heat treatment is proeutectoid cementite and fine pearlite. According to Figure 10.30*a*, the hardness of a 1.13 wt% C alloy consisting of fine pearlite is about 310 HB (by extrapolation).

10.39 *Determine the approximate tensile strengths and ductilities (%RA) for specimens of a eutectoid iron–carbon alloy that have experienced the heat treatments described in parts (a) through (d) of Problem 10.24.*

Solution

(a) The microstructural product of this heat treatment is 100% coarse pearlite. According to Figure 10.30*a* the hardness of an alloy of eutectoid composition (0.76 wt%C) that has a coarse pearlitic microstructure is about 205 HB. To convert this hardness value to tensile strength requires us to use Equation 6.20a; this conversion is made as follows:

$$TS(\text{MPa}) = 3.45 \times \text{HB}$$

$$= (3.45)(205) = 707 \text{ MPa} \ \ (102{,}500 \text{ psi})$$

Determination of the ductility of this alloy is possible using the "Coarse pearlite" curve of Figure 10.30*b*, which, for an alloy of eutectoid composition is about 27%RA.

(b) The microstructural product of this heat treatment is 100% fine pearlite. According to Figure 10.30*a* the hardness of an alloy of eutectoid composition (0.76 wt%C) that has a fine pearlitic microstructure is about 270 HB. To convert this hardness value to tensile strength requires us to use Equation 6.20a; this conversion is made as follows:

$$TS(\text{MPa}) = 3.45 \times \text{HB}$$

$$= (3.45)(270) = 932 \text{ MPa} \ \ (135{,}000 \text{ psi})$$

Determination of the ductility of this alloy is possible using the "Fine pearlite" curve of Figure 10.30*b*, which, for an alloy of eutectoid composition is about 20%RA.

(c) The microstructural products of this heat treatment are fine pearlite and martensite. From Figure 10.27, a cooling rate of 50°C/s is slightly greater than the 35°C/s at which martensite begins to form. Therefore, let us assume that 85% of the specimen is fine pearlite and the remaining 15% is martensite. Because the microstructure consists of two microconstituents, we use rule-of-mixtures expressions similar to Equation 10.21 to determine both hardness and ductility values.

For hardness, the rule-of-mixtures equation is as follows:

$$\text{HB(alloy)} = W_{fp}\text{HB}_{fp} + W_M\text{HB}_M$$

in which

W_{fp} and W_M represent mass fractions of fine pearlite and martensite, respectively

HB_{fp} and HB_M denote Brinell hardness values for fine pearlite and martensite microconstituents, respectively.

According to Figure 10.30*a* the hardness of an alloy of eutectoid composition (0.76 wt%C) that has a fine pearlitic microstructure is about 270 HB. And from Figure 10.32, the hardness of a eutectoid (0.76 wt% C) iron-carbon alloy having a martensitic structure is about 700 HB. For this heat treatment W_{fp} = 0.85 and W_M = 0.15. Therefore, the Brinell hardness of this alloy is determined using the above equation as follows:

$$\mathrm{HB(alloy)} = W_{fp}\mathrm{HB}_{fp} + W_M\mathrm{HB}_M$$

$$= (0.85)(270\ \mathrm{HB}) + (0.15)(700\ \mathrm{HB})$$

$$= 335\ \mathrm{HB}$$

To convert this hardness value to tensile strength requires us to use Equation 6.20a; this conversion is made as follows:

$$TS(\mathrm{MPa}) = 3.45 \times \mathrm{HB}$$

$$= (3.45)(335) = 1155\ \mathrm{MPa}\ \ (167{,}500\ \mathrm{psi})$$

Likewise for the ductility, the appropriate rule-of-mixtures is expression is

$$\%\mathrm{RA(alloy)} = W_{fp}(\%\mathrm{RA}_{fp}) + W_M(\%\mathrm{RA}_M)$$

Determination of the ductility of this alloy is possible using the "Fine pearlite" curve of Figure 10.30*b*, which, for an alloy of eutectoid composition is about 20%RA. Furthermore, the ductility of martensite is negligible, which we will take as 0%RA. Therefore, using the above equation we compute the ductility of this alloy as follows:

$$\%\mathrm{RA(alloy)} = W_{fp}(\%\mathrm{RA}_{fp}) + W_M(\%\mathrm{RA}_M)$$

$$= (0.85)(20\%\mathrm{RA}) + (0.15)(0\%\mathrm{RA})$$

$$= 17\%\mathrm{RA}$$

(d) The microstructural product of this heat treatment is 100% martensite. The Brinell hardness of an alloy of eutectic composition (0.76 wt% C) is about 700 HB, as noted in Figure 10.32. To convert this hardness value to tensile strength requires us to use Equation 6.20a; this conversion is made as follows:

$$TS(\text{MPa}) = 3.45 \times \text{HB}$$

$$= (3.45)(700) = 2415\ \text{MPa}\ \ (350{,}000\ \text{psi})$$

The ductility of an alloy composed entirely of martensite is negligible, therefore we assume approximately 0%RA.

DESIGN PROBLEMS

Continuous-Cooling Transformation Diagrams

Mechanical Behavior of Iron–Carbon Alloys

10.D1 *Is it possible to produce an iron–carbon alloy of eutectoid composition that has a minimum hardness of 200 HB and a minimum ductility of 25%RA? If so, describe the continuous-cooling heat treatment to which the alloy would be subjected to achieve these properties. If it is not possible, explain why.*

Solution

This problem inquires as to the possibility of producing an iron-carbon alloy of eutectoid composition that has a minimum hardness of 200 HB and a minimum ductility of 25%RA. If the alloy is possible, then the continuous cooling heat treatment is to be stipulated.

According to Figures 10.30*a* and 10.30*b*, the following is a tabulation of Brinell hardnesses and percents reduction of area for fine and coarse pearlites and spheroidite for a 0.76 wt% C alloy.

Microstructure	HB	%RA
Fine pearlite	270	20
Coarse pearlite	205	28
Spheroidite	180	67

Therefore, coarse pearlite meets both of these criteria. The continuous cooling heat treatment that will produce coarse pearlite for an alloy of eutectoid composition is indicated in Figure 10.27. The cooling rate would need to be considerably less than 35°C/s, probably on the order of 0.1°C/s.

10.D2 *For a eutectoid steel, describe isothermal heat treatments that would be required to yield specimens having the following tensile strength-ductility (%RA) combinations:*

(a) 900 MPa and 30%RA

(b) 700 MPa and 25%RA

Solution

This problem asks for us to specify isothermal heat treatments to yield two tensile strength-ductility combinations.

(a) For this portion of the problem the required tensile strength is 900 MPa and the ductility is 30%RA. Because the heat treatment is to be isothermal and alloy is one of eutectoid composition, we use Figures 10.31*a* and 10.31*b*. From Figure 10.31*a*, in order to achieve a tensile strength of 900 MPa the isothermal heat treatment must be conducted at about 660°C. On the other hand, for a ductility of 30%RA, the heat treatment temperature is also 660°C, as indicated in Figure 10.31*b*.

(b) For this portion of the problem, the tensile strength-ductility combination is 700 MPa and 25%RA. For a tensile strength of 700 MPa, the heat treatment temperature is 690°C (Figure 10.31*a*). And, using Figure 10.31*b* an isothermal heat treatment also at about 690°C is required.

10.D3 *Is it possible to produce iron-carbon alloys of eutectoid composition that, using isothermal heat treatments, have the following tensile strength-ductility (%RA) combinations? If so, for each combination describe the heat treatment required to achieve these properties. Or, if this is not possible, explain why.*

(a) 1800 MPa and 30%RA

(b) 1700 MPa and 45%RA

(c) 1400 MPa and 50%RA

Solution

This problem asks for us to specify isothermal heat treatments to yield three tensile strength-ductility combinations.

(a) For this portion of the problem the required tensile strength is 1800 MPa and the ductility is 30%RA. Because the heat treatment is to be isothermal and alloy is one of eutectoid composition, we use Figures 10.31*a* and 10.31*b*. From Figure 10.31*a*, in order to achieve a tensile strength of 1800 MPa the isothermal heat treatment must carried out at a temperature less than 300°C. On the other hand, for a ductility of 30%RA, the minimum heat treatment temperature is about 260°C, as indicated in Figure 10.31*b*. Therefore, it is possible to produce the required combination of properties; the heat treatment must be conducted between 260°C and 300°C.

(b) For this part of the problem the tensile strength must be at least 1700 MPa, while the maximum required ductility is 45%RA. From Figure 10.31*a*, in order to achieve a tensile strength of 1700 MPa the isothermal heat treatment must carried out at a temperature less than 320°C. On the other hand, for a ductility of 45%RA, the minimum heat treatment temperature is about 350°C (and the maximum temperature is 500°C), as indicated in Figure 10.31*b*. Therefore, it is *not possible* to produce an alloy of eutectoid composition that meets these two criteria because the maximum temperature for a 1700 MPa tensile strength (320°C) is less than the minimum temperature required for the ductility (350°C)

(c) The isothermal heat treatment called for in this part of the problem must produce a tensile strength of at least 1400 MPa and a ductility of 50%RA. From Figure 10.31*a*, in order to achieve a tensile strength of 1400 MPa the isothermal heat treatment must carried out at a temperature less than 380°C. On the other hand, for a ductility of 50%RA, the minimum heat treatment temperature is also at about 380°C. Therefore, it is possible to produce the required combination of properties; the heat treatment must be conducted at 380°C.

10.D4 *For a eutectoid steel, describe continuous-cooling heat treatments that would be required to yield specimens having the following Brinell hardness-ductility (%RA) combinations:*

(a) 680 HB and ~0%RA

(b) 260 HB and 20 %RA

(c) 200 HB and 28 %RA

(d) 160 HB and 67%RA

Solution

This problem asks for us to specify continuous-cooling heat treatments to yield four Brinell hardness—ductility combinations for an iron-carbon alloy of eutectoid composition.

(a) For this portion of the problem the required hardness is 680 HB and the ductility is approximately 0%RA. According to Figure 10.32 a martensitic structure is required to give a hardness of 680 HB. Also, as noted in this chapter, the ductility of a steel of this composition is extremely low. From Figure 10.27, a continuous-cooling diagram for a eutectoid iron-carbon alloy, a cooling rate in excess of 140°C/s is required to yield a 100% martensite structure.

(b) A 260 HB-20%RA hardness-ductility is required for this portion of the problem. From Figure 10.30*a*, only a eutectoid alloy that has a fine-pearlite microstructure yields a hardness of at least 260 HB. On the other hand, according to Figure 10.30*b*, the ductility of 20%RA is achieved by a fine-pearlitic steel of the eutectoid composition (0.76 wt% C). Therefore, the microstructure should consist of fine pearlite. From Figure 10.27, the continuous-cooling diagram for a eutectoid steel, fine pearlite is the result of a continuous-cooling rate slightly less than 35°C/s.

(c) We need to specify a heat treatment to yield an alloy that has a hardness of 200 HB and a ductility of 28%RA. It may be noted from Figure 10.30*a* that, for a eutectoid composition (0.76 wt% C), both fine and coarse pearlites give a hardness of 200 HB. However, the ductility of coarse pearlite at this same composition is about 28%RA (Figure 10.30*b*), which is suitable. Fine pearlite does not satisfy this criterion since its ductility is only about 20%RA. According to Figure 10.27, in order to achieve a coarse pearlitic structure, the cooling rate must be considerably less than 35°C/s, say of the order of 1 to 5°C/s.

(d) For this portion of the problem, a 160 HB-67%RA combination is required. As may be noted on Figure 10.30*a*, all of spheroidite, coarse pearlite, and fine pearlite yield hardnesses of at least 160 HB for an alloy of composition 0.76 wt% C. However, from Figure 10.30*b* only spheroidite of the eutectoid composition has a ductility of 67%RA, which satisfies the requirement. Ductilities of coarse and fine pearlite are much lower—about 20 and 27%RA, respectively. With regard to heat treatment, it is probably best to first cool at a rate sufficient to produce pearlite (either fine or coarse)—i.e., less that about 35°C/s, and then reheat the specimen at about 700°C for a time within the range of about 18 to 24 h.

10.D5 *Is it possible to produce an iron–carbon alloy that has a minimum tensile strength of 620 MPa (90,000 psi) and a minimum ductility of 50% RA? If so, what will be its composition and microstructure (coarse and fine pearlites and spheroidite are alternatives)? If this is not possible, explain why.*

Solution

This problem asks if it is possible to produce an iron-carbon alloy that has a minimum tensile strength of 620 MPa (90,000 psi) and a minimum ductility of 50%RA. If such an alloy is possible, its composition and microstructure are to be stipulated.

From Equation 6.20a, a tensile strength of 620 MPa corresponds to a Brinell hardness of

$$\mathrm{HB} = \frac{TS(\mathrm{MPa})}{3.45} = \frac{620\ \mathrm{MPa}}{3.45} = 180$$

According to Figures 10.30*a* and 10.30*b*, the following is a tabulation of the composition ranges for fine and coarse pearlites and spheroidite that meet the stipulated criteria.

Microstructure	Compositions for HB ≥ 180	Compositions for %RA ≥ 50%
Fine pearlite	> 0.40 %C	< 0.35 %C
Coarse pearlite	> 0.50 %C	< 0.40 %C
Spheroidite	> 0.80 %C	0-1.0 %C

Therefore, it is possible to have an alloy that meets both hardness and ductility criteria—however, only spheroidite has a composition range overlap for both of the hardness and ductility restrictions; and the spheroidite would necessarily have to have a carbon content greater than 0.80 wt% C.

10.D6 *It is desired to produce an iron–carbon alloy that has a minimum hardness of 200 HB and a minimum ductility of 35% RA. Is such an alloy possible? If so, what will be its composition and microstructure (coarse and fine pearlites and spheroidite are alternatives)? If this is not possible, explain why.*

Solution

This problem inquires as to the possibility of producing an iron-carbon alloy having a minimum hardness of 200 HB and a minimum ductility of 35%RA. The composition and microstructure are to be specified; possible microstructures include fine and coarse pearlites and spheroidite.

To solve this problem, we must consult Figures 10.30*a* and 10.30*b*. The following is a tabulation of the composition ranges for fine and coarse pearlites and spheroidite that meet the stipulated criteria.

Microstructure	Compositions for HB ≥ 200	Compositions for %RA ≥ 35%
Fine pearlite	> 0.47 %C	< 0.53 %C
Coarse pearlite	> 0.70 %C	< 0.61 %C
Spheroidite	not possible	<1.0 %C

Thus, fine pearlite is the only possibility. Its composition would need to be between 0.47 and 0.53 wt% C. A spheroidite microstructure is not possible since a hardness of 200 HB is not attainable. Furthermore, coarse pearlite is not possible because there is not a composition overlap for both hardness and ductility restrictions.

Tempered Martensite

10.D7 *(a) For a 1080 steel that has been water quenched, estimate the tempering time at 535°C (1000°F) to achieve a hardness of 45 HRC.*

(b) What will be the tempering time at 425°C (800°F) necessary to attain the same hardness?

<u>Solution</u>

This problem asks us to consider the tempering of a water-quenched 1080 steel to achieve a hardness of 45 HRC. It is necessary to use Figure 10.35.

(a) The time necessary at 535°C is about 70 s. (Please note that the time axis is scaled logarithmically.)

(b) At 425°C, the time required is approximately 40,000 s (about 11 h).

10.D8 *An alloy steel (4340) is to be used in an application requiring a minimum tensile strength of 1515 MPa (220,000 psi) and a minimum ductility of 40% RA. Oil quenching followed by tempering is to be used. Briefly describe the tempering heat treatment.*

Solution

We are to consider the tempering of an oil-quenched 4340 steel. From Figure 10.34, for a minimum tensile strength of 1515 MPa (220,000 psi) a tempering temperature of less than 400°C (750°F) is required. Also, for a minimum ductility of 40%AR, tempering must be carried out at a temperature greater than about 300°C (570°F). Therefore, tempering must occur at between 300°C and 400°C (570°F and 750°F) for 1 h.

10.D9 *For a 4340 steel alloy, describe continuous-cooling/tempering heat treatments that would be required to yield specimens having the following yield/tensile strength-ductility property combinations:*

(a) tensile strength of 1100 MPa, ductility of 50%RA

(b) yield strength of 1200 MPa, ductility of 45%RA

(c) tensile strength of 1300 MPa, ductility of 45%RA

Solution

It is first necessary to cool each specimen at a rate of at least 8.3°C/s (Figure 10.28) in order to produce 100% martensite. Next, using two of the three curves in Figure 10.34 it is possible to determine tempering temperature (for a tempering time of 1h) for both the required tensile/yield strength-ductility combinations.

(a) For a tensile strength of 1100 MPa, a tempering temperature less than about 560°C is required. On the other hand, for a ductility of 50%RA, the tempering temperature must be greater than about 510°C. Therefore, in order to obtain this tensile strength-ductility combination, tempering needs to be carried out between 510°C and 560°C.

(b) For a yield strength of 1200 MPa, a tempering temperature less than about 495°C is required. On the other hand, for a ductility of 45%RA, the tempering temperature must be greater than about 435°C. Therefore, in order to obtain this tensile strength-ductility combination, tempering needs to be carried out between 435°C and 495°C.

(c) For a tensile strength of 1300 MPa, a tempering temperature less than about 475°C is required. On the other hand, for a ductility of 45%RA, the tempering temperature must be greater than about 435°C. Therefore, in order to obtain this tensile strength-ductility combination, tempering needs to be carried out between 435°C and 475°C.

10.D10 *Is it possible to produce an oil-quenched and tempered 4340 steel that has a minimum yield strength of 1240 MPa (180,000 psi) and a ductility of at least 50%RA? If this is possible, describe the tempering heat treatment. If it is not possible, then explain why.*

Solution

This problem asks if it is possible to produce an oil-quenched and tempered 4340 steel that has a minimum yield strength of 1240 MPa (180,000 psi) and a minimum ductility of 50%RA, and, if so, to describe the tempering heat treatment. In Figure 10.34 is shown the tempering characteristics of this alloy. According to this figure, in order to achieve a minimum yield strength of 1240 MPa a tempering temperature of less that about 475°C is required. On the other hand, tempering must be carried out at greater than about 510°C for a minimum ductility of 50%RA. Since there is no overlap of these temperature ranges, an oil-quenched and tempered 4340 alloy possessing these characteristics is not possible.

FUNDAMENTALS OF ENGINEERING QUESTIONS AND PROBLEMS

10.1FE *Which of the following describes recrystallization?*

(A) Diffusion dependent with a change in phase composition

(B) Diffusionless

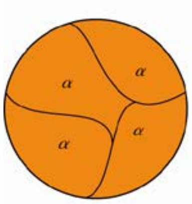
(C) Diffusion dependent with no change in phase composition

(D) All of the above

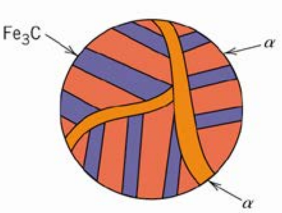
Solution

The correct answer is C. Recrystallization is *diffusion-dependent with no change in phase composition*.

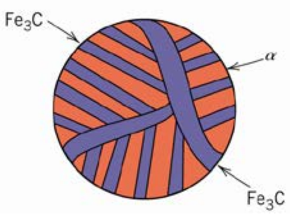
10.2FE *Schematic room-temperature microstructures for four iron–carbon alloys are as follows. Rank these microstructures (by letter) from the hardest to the softest.*



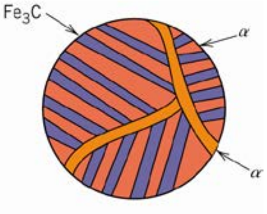
(A)



(B)



(C)



(D)

(a) $A > B > C > D$

(b) $C > D > B > A$

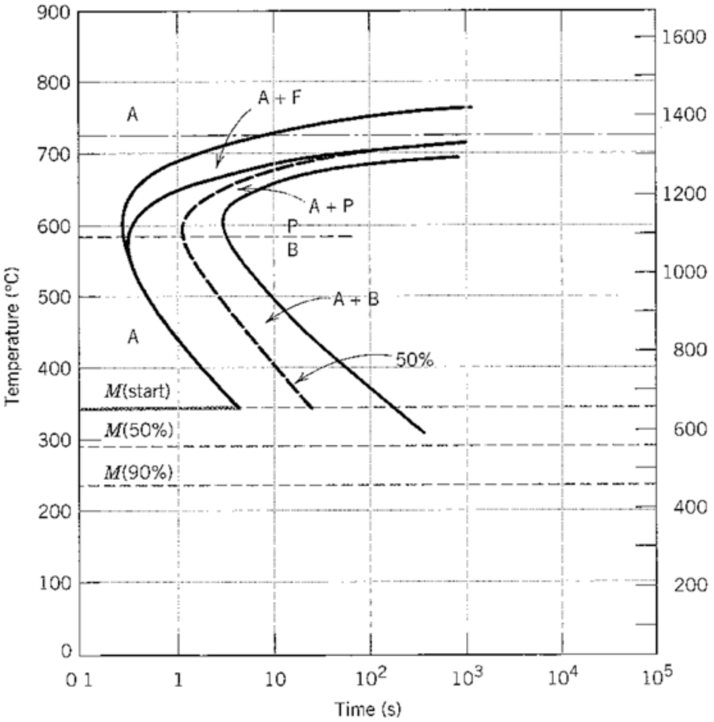
(c) $A > B > D > C$

(d) *None of the above*

Solution

The correct answer is B**:** C > D > B > A. Specimen C will be the hardest because it has the highest carbon content inasmuch as proeutectoid Fe_3C is present; also the pearlite is fine pearlite. Specimens B and D have approximately the same carbon content since the proportions of proeutectoid ferrite in both are about the same. However, carbon contents for B and D are lower than for specimen C because of the presence of proeutectoid ferrite. Specimen D is harder than B because its pearlite is fine, whereas B's is coarse. Finally, specimen A is the softest since it is composed entirely of α-ferrite and, thus, has the lowest carbon content.

10.3FE *On the basis of accompanying isothermal transformation diagram for a 0.45 wt% C iron-carbon alloy, which heat treatment could be used to isothermally convert a microstructure that consists of proeutectoid ferrite and fine pearlite into one that is composed of proeutectoid ferrite and martensite?*



(A) Austenitize the specimen at approximately 700°C, rapidly cool to about 675°C, hold at this temperature for 1 to 2 s, and then rapidly quench to room temperature

(B) Rapidly heat the specimen to about 675°C, hold at this temperature for 1 to 2 s, then rapidly quench to room temperature

(C) Austenitize the specimen at approximately 775°C, rapidly cool to about 500°C, hold at this temperature for 1 to 2 s, and then rapidly quench to room temperature

(D) Austenitize the specimen at approximately 775°C, rapidly cool to about 675°C, hold at this temperature for 1 to 2 s, and then rapidly quench to room temperature

Solution

The correct answer is D. Reaustenitize the specimen at approximately 775°C, and then rapidly cool to about 675°C, hold for 1 to 2 s to form proeutectoid ferrite, then rapidly quench to room temperature to convert the remaining austenite to martensite.

CHAPTER 11

APPLICATIONS AND PROCESSING OF METAL ALLOYS

PROBLEM SOLUTIONS

Ferrous Alloys

11.1 *(a) List the four classifications of steels.*

(b) For each, briefly describe the properties and typical applications.

Answer

The four classifications of steels, their properties, and typical applications are as follows:

Low Carbon Steels

Properties: nonresponsive to heat treatments; relatively soft and weak; machinable and weldable.

Typical applications: automobile bodies, structural shapes, pipelines, buildings, bridges, and tin cans.

Medium Carbon Steels

Properties: heat treatable, relatively large combinations of mechanical characteristics.

Typical applications: railway wheels and tracks, gears, crankshafts, and machine parts.

High Carbon Steels

Properties: hard, strong, and relatively brittle.

Typical applications: chisels, hammers, knives, and hacksaw blades.

High Alloy Steels (Stainless and Tool)

Properties: hard and wear resistant; resistant to corrosion in a large variety of environments.

Typical applications: cutting tools, drills, cutlery, food processing, and surgical tools.

11.2 *(a) Cite three reasons why ferrous alloys are used so extensively.*

(b) Cite three characteristics of ferrous alloys that limit their use.

Answer

(a) Ferrous alloys are used extensively because:

(1) Iron ores exist in abundant quantities.

(2) Economical extraction, refining, and fabrication techniques are available.

(3) The alloys may be tailored to have a wide range of properties.

(b) Disadvantages of ferrous alloys are:

(1) They are susceptible to corrosion.

(2) They have relatively high densities.

(3) They have relatively low electrical conductivities.

11.3 *What is the function of alloying elements in tool steels?*

Answer

The alloying elements in tool steels (e.g., Cr, V, W, and Mo) combine with the carbon to form very hard and wear-resistant carbide compounds.

11.4 *Compute the volume percent of graphite, V_{Gr}, in a 2.5 wt% C cast iron, assuming that all the carbon exists as the graphite phase. Assume densities of 7.9 and 2.3 g/cm^3 for ferrite and graphite, respectively.*

Solution

To solve this problem it first becomes necessary to compute mass fractions using the lever rule. From the iron-carbon phase diagram (Figure 11.2), the tie-line in the α and graphite phase field extends from essentially 0 wt% C to 100 wt% C. Thus, for a 2.5 wt% C cast iron the mass fractions of ferrite and graphite phases (W_α and W_{Gr}, respectively) are determined using this tie-line and the following expressions:

$$W_\alpha = \frac{C_{\mathrm{Gr}} - C_0}{C_{\mathrm{Gr}} - C_\alpha} = \frac{100 - 2.5}{100 - 0} = 0.975$$

$$W_{\mathrm{Gr}} = \frac{C_0 - C_\alpha}{C_{\mathrm{Gr}} - C_\alpha} = \frac{2.5 - 0}{100 - 0} = 0.025$$

Conversion from weight fraction to volume fraction of graphite is possible using Equation 9.6a as

$$V_{\mathrm{Gr}} = \frac{\dfrac{W_{\mathrm{Gr}}}{\rho_{\mathrm{Gr}}}}{\dfrac{W_\alpha}{\rho_\alpha} + \dfrac{W_{\mathrm{Gr}}}{\rho_{\mathrm{Gr}}}}$$

$$= \frac{\dfrac{0.025}{2.3\ \mathrm{g/cm^3}}}{\dfrac{0.975}{7.9\ \mathrm{g/cm^3}} + \dfrac{0.025}{2.3\ \mathrm{g/cm^3}}}$$

= 0.081 or 8.1 vol%

11.5 *On the basis of microstructure, briefly explain why gray iron is brittle and weak in tension.*

Answer

Gray iron is weak and brittle in tension because the tips of the graphite flakes act as points of stress concentration.

11.6 *Compare gray and malleable cast irons with respect to*

(a) composition and heat treatment

(b) microstructure

(c) mechanical characteristics

Answer

This question asks us to compare various aspects of gray and malleable cast irons.

(a) With respect to composition and heat treatment:

Gray iron--2.5 to 4.0 wt% C and 1.0 to 3.0 wt% Si. For most gray irons there is no heat treatment after solidification.

Malleable iron--2.5 to 4.0 wt% C and less than 1.0 wt% Si. White iron is heated in a nonoxidizing atmosphere and at a temperature between 800 and 900°C for an extended time period.

(b) With respect to microstructure:

Gray iron--Graphite flakes are embedded in a ferrite or pearlite matrix.

Malleable iron--Graphite clusters are embedded in a ferrite or pearlite matrix.

(c) With respect to mechanical characteristics:

Gray iron--Relatively weak and brittle in tension; good capacity for damping vibrations.

Malleable iron--Moderate strength and ductility.

11.7 *Compare white and nodular cast irons with respect to*

(a) composition and heat treatment

(b) microstructure

(c) mechanical characteristics.

Answer

This question asks us to compare white and nodular cast irons.

(a) With regard to composition and heat treatment:

White iron--2.5 to 4.0 wt% C and less than 1.0 wt% Si. No heat treatment; however, cooling is rapid during solidification.

Nodular cast iron--2.5 to 4.0 wt% C, 1.0 to 3.0 wt% Si, and a small amount of Mg or Ce. A heat treatment at about 700°C may be necessary to produce a ferritic matrix.

(b) With regard to microstructure:

White iron--There are regions of cementite interspersed within pearlite.

Nodular cast iron--Nodules of graphite are embedded in a ferrite or pearlite matrix.

(c) With respect to mechanical characteristics:

White iron--Extremely hard and brittle.

Nodular cast iron--Moderate strength and ductility.

11.8 *Is it possible to produce malleable cast iron in pieces having large cross-sectional dimensions? Why or why not?*

Answer

It is *not possible* to produce malleable iron in pieces having large cross-sectional dimensions. White cast iron is the precursor of malleable iron, and a rapid cooling rate is necessary for the formation of white iron, which may not be accomplished at interior regions of thick cross-sections.

Nonferrous Alloys

11.9 *What is the principal difference between wrought and cast alloys?*

Answer

The principal difference between wrought and cast alloys is as follows: wrought alloys are ductile enough so as to be hot or cold worked during fabrication, whereas cast alloys are brittle to the degree that shaping by deformation is not possible and they must be fabricated by casting.

11.10 *Why must rivets of a 2017 aluminum alloy be refrigerated before they are used?*

Answer

Rivets of a 2017 aluminum alloy must be refrigerated before they are used because, after being solution heat treated, they precipitation harden at room temperature. Once precipitation hardened, they are too strong and brittle to be driven.

11.11 *What is the chief difference between heat-treatable and non-heat-treatable alloys?*

Answer

The chief difference between heat-treatable and non-heat-treatable alloys is that heat-treatable alloys may be strengthened by a heat treatment wherein a precipitate phase is formed (precipitation hardening) or a martensitic transformation occurs. Non-heat-treatable alloys are not amenable to strengthening by such treatments.

11.12 *Give the distinctive features, limitations, and applications of the following alloy groups: titanium alloys, refractory metals, superalloys, and noble metals.*

Answer

This question asks us for the distinctive features, limitations, and applications of several alloy groups.

Titanium Alloys

Distinctive features: relatively low density, high melting temperatures, and high strengths are possible.

Limitation: because of chemical reactivity with other materials at elevated temperatures, these alloys are expensive to refine.

Applications: aircraft structures, space vehicles, and in chemical and petroleum industries.

Refractory Metals

Distinctive features: extremely high melting temperatures; large elastic moduli, hardnesses, and strengths.

Limitation: some experience rapid oxidation at elevated temperatures.

Applications: extrusion dies, structural parts in space vehicles, incandescent light filaments, x-ray tubes, and welding electrodes.

Superalloys

Distinctive features: able to withstand high temperatures and oxidizing atmospheres for long time periods.

Applications: aircraft turbines, nuclear reactors, and petrochemical equipment.

Noble Metals

Distinctive features: highly resistant to oxidation, especially at elevated temperatures; soft and ductile.

Limitation: expensive.

Applications: jewelry, dental restoration materials, coins, catalysts, and thermocouples.

Forming Operations

11.13 *Cite advantages and disadvantages of hot working and cold working.*

Answer

The advantages of cold working are:

(1) A high quality surface finish.
(2) The mechanical properties may be varied.
(3) Close dimensional tolerances.

The disadvantages of cold working are:

(1) High deformation energy requirements.
(2) Large deformations must be accomplished in steps, which may be expensive.
(3) A loss of ductility.

The advantages of hot working are:

(1) Large deformations are possible, which may be repeated.
(2) Deformation energy requirements are relatively low.

The disadvantages of hot working are:

(1) A poor surface finish.
(2) A variety of mechanical properties is not possible.

11.14 *(a) Cite advantages of forming metals by extrusion as opposed to rolling.*

(b) Cite some disadvantages.

Answer

(a) The advantages of extrusion as opposed to rolling are as follows:

(1) Pieces having more complicated cross-sectional geometries may be formed.

(2) Seamless tubing may be produced.

(b) The disadvantages of extrusion over rolling are as follows:

(1) Nonuniform deformation over the cross-section.

(2) A variation in properties may result over a cross-section of an extruded piece.

Casting

11.15 *List four situations in which casting is the preferred fabrication technique.*

Answer

Four situations in which casting is the preferred fabrication technique are as follows:

(1) For large pieces and/or complicated shapes.

(2) When mechanical strength is not an important consideration.

(3) For alloys having low ductilities.

(4) When it is the most economical fabrication technique.

11.16 *Compare sand, die, investment, lost-foam, and continuous casting techniques.*

Answer

For *sand casting*, sand is the mold material, a two-piece mold is used, ordinarily the surface finish is not an important consideration, the sand may be reused (but the mold may not), casting rates are low, and large pieces are usually cast.

For *die casting*, a permanent mold is used, casting rates are high, the molten metal is forced into the mold under pressure, a two-piece mold is used, and small pieces are normally cast.

For *investment casting*, a single-piece mold is used, which is not reusable; it results in high dimensional accuracy, good reproduction of detail, and a fine surface finish; and casting rates are low.

For *lost foam casting*, the pattern is polystyrene foam, whereas the mold material is sand. Complex geometries and tight tolerances are possible. Casting rates are higher than for investment, and there are few environmental wastes.

For *continuous casting*, at the conclusion of the extraction process, the molten metal is cast into a continuous strand having either a rectangular or circular cross-section; these shapes are desirable for subsequent secondary metal-forming operations. The chemical composition and mechanical properties are relatively uniform throughout the cross-section.

Miscellaneous Techniques

11.17 *If it is assumed that, for steel alloys, the average cooling rate of the heat-affected zone in the vicinity of a weld is 10°C/s, compare the microstructures and associated properties that will result for 1080 (eutectoid) and 4340 alloys in their HAZs.*

Solution

This problem asks that we specify and compare the microstructures and mechanical properties in the heat-affected weld zones for 1080 and 4340 alloys assuming that the average cooling rate is 10°C/s. Figure 10.27 shows the continuous cooling transformation diagram for an iron-carbon alloy of eutectoid composition (1080), and, in addition, cooling curves that delineate changes in microstructure. For a cooling rate of 10°C/s (which is less than 35°C/s) the resulting microstructure will be totally pearlite--probably a reasonably fine pearlite. On the other hand, in Figure 10.28 is shown the CCT diagram for a 4340 steel. From this diagram it may be noted that a cooling rate of 10°C/s produces a totally martensitic structure. Pearlite is softer and more ductile than martensite, and, therefore, is most likely more desirable.

11.18 *Describe one problem that might exist with a steel weld that was cooled very rapidly.*

Answer

If a steel weld is cooled very rapidly, martensite may form, which is very brittle. In some situations, cracks may form in the weld region as it cools.

11.19 *In your own words describe the following heat-treatment procedures for steels and, for each, the intended final microstructure:*

(a) full annealing

(b) normalizing

(c) quenching

(d) tempering.

Answer

(a) Full annealing--Heat to about 50°C above the A_3 line, Figure 11.11 (if the concentration of carbon is less than the eutectoid) or above the A_1 line (if the concentration of carbon is greater than the eutectoid) until the alloy comes to equilibrium; then furnace cool to room temperature. The final microstructure is coarse pearlite; the grain size is relatively small and the grain structure is uniform.

(b) Normalizing--Heat to at least 55°C above the A_3 line Figure 11.11 (if the concentration of carbon is less than the eutectoid) or above the A_{cm} line (if the concentration of carbon is greater than the eutectoid) until the alloy completely transforms to austenite, then cool in air. The final microstructure is fine pearlite.

(c) Quenching--Heat to a temperature within the austenite phase region and allow the specimen to fully austenitize, then quench to room temperature in oil or water. The final microstructure is martensite.

(d) Tempering--Heat a quenched (martensitic) specimen, to a temperature between 250°C and 650°C, for the time necessary to achieve the desired hardness. The final microstructure is tempered martensite.

11.20 *Cite three sources of internal residual stresses in metal components. What are two possible adverse consequences of these stresses?*

Answer

Three sources of residual stresses in metal components are plastic deformation processes, nonuniform cooling of a piece that was cooled from an elevated temperature, and a phase transformation in which parent and product phases have different densities.

Two adverse consequences of these stresses are distortion (or warpage) and fracture.

11.21 *Give the approximate minimum temperature at which it is possible to austenitize each of the following iron–carbon alloys during a normalizing heat treatment:*

(a) 0.15 wt% C

(b) 0.50 wt% C

(c) 1.10 wt% C.

Solution

This question asks that we cite the approximate minimum temperature at which it is desirable to austenitize several iron-carbon alloys during a normalizing heat treatment. In order to do this problem it is necessary to use Figure 11.11.

(a) For 0.15 wt% C, heat to at least 915°C (1680°F) since the A_3 temperature is 860°C (1580°F).

(b) For 0.50 wt% C, heat to at least 825°C (1520°F) since the A_3 temperature is 770°C (1420°F).

(c) For 1.10 wt% C, heat to at least 900°C (1655°F) since the A_{cm} temperature is 845°C (1555°F).

11.22 *Give the approximate temperature at which it is desirable to heat each of the following iron–carbon alloys during a full anneal heat treatment:*

(a) 0.20 wt% C

(b) 0.60 wt% C

(c) 0.76 wt% C

(d) 0.95 wt% C.

Solution

We are asked for the approximate temperature at which several iron-carbon alloys should be austenitized during a full-anneal heat treatment. In order to do this problem it is necessary to use Figure 11.11.

(a) For 0.20 wt% C, heat to about 890°C (1635°F) since the A_3 temperature is 840°C (1545°F).

(b) For 0.60 wt% C, heat to about 800°C (1470°F) since the A_3 temperature is 750°C (1380°F).

(c) For 0.76 wt% C, heat to about 777°C (1430°F) since the A_1 temperature is 727°C (1340°F).

(d) For 0.95 wt% C, heat to about 777°C (1430°F) since the A_1 temperature is 727°C (1340°F).

11.23 *What is the purpose of a spheroidizing heat treatment? On what classes of alloys is it normally used?*

Answer

The purpose of a spheroidizing heat treatment is to produce a very soft and ductile steel alloy having a spheroiditic microstructure. It is normally used on medium- and high-carbon steels, which, by virtue of carbon content, are relatively hard and strong.

Heat Treatment of Steels

11.24 *Briefly explain the difference between* hardness *and* hardenability.

Answer

Hardness is a measure of a material's resistance to localized surface deformation, whereas hardenability is a measure of the depth to which a ferrous alloy may be hardened by the formation of martensite. Hardenability is determined from hardness tests.

11.25 *What influence does the presence of alloying elements (other than carbon) have on the shape of a hardenability curve? Briefly explain this effect.*

Answer

The presence of alloying elements (other than carbon) causes a much more gradual decrease in hardness with position from the quenched end for a hardenability curve. The reason for this effect is that alloying elements retard the formation of pearlitic and bainitic structures which are not as hard as martensite.

11.26 *How would you expect a decrease in the austenite grain size to affect the hardenability of a steel alloy? Why?*

Answer

A decrease of austenite grain size will *decrease* the hardenability. Pearlite normally nucleates at grain boundaries, and the smaller the grain size, the greater the grain boundary area, and, consequently, the easier it is for pearlite to form.

11.27 *Name two thermal properties of a liquid medium that influence its quenching effectiveness.*

<u>Answer</u>

The two thermal properties of a liquid medium that influence its quenching effectiveness are (1) thermal conductivity and (2) heat capacity.

11.28 *Construct radial hardness profiles for the following:*

(a) A cylindrical specimen of an 8640 steel alloy of diameter 75 mm (3 in.) that has been quenched in moderately agitated oil

(b) A cylindrical specimen of a 5140 steel alloy of diameter 50 mm (2 in.) that has been quenched in moderately agitated oil

(c) A cylindrical specimen of an 8630 steel alloy of diameter 90 mm (3 $\frac{1}{2}$ in.) that has been quenched in moderately agitated water

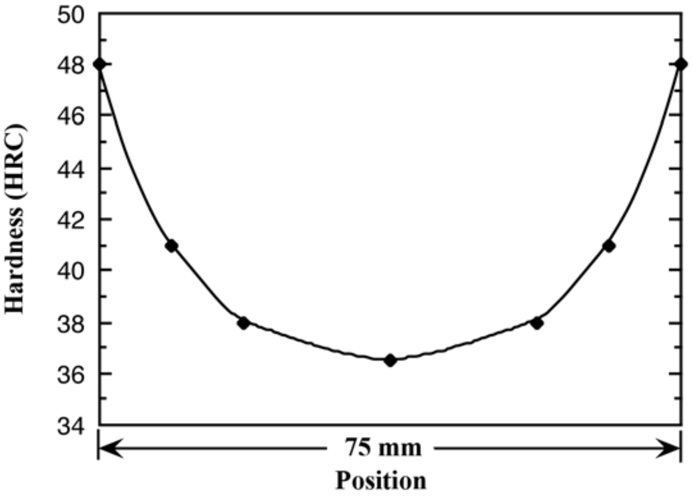
(d) A cylindrical specimen of an 8660 steel alloy of diameter 100 mm (4 in.) that has been quenched in moderately agitated water

Solution

(a) This part of the problem calls for us to construct a radial hardness profile for a 75 mm (3 in.) diameter cylindrical specimen of an 8640 steel that has been quenched in moderately agitated oil. In the manner of Example Problem 11.1, the equivalent distances and hardnesses tabulated below were determined from Figures 11.15 and 11.18*b*.

Radial Position	Equivalent Distance, mm	HRC Hardness
Surface	13	48
3/4 *R*	18	41
Midradius	22	38
Center	26	36

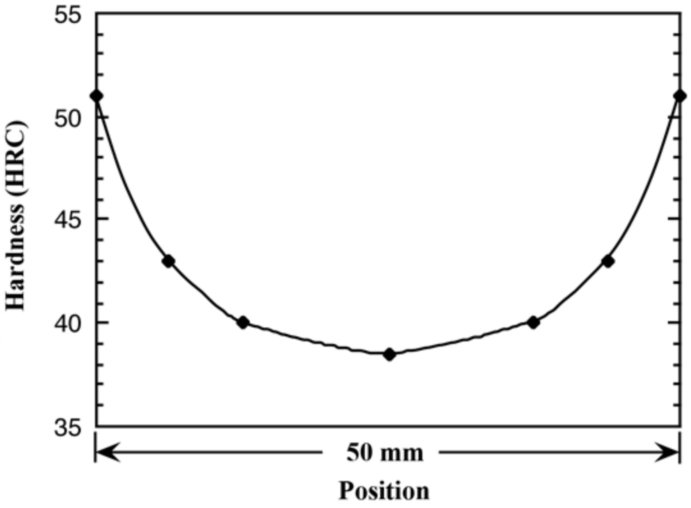
The resulting hardness profile is plotted below.



(b) The radial hardness profile for a 50 mm (2 in.) diameter specimen of a 5140 steel that has been quenched in moderately agitated oil is desired. The equivalent distances and hardnesses tabulated below were determined using Figures 11.15 and 11.18*b*.

Radial Position	Equivalent Distance, mm	HRC Hardness
Surface	7	51
3/4 *R*	12	43
Midradius	14	40
Center	16	38.5

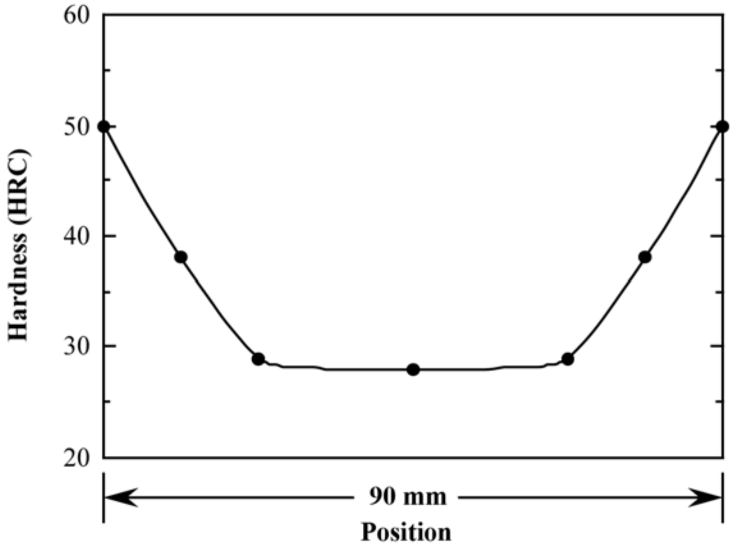
The resulting hardness profile is plotted below.



(c) The radial hardness profile for a 90-mm (3-1/2 in.) diameter specimen of an 8630 steel that has been quenched in moderately agitated water is desired. The equivalent distances and hardnesses for the various radial positions, as determined using Figures 11.16 and 11.18*a* are tabulated below.

Radial Position	Equivalent Distance, mm	HRC Hardness
Surface	3	50
3/4 *R*	10	38
Midradius	17	29
Center	22	27

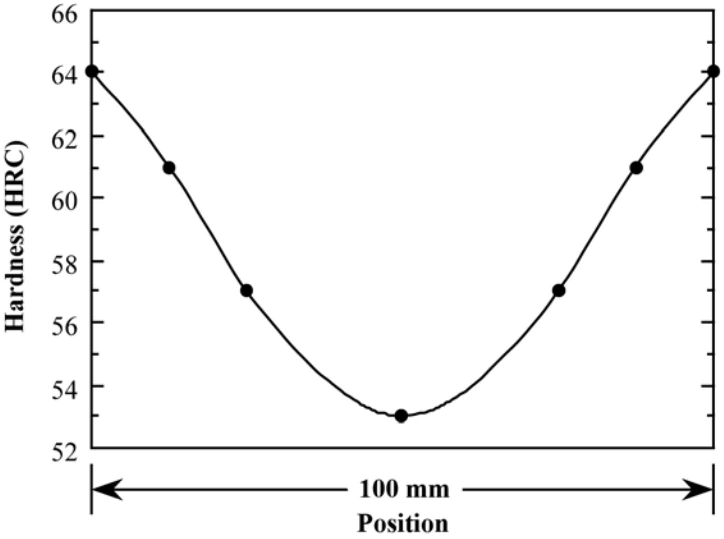
The resulting hardness profile is plotted here.



(d) The radial hardness profile for a 100-mm (4-in.) diameter specimen of a 8660 steel that has been quenched in moderately agitated water is desired. The equivalent distances and hardnesses for the various radial positions, as determined using Figures 11.16 and 11.18*a*, are tabulated below.

Radial Position	Equivalent Distance, mm	HRC Hardness
Surface	3	64
3/4 *R*	11	61
Midradius	20	57
Center	26	53

The resulting hardness profile is plotted here.


66
64
62
60
58
56
54
52
Hardness (HRC)
100 mm
Position

11.29 *Compare the effectiveness of quenching in moderately agitated water and oil, by graphing on a single plot radial hardness profiles for cylindrical specimens of an 8640 steel of diameter 75 mm (3 in.) that have been quenched in both media.*

Solution

We are asked to compare the effectiveness of quenching in moderately agitated water and oil by graphing, on a single plot, the hardness profiles for 75-mm (3-in.) diameter cylindrical specimens of an 8640 steel that had been quenched in both media.

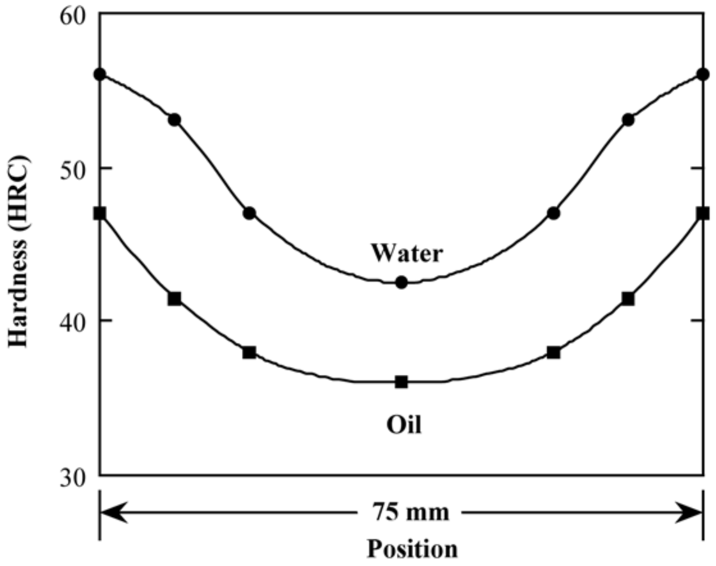
For moderately agitated water, the equivalent distances and hardnesses for the several radial positions (Figures 11.18*a* and 11.16) are tabulated below.

Radial Position	Equivalent Distance, mm	HRC Hardness
Surface	3	56
3/4 *R*	8	53
Midradius	13	47
Center	17	42.5

While for moderately agitated oil, the equivalent distances and hardnesses for the several radial positions (Figures 11.18*b* and 11.16) are tabulated below.

Radial Position	Equivalent Distance, mm	HRC Hardness
Surface	13	47
3/4 *R*	19	41.5
Midradius	22	38
Center	25	36

These data are plotted here.


60
50
40
30
Hardness (HRC)
Water
Oil
75 mm
Position

11.30 *Compare precipitation hardening (Section 11.9) and the hardening of steel by quenching and tempering (Sections 10.5, 10.6, and 10.8) with regard to the following:*

(a) The total heat treatment procedure

(b) The microstructures that develop

(c) How the mechanical properties change during the several heat treatment stages

Answer

(a) With regard to the total heat treatment procedure, the steps for the *hardening of steel* are as follows:

1. Austenitize above the upper critical temperature.
2. Quench to a relatively low temperature.
3. Temper at a temperature below the eutectoid.
4. Cool to room temperature.

With regard to *precipitation hardening*, the steps are as follows:

1. Solution heat treat by heating into the solid solution phase region.
2. Quench to a relatively low temperature.
3. Precipitation harden by heating to a temperature that is within the solid two-phase region.
4. Cool to room temperature.

(b) For the *hardening of steel*, the microstructures that form at the various heat treating stages in part (a) are:

1. Austenite
2. Martensite
3. Tempered martensite
4. Tempered martensite

For *precipitation hardening*, the microstructures that form at the various heat treating stages in part (a) are:

1. Single phase
2. Single phase--supersaturated
3. Small plate-like particles of a new phase within a matrix of the original phase.
4. Same as (3)

(c) For the *hardening of steel*, the mechanical characteristics for the various steps in part (a) are as follows:

1. Not important
2. The steel becomes hard and brittle upon quenching.
3. During tempering, the alloy softens slightly and becomes more ductile.
4. No significant changes upon cooling to or maintaining at room temperature.

For *precipitation hardening*, the mechanical characteristics for the various steps in part (a) are as follows:

1. Not important

(2) The alloy is relatively soft.

(3) The alloy hardens with increasing time (initially), and becomes more brittle; it may soften with overaging.

(4) The alloy may continue to harden or overage at room temperature.

11.31 *What is the principal difference between natural and artificial aging processes?*

Answer

For precipitation hardening, natural aging is allowing the precipitation process to occur at the ambient temperature; artificial aging is carried out at an elevated temperature.

DESIGN PROBLEMS

Ferrous Alloys

Nonferrous Alloys

11.D1 *The following is a list of metals and alloys:*

Plain carbon steel
Brass
Gray cast iron
Platinum
Stainless steel
Titanium alloy
Magnesium
Zinc
Tool steel
Aluminum
Tungsten

Select from this list the one metal or alloy that is best suited for each of the following applications, and cite at least one reason for your choice:

(a) The block of an internal combustion engine
(b) Condensing heat exchanger for steam
(c) Jet engine turbofan blades
(d) Drill bit
(e) Cryogenic (i.e., very low temperature) container
(f) As a pyrotechnic (i.e., in flares and fireworks)
(g) High-temperature furnace elements to be used in oxidizing atmospheres

Solution

This problem calls for us to select, from a list of alloys, the best alloy for each of several applications and then to justify each choice.

(a) Gray cast iron would be the best choice for an engine block because it is relatively easy to cast, is wear resistant, has good vibration damping characteristics, and is relatively inexpensive.

(b) Stainless steel would be the best choice for a heat exchanger to condense steam because it is corrosion resistant to the steam and condensate.

(c) Titanium alloys are the best choice for high-speed aircraft jet engine turbofan blades because they are light weight, strong, and easily fabricated very resistant to corrosion. However, one drawback is their cost.

(d) A tool steel would be the best choice for a drill bit because it is very hard retains its hardness at high temperature and is wear resistant, and, thus, will retain a sharp cutting edge.

(e) For a cryogenic (low-temperature) container, an aluminum alloy would be the best choice; aluminum alloys have an FCC crystal structure, and therefore, are ductile at very low temperatures.

(f) As a pyrotechnic in flares and fireworks, magnesium is the best choice because it ignites easily and burns readily in air with a very bright flame.

(g) Platinum is the best choice for high-temperature furnace elements to be used in oxidizing atmospheres because it is very ductile, has a relatively very high melting temperature, and is highly resistant to oxidation.

11.D2 *A group of new materials are the metallic glasses (or amorphous metals). Write an essay about these materials in which you address the following issues:*

(a) compositions of some of the common metallic glasses

(b) characteristics of these materials that make them technologically attractive

(c) characteristics that limit their use

(d) current and potential uses

(e) at least one technique that is used to produce metallic glasses.

Answer

(a) Compositionally, the metallic glass materials are rather complex; several compositions are as follows: $Fe_{80}B_{20}$, $Fe_{72}Cr_8P_{13}C_7$, $Fe_{67}Co_{18}B_{14}Si$, $Pd_{77.5}Cu_{6.0}Si_{16.5}$, and $Fe_{40}Ni_{38}Mo_4B_{18}$.

(b) These materials are exceptionally strong and tough, extremely corrosion resistant, and are easily magnetized.

(c) Principal drawbacks for these materials are 1) complicated and exotic fabrication techniques are required; and 2) inasmuch as very rapid cooling rates are required, at least one dimension of the material must be small--i.e., they are normally produced in ribbon form.

(d) Potential uses include transformer cores, magnetic amplifiers, heads for magnetic tape players, reinforcements for pressure vessels and tires, shields for electromagnetic interference, security tapes for library books.

(e) Production techniques include centrifuge melt spinning, planar-flow casting, rapid pressure application, arc melt spinning.

11.*D3 Of the following alloys, pick the one(s) that may be strengthened by heat treatment, cold work, or both: 410 stainless steel, 4340 steel, F10004 cast iron, C26000 cartridge brass, 356.0 aluminum, ZK60A magnesium, R56400 titanium, 1100 aluminum, and zinc.*

Answer

Those alloys that may be heat treated are either those noted as "heat treatable" (Tables 11.6 and 11.8 through 11.10), or as martensitic stainless steels (Table 11.4). Alloys that may be strengthened by cold working must not be exceptionally brittle (which may be the case for cast irons, Table 11.5); furthermore, must have recrystallization temperatures above room temperature (which immediately eliminates zinc). The alloys that fall within the three classifications are as follows:

Heat Treatable	Cold Workable	Both
410 stainless steel	410 stainless steel	410 stainless steel
4340 steel	4340 steel	4340 steel
ZK60A magnesium	ZK60A magnesium	ZK60A magnesium
356.0 aluminum	C26000 cartridge brass	
	R56400 Ti	
	1100 aluminum	

11.D4 *A structural member 250 mm (10 in.) long must be able to support a load of 44,400 N (10,000 lb$_f$) without experiencing any plastic deformation. Given the following data for brass, steel, aluminum, and titanium, rank them from least to greatest weight in accordance with these criteria.*

Alloy	***Yield Strength [MPa (ksi)]***	***Density (g/cm^3)***
Brass	*345 (50)*	*8.5*
Steel	*690 (100)*	*7.9*
Aluminum	*275 (40)*	*2.7*
Titanium	*480 (70)*	*4.5*

Solution

This problem asks us to rank four alloys (brass, steel, titanium, and aluminum), from least to greatest weight for a structural member to support a 44,400 N (10,000 lb$_f$) load without experiencing plastic deformation. From Equation 6.1, the cross-sectional area (A_0) must necessarily carry the load (F) without exceeding the yield strength (σ_y), as

$$A_0 = \frac{F}{\sigma_y}$$

Now, given the length l, the volume of material required (V) is just

$$V = lA_0 = \frac{lF}{\sigma_y}$$

Finally, the mass of the member (m) is

$$m = V\rho = \frac{\rho l F}{\sigma_y}$$

Here ρ is the density. Using the values given for these alloys [and assuming a length l of 25 cm (10 in.)], mass values for these four alloys are determined as follows:

$$m(\text{brass}) = \frac{(8.5\ \text{g/cm}^3)(25\ \text{cm})(44{,}400\ \text{N})}{(345 \times 10^6\ \text{N/m}^2)\left(\dfrac{1\ \text{m}}{10^2\ \text{cm}}\right)^2} = 273\ \text{g}$$

$$m(\text{steel}) = \frac{(7.9\ \text{g/cm}^3)(25\ \text{cm})(44{,}400\ \text{N})}{(690 \times 10^6\ \text{N/m}^2)\left(\dfrac{1\ \text{m}}{10^2\ \text{cm}}\right)^2} = 127\ \text{g}$$

$$m(\text{aluminum}) = \frac{(2.7\ \text{g/cm}^3)(25\ \text{cm})(44{,}400\ \text{N})}{(275 \times 10^6\ \text{N/m}^2)\left(\dfrac{1\ \text{m}}{10^2\ \text{cm}}\right)^2} = 109\ \text{g}$$

$$m(\text{titanium}) = \frac{(4.5\ \text{g/cm}^3)(25\ \text{cm})(44{,}400\ \text{N})}{(480 \times 10^6\ \text{N/m}^2)\left(\dfrac{1\ \text{m}}{10^2\ \text{cm}}\right)^2} = 104\ \text{g}$$

Thus, titanium would have the minimum weight (or mass), followed by aluminum, steel, and brass.

11.D5 *Discuss whether it would be advisable to hot work or cold work the following metals and alloys on the basis of melting temperature, oxidation resistance, yield strength, and degree of brittleness: platinum, molybdenum, lead, 304 stainless steel, and copper.*

Answer

This question asks for us to decide whether or not it would be advisable to hot-work or cold-work several metals and alloys.

Platinum is one of the noble metals. Even though it has a high melting temperature and good resistance to oxidation, at room temperature it is relatively soft and ductile, and is amenable to cold working.

Molybdenum, one of the refractory metals, is hard and strong at room temperature, has a high recrystallization temperature, and experiences oxidation at elevated temperatures. Cold-working is difficult because of its strength, and hot-working is not practical because of oxidation problems. Most molybdenum articles are fabricated by powder metallurgy, or by using cold-working followed by annealing cycles.

Lead would almost always be hot-worked. Even deformation at room temperature would be considered hot-working inasmuch as its recrystallization temperature is below room temperature (Table 7.2).

304 stainless steel is relatively resistant to oxidation. However, it is very ductile and has a moderate yield strength (Table 11.4), therefore, it may be cold-worked, but hot-working is also a possibility.

Copper is relatively soft and very ductile and ductile at room temperature (see, for example, C11000 copper in Table 11.6); therefore, it may be cold-worked.

Heat Treatment of Steels

11.D6 *A cylindrical piece of steel 38 mm (1 $\frac{1}{2}$ in.) in diameter is to be quenched in moderately agitated oil. Surface and center hardnesses must be at least 50 and 40 HRC, respectively. Which of the following alloys will satisfy these requirements: 1040, 5140, 4340, 4140, and 8640? Justify your choice(s).*

Answer

A 38-mm (1 $\frac{1}{2}$ in.) diameter steel specimen is to be quenched in moderately agitated oil. We are to decide which of five different steels will have surface and center hardnesses of at least 50 and 40 HRC, respectively.

In moderately agitated oil, the equivalent distances from the quenched end for a 38 mm diameter bar for surface and center positions are 5 mm (3/16 in.) and 12 mm (15/32 in.), respectively (Figure 11.18*b*). The hardnesses at these two positions for the alloys cited (as determined using Figure 11.15) are given below.

Alloy	Surface Hardness (HRC)	Center Hardness (HRC)
1040	40	24
5140	53	42
4340	57	55
4140	56	53
8640	55	48

Thus, alloys 4340, 4140, 8640, and 5140 will satisfy the criteria for both surface and center hardnesses.

11.D7 *A cylindrical piece of steel 57 mm (2 $\frac{1}{4}$ in.) in diameter is to be austenitized and quenched such that a minimum hardness of 45 HRC is to be produced throughout the entire piece. Of the alloys 8660, 8640, 8630, and 8620, which will qualify if the quenching medium is (a) moderately agitated water and (b) moderately agitated oil? Justify your choice(s).*

Answer

(a) This portion of the problem calls for us to decide which of 8660, 8640, 8630, and 8620 alloys may be fabricated into a cylindrical piece 57 mm ($2\frac{1}{4}$ in.) in diameter which, when quenched in mildly agitated water, will produce a minimum hardness of 45 HRC throughout the entire piece.

The center of the steel cylinder will cool the slowest and therefore will be the softest. In moderately agitated water the equivalent distance from the quenched end for a 57 mm diameter bar for the center position is about 11 mm (7/16 in.) (Figure 11.18*a*). The hardnesses at this position for the alloys cited (Figure 11.16) are given below.

Alloy	Center Hardness (HRC)
8660	61
8640	50
8630	36
8620	25

Therefore, only 8660 and 8640 alloys will have a minimum of 45 HRC at the center, and therefore, throughout the entire cylinder.

(b) This part of the problem asks us to do the same thing for moderately agitated oil. In moderately agitated oil the equivalent distance from the quenched end for a 57 mm diameter bar at the center position is about 17.5 mm (11.16 in.) (Figure 11.18*b*). The hardnesses at this position for the alloys cited (Figure 11.16) are given below.

Alloy	Center Hardness (HRC)
8660	58
8640	42
8630	30
8620	21

Therefore, only the 8660 alloy will have a minimum of 45 HRC at the center, and therefore, throughout the entire cylinder.

11.D8 *A cylindrical piece of steel 44 mm (1 $\frac{3}{4}$ in.) in diameter is to be austenitized and quenched such that a microstructure consisting of at least 50% martensite will be produced throughout the entire piece. Of the alloys 4340, 4140, 8640, 5140, and 1040, which qualify if the quenching medium is (a) moderately agitated oil and (b) moderately agitated water? Justify your choice(s).*

Answer

A 44-mm (1 $\frac{3}{4}$- in.) diameter cylindrical steel specimen is to be heat treated such that the microstructure throughout will be at least 50% martensite. We are to decide which of several alloys will satisfy this criterion if the quenching medium is moderately agitated (a) oil, and (b) water.

(a) Since the cooling rate is lowest at the center, we want a minimum of 50% martensite at the center position. From Figure 11.18*b*, the cooling rate is equal to an equivalent distance from the quenched end of 14 mm (5/8 in.). According to Figure 11.15, the hardness corresponding to 50% martensite for these alloys is 42 HRC. Thus, all we need do is to determine which of the alloys have a hardness of 42 HRC at an equivalent distance from the quenched end of 14 mm (5/8 in.). At an equivalent distance of 14 mm, the following hardnesses are determined from Figure 11.15 for the various alloys.

Alloy	Hardness (HRC)
4340	55
4140	52
8640	46
5140	40
1040	23

Thus, only alloys 4340, 4140 and 8640 will qualify (i.e., have hardnesses greater than 42 HRC).

(b) For moderately agitated water, the cooling rate at the center of a 44-mm (1- $\frac{3}{4}$ in.) diameter specimen is 9 mm (11/32 in.) equivalent distance from the quenched end (Figure 11.18*a*). At this position, the following hardnesses are determined from Figure 11.15 for the several alloys.

Alloy	Hardness (HRC)
4340	57
4140	55
8640	53
5140	48
1040	30

It is still necessary to have a hardness of 42 HRC or greater at the center; thus, alloys 4340, 4140, 8640, and 5140 qualify.

11.D9 *A cylindrical piece of steel 50 mm (2 in.) in diameter is to be quenched in moderately agitated water. Surface and center hardnesses must be at least 50 and 40 HRC, respectively. Which of the following alloys satisfy these requirements: 1040, 5140, 4340, 4140, 8620, 8630, 8640, and 8660? Justify your choice(s).*

Answer

A 50-mm (2-in.) diameter cylindrical steel specimen is to be quenched in moderately agitated water. We are to decide which of eight different steels will have surface and center hardnesses of at least 50 and 40 HRC, respectively.

In moderately agitated water, the equivalent distances from the quenched end for a 50-mm diameter bar for surface and center positions are 1.5 mm (1/16 in.) and 10 mm (3/8 in.), respectively (Figure 11.18*a*). The hardnesses at these two positions for the alloys cited are given below (as determined from Figures 11.15 and 11.16).

Alloy	Surface Hardness (HRC)	Center Hardness (HRC)
1040	53	27
5140	57	45
4340	57	56
4140	57	54
8620	44	27
8630	52	38
8640	57	51
8660	64	62

Thus, alloys 5140, 4340, 4140, 8640, and 8660 will satisfy the criteria for both surface hardness (minimum 50 HRC) and center hardness (minimum 40 HRC).

11.D10 *A cylindrical piece of 4140 steel is to be austenitized and quenched in moderately agitated oil. If the microstructure is to consist of at least 80% martensite throughout the entire piece, what is the maximum allowable diameter? Justify your answer.*

Answer

We are asked to determine the maximum diameter possible for a cylindrical piece of 4140 steel that is to be quenched in moderately agitated oil such that the microstructure will consist of at least 80% martensite throughout the entire piece. From Figure 11.15, the equivalent distance from the quenched end of a 4140 steel to give 80% martensite (or a 50 HRC hardness) is 16 mm (5/8 in.). Thus, the quenching rate at the center of the specimen should correspond to this equivalent distance. Using Figure 11.18*b*, the center specimen curve takes on a value of 16 mm (5/8 in.) equivalent distance at a diameter of about 50 mm (2 in.).

11.D11 *A cylindrical piece of 8660 steel is to be austenitized and quenched in moderately agitated oil. If the hardness at the surface of the piece must be at least 58 HRC, what is the maximum allowable diameter? Justify your answer.*

Answer

We are to determine, for a cylindrical piece of 8660 steel, the maximum allowable diameter possible in order yield a surface hardness of 58 HRC, when the quenching is carried out in moderately agitated oil.

From Figure 11.16, the equivalent distance from the quenched end of an 8660 steel to give a hardness of 58 HRC is about 18 mm (3/4 in.). Thus, the quenching rate at the surface of the specimen should correspond to this equivalent distance. Using Figure 11.18*b*, the surface specimen curve takes on a value of 18 mm equivalent distance at a diameter of about 95 mm (3.75 in.).

11.D12 *Is it possible to temper an oil-quenched 4140 steel cylindrical shaft 25 mm (1 in.) in diameter so as to give a minimum yield strength of 950 MPa (140,000 psi) and a minimum ductility of 17%EL? If so, specify a tempering temperature. If this is not possible, then explain why.*

Answer

This problem asks if it is possible to temper an oil-quenched 4140 steel cylindrical shaft 25 mm (1 in.) in diameter so as to give a minimum yield strength of 950 MPa (140,000 psi) and a minimum ductility of 17%EL. In order to solve this problem it is necessary to use Figures 11.21*b* and 11.21*c*, which plot, respectively, yield strength and ductility versus tempering temperature. For the 25 mm diameter line of Figure 11.21*b*), tempering temperatures less than about 575°C are required to give a yield strength of at least 950 MPa. Furthermore, from Figure 11.21*c*, for the 25 mm diameter line, tempering temperatures greater than about 550°C will give ductilities greater than 17%EL. Hence, it *is possible* to temper this alloy to produce the stipulated minimum yield strength and ductility; the tempering temperature will lie between 550°C and 575°C.

11.D13 *Is it possible to temper an oil-quenched 4140 steel cylindrical shaft 50 mm (2 in.) in diameter so as to give a minimum tensile strength of 900 MPa (130,000 psi) and a minimum ductility of 20%EL? If so, specify a tempering temperature. If this is not possible, then explain why.*

Answer

This problem asks if it is possible to temper an oil-quenched 4140 steel cylindrical shaft 50 mm (2 in.) in diameter so as to give a minimum tensile strength of 900 MPa (130,000 psi) and a minimum ductility of 20%EL. In order to solve this problem it is necessary to use Figures 11.21*a* and 11.21*c*, which plot, respectively, tensile strength and ductility versus tempering temperature. For the 50 mm diameter line of Figure 11.21*a*, tempering temperatures less than about 590°C are required to give a tensile strength of at least 900 MPa. Furthermore, from Figure 11.21*c*, for the 50 mm diameter line, tempering temperatures greater than about 600°C will give ductilities greater than 20%EL. Hence, it *is not possible* to temper this alloy to produce the stipulated minimum tensile strength and ductility. To meet the tensile strength minimum, T(tempering) < 590°C, whereas for ductility minimum, T(tempering) > 600°C; thus, there is no overlap of these tempering temperature ranges.

Precipitation Hardening

11.D14 *Copper-rich copper–beryllium alloys are precipitation hardenable. After consulting the portion of the phase diagram shown in Figure 11.31, do the following:*

(a) Specify the range of compositions over which these alloys may be precipitation hardened.

(b) Briefly describe the heat-treatment procedures (in terms of temperatures) that would be used to precipitation harden an alloy having a composition of your choosing yet lying within the range given for part (a).

Answer

This problem is concerned with the precipitation-hardening of copper-rich Cu-Be alloys. It is necessary for us to use the Cu-Be phase diagram (Figure 11.31).

(a) The range of compositions over which these alloys may be precipitation hardened is between approximately 0.2 wt% Be (the maximum solubility of Be in Cu at about 300°C) and 2.7 wt% Be (the maximum solubility of Be in Cu at 866°C).

(b) The heat treatment procedure, of course, will depend on the composition chosen. First of all, the solution heat treatment must be carried out at a temperature within the α phase region, after which, the specimen is quenched to room temperature. Finally, the precipitation heat treatment is conducted at a temperature within the $\alpha + \gamma_2$ phase region.

For example, for a 1.5 wt% Be-98.5 wt% Cu alloy, the solution heat treating temperature must be between about 600°C (1110°F) and 900°C (1650°F), while the precipitation heat treatment would be below 600°C (1110°F), and probably above 300°C (570°F). Below 300°C, diffusion rates are low, and heat treatment times would be relatively long.

11.D15 *A solution heat-treated 2014 aluminum alloy is to be precipitation hardened to have a minimum yield strength of 345 MPa (50,000 psi) and a ductility of at least 12%EL. Specify a practical precipitation heat treatment in terms of temperature and time that would give these mechanical characteristics. Justify your answer.*

Answer

We are asked to specify a practical heat treatment for a 2014 aluminum alloy that will produce a minimum yield strength of 345 MPa (50,000 psi), and a minimum ductility of 12%EL. From Figure 11.28*a*, the following heat treating temperatures and time ranges are possible to the give the required yield strength (Note: keep in mind that the time axis is scaled logarithmically.)

Temperature (°C)	Time Range (h)
260	not possible
204	0.3-15
149	10-700
121	300-?

With regard to temperatures and times to give the desired ductility (Figure 11.28*b*):

Temperature (°C)	Time Range (h)
260	<0.02, >10
204	<0.4, >300
149	<20
121	<1000

From these tabulations, the following may be concluded:

It is not possible to heat treat this alloy at 260°C so as to produce the desired set of properties—attainment of a yield strength of 345 MPa is not possible at this temperature.

At 204°C, the heat treating time would need to be about 0.4 h, which is practical.

At 149°C, the time range is between 10 and 20 h, which is a little on the long side.

Finally, at 121°C, the time range is unpractically long (300 to 1000 h).

11.D16 *Is it possible to produce a precipitation hardened 2014 aluminum alloy having a minimum yield strength of 380 MPa (55,000 psi) and a ductility of at least 15%EL? If so, specify the precipitation heat treatment. If it is not possible then explain why.*

Answer

This problem inquires as to the possibility of producing a precipitation-hardened 2014 aluminum alloy having a minimum yield strength of 380 MPa (55,000 psi) and a ductility of at least 15%EL. In order to solve this problem it is necessary to consult Figures 11.28*a* and 11.28*b*. Below are tabulated the times required at the various temperatures to achieve the stipulated yield strength. (Note: keep in mind that the time axis is scaled logarithmly.).

Temperature (°C)	Time Range (h)
260	not possible
204	0.5-7
149	10-250
121	400-2500

With regard to temperatures and times to give the desired ductility:

Temperature (°C)	Time Range (h)
260	<0.005
204	<0.13
149	<10
121	<500

Therefore, an alloy having this combination of yield strength and ductility is marginally possible. A heat treatment at 149°C for 10 h would probably just achieve the stipulated ductility and yield strength. At 121°C the tempering time would lie between 400 h and 500 h, times that are impractically long.

FUNDAMENTALS OF ENGINEERING QUESTIONS AND PROBLEMS

11.1FE *Which of the following elements is the primary constituent of ferrous alloys?*

(A) Copper

(B) Carbon

(C) Iron

(D) Titanium

Answer

The correct answer is C. *Iron* (Fe) is the primary constituent of ferrous alloys.

11.2FE *Which of the following microconstituents/phases is (are) typically found in a low-carbon steel?*

(A) Austenite

(B) Pearlite

(C) Ferrite

(D) Both pearlite and ferrite

Answer

The correct answer is D**.** *Pearlite* and *ferrite* are the microconstituents/phases typically found in a low-carbon steel.

11.3FE *Which of the following characteristics distinguishes the stainless steels from other steel types?*

(A) They are more corrosion resistant.

(B) They are stronger.

(C) They are more wear resistant.

(D) They are more ductile.

Answer

The correct answer is A. Stainless steels *are more corrosion resistant* than other steels.

11.*4FE Hot working takes place at a temperature above a metal's*

(A) melting temperature

(B) recrystallization temperature

(C) eutectoid temperature

(D) glass transition temperature

Answer

The correct answer is B. Hot working takes place at a temperature that is above a metal's *recrystallization temperature*.

11.5FE *Which of the following may occur during an annealing heat treatment?*

(A) Stresses may be relieved.

(B) Ductility may increase.

(C) Toughness may increase.

(D) All of the above.

Answer

The correct answer is D. During an annealing heat treatment: *stresses may be relieved*, *ductility may increase,* and *toughness may increase*.

11.6FE *Which of the following influences the hardenability of a steel?*

(A) Composition of the steel

(B) Type of quenching medium

(C) Character of the quenching medium

(D) Size and shape of the specimen

Answer

The correct answer is A**.** The hardenability of a steel is influenced by *its composition*.

CHAPTER 12

STRUCTURES AND PROPERTIES OF CERAMICS

PROBLEM SOLUTIONS

*Crystal Structures_*

12.1 *For a ceramic compound, what are the two characteristics of the component ions that determine the crystal structure?*

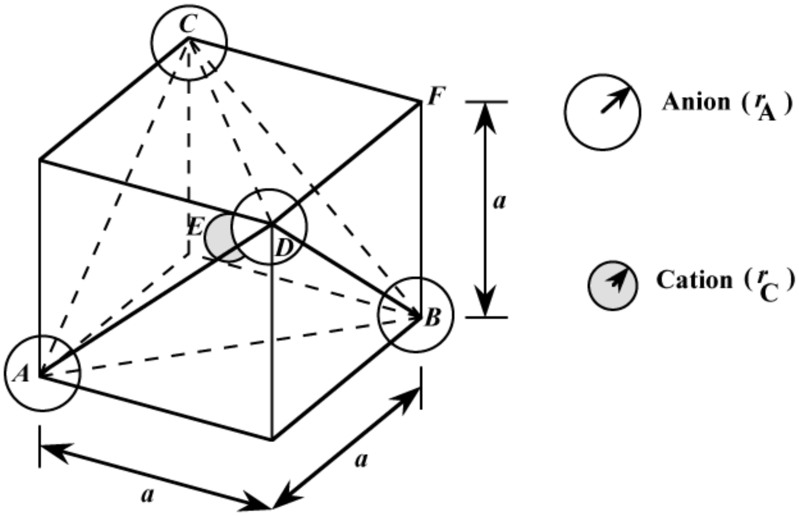
Answer

The two characteristics of component ions that determine the crystal structure of a ceramic compound are: (1) the magnitude of the electrical charge on each ion, and (2) the relative sizes of the cations and anions.

12.2 *Show that the minimum cation-to-anion radius ratio for a coordination number of 4 is 0.225.*

Solution

In this problem we are asked to show that the minimum cation-to-anion radius ratio for a coordination number of four is 0.225. If lines are drawn from the centers of the anions, then a tetrahedron is formed. The tetrahedron may be inscribed within a cube as shown below.



The spheres at the apexes of the tetrahedron are drawn at the corners of the cube, and designated as positions *A*, *B*, *C*, and *D*. (These are reduced in size for the sake of clarity.) The cation resides at the center of the cube, which is designated as point *E*. Let us now express the cation and anion radii in terms of the cube edge length, designated as *a*. The spheres located at positions *A* and *B* touch each other along the bottom face diagonal. Thus,

$$\overline{AB} = 2r_A$$

But

$$(\overline{AB})^2 = a^2 + a^2 = 2a^2$$

Or, combining the above two equations:

$$\overline{AB} = a\sqrt{2} = 2r_A \qquad \text{(S.12.2a)}$$

Which leads to the following:

$$a = \frac{2r_A}{\sqrt{2}} \qquad \text{(S.12.2b)}$$

There will also be an anion located at the corner, point *F* (not drawn), and the cube diagonal $\overline{AEF}$ will be related to the ionic radii as

$$\overline{AEF} = 2(r_A + r_C) \qquad \text{(S.12.2c)}$$

(The line *AEF* has not been drawn to avoid confusion.) From the triangle *ABF*

$$(\overline{AB})^2 + (\overline{FB})^2 = (\overline{AEF})^2 \qquad \text{(S.12.2d)}$$

But, the length of line $\overline{FB}$ is equal to

$$\overline{FB} = a = \frac{2r_A}{\sqrt{2}} \qquad \text{(S.12.2e)}$$

and, as noted above (Equation S.12.2a), the length of line $\overline{AB}$is as follows:

$$\overline{AB} = 2r_A$$

Thus, combining Equations S.12.2a, S.12.2.c, and S.12.2e with Equation S.12.2d leads to the following:

$$(2r_A)^2 + \left(\frac{2r_A}{\sqrt{2}}\right)^2 = \left[2(r_A + r_C)\right]^2$$

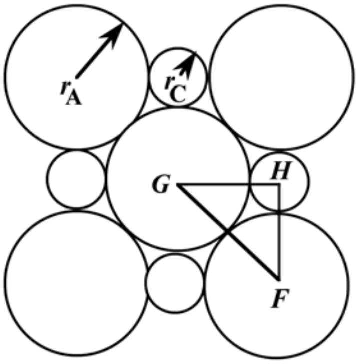
Solving for the r_C/r_A ratio from this expression yields

$$\frac{r_C}{r_A} = \frac{\sqrt{6} - 2}{2} = 0.225$$

12.3 *Show that the minimum cation-to-anion radius ratio for a coordination number of 6 is 0.414. [Hint: Use the NaCl crystal structure (Figure 12.2), and assume that anions and cations are just touching along cube edges and across face diagonals.]*

Solution

This problem asks us to show that the minimum cation-to-anion radius ratio for a coordination number of 6 is 0.414 (using the rock salt crystal structure). Below is shown one of the faces of the rock salt crystal structure in which anions and cations just touch along the edges, and also the face diagonals.



From triangle *FGH*,

$$\overline{GF} = 2r_A$$

Whereas

$$\overline{FH} = \overline{GH} = r_A + r_C$$

Since *FGH* is a right triangle, it is the case that

$$(\overline{GH})^2 + (\overline{FH})^2 = (\overline{GF})^2$$

Upon substitution into this equation, expressions for $\overline{GF}$, $\overline{FH}$, and $\overline{GH}$ cite above gives the following:

$$(r_A + r_C)^2 + (r_A + r_C)^2 = (2r_A)^2$$

which leads to

$$r_A + r_C = \frac{2r_A}{\sqrt{2}}$$

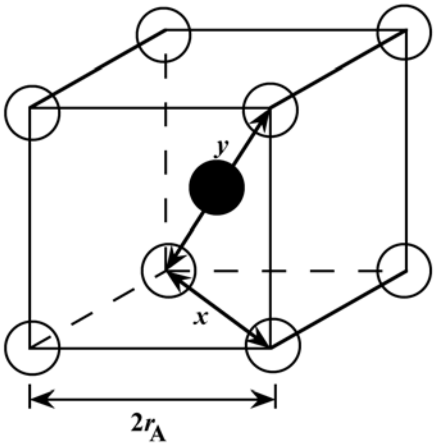
Or, solving for r_C/r_A

$$\frac{r_C}{r_A} = \left(\frac{2}{\sqrt{2}} - 1\right) = 0.414$$

12.4 *Demonstrate that the minimum cation-to-anion radius ratio for a coordination number of 8 is 0.732.*

Solution

This problem asks us to show that the minimum cation-to-anion radius ratio for a coordination number of 8 is 0.732. From the following sketch of a cubic unit cell, it may be noted that the atom represented by the dark circle has eight nearest-neighbor atoms—denoted by the open circles at the corners of the unit cell.



From this unit cell it is the case that the unit cell edge length is 2r_A. Furthermore, from the base of the unit cell

$$x^2 = (2r_A)^2 + (2r_A)^2 = 8r_A^2$$

which means that

$$x = 2r_A\sqrt{2}$$

Now from the triangle that involves *x*, *y*, and the unit cell edge, the following may be written:

$$x^2 + (2r_A)^2 = y^2 = (2r_A + 2r_C)^2$$

Or, upon substitution for the expression for *x* given above

$$(2r_A\sqrt{2})^2 \; + \; 4r_A^2 \; = \; (2r_A \; + \; 2r_C)^2$$

This equation reduces to the following:

$$2r_A(\sqrt{3} \; - \; 1) = 2r_C$$

Or, solving for the r_C-$r_A$ration yields

$$\frac{r_C}{r_A} = \sqrt{3} \; - \; 1 \; = \; 0.732$$

12.5 *On the basis of ionic charge and ionic radii given in Table 12.3, predict crystal structures for the following materials:*

(a) CaO

(b) MnS

(c) KBr

(d) CsBr

Justify your selections.

Solution

This problem calls for us to predict crystal structures for several ceramic materials on the basis of ionic charge and ionic radii.

(a) For CaO, using data from Table 12.3

$$\frac{r_{\mathrm{Ca}^{2+}}}{r_{\mathrm{O}^{2-}}} = \frac{0.100 \text{ nm}}{0.140 \text{ nm}} = 0.714$$

Now, from Table 12.2, the coordination number for each cation (Ca^{2+}) is six, and, using Table 12.4, the predicted crystal structure is *sodium chloride.*

(b) For MnS, using data from Table 12.3

$$\frac{r_{\mathrm{Mn}^{2+}}}{r_{\mathrm{S}^{2-}}} = \frac{0.067 \text{ nm}}{0.184 \text{ nm}} = 0.364$$

The coordination number is four (Table 12.2), and the predicted crystal structure is *zinc blende* (Table 12.4).

(c) For KBr, using data from Table 12.3

$$\frac{r_{\mathrm{K}^{+}}}{r_{\mathrm{Br}^{-}}} = \frac{0.138 \text{ nm}}{0.196 \text{ nm}} = 0.704$$

The coordination number is six (Table 12.2), and the predicted crystal structure is *sodium chloride* (Table 12.4).

(d) For CsBr, using data from Table 12.3

$$\frac{r_{\mathrm{Cs}^{+}}}{r_{\mathrm{Br}^{-}}} = \frac{0.170 \text{ nm}}{0.196 \text{ nm}} = 0.867$$

The coordination number is eight (Table 12.2), and the predicted crystal structure is cesium chloride (Table 12.4).

12.6 *Which of the cations in Table 12.3 would you predict to form fluorides having the cesium chloride crystal structure? Justify your choices.*

Solution

We are asked to cite the cations in Table 12.3 which would form fluorides having the cesium chloride crystal structure. First of all, the possibilities would include only the monovalent cations Cs^+, K^+, and Na^+. Furthermore, the coordination number for each cation must be 8, which means that $0.732 < r_C/r_A < 1.0$ (Table 12.2). From Table 12.3 the r_C/r_A ratios for these three cations and the F^- ion are as follows:

$$\frac{r_{Cs^+}}{r_{F^-}} = \frac{0.170\text{ nm}}{0.133\text{ nm}} = 1.28$$

$$\frac{r_{K^+}}{r_{F^-}} = \frac{0.138\text{ nm}}{0.133\text{ nm}} = 1.04$$

$$\frac{r_{Na^+}}{r_{F^-}} = \frac{0.102\text{ nm}}{0.133\text{ nm}} = 0.77$$

Thus, on the basis of the $0.732 < r_C/r_A < 1.0$ criterion, only sodium fluoride will form the CsCl crystal structure.

12.7 *Using the Molecule Definition Utility found in both "Metallic Crystal Structures and Crystallography" and "Ceramic Crystal Structures" modules of VMSE, located on the book's web site [www.wiley.com/college/callister (Student Companion Site)], generate (and print out) a three-dimensional unit cell for lead oxide, PbO, given the following: (1) The unit cell is tetragonal with a = 0.397 nm and c = 0.502 nm, (2) oxygen atoms are located at the following point coordinates:*

0 0 0	*0 0 1*
1 0 0	*1 0 1*
0 1 0	*0 1 1*
$\frac{1}{2}\,\frac{1}{2}\,0$	$\frac{1}{2}\,\frac{1}{2}\,1$

and (3) Pb atoms are located at the following point coordinates:

$\frac{1}{2}\;0\;0.763$	$0\;\frac{1}{2}\;0.237$
$\frac{1}{2}\;1\;0.763$	$1\;\frac{1}{2}\;0.237$

Solution

First of all, open the "Molecular Definition Utility"; it may be found in either of "Metallic Crystal Structures and Crystallography" or "Ceramic Crystal Structures" modules. After opening either of these modules, then open the "Molecule Definition Utility" submodule. Detailed instructions are provided for each step; therefore, our instructions will be general in nature.

Three steps are provided for generating crystal structures: Step 1—Define atom types; Step 2—Position atoms; Step 3—Define bonds between atoms.

In Step 1 each atom/ion type is given a name, a color, and a size—size may be specified in terms of nanometers; they each atom type is registered.

For Step 2 positions of all atoms/ions of each type are specified. In the problem statement point coordinate indices are provided (see Section 3.8); these need to be converted into lattice positions—i.e., multiplied by the appropriate *a* or *c* lattice parameter. Therefore, these atom positions are entered in nanometers—relative to the three X, Y, and Z axes. After entering the lattice position for each ion, that ion is displayed by clicking on the "Register Atom Position" button.

The X, Y, and Z lattice position entries for the 10 sets of point coordinates for the oxygen ions are as follows:

0, 0, and 0	0, 0, and 0.502
0.397, 0, and 0	0.397, 0, and 0.502
0, 0.397, and 0	0, 0.397, and 0.502

0.397, 0.397, and 0

0.1985, 0.1985, and 0

0.397, 0.397, and 0.502

0.1985, 0.1985, and 0.502

Likewise, for the lead ions, X, Y, and Z lattice position entries for the four sets of points coordinates are the following:

0.1985, 0, and 0.383

0.1985, 0.397, and 0.383

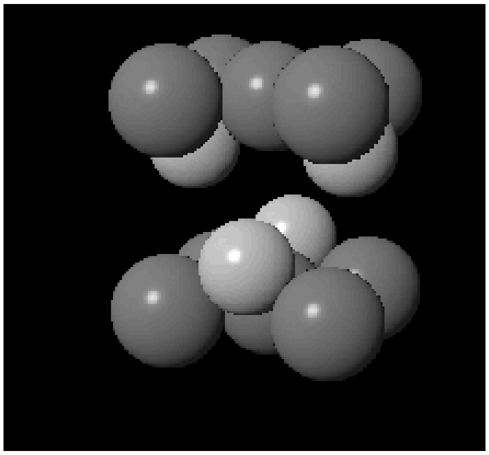
0, 0.1985, and 0.1190

0.397, 0.1985, and 0.1190

Step 3 allows the user to define the nature of the bonds between atoms. For the ceramic and metallic crystal structures, interatomic bonds are not normally displayed.

At any time during this process, the image may be rotated by using mouse click-and-drag.

For this problem the image should appear something like the one shown below:



Here the darker spheres represent oxygen ions, while lead ions are depicted by the lighter balls.

[Note: Unfortunately, with this version of the Molecular Definition Utility, it is not possible to save either the data or the image that you have generated. You may use screen capture (or screen shot) software to record and store your image.]

12.8 *The zinc blende crystal structure is one that may be generated from close-packed planes of anions.*

(a) Will the stacking sequence for this structure be FCC or HCP? Why?

(b) Will cations fill tetrahedral or octahedral positions? Why?

(c) What fraction of the positions will be occupied?

Solution

This question is concerned with the zinc blende crystal structure in terms of close-packed planes of anions.

(a) The stacking sequence of close-packed planes of anions for the zinc blende crystal structure will be the same as FCC (and not HCP) because the anion packing is FCC (Table 12.4).

(b) The cations will fill tetrahedral positions since the coordination number for cations is four (Table 12.4).

(c) Only one-half of the tetrahedral positions will be occupied because there are two tetrahedral sites per anion, and yet only one cation per anion.

12.9 *The corundum crystal structure, found for* Al_2O_3*, consists of an HCP arrangement of* O^{2-} *ions; the* Al^{3+} *ions occupy octahedral positions.*

(a) What fraction of the available octahedral positions are filled with Al^{3+} *ions?*

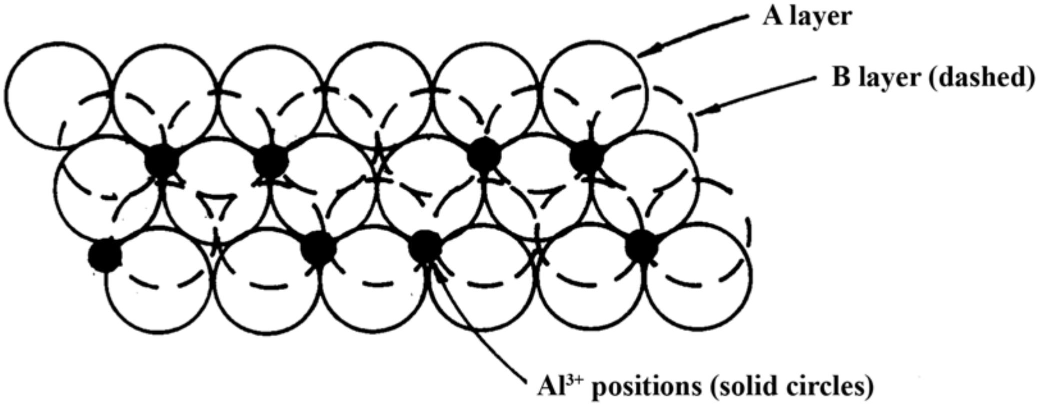
(b) Sketch two close-packed O^{2-}*planes stacked in an AB sequence, and note octahedral positions that will be filled with the* Al^{3+} *ions.*

Solution

This question is concerned with the corundum crystal structure in terms of close-packed planes of anions.

(a) For this crystal structure, two-thirds of the octahedral positions will be filled with Al^{3+} ions since there is one octahedral site per O^{2-} ion, and the ratio of Al^{3+} to O^{2-} ions is two-to-three.

(b) Two close-packed O^{2-} planes and the octahedral positions between these planes that will be filled with Al^{3+} ions are sketched below.



12.10 *Beryllium oxide (BeO) may form a crystal structure that consists of an HCP arrangement of* O^{2-} *ions. If the ionic radius of* Be^{2+} *is 0.035 nm, then*

(a) Which type of interstitial site will the Be^{2+} *ions occupy?*

(b) What fraction of these available interstitial sites will be occupied by Be^{2+} *ions?*

Solution

(a) This portion of the problem asks that we specify which type of interstitial site the Be^{2+} ions occupy in BeO if the ionic radius of Be^{2+} is 0.035 nm and the O^{2-} ions form an HCP arrangement. Since, from Table 12.3, $r_{O^{2-}}$ = 0.140 nm, then

$$\frac{r_{Be^{2+}}}{r_{O^{2-}}} = \frac{0.035\text{ nm}}{0.140\text{ nm}} = 0.250$$

Inasmuch as r_C/r_A is between 0.225 and 0.414, the coordination number for Be^{2+} is 4 (Table 12.2); therefore, tetrahedral interstitial positions are occupied.

(b) We are now asked what fraction of these available interstitial sites are occupied by Be^{2+} ions. Since there are two tetrahedral sites per O^{2-} ion, and the ratio of Be^{2+} to O^{2-} is 1:1, one-half of these sites are occupied with Be^{2+} ions.

12.11 *Iron titanate,* $FeTiO_3$*, forms in the ilmenite crystal structure that consists of an HCP arrangement of* O^{2-}*ions.*

(a) Which type of interstitial site will the Fe^{2+} *ions occupy? Why?*

(b) Which type of interstitial site will the Ti^{4+} *ions occupy? Why?*

(c) What fraction of the total tetrahedral sites will be occupied?

(d) What fraction of the total octahedral sites will be occupied?

Solution

(a) We are first of all asked to cite, for $FeTiO_3$, which type of interstitial site the Fe^{2+} ions will occupy. From Table 12.3, the cation-anion radius ratio is

$$\frac{r_{\mathrm{Fe}^{2+}}}{r_{\mathrm{O}^{2-}}} = \frac{0.077 \text{ nm}}{0.140 \text{ nm}} = 0.550$$

Since this ratio is between 0.414 and 0.732, the Fe^{2+} ions will occupy octahedral sites (Table 12.2).

(b) Similarly, for the Ti^{4+} ions, the titanium-oxygen ionic radius ratio is as follows:

$$\frac{r_{\mathrm{Ti}^{4+}}}{r_{\mathrm{O}^{2-}}} = \frac{0.061 \text{ nm}}{0.140 \text{ nm}} = 0.436$$

Since this ratio is between 0.414 and 0.732, the Ti^{4+} ions will also occupy octahedral sites.

(c) Since both Fe^{2+} and Ti^{4+} ions occupy octahedral sites, no tetrahedral sites will be occupied.

(d) For every $FeTiO_3$ formula unit, there are three O^{2-} ions, and, therefore, three octahedral sites; since there is one ion each of Fe^{2+} and Ti^{4+}per formula unit, two-thirds of these octahedral sites will be occupied.

12.12 *For each of the following crystal structures, represent the indicated plane in the manner of Figures 3.12 and 3.13, showing both anions and cations:*

(a) (100) plane for the cesium chloride crystal structure

(b) (200) plane for the cesium chloride crystal structure

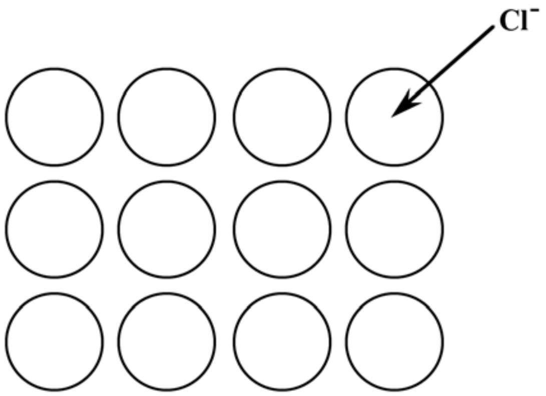
(c) (111) plane for the diamond cubic crystal structure

(d) (110) plane for the fluorite crystal structure

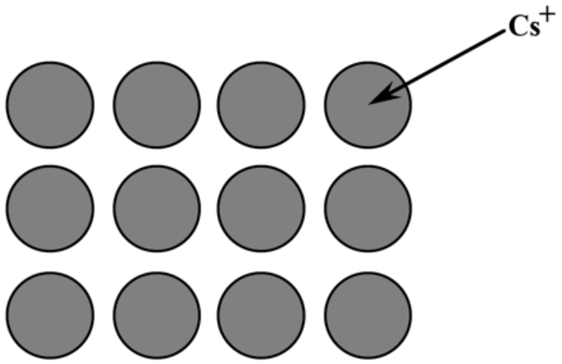
Solution

This problem asks that we represent specific crystallographic planes for various ceramic crystal structures.

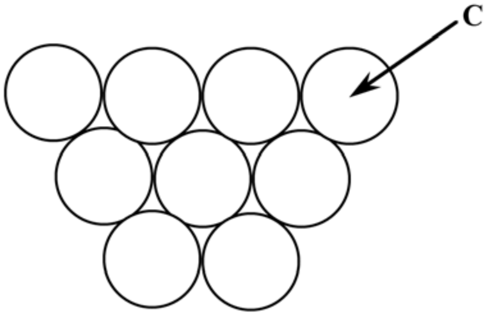
(a) A (100) plane for the cesium chloride crystal structure would appear as



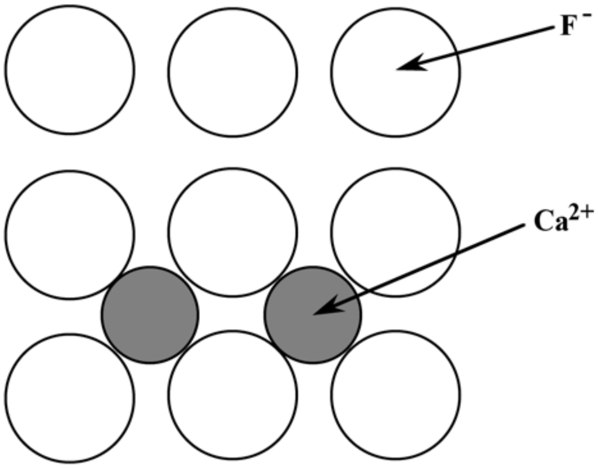
(b) A (200) plane for the cesium chloride crystal structure would appear as



(c) A (111) plane for the diamond cubic crystal structure would appear as



(d) A (110) plane for the fluorite crystal structure would appear as



Ceramic Density Computations

12.13 *Compute the atomic packing factor for the rock salt crystal structure in which r_C/r_A = 0.414.*

<u>Solution</u>

This problem asks that we compute the atomic packing factor for the rock salt crystal structure when r_C/r_A = 0.414. The definition of the atomic packing (APF) is given in Equation 3.3 as follows:

$$\text{APF} = \frac{V_S}{V_C}$$

where V_S and V_C are, respectively sphere volume of ions within the unit cell and unit cell volume. With regard to the sphere volume, there are four cation and four anion spheres per unit cell (because the rock salt crystal structure consists of two interpenetrating FCC networks). Thus,

$$V_S = (4)\left(\frac{4}{3}\pi r_A^3\right) + (4)\left(\frac{4}{3}\pi r_C^3\right)$$

But, since r_C/r_A = 0.414, then the above equation may be rewritten as follows:

$$V_S = \frac{16}{3}\pi r_A^3\left[1 + (0.414)^3\right] = (17.94)\ r_A^3$$

Now, for r_C/r_A = 0.414 the corner anions in Table 12.2 just touch one another along the cubic unit cell edges such that

$$V_C = a^3 = \left[2(r_A + r_C)\right]^3$$

$$= \left[2(r_A + 0.414 r_A)\right]^3 = (22.62) r_A^3$$

Thus

$$\text{APF} = \frac{V_S}{V_C} = \frac{(17.94)\ r_A^3}{(22.62)\ r_A^3} = 0.793$$

12.14 *The unit cell for* Al_2O_3 *has hexagonal symmetry with lattice parameters a = 0.4759 nm and c =1.2989 nm. If the density of this material is 3.99 g/cm*^{3}*, calculate its atomic packing factor. For this computation use ionic radii listed in Table 12.3.*

Solution

This problem asks for us to calculate the atomic packing factor for aluminum oxide given values for *a* and *c* lattice parameters, and the density. To begin, the atomic packing (APF) is defined in Equation 3.3 as follows:

$$\text{APF} = \frac{V_S}{V_C}$$

where V_S and V_C are, respectively sphere volume of ions within the unit cell and unit cell volume. Let us first begin by determining the value of V_C for Al_2O_3. The first thing we need to do is determine *n'*, the number of formula (Al_2O_3) units in the unit cell, which is one of the parameters in Equation 12.1. However, this necessitates that we calculate the value of V_C, the unit cell volume. The unit cell volume for the HCP crystal was given in Equation 3.7a as follows:

$$V_C = \frac{3a^2c\sqrt{3}}{2} \tag{3.7a}$$

Values for *a* and *c* are given in the problem statement as 0.4759 nm $(\text{or } 4.759 \times 10^{-8}\ \text{cm})$ and 1.2989 nm $(\text{or } 1.2989 \times 10^{-7}\ \text{cm})$, respectively. Thus, the unit cell volume is computed as follows:

$$V_C = \frac{(3)(4.759 \times 10^{-8}\ \text{cm})^2(1.2989 \times 10^{-7}\ \text{cm})(\sqrt{3})}{2}$$

$$= 7.64 \times 10^{-22}\ \text{cm}^3$$

Now, solving for *n'* (Equation 12.1) leads to the following expression:

$$n' = \frac{\rho N_A V_C}{\sum A_{\text{Al}} + \sum A_{\text{O}}}$$

Here

$\sum A_{\text{Al}}$ = the sum of the atomic weights of all aluminum ions in Al_2O_3= $2A_{\text{Al}}$ = (2)(26.98 g/mol)

$\sum A_{\text{O}}$ = the sum of the atomic weights of all oxygen ions in Al_2O_3 = $3A_{\text{O}}$ = (3)(16.00 g/mol)

ρ = the density of Al_2O_3, given in the problem statement as 3.99 g/cm^3

N_A = Avogardo's number = 6.022×10^{23} formula units/mol

Thus the value of *n'* is computed as follows:

$$n' = \frac{(3.99\ \text{g/cm}^3)(6.022\ \times\ 10^{23}\ \text{formula units/mol})(7.64\ \times\ 10^{-22}\ \text{cm}^3/\text{unit cell})}{(2)(26.98\ \text{g/mol}) + (3)(16.00\ \text{g/mol})}$$

= 18.0 formula units/unit cell

Which means there are 18 Al_2O_3 units per unit cell, or 36 Al^{3+} ions and 54 O^{2-} ions. From Table 12.3, the radii of these two ion types are 0.053 and 0.140 nm, respectively. Thus, the total sphere volume in Equation 3.3 (which we denote as V_S), is just

$$V_S = (36)\left(\frac{4}{3}\pi\right)(5.3 \times 10^{-9}\text{cm})^3 + (54)\left(\frac{4}{3}\pi\right)(1.4 \times 10^{-8}\text{cm})^3$$

$$= 6.43\ \times\ 10^{-22}\ \text{cm}^3$$

Finally, the APF is equal to

$$\text{APF} = \frac{V_S}{V_C} = \frac{6.43\ \times\ 10^{-22}\ \text{cm}^3}{7.64\ \times\ 10^{-22}\ \text{cm}^3} = 0.842$$

12.15 *Compute the atomic packing factor for cesium chloride using the ionic radii in Table 12.3 and assuming that the ions touch along the cube diagonals.*

Solution

We are asked in this problem to compute the atomic packing factor for the CsCl crystal structure. This requires that we take the ratio of the sphere volume within the unit cell and the total unit cell volume. From Figure 12.3 there is the equivalence of one Cs and one Cl ion per unit cell; the ionic radii of these two ions are 0.170 nm and 0.181 nm, respectively (Table 12.3). Thus, the sphere volume, V_S, is a function of the atomic radii of Cs and Cl (r_{Cs} and r_{Cl}, respectively) as

$$V_S = \frac{4}{3}(\pi)r_{\mathrm{Cs}}^3 + \frac{4}{3}(\pi)r_{\mathrm{Cl}}^3$$

$$= \frac{4}{3}(\pi)\left(r_{\mathrm{Cs}}^3 + r_{\mathrm{Cl}}^3\right)$$

$$= \frac{4}{3}(\pi)\left[(0.170 \text{ nm})^3 + (0.181 \text{ nm})^3\right] = 0.0454 \text{ nm}^3$$

The unit cell for CsCl is cubic, which means that the unit cell volume, V_C, is equal to

$$V_C = a^3$$

Here a is the unit cell edge length. This a parameter is related to the atomic radii of Cs and Cl according to a modified form of Equation 3.4 (for the BCC crystal structure, the relationship between the atomic radius, R and the unit cell edge length a). This expression for the CsCl crystal structure is as follows:

$$a = \frac{2r_{\mathrm{Cs}^+} + 2r_{\mathrm{Cl}^-}}{\sqrt{3}}$$

Incorporation of values for the ionic radii for both Cs and Cl leads to the following value for a:

$$a = \frac{2(0.170 \text{ nm}) + 2(0.181 \text{ nm})}{\sqrt{3}}$$

$$= 0.405 \text{ nm}$$

Thus, the unit cell volume for CsCl is computed as follows:

$$V_C = a^3$$

$$= (0.405\ \text{nm})^3 = 0.0664\ \text{nm}^3$$

And, finally the atomic packing factor for CsCl is just equal to the following:

$$\text{APF} = \frac{V_S}{V_C} = \frac{0.0454\ \text{nm}^3}{0.0664\ \text{nm}^3} = 0.684$$

12.16 *Calculate the theoretical density of NiO, given that it has the rock salt crystal structure.*

Solution

This density of NiO may be computed using Equation 12.1, which for this problem, is of the form

$$\rho = \frac{n'\left(\sum A_{\mathrm{Ni}} + \sum A_{\mathrm{O}}\right)}{V_C N_{\mathrm{A}}}$$

But because the formula unit is "NiO" then

$$\sum A_{\mathrm{Ni}} = A_{\mathrm{Ni}} = 58.69 \text{ g/mol}$$
$$\sum A_{\mathrm{O}} = A_{\mathrm{O}} = 16.00 \text{ g/mol}$$

This means that, for this problem, Equation 12.1 becomes the following:

$$\rho = \frac{n'\left(A_{\mathrm{Ni}} + A_{\mathrm{O}}\right)}{V_C N_{\mathrm{A}}} \tag{12.1a}$$

Since the crystal structure is rock salt, *n*' = 4 formula units per unit cell (because the rock salt crystal structure consists of two interpenetrating FCC structures—in this case, one for Ni^{2+} ions; the other for the and O^{2-} ions). At this point it becomes necessary to determine the value of the unit cell volume V_C. Because the unit cell has cubic symmetry, V_C and the unit cell edge length *a* are related as

$$V_C = a^3$$

From Example Problem 12.3, it may be noted, for the rock salt crystal structure, that *a*, the unit cell edge length is related to (in this case) the ionic radii of Ni and O ions ($r_{\mathrm{Ni}^{2+}}$ and $r_{\mathrm{O}^{2-}}$, respectively) as follows:

$$a = 2r_{\mathrm{Ni}^{2+}} + 2r_{\mathrm{O}^{2-}}$$

Which means that

$$V_C = a^3 = \left(2r_{\mathrm{Ni}^{2+}} + 2r_{\mathrm{O}^{2-}}\right)^3$$

The ionic radii of Ni^{2+} and O^{2-} from Table 12.3 are 0.069 nm and 0.140 nm, respectively. Therefore,

$$V_C = a^3 = \left(2r_{\mathrm{Ni}^{2+}} + 2r_{\mathrm{O}^{2-}}\right)^3 = \left[2(0.069 \text{ nm}) + 2(0.140 \text{ nm})\right]^3$$

$$= 0.0730\ \frac{\text{nm}^3}{\text{unit cell}} = 0.0730\ \frac{\text{nm}^3}{\text{unit cell}}\left(\frac{1\ \text{cm}}{10^7\ \text{nm}}\right)^3$$

$$= 7.30 \times 10^{-23}\ \text{cm}^3/\text{unit cell}$$

Finally, it is possible for us to compute the density of NiO incorporating Avogadro's number and values of the other parameters in Equation 12.1a, as follows:

$$\rho = \frac{(4\ \text{formula units/unit cell})(58.69\ \text{g/mol} + 16.00\ \text{g/mol})}{\left(7.30 \times 10^{-23}\ \text{cm}^3/\text{unit cell}\right)\left(6.022 \times 10^{23}\ \text{formula units/mol}\right)}$$

$$= 6.80\ \text{g/cm}^3$$

12.17 *Iron oxide (FeO) has the rock salt crystal structure and a density of 5.70 g/cm*^{3}.

(a) Determine the unit cell edge length.

(b) How does this result compare with the edge length as determined from the radii in Table 12.3, assuming that the Fe^{2+} *and* O^{2-} *ions just touch each other along the edges?*

Solution

(a) This part of the problem calls for us to determine the unit cell edge length for FeO. The density of FeO is 5.70 g/cm^3 and the crystal structure is rock salt. From Equation 12.1 the density of Fe, is of the form

$$\rho = \frac{n'\left(\sum A_{\text{Fe}} + \sum A_{\text{O}}\right)}{V_C N_{\text{A}}}$$

But because the formula unit is "FeO" then

$$\sum A_{\text{Fe}} = A_{\text{Fe}} = 55.85 \text{ g/mol}$$
$$\sum A_{\text{O}} = A_{\text{O}} = 16.00 \text{ g/mol}$$

This means that, for this problem, Equation 12.1 becomes the following:

$$\rho = \frac{n'\left(A_{\text{Fe}} + A_{\text{O}}\right)}{V_C N_{\text{A}}} \tag{12.1b}$$

Since the crystal structure is rock salt, n' = 4 formula units per unit cell (because the rock salt crystal structure consists of two interpenetrating FCC structures—in this case, one for Fe^{2+} ions; the other for the and O^{2-} ions). Because the unit cell has cubic symmetry, V_C and the unit cell edge length a are related as

$$V_C = a^3$$

This means that Equation 12.1b takes the form:

$$\rho = \frac{n'\left(A_{\text{Fe}} + A_{\text{O}}\right)}{a^3 N_{\text{A}}}$$

And solving this expression for a, the unit cell edge length (while incorporating atomic weight values—A_{Fe} = 55.85 g/mol and A_{O} = 16.00 g/mol) leads to

$$a = \left[\frac{n'\left(A_{\text{Fe}} + A_{\text{O}}\right)}{\rho N_{\text{A}}}\right]^{1/3}$$

$$= \left[\frac{(\text{4 formula units/unit cell})(55.85\ \text{g/mol} + 16.00\ \text{g/mol})}{(5.70\ \text{g/cm}^3)(6.022\times10^{23}\ \text{formula units/mol})}\right]^{1/3}$$

$$= 4.37 \times 10^{-8}\ \text{cm} = 0.437\ \text{nm}$$

(b) The edge length is to be determined from the Fe^{2+} and O^{2-} radii for this portion of the problem. From Example Problem 12.3, it may be noted, for the rock salt crystal structure, that *a*, the unit cell edge length is related to (in this case) the ionic radii of Fe and O ions $(r_{Fe^{2+}}$ and $r_{O^{2-}}$, respectively) as follows:

$$a = 2r_{Fe^{2+}} + 2r_{O^{2-}}$$

From Table 12.3,

$r_{Fe^{2+}} = 0.077$ nm

$r_{O^{2-}} = 0.140$ nm

Therefore, the unit cell edge length, as determined from ionic radii, is

$$a = 2r_{Fe^{2+}} + 2r_{O^{2-}}$$

$$= 2(0.077\ \text{nm}) + 2(0.140\ \text{nm}) = 0.434\ \text{nm}$$

This value is in excellent agreement with the value of *a* determined from part (a)—i.e., 0.437 nm.

12.18 *One crystalline form of silica (SiO_2) has a cubic unit cell, and from x-ray diffraction data it is known that the cell edge length is 0.700 nm. If the measured density is 2.32 g/cm^3, how many Si^{4+} and O^{2-}ions are there per unit cell?*

Solution

We are asked to determine the number of Si^{4+} and O^{2-} ions per unit cell for a crystalline form of silica (SiO_2). For this material, a = 0.700 nm and ρ = 2.32 g/cm^3. Solving for n' from Equation 12.1, we obtain the following:

$$n' = \frac{\rho V_C N_A}{\sum A_{Si} + \sum A_O} \qquad (12.1c)$$

Now if a formula (SiO_2) unit there is 1 Si^{4+} and 2O^{2-} ions. Therefore

$$\sum A_{Si} = A_{Si} = 28.09 \text{ g/mol}$$
$$\sum A_O = 2A_O = 2(16.00 \text{ g/mol}) = 32.00 \text{ g/mol}$$

(The atomic weight values for Si and O came from inside the front cover.)

Also, because the unit cell has cubic symmetry, it is the case that

$$V_C = a^3$$

Here, a is the unit cell edge length—viz., 0.700 nm $(\text{or } 7.00 \times 10^{-8} \text{ cm})$. Now, realizing that the density, ρ, has a value of 2.32 g/cm^3, the value of n' is determined from Equation 12.1c as follows"

$$n' = \frac{\rho V_C N_A}{\sum A_{Si} + \sum A_O}$$

$$= \frac{(2.32 \text{ g/cm}^3)(7.00 \times 10^{-8} \text{ cm})^3(6.022 \times 10^{23} \text{ formula units/mol})}{28.09 \text{ g/mol} + 32.00 \text{ g/mol}}$$

= 7.97 or almost 8

Therefore, there are 8 Si^{4+} ions and 16 O^{2-} ions per SiO_2 unit cell.

12.19 *(a) Using the ionic radii in Table 12.3, compute the theoretical density of CsCl. (Hint: Use a modification of the result of Problem 3.3.)*

(b) The measured density is 3.99 g/cm^3. How do you explain the slight discrepancy between your calculated value and the measured value?

Solution

(a) We are asked to compute the density of CsCl. To solve this problem it is necessary to use Equation 12.1—namely

$$\rho = \frac{n'\left(\sum A_{\mathrm{Cs}} + \sum A_{\mathrm{Cl}}\right)}{V_C N_{\mathrm{A}}} \tag{12.1d}$$

But because the formula unit is "CsCl" then

$$\sum A_{\mathrm{Cs}} = A_{\mathrm{Cs}} = 132.91 \text{ g/mol}$$

$$\sum A_{\mathrm{Cl}} = A_{\mathrm{Cl}} = 35.45 \text{ g/mol}$$

Now, in order to compute the unit cell volume, V_C, we make use of the result of Problem 3.3. This problem asks for us to confirm, for the BCC crystal structure, the equation that relates the unit cell edge length (*a*) and the atomic radius (*R*)—that is

$$a = \frac{4R}{\sqrt{3}} \tag{3.4}$$

For this demonstration in Problem 3.3, the "4*R*" in this equation is the length of a cube diagonal. For the CsCl crystal structure, this cube diagonal length is equal to $2r_{\mathrm{Cs}^+} + 2r_{\mathrm{Cl}^-}$ where

r_{Cs^+} = the radius of a Cs ion = 0.170 nm (Table 12.3)

r_{Cl^-} = the radius of a Cl ion = 0.181 nm (Table 12.3)

Thus, the modified form of Equation 3.4 (above) is

$$a = \frac{2r_{\mathrm{Cs}^+} + 2r_{\mathrm{Cl}^-}}{\sqrt{3}}$$

$$= \frac{2(0.170 \text{ nm}) + 2(0.181 \text{ nm})}{\sqrt{3}}$$

$$= 0.405 \text{ nm} = 4.05 \times 10^{-8} \text{ cm}$$

Since the unit cell volume, $V_C = a^3$, and for the CsCl crystal structure, $n' = 1$ formula unit/unit cell, we solve for the density of CsCl using Equation 12.1d as follows:

$$\rho = \frac{n'(A_{\text{Cs}} + A_{\text{Cl}})}{V_C N_{\text{A}}} = \frac{n'(A_{\text{Cs}} + A_{\text{Cl}})}{a^3 N_{\text{A}}}$$

$$\rho = \frac{(\text{1 formula unit/unit cell})(132.91\ \text{g/mol} + 35.45\ \text{g/mol})}{(4.05 \times 10^{-8}\ \text{cm})^3/\text{unit cell}\,(6.022 \times 10^{23}\ \text{formula units/mol})}$$

$$= 4.21\ \text{g/cm}^3$$

(b) This value of the density is greater than the measured density (3.99 g/cm^3). The reason for this discrepancy is that the ionic radii in Table 12.3, used for this computation, were for a coordination number of six, when, in fact, the coordination number of both Cs^+ and Cl^- is eight. The ionic radii should be slightly greater, leading to a larger V_C value, and a lower density.

12.20 *From the data in Table 12.3, compute the theoretical density of* CaF_2*, which has the fluorite structure.*

Solution

This problem asks that we compute the density of CaF_2. In order to solve this problem it is necessary to use Equation 12.1, which for our problem takes the form:

$$\rho = \frac{n'\left(\sum A_{\mathrm{Ca}} + \sum A_{\mathrm{F}}\right)}{V_C N_{\mathrm{A}}} \tag{12.1e}$$

But because the formula unit is "CaF_2" then

$$\sum A_{\mathrm{Ca}} = A_{\mathrm{Ca}} = \mathbf{40.08\ g/mol}$$

$$\sum A_{\mathrm{F}} = 2A_{\mathrm{F}} = (2)(19.00\ \mathrm{g/mol}) = 38.00\ \mathrm{g/mol}$$

It is now necessary to determine the unit cell volume, V_C. A unit cell of the fluorite structure is shown in Figure 12.5. It may be seen that there are four CaF_2 units per unit cell (i.e., *n'* = 4 formula units/unit cell). For each of the eight small cubes (or sub-cells) in the unit cell (as demonstrated in the solution to Problem 12.19), the sub-cell edge length *a* is equal to

$$a = \frac{2r_{\mathrm{Ca}^{2+}} + 2r_{\mathrm{F}^-}}{\sqrt{3}}$$

and, from Table 12.3

$r_{\mathrm{Ca}^{2+}} = 0.100\ \mathrm{nm}$

$r_{\mathrm{F}^-} = 0.133\ \mathrm{nm}$

Therefore,

$$a = \frac{2(0.100\ \mathrm{nm}) + 2(0.133\ \mathrm{nm})}{\sqrt{3}} = 0.269\ \mathrm{nm} = 2.69 \times 10^{-8}\ \mathrm{cm}$$

And the volume of the unit cell is just

$$V_C = (2a)^3 = \left[(2)(2.69 \times 10^{-3}\ \mathrm{cm})\right]^3 = 1.56 \times 10^{-22}\ \mathrm{cm}^3$$

Also, from Figure 12.5, it may be noted that the unit cell is composed of 4 formula units (CaF_2's), which means that *n'* in Equation 12.1e is 4. Now it is possible to solve for the density of calcium fluoride using Equation 12.1e as follows:

$$\rho = \frac{n'(A_{\mathrm{Ca}} + 2A_{\mathrm{F}})}{V_C N_{\mathrm{A}}}$$

$$= \frac{(4 \text{ formula units/unit cell})\left[40.08 \text{ g/mol} + (2)(19.00 \text{ g/mol})\right]}{\left(1.56 \times 10^{-22} \text{ cm}^3\text{/unit cell}\right)\left(6.022 \times 10^{23} \text{ formula units/mol}\right)}$$

$$= 3.32 \text{ g/cm}^3$$

The measured density is 3.18 g/cm^3.

12.21 *A hypothetical AX type of ceramic material is known to have a density of 2.10 g/cm^3 and a unit cell of cubic symmetry with a cell edge length of 0.57 nm. The atomic weights of the A and X elements are 28.5 and 30.0 g/mol, respectively. On the basis of this information, which of the following crystal structures is (are) possible for this material: sodium chloride, cesium chloride, or zinc blende? Justify your choice(s).*

Solution

We are asked to specify possible crystal structures for an AX type of ceramic material given its density (2.10 g/cm^3), that the unit cell has cubic symmetry with edge length of 0.57 nm, and the atomic weights of the A and X elements (28.5 and 30.0 g/mol, respectively). Solving for *n'* in Equation 12.1 leads to the following

$$n' = \frac{\rho V_C N_A}{\sum A_C + \sum A_A}$$

$$= \frac{(2.10\ \text{g/cm}^3)\left[(5.70 \times 10^{-8}\ \text{cm})^3/\text{unit cell}\right](6.022 \times 10^{23}\ \text{formula units/mol})}{(30.0\ \text{g/mol} + 28.5\ \text{g/mol})}$$

= 4.00 formula units/unit cell

Of the three possible crystal structures, only sodium chloride and zinc blende have four formula units per unit cell, and therefore, are possibilities.

12.22 *The unit cell for Fe_3O_4 (FeO-Fe_2O_3) has cubic symmetry with a unit cell edge length of 0.839 nm. If the density of this material is 5.24 g/cm^3, compute its atomic packing factor. For this computation, you will need to use the ionic radii listed in Table 12.3.*

Solution

This problem asks us to compute the atomic packing factor for Fe_3O_4 given its density and unit cell edge length. It is first necessary to determine the number of formula units in the unit cell in order to calculate the sphere volume. Solving for *n'* from Equation 12.1 leads to

$$n' = \frac{\rho V_C N_A}{\sum A_{Fe} + \sum A_O}$$

A formula unit of Fe_3O_4 consists of 3 iron ions and 4 oxygen ions; inasmuch as the atomic weights of iron and oxygen (A_{Fe} and A_O) are 55.85 g/mol and 16.00 g/mol, respectively (as cited inside the front cover of the book)—therefore,

$$\sum A_{\text{Fe}} = (3)(55.85\text{ g/mol}) = 167.55\text{ g/mol}$$

$$\sum A_{\text{O}} = (4)(16.00\text{ g/mol}) = 64.00\text{ g/mol}$$

In addition, the unit cell volume, V_C, is equal to a^3 where a is the unit cell edge length (0.839 nm as given in the problem statement). Since the density value is 5.24 g/cm^3 (as also provided in the problem statement), we calculate n' using the above equation as follows:

$$n' = \frac{\rho V_C N_A}{\sum A_{\text{Fe}} + \sum A_{\text{O}}}$$

$$= \frac{(5.24\text{ g/cm}^3)\left[(8.39 \times 10^{-8}\text{ cm})^3/\text{unit cell}\right](6.022 \times 10^{23}\text{ formula units/mol})}{(167.55\text{ g/mol}) + (64.00\text{ g/mol})}$$

$$= 8.0 \text{ formula units/unit cell}$$

Thus, in each FeO-Fe_2O_3 unit cell there are 8 Fe^{2+}, 16 Fe^{3+}, and 32 O^{2-} ions. From Table 12.3, $r_{\text{Fe}^{2+}}$ = 0.077 nm, $r_{\text{Fe}^{3+}}$ = 0.069 nm, and $r_{\text{O}^{2-}}$ = 0.140 nm. Thus, the total sphere volume in Equation 3.3 (which we denote as V_S), is the sum of the sphere volume of the 8 Fe^{2+}, 16 Fe^{3+}, and 32 O^{2-} ions as follows:

$$V_S = (8)\left(\frac{4}{3}\pi\right)(7.7 \times 10^{-9}\text{cm})^3 + (16)\left(\frac{4}{3}\pi\right)(6.9 \times 10^{-9}\text{cm})^3$$

$$+ (32)\left(\frac{4}{3}\pi\right)(1.40 \times 10^{-8}\text{ cm})^3$$

$$= 4.05 \times 10^{-22}\text{ cm}^3$$

And, as noted above, the unit cell volume (V_C) is just a^3, which means that

$$V_C = a^3 = (8.39 \times 10^{-8}\text{ cm})^3 = 5.90 \times 10^{-22}\text{ cm}^3$$

Finally, the atomic packing factor (APF) from Equation 3.3 is just

$$\text{APF} = \frac{V_S}{V_C} = \frac{4.05 \times 10^{-22}\text{ cm}^3}{5.90 \times 10^{-22}\text{ cm}^3} = 0.686$$

Silicate Ceramics

12.23 *In terms of bonding, explain why silicate materials have relatively low densities.*

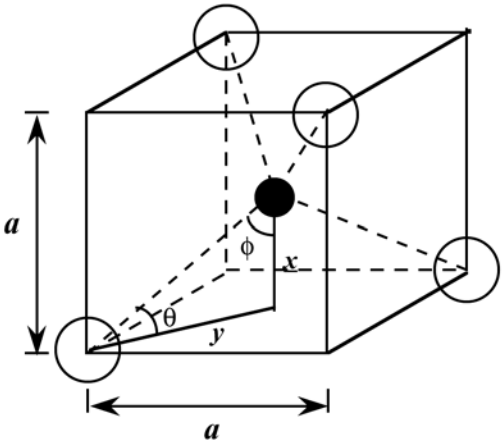
Answer

The silicate materials have relatively low densities because the atomic bonds have a high degree of covalency (Table 12.1), and, therefore, are directional. This limits the packing efficiency of the atoms, and therefore, the magnitude of the density.

12.24 *Determine the angle between covalent bonds in an* SiO_4^{4-} *tetrahedron.*

Solution

Below is shown a SiO_4^{4-} tetrahedron situated within a cube; oxygen atoms are represented by open circles, the Si atom by the dark circle.



Now if we extend the base diagonal (having a length of *y*) from one corner to the other, then

$$(2y)^2 = a^2 + a^2 = 2a^2$$

where *a* is the unit cell edge length. Now, solving the above expression for *y* gives

$$y = \frac{a\sqrt{2}}{2}$$

Furthermore, from he above illustration it may be noted that $x = a/2$, which means that

$$\tan\theta = \frac{x}{y} = \frac{\frac{a}{2}}{\frac{a\sqrt{2}}{2}} = \frac{1}{\sqrt{2}}$$

Now solving the above expression for the angle θ yields the following:

$$\theta = \tan^{-1}\left(\frac{1}{\sqrt{2}}\right) = 35.26°$$

Now, from the illustration shown above, we solve for the value of the angle ϕ realizing that the angle between the *x* and *y* line segments is a right angle (90°); therefore since the total of the angles in a triangle is 180° then

$$\phi = 180° - 90° - \theta$$

$$= 180° - 90° - 35.26° = 54.74°$$

Finally, from the above illustration the bond angle between two silicon atoms (those two atoms located on the base of this unit cell) is just 2ϕ, or $2\phi = (2)(54.74°) = 109.48°$.

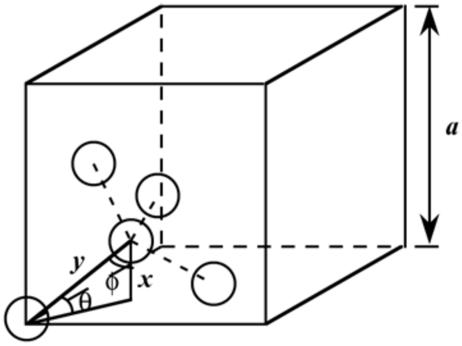
Carbon

12.25 *Compute the theoretical density of diamond, given that the C—C distance and bond angle are 0.154 nm and 109.5°, respectively. How does this value compare with the measured density?*

Solution

This problem asks that we compute the theoretical density of diamond given that the C—C distance and bond angle are 0.154 nm and 109.5°, respectively. To compute the density of diamond it is necessary that we use Equation 12.1. However, in order to do this it is necessary to determine the unit cell edge length (*a*) from the given C—C distance. Once we know the value of *a* it is possible to calculate the unit cell volume (V_C) since, because the unit cell is a cube, $V_C = a^3$.

The drawing below shows the cubic unit cell with those carbon atoms that bond to one another in one-quarter of the unit cell.



From this figure, ϕ is one-half of the bond angle or ϕ = 109.5°/2 = 54.75°; but since the triangle having sides labeled *x* and *y* is a right triangle then

$$\theta + \phi = 90°$$

or that

$$\theta = 90° - 54.75° = 35.25°$$

Also, we are given in the problem statement that y = 0.154 nm, the carbon-carbon bond distance. Furthermore, it is the case that $x = a/4$, and therefore,

$$x = \frac{a}{4} = y \sin \theta$$

Or

$$a = 4y \sin \theta = (4)(0.154 \text{ nm})(\sin 35.25°) = 0.356 \text{ nm}$$

$$= 3.56 \times 10^{-8} \text{ cm}$$

As noted above, the unit cell volume, V_C is just a^3, that is

$$V_C = a^3 = (3.56 \times 10^{-8} \text{ cm})^3 = 4.51 \times 10^{-23} \text{ cm}^3$$

It is necessary that we use a modified form of Equation 12.1, because there is only one atom type—that is

$$\rho = \frac{n'A_C}{V_C N_A} \tag{12.1f}$$

where A_C is the atomic weight of carbon (12.01 g/mol). The parameter n' in this equation represents the number of carbon atoms per unit cell. The unit cell for diamond, Figure 12.16, consists of a face-centered cubic arrangement of carbon atoms, and, in addition, 4 carbon atoms that are situated within the interior of the unit cell. From Equation 3.2 (Section 3.4) the number of equivalent atoms in a FCC unit cell is 4; which means that n'= 8 when we add in the 4 interior carbon atoms. Therefore, the density of diamond is computed using the above Equation 12.1f, as follows:

$$\rho = \frac{n'A_C}{V_C N_A}$$

$$= \frac{(8 \text{ atoms/unit cell})(12.01 \text{ g/g-atom})}{(4.51 \times 10^{-23} \text{ cm}^3\text{/unit cell})(6.022 \times 10^{23} \text{ atoms/g-atom})}$$

$$= 3.54 \text{ g/cm}^3$$

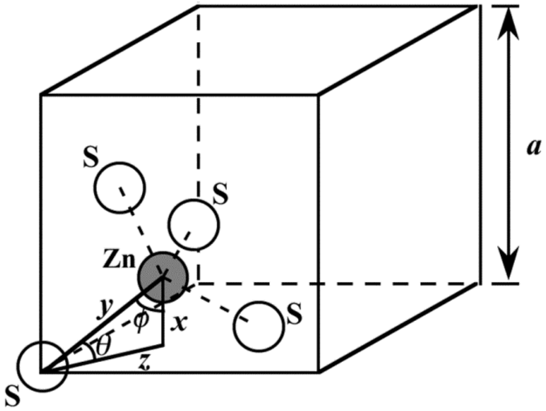
The measured density is 3.51 g/cm^3.

12.26 *Compute the theoretical density of ZnS, given that the Zn—S distance and bond angle are 0.234 nm and 109.5°, respectively. How does this value compare with the measured density?*

Solution

This problem asks that we compute the theoretical density of ZnS given that the Zn—S distance and bond angle are 0.234 nm and 109.5°, respectively. To compute the density of zinc sulfide it is necessary that we use Equation 12.1. However, in order to do this it is necessary to determine the unit cell edge length (a) from the given Zn—S distance. Once we know the value of a it is possible to calculate the unit cell volume (V_C) since, because the unit cell is a cube, $V_C = a^3$.

The drawing below shows the cubic unit cell that shows one Zn atom, which bonds to four sulfur atoms within one-quarter of the unit cell.



From this figure, ϕ is one-half of the bond angle between the Zn atom and the two S atoms in the bottom plane. Thus $\phi = 109.5°/2 = 54.75°$; but since the triangle having sides labeled x, y, and z is a right triangle, and the angle between sides x and z is 90°, □□□□

$$\theta + \phi = 90°$$

or

$$\theta = 90° - 54.75° = 35.25°$$

Also, we are given in the problem statement that $y = 0.234$ nm, the Zn-S bond distance.
Furthermore, it is the case that $x = a/4$, and therefore,

$$x = \frac{a}{4} = y \sin \theta$$

Or

$$a = 4y \sin \theta = (4)(0.234 \text{ nm})(\sin 35.25°) = 0.540 \text{ nm}$$

$$= 5.40 \times 10^{-8} \text{ cm}$$

As noted above, the unit cell volume, V_C is just a^3, that is

$$V_C = a^3 = (5.40 \times 10^{-8} \text{ cm})^3 = 1.575 \times 10^{-22} \text{ cm}^3$$

Now, for this problem, Equation 12.1 reads as follows:

$$\rho = \frac{n'\left(\sum A_{\text{Zn}} + \sum A_{\text{S}}\right)}{V_C N_{\text{A}}} \tag{12.1g}$$

where

$\sum A_{\text{Zn}}$ equals the sum of the atomic weights of all Zn atoms in a formula (ZnS) unit, which is just the atomic weight of Zn (A_{Zn} = 65.41 g/mol) because there is only 1 Zn atom in an ZnS unit. Similarly

$\sum A_{\text{S}}$ equals the sum of the atomic weights of all S atoms in a ZnS unit = A_{S} = 32.06 g/mol.

Now, the parameter *n'* in this equation represents the number of Zn-S units per unit cell. Because the unit cell for ZnS contains equal numbers of Zn and S atoms, it is necessary only to determine the number of either Zn or S atoms in the unit cell. From Figure 12.4, which represents a unit cell for ZnS, it may be noted that the sulfur atoms form a face-centered cubic structure. From Equation 3.2 (Section 3.4) the number of equivalent atoms in a FCC unit cell is 4, and thus there are 4 ZnS units per unit cell, or that *n'* = 4. Therefore, the density of ZnS is computed using the above Equation 12.1g, as follows:

$$\rho = \frac{n'\left(\sum A_{\text{Zn}} + \sum A_{\text{S}}\right)}{V_C N_{\text{A}}}$$

$$= \frac{(4 \text{ Zn-S units/unit cell})(65.41 \text{ g/mol} + 32.06 \text{ g/mol})}{\left(1.575 \times 10^{-22} \text{ cm}^3\text{/unit cell}\right)\left(6.022 \times 10^{23} \text{ atoms/mol}\right)}$$

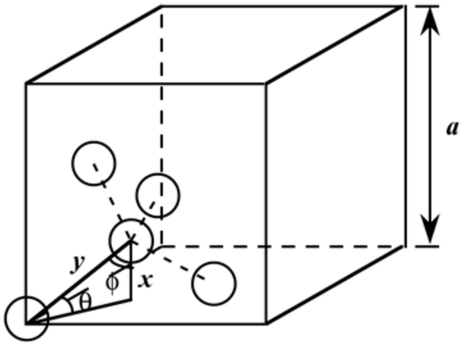
$$= 4.11 \text{ g/cm}^3$$

The measured density is 4.10 g/cm^3.

12.27 *Compute the atomic packing factor for the diamond cubic crystal structure (Figure 12.16). Assume that bonding atoms touch one another, that the angle between adjacent bonds is 109.5°, and that each atom internal to the unit cell is positioned a/4 of the distance away from the two nearest cell faces (a is the unit cell edge length).*

Solution

We are asked in this problem to compute the atomic packing factor for the diamond cubic crystal structure, given that the angle between adjacent bonds is 109.5°. Let us consider he drawing below, which represents the diamond cubic unit cell with those carbon atoms that bond to one another in one-quarter of the unit cell.



Using the above sketch the first thing that we must do is to determine the unit cell volume V_C in terms of the atomic radius *r*. The carbon atom that resides at the intersection between lines *x* and *y* is one-quarter of the distance between from the top and bottom faces, as noted in the problem statement—that is, *x* = *a*/4. Furthermore, from the triangle comprised of sizes denoted *x*, *y*, and *z* the following relationship exists:

$$\sin\theta = \frac{x}{y}$$

or that $x = y\sin\theta$. And, since *x* = *a*/4 it is the case that

$$x = \frac{a}{4} = y \sin \theta$$

Or

$$a = 4y \sin \theta \qquad \text{(S12.27)}$$

Because the two C atoms that are located at the end of the line segment labeled "*y*" touch one another, it the case that *y* = 2*r*. Furthermore, from the above sketch, it may be noted that ϕ is one-half of the bond angle or $\phi = 109.5°/2 = 54.75°$; but since this triangle having sides labeled *x*, *y*, and *z* is a right triangle then

$$\theta + \phi = 90^\circ$$

or that

$$\theta = 90^\circ - 54.75^\circ = 35.25^\circ$$

Thus, we may compute the unit cell edge length using Equation S12.27 as follows:

$$a = 4y \sin\theta$$

$$= (4)(2r)(\sin 35.25^\circ) = 4.62r$$

Furthermore, since the unit cell is cubic, $V_C = a^3$, and therefore

$$V_C = (4.617r)^3 = 98.42\ r^3$$

Now, it is necessary to determine the sphere volume in the unit cell, V_S, in terms of r. For this unit cell (Figure 12.16) there are 4 interior atoms, 6 face atoms, and 8 corner atoms. Thus, from Equation 3.2, the number of equivalent atoms per unit cell is

$$N = N_i + \frac{N_f}{2} + \frac{N_c}{8}$$

$$= 4 + \frac{6}{2} + \frac{8}{8}$$

$$= 8 \text{ atoms/unit cell}$$

Therefore, inasmuch as the volume of a sphere of radius r is equal to

$$V = \frac{4}{3}\pi r^3$$

The total sphere volume within a unit cell V_S is equal to

$$V_S = (8)\left(\frac{4}{3}\pi r^3\right) = 33.51\ r^3$$

Finally, the atomic packing factor is determined using Equation 3.3 as follows:

$$\text{APF} = \frac{V_S}{V_C} = \frac{33.51\ r^3}{98.42\ r^3} = 0.340$$

Imperfections in Ceramics

12.28 *Would you expect Frenkel defects for anions to exist in ionic ceramics in relatively large concentrations? Why or why not?*

Answer

Frenkel defects for anions would not exist in appreciable concentrations because the anion (of an anion vacancy-anion interstitial pair) is quite large and is highly unlikely to exist as an interstitial.

12.29 *Calculate the fraction of lattice sites that are Schottky defects for cesium chloride at its melting temperature (645°C). Assume an energy for defect formation of 1.86 eV.*

Solution

In order to solve this problem it is necessary to use Equation 12.3 and solve for the N_s/N ratio. Rearrangement of Equation 12.3 and substituting values for temperature and the energy of defect formation (Q_s) given in the problem statement leads to

$$\frac{N_s}{N} = \exp\left(-\frac{Q_s}{2kT}\right)$$

$$= \exp\left[-\frac{1.86 \text{ eV}}{(2)(8.62 \times 10^{-5} \text{ eV/K})(645 + 273 \text{ K})}\right]$$

$$= 7.87 \times 10^{-6}$$

12.30 *Calculate the number of Frenkel defects per cubic meter in silver chloride at 350°C. The energy for defect formation is 1.1 eV, whereas the density for AgCl is 5.50 g/cm^3 at 350°C.*

Solution

Solution of this problem is possible using Equation 12.2. However, we must first determine the value of N, the number of lattice sites per cubic meter, which is possible using a modified form of Equation 4.2, which is given as follows:

$$N = \frac{N_A \rho}{A_{Ag} + A_{Cl}}$$

in which A_{Ag} and A_{Cl} are, respectively, the atomic weights of Ag and Cl (i.e., 107.87 g/mol and 35.45 g/mol). Thus, using the above equation we calculate the value for N

$$N = \frac{(6.022 \times 10^{23} \text{ atoms/mol})(5.50 \text{ g/cm}^3)(10^6 \text{ cm}^3/\text{m}^3)}{107.87 \text{ g/mol} + 35.45 \text{ g/mol}}$$

$$= 2.31 \times 10^{28} \text{ lattice sites/m}^3$$

And, finally the value of N_{fr} is computed using Equation 12.2 as

$$N_{fr} = N \exp\left(-\frac{Q_{fr}}{2kT}\right)$$

$$= (2.31 \times 10^{28} \text{ lattice sites/m}^3) \exp\left[-\frac{1.1 \text{ eV}}{(2)(8.62 \times 10^{-5} \text{ eV/K})(350 + 273 \text{ K})}\right]$$

$$= 8.24 \times 10^{23} \text{ defects/m}^3$$

12.31 *Using the following data that relate to the formation of Schottky defects in some oxide ceramic (having the chemical formula MO), determine the following:*

(a) The energy for defect formation (in eV)

(b) The equilibrium number of Schottky defects per cubic meter at 1000°C

(c) The identity of the oxide (i.e., what is the metal M?)

T (°C)	ρ (g/cm^3)	N_s (m^{-3})
750	3.50	5.7×10^9
1000	3.45	?
1500	3.40	5.8×10^{17}

Solution

This problem provides for some oxide ceramic, at temperatures of 750°C and 1500°C, values for density and the number of Schottky defects per cubic meter. The (a) portion of the problem asks that we compute the energy for defect formation. To begin, let us combine a modified form of Equation 4.2—viz.

$$N = \left(\frac{N_A \rho}{A_M + A_O}\right)$$

where A_M and A_O are the atomic weights of the metal M and oxygen, respectively, with Equation 12.3

$$N_s = N \exp\left(-\frac{Q_s}{2kT}\right)$$

which leads to the following:

$$N_s = \left(\frac{N_A \rho}{A_M + A_O}\right) \exp\left(-\frac{Q_s}{2kT}\right)$$

Inasmuch as this is a hypothetical oxide material, we don't know the atomic weight of metal M, nor the value of Q_s in the above equation. Therefore, let us write equations of the above form for two temperatures, T_1 and T_2. These expressions are as follows:

$$N_{s1} = \left(\frac{N_A \rho_1}{A_M + A_O}\right) \exp\left(-\frac{Q_s}{2kT_1}\right) \qquad (12.S1a)$$

$$N_{s2} = \left(\frac{N_A \rho_2}{A_M + A_O}\right) \exp\left(-\frac{Q_s}{2kT_2}\right) \qquad (12.S1b)$$

Dividing the first of these equations by the second leads to

$$\frac{N_{s1}}{N_{s2}} = \frac{\left(\dfrac{N_A \rho_1}{A_M + A_O}\right) \exp\left(-\dfrac{Q_s}{2kT_1}\right)}{\left(\dfrac{N_A \rho_2}{A_M + A_O}\right) \exp\left(-\dfrac{Q_s}{2kT_2}\right)}$$

which, after some algebraic manipulation, reduces to the form

$$\frac{N_{s1}}{N_{s2}} = \frac{\rho_1}{\rho_2} \exp\left[-\frac{Q_s}{2k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] \tag{12.S2}$$

Now, taking natural logarithms of both sides of this equation gives

$$\ln\left(\frac{N_{s1}}{N_{s2}}\right) = \ln\left(\frac{\rho_1}{\rho_2}\right) - \frac{Q_s}{2k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

And solving for Q_s from the above equation leads to the expression

$$Q_s = \frac{-2k\left[\ln\left(\dfrac{N_{s1}}{N_{s2}}\right) - \ln\left(\dfrac{\rho_1}{\rho_2}\right)\right]}{\dfrac{1}{T_1} - \dfrac{1}{T_2}}$$

Let us take T_1 = 750°C and T_2 = 1500°C, and we may compute the value of Q_s as follows:

$$Q_s = \frac{-(2)(8.62 \times 10^{-5}\ \text{eV/K})\left[\ln\left(\dfrac{5.7 \times 10^{9}\ \text{m}^{-3}}{5.8 \times 10^{17}\ \text{m}^{-3}}\right) - \ln\left(\dfrac{3.50\ \text{g/cm}^3}{3.40\ \text{g/cm}^3}\right)\right]}{\dfrac{1}{750 + 273\ \text{K}} - \dfrac{1}{1500 + 273\ \text{K}}}$$

$$= 7.70\ \text{eV}$$

(b) It is now possible to solve for N_s at 1000°C using Equation 12.S2 above. This time let's take T_1 = 1000°C and T_2 = 750°C. Thus, solving for N_{s1}, substituting values provided in the problem statement and Q_s determined above yields

$$N_{s1} = \frac{N_{s2}\,\rho_1}{\rho_2} \exp\left[-\frac{Q_s}{2k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]$$

$$= \frac{(5.7 \times 10^{9}\ \text{m}^{-3})(3.45\ \text{g/cm}^{3})}{3.50\ \text{g/cm}^{3}} \exp\left[-\frac{7.70\ \text{eV}}{(2)(8.62 \times 10^{-5}\ \text{eV/K})}\left(\frac{1}{1000 + 273\ \text{K}} - \frac{1}{750 + 273\ \text{K}}\right)\right]$$

$$= 2.98 \times 10^{13}\ \text{m}^{-3}$$

(c) And, finally, we want to determine the identity of metal M. This is possible by computing the atomic weight of M (A_M) from Equation 12.S1a. Rearrangement of this expression leads to

$$\left(\frac{N_A \rho_1}{A_M + A_O}\right) = N_{s1} \exp\left(\frac{Q_s}{2kT_1}\right)$$

And, after further algebraic manipulation yields the following equation:

$$\left[\frac{N_A \rho_1}{N_{s1} \exp\left(\dfrac{Q_s}{2kT_1}\right)}\right] = A_M + A_O$$

And, solving this expression for A_M gives

$$A_M = \left[\frac{N_A \rho_1}{N_{s1} \exp\left(\dfrac{Q_s}{2kT_1}\right)}\right] - A_O$$

Now, assuming that T_1 = 750°C, the value of A_M is

$$A_M = \left\{\frac{(6.022 \times 10^{23}\ \text{ions/mol})(3.50\ \text{g/cm}^{3})(10^{6}\ \text{cm}^{3}/\text{m}^{3})}{(5.7 \times 10^{9}\ \text{ions/m}^{3}) \exp\left[\dfrac{7.7\ \text{eV}}{(2)(8.62 \times 10^{-5}\ \text{eV/K})(750 + 273\ \text{K})}\right]}\right\} - 16.00\ \text{g/mol}$$

$$= 24.45\ \text{g/mol}$$

Upon consultation of the periodic table in Figure 2.8, the divalent metal (i.e., that forms M^{2+} ions) that has an atomic weight closest to 24.45 g/mol is magnesium (with an atomic weight of 24.31 g/mol). Thus, this metal oxide is MgO.

12.32 *In your own words, briefly define the term* stoichiometric.

Answer

Stoichiometric means having exactly the ratio of anions to cations as specified by the chemical formula for the compound.

12.33 *If cupric oxide (CuO) is exposed to reducing atmospheres at elevated temperatures, some of the* Cu^{2+} *ions will become* Cu^{+}.

(a) Under these conditions, name one crystalline defect that you would expect to form in order to maintain charge neutrality.

(b) How many Cu^{+} *ions are required for the creation of each defect?*

(c) How would you express the chemical formula for this nonstoichiometric material?

Solution

(a) For a $Cu^{2+}O^{2-}$ compound in which a small fraction of the copper ions exist as Cu^{+}, for each Cu^{+} formed there is one less positive charge introduced (or one more negative charge). In order to maintain charge neutrality, we must either add an additional positive charge or subtract a negative charge. This may be accomplished be either creating Cu^{2+} interstitials or O^{2-} vacancies.

(b) There will be two Cu^{+} ions required for each of these defects.

(c) The chemical formula for this nonstoichiometric material is $\mathbf{Cu_{1+\mathit{x}}O}$ or $\mathbf{CuO_{1-\mathit{x}}}$, where x is some small fraction.

12.34 *Do the Hume-Rothery rules (Section 4.3) also apply to ceramic systems? Explain your answer.*

Answer

For metals, for appreciable solid solubility of one metal in another, the following characteristics of the metals must be the same or similar:

1. *Atomic size* (< ±15%)
2. *Crystal structure*
3. *Electronegativity*
4. *Valence*

A similar set of rules exist for one ceramics—that is, in order to have appreciable solid solubility of one ceramic compound in another the following rules must be satisfied:

1. Atomic size factor—similar to that for metallic systems for both cations and anions
2. Valence factor—valences (charges on) anions should be the same; also the same for cations
3. Crystal structures of the two compounds should be the same or similar
4. Other ceramic compounds may form (i.e., solid solubility is limited) when there is a difference in the electronic structure between the cations and/or anions of the two compounds.

12.35 *Which of the following oxides would you expect to form substitutional solid solutions that have complete (i.e., 100%) solubility with MgO? Explain your answers.*

(a) FeO

(b) BaO

(c) PbO

(d) CoO

Answer

In order to have a high degree (or 100% solubility) of one ceramic compound in another ceramic compound, the following criteria must be met: the relative sizes of cations/anions must be similar (< ±15%); the valence (or charges) on the cations and anions of both compounds must be the same; and the crystals structures of the two compounds must the same or similar. Inasmuch as crystal structure information for the compounds in this problem, for the most part, is not provided in the text, we will base our criteria only on the relative ion sizes and charges on the anions and cations. Because all of these ceramics are oxides and the charge on all of the cations is +2, in making solubility determinations, only the relative sizes of the cations will be considered.

(a) For FeO, the ionic radii of the Mg^{2+} and Fe^{2+} (found inside the front cover of the book) are 0.072 nm and 0.077 nm, respectively. Therefore the percentage difference in ionic radii, $\Delta r\%$ is determined as follows:

$$\Delta r\% = \frac{r_{\mathrm{Fe}^{2+}} - r_{\mathrm{Mg}^{2+}}}{r_{\mathrm{Fe}^{2+}}} \times 100$$

$$= \frac{0.077 \text{ nm} - 0.072 \text{ nm}}{0.077 \text{ nm}} \times 100 = 6.5\%$$

which value is with the acceptable range for a high degree of solubility. Furthermore, as Table 12.4 notes, the crystal structures of both MgO and FeO are rock salt; therefore, it is expected that FeO and MgO form high degrees of solid solubility. Experimentally, these two ceramics exhibit 100% solubility.

(b) For BaO, the ionic radii of the Mg^{2+} and Ba^{2+} (found inside the front cover of the book) are 0.072 nm and 0.136 nm, respectively. Therefore the percentage difference in ionic radii, $\Delta r\%$ is determined as follows:

$$\Delta r\% = \frac{r_{\mathrm{Ba}^{2+}} - r_{\mathrm{Mg}^{2+}}}{r_{\mathrm{Ba}^{2+}}} \times 100$$

$$= \frac{0.136 \text{ nm} - 0.072 \text{ nm}}{0.136 \text{ nm}} \times 100 = 47\%$$

This Δ*r*% value is much larger than the ±15% range, and, therefore, BaO is not expected to experience any appreciable solubility in MgO. Experimentally, the solubility of BaO in MgO is very small; this is also the case for the solubility of MgO in BaO.

(c) For PbO, the ionic radii of the Mg^{2+} and Pb^{2+} (found inside the front cover of the book) are 0.072 nm and 0.120 nm, respectively. Therefore the percentage difference in ionic radii, Δ*r*% is determined as follows:

$$\Delta r\% = \frac{r_{Pb^{2+}} - r_{Mg^{2+}}}{r_{Pb^{2+}}} \times 100$$

$$= \frac{0.120 \text{ nm} - 0.072 \text{ nm}}{0.120 \text{ nm}} \times 100 = 40\%$$

This Δ*r*% value is much larger than the ±15% range, and, therefore, PbO is not expected to experience any appreciable solubility in MgO.

(d) For CoO, the ionic radii of the Mg^{2+} and Co^{2+} (found inside the front cover of the book) are 0.072 nm and 0.072 nm, respectively. Therefore the percentage difference in ionic radii, Δ*r*% is determined as follows:

$$\Delta r\% = \frac{r_{Co^{2+}} - r_{Mg^{2+}}}{r_{Co^{2+}}} \times 100$$

$$= \frac{0.072 \text{ nm} - 0.072 \text{ nm}}{0.072 \text{ nm}} \times 100 = 0\%$$

which value is, of course, within the acceptable range for a high degree (probably 100%) of solubility.

12.36 *(a) Suppose that CaO is added as an impurity to* Li_2O*. If the* Ca^{2+} *substitutes for* Li^+*, what kind of vacancies would you expect to form? How many of these vacancies are created for every* Ca^{2+} *added?*

(b) Suppose that CaO is added as an impurity to $CaCl_2$*. If the* O^{2-} *substitutes for* Cl^-*, what kind of vacancies would you expect to form? How many of these vacancies are created for every* O^{2-} *added*?

Solution

(a) For Ca^{2+} substituting for Li^+ in Li_2O, lithium vacancies would be created. For each Ca^{2+} substituting for Li^+, one positive charge is added; in order to maintain charge neutrality, a single positive charge may be removed. Positive charges are eliminated by creating lithium vacancies, and for every Ca^{2+} ion added, a single lithium vacancy is formed.

(b) For O^{2-} substituting for Cl^- in $CaCl_2$, chlorine vacancies would be created. For each O^{2-} substituting for a Cl^-, one negative charge is added; negative charges are eliminated by creating chlorine vacancies. In order to maintain charge neutrality, one O^{2-} ion will lead to the formation of one chlorine vacancy.

12.37 *What point defects are possible for* Al_2O_3 *as an impurity in MgO? How many* Al^{3+} *ions must be added to form each of these defects?*

Solution

For every Al^{3+} ion that substitutes for Mg^{2+} in MgO, a single positive charge is added. Thus, in order to maintain charge neutrality, either a positive charge must be removed or a negative charge must be added.

Negative charges are added by creating O^{2-} interstitials, which are not likely to form.

Positive charges may be removed by forming Mg^{2+} vacancies, and one magnesium vacancy would be formed for every two Al^{3+} ions added.

Ceramic Phase Diagrams

12.38 *For the ZrO_2–CaO system (Figure 12.24), write all eutectic and eutectoid reactions for cooling.*

Solution

There is only one eutectic for the portion of the ZrO_2-CaO system shown in Figure 12.24, which, upon cooling, is

$$\textbf{Liquid} \rightarrow \textbf{cubic } \mathbf{ZrO_2} + \mathbf{CaZrO_3}$$

There are two eutectoids, which reactions are as follows:

$$\textbf{tetragonal} \rightarrow \textbf{monoclinic } \mathbf{ZrO_2} + \textbf{cubic } \mathbf{ZrO_2}$$

$$\textbf{cubic} \rightarrow \textbf{monoclinic } \mathbf{ZrO_2} + \mathbf{CaZr_4O_9}$$

12.39 *From Figure 12.23, the phase diagram for the MgO–*Al_2O_3 *system, it may be noted that the spinel solid solution exists over a range of compositions, which means that it is nonstoichiometric at compositions other than 50 mol% MgO–50 mol%* Al_2O_3.

(a) The maximum nonstoichiometry on the Al_2O_3*-rich side of the spinel phase field exists at about 2000°C (3630°F), corresponding to approximately 82 mol% (92 wt%)* Al_2O_3*. Determine the type of vacancy defect that is produced and the percentage of vacancies that exist at this composition.*

(b) The maximum nonstoichiometry on the MgO-rich side of the spinel phase field exists at about 2000°C (3630°F), corresponding to approximately 39 mol% (62 wt%) Al_2O_3*. Determine the type of vacancy defect that is produced and the percentage of vacancies that exist at this composition.*

Solution

(a) For this portion of the problem we are to determine the type of vacancy defect that is produced on the Al_2O_3-rich side of the spinel phase field (Figure 12.23) and the percentage of these vacancies at the maximum nonstoichiometry (82 mol% Al_2O_3). On the alumina-rich side of this phase field, there is an excess of Al^{3+} ions, which means that some of the Al^{3+} ions substitute for Mg^{2+} ions. In order to maintain charge neutrality, Mg^{2+} vacancies are formed, and for every Mg^{2+} vacancy formed, two Al^{3+} ions substitute for three Mg^{2+} ions.

Now, we will calculate the percentage of Mg^{2+} vacancies that exist at 82 mol% Al_2O_3. Let us arbitrarily choose as our basis 50 MgO-Al_2O_3 units of the stoichiometric material, which consists of 50 Mg^{2+} ions and 100 Al^{3+} ions. Furthermore, let us designate the number of Mg^{2+} vacancies as x, which means that $2x$ Al^{3+} ions have been added and $3x$ Mg^{2+} ions have been removed (two of which are filled with Al^{3+} ions). Using our 50 MgO-Al_2O_3 unit basis, the number of moles of Al_2O_3 in the nonstoichiometric material is $(100 + 2x)/2$; similarly the number of moles of MgO is $(50 – 3x)$. Thus, the expression for the mol% of Al_2O_3 is just

$$\text{mol\% } Al_2O_3 = \left[\frac{\dfrac{100 + 2x}{2}}{\dfrac{100 + 2x}{2} + (50 - 3x)}\right] \times 100$$

If we solve for x when the mol% of Al_2O_3 = 82, then x = 12.1. Thus, adding $2x$ or (2)(12.1) = 24.2 Al^{3+} ions to the original material consisting of 100 Al^{3+} and 50 Mg^{2+} ions will produce 12.1 Mg^{2+} vacancies. Therefore, the percentage of vacancies is just

$$\text{\% vacancies} = \frac{12.1}{100 + 50} \times 100 = 8.1\%$$

(b) Now, we are asked to make the same determinations for the MgO-rich side of the spinel phase field, for 39 mol% Al_2O_3. In this case, Mg^{2+} ions are substituting for Al^{3+} ions. Since the Mg^{2+} ion has a lower charge than the Al^{3+} ion, in order to maintain charge neutrality, negative charges must be eliminated, which may be accomplished by introducing O^{2-} vacancies. For every 2 Mg^{2+} ions that substitute for 2 Al^{3+} ions, one O^{2-} vacancy is formed.

Now, we will calculate the percentage of O^{2-} vacancies that exist at 39 mol% Al_2O_3. Let us arbitrarily choose as our basis 50 MgO-Al_2O_3 units of the stoichiometric material, which consists of 50 Mg^{2+} ions 100 Al^{3+} ions. Furthermore, let us designate the number of O^{2-} vacancies as *y*, which means that 2*y* Mg^{2+} ions have been added and 2*y* Al^{3+} ions have been removed. Using our 50 MgO- Al_2O_3 unit basis, the number of moles of Al_2O_3 in the nonstoichiometric material is (100 – 2*y*)/2; similarly the number of moles of MgO is (50 + 2*y*). Thus, the expression for the mol% of Al_2O_3 is just

$$\text{mol\% } Al_2O_3 = \left[\frac{\dfrac{100 - 2y}{2}}{\dfrac{100 - 2y}{2} + (50 + 2y)}\right] \times 100$$

If we solve for *y* when the mol% of Al_2O_3 = 39, then *y* = 7.91. Thus, 7.91 O^{2-} vacancies are produced in the original material that had 200 O^{2-} ions. Therefore, the percentage of vacancies is just

$$\% \text{ vacancies} = \frac{7.91}{200} \times 100 = 3.96\%$$

12.40 *When kaolinite clay [$Al_2(Si_2O_5)(OH)_4$] is heated to a sufficiently high temperature, chemical water is driven off.*

(a) Under these circumstances, what is the composition of the remaining product (in weight percent Al_2O_3)?

(b) What are the liquidus and solidus temperatures of this material?

Solution

(a) The chemical formula for kaolinite clay may also be written as Al_2O_3–$2SiO_2$-$2H_2O$. Thus, if we remove the chemical water, the formula becomes Al_2O_3–$2SiO_2$. The formula weight for Al_2O_3 is just (2)(26.98 g/mol) + (3)(16.00 g/mol) = 101.96 g/mol; and for SiO_2 the formula weight is 28.09 g/mol + (2)(16.00 g/mol) = 60.09 g/mol. Thus, the composition of this product, in terms of the concentration of Al_2O_3, $C_{\mathrm{Al_2O_3}}$, in weight percent is just

$$C_{\mathrm{Al_2O_3}} = \frac{101.96 \text{ g/mol}}{101.96 \text{ g/mol} + (2)(60.09 \text{ g/mol})} \times 100 = 45.9 \text{ wt\%}$$

(b) The liquidus and solidus temperatures for this material as determined from the SiO_2–Al_2O_3 phase diagram, Figure 12.25, are 1825°C and 1587°C, respectively.

Brittle Fracture of Ceramics

12.41 *Briefly answer the following:*

(a) Why may there be significant scatter in the fracture strength for some given ceramic material?

(b) Why does the fracture strength increase with decreasing specimen size?

Answer

(a) There may be significant scatter in the fracture strength for some given ceramic material because the fracture strength depends on the probability of the existence of a flaw that is capable of initiating a crack; this probability varies from specimen to specimen of the same material.

(b) The fracture strength increases with decreasing specimen size because as specimen size decreases, the probably of the existence of a flaw of that is capable of initiating a crack diminishes.

12.42 *The tensile strength of brittle materials may be determined using a variation of Equation 8.1. Compute the critical crack tip radius for a glass specimen that experiences tensile fracture at an applied stress of 70 MPa (10,000 psi). Assume a critical surface crack length of* 10^{-2} *mm and a theoretical fracture strength of E/10, where E is the modulus of elasticity.*

Solution

We are asked for the critical crack tip radius for a glass. From Equation 8.1

$$\sigma_m = 2\sigma_0\left(\frac{a}{\rho_t}\right)^{1/2}$$

Fracture will occur when σ_m reaches the fracture strength of the material, which is given as $E/10$; thus

$$\frac{E}{10} = 2\sigma_0\left(\frac{a}{\rho_t}\right)^{1/2}$$

Or, solving for ρ_t

$$\rho_t = \frac{400\, a\sigma_0^2}{E^2}$$

From Table 12.5, for glass E = 69 GPa (or 69 × 10^3 MPa)—thus, we compute the value of ρ_t as follows:

$$\rho_t = \frac{(400)(1 \times 10^{-2}\text{ mm})(70\text{ MPa})^2}{(69 \times 10^3\text{ MPa})^2}$$

$$= 4.1 \times 10^{-6}\text{ mm} = 4.1\text{ nm}$$

12.43 *The fracture strength of glass may be increased by etching away a thin surface layer. It is believed that the etching may alter surface crack geometry (i.e., reduce the crack length and increase the tip radius). Compute the ratio of the etched and original crack-tip radii for a fourfold increase in fracture strength if half of the crack length is removed.*

Solution

This problem asks that we compute the crack tip radius ratio before and after etching. Let

$$\rho_t = \text{original crack tip radius, and}$$
$$\rho'_t = \text{etched crack tip radius}$$

Also, as given in the problem statement

$$\sigma'_f = \sigma_f$$

$$a' = \frac{a}{2}$$

$$\sigma'_0 = 4\sigma_0$$

When we incorporate the above relationships into two expressions of Equation 8.1 as follows:

$$\sigma_f = 2\sigma_0\left(\frac{a}{\rho_t}\right)^{1/2} = \sigma'_f = 2\sigma'_0\left(\frac{a'}{\rho'_t}\right)^{1/2}$$

We now solve for the $\dfrac{\rho'_t}{\rho_t}$ ratio, which yields the following:

$$\frac{\rho'_t}{\rho_t} = \left(\frac{\sigma'_0}{\sigma_0}\right)^2\left(\frac{a'}{a}\right) = \left(\frac{4\sigma_0}{\sigma_0}\right)^2\left(\frac{a/2}{a}\right) = 8$$

which is the solution requested in the problem statement.

Stress–Strain Behavior

12.44 *A three-point bending test is performed on a spinel ($MgAl_2O_4$) specimen having a rectangular cross section of height d = 3.8 mm (0.15 in.) and width b = 9 mm (0.35 in.); the distance between support points is 25 mm (1.0 in.).*

(a) Compute the flexural strength if the load at fracture is 350 N (80 lb_f).

(b) The point of maximum deflection Δy occurs at the center of the specimen and is described by

$$\Delta y = \frac{FL^3}{48EI} \qquad (12.11)$$

where E is the modulus of elasticity and I is the cross-sectional moment of inertia. Compute Δy at a load of 310 N (70 lb_f).

<u>Solution</u>

(a) For this portion of the problem we are asked to compute the flexural strength for a spinel specimen that is subjected to a three-point bending test. The flexural strength for a rectangular cross-section (Equation 12.7a) is just

$$\sigma_{fs} = \frac{3F_f L}{2bd^2}$$

for a rectangular cross-section. Incorporating values for the parameters in this equation that are provided in the problem statement, gives the following flexural strength:

$$\sigma_{fs} = \frac{(3)(350\text{ N})(25 \times 10^{-3}\text{ m})}{(2)(9.0 \times 10^{-3}\text{ m})(3.8 \times 10^{-3}\text{ m})^2} = 101 \text{ MPa} \quad (15{,}200 \text{ psi})$$

(b) We are now asked to compute the maximum deflection using Equation 12.11. From Table 12.5, the elastic modulus (*E*) for spinel is 260 GPa (38 × 10^6 psi). Also, the moment of inertia for a rectangular cross section (Figure 12.30) is just

$$I = \frac{bd^3}{12}$$

Incorporating this expression for *I* into Equation 12.11 and also the value for *E*, and values of *F*, *L*, *b*, and *d* given in the problem statement [310 N, 25 mm (25 × 10^{-3} m), 9 mm (9 × 10^{-3} m), and 3.8 mm (3.8 10^{-3} m), respectively] the value of Δ*y* is computed as follows:

$$\Delta y = \frac{FL^3}{48E\left(\dfrac{bd^3}{12}\right)} = \frac{FL^3}{4Ebd^3}$$

$$= \frac{(310\ \mathrm{N})(25\ \times 10^{-3}\mathrm{m})^3}{(4)(260\ \times 10^9\,\mathrm{N/m^2})(9.0\ \times 10^{-3}\mathrm{m})(3.8\ \times 10^{-3}\mathrm{m})^3}$$

$$= 9.4\ \times\ 10^{-6}\ \mathrm{m} = 9.4\ \times\ 10^{-3}\ \mathrm{mm}\quad (3.9\ \times\ 10^{-4}\ \mathrm{in.})$$

12.45 *A circular specimen of MgO is loaded using a three-point bending mode. Compute the minimum possible radius of the specimen without fracture, given that the applied load is 5560 N (1250 lb$_f$), the flexural strength is 105 MPa (15,000 psi), and the separation between load points is 45 mm (1.75 in.).*

Solution

We are asked to calculate the maximum radius of a circular specimen of MgO that is loaded using three-point bending. Solving for the specimen radius, *R*, from Equation 12.7b leads to the following:

$$R = \left[\frac{F_f L}{\sigma_{fs} \pi}\right]^{1/3}$$

which, when substituting the parameters stipulated in the problem statement, yields

$$R = \left[\frac{(5560\ N)(45 \times 10^{-3}\,\mathrm{m})}{(105 \times 10^{6}\,\mathrm{N/m^2})(\pi)}\right]^{1/3}$$

$$= 9.1 \times 10^{-3}\ \mathrm{m} = 9.1\ \mathrm{mm} \quad (0.36\ \mathrm{in.})$$

Thus, the minimum allowable specimen radius is 9.1 mm (0.36 in.)

12.46 *A three-point bending test was performed on an aluminum oxide specimen having a circular cross section of radius 5.0 mm (0.20 in.); the specimen fractured at a load of 3000 N (675 lb*$_f$*) when the distance between the support points was 40 mm (1.6 in.). Another test is to be performed on a specimen of this same material, but one that has a square cross section of 15 mm (0.6 in.) length on each edge. At what load would you expect this specimen to fracture if the support point separation is maintained at 40 mm (1.6 in.)?*

Solution

For this problem, the load is given at which a circular specimen of aluminum oxide fractures when subjected to a three-point bending test; we are then are asked to determine the load at which a specimen of the same material having a square cross-section fractures. It is first necessary to compute the flexural strength of the cylindrical specimen from Equation 12.7b; then, using this value, calculate the value of F_f in Equation 12.7a (for the specimen having a square cross-section). From Equation 12.7b, and using the first set of data provided in the problem statement, we compute the flexural strength as follows:

$$\sigma_{fs} = \frac{F_f L}{\pi R^3}$$

$$= \frac{(3000\ \text{N})(40 \times 10^{-3}\ \text{m})}{(\pi)(5.0 \times 10^{-3}\ \text{m})^3} = 306 \times 10^6\ \text{N/m}^2 = 306\ \text{MPa} \quad (42{,}970\ \text{psi})$$

Now, solving for F_f for the second specimen using Equation 12.7a, realizing that $b = d = 15$ mm (15×10^{-3} m), yields

$$F_f = \frac{2\sigma_{fs} d^3}{3L}$$

$$= \frac{(2)(306 \times 10^6\ \text{N/m}^2)(15 \times 10^{-3}\text{m})^3}{(3)(40 \times 10^{-3}\text{m})} = 17{,}200\ \text{N} \quad (3870\ \text{lb}_\text{f})$$

12.47 *(a) A three-point transverse bending test is conducted on a cylindrical specimen of aluminum oxide having a reported flexural strength of 300 MPa (43,500 psi). If the specimen radius is 5.0 mm (0.20 in.) and the support point separation distance is 15.0 mm (0.61 in.), would you expect the specimen to fracture when a load of 7500 N (1690* lb_f*) is applied? Justify your answer.*

(b) Would you be 100% certain of the answer in part (a)? Why or why not?

Solution

(a) This portion of the problem asks that we determine whether or not a cylindrical specimen of aluminum oxide having a flexural strength of 300 MPa and a radius of 5.0 mm will fracture when subjected to a load of 7500 N in a three-point bending test; the support point separation is given as 15.0 mm. Using Equation 12.7b we will calculate the value of σ, in this case the flexural stress; if this value is greater than the flexural strength, σ_{fs} (300 MPa), then fracture is expected to occur. Employment of Equation 12.7b to compute the flexural stress yields

$$\sigma = \frac{FL}{\pi R^3} = \frac{(7500 \text{ N})(15 \times 10^{-3} \text{ m})}{(\pi)(5 \times 10^{-3} \text{ m})^3}$$

$$= 286.5 \times 10^6 \text{ N/m}^2 = 286.5 \text{ MPa} \quad (40{,}300 \text{ psi})$$

Since this value (286.5 MPa) is less than the given value of σ_{fs} (300 MPa), then fracture is not predicted.

(b) However, the certainty of this prediction is not 100% because there is always some variability in the flexural strength for ceramic materials, and since this value of the flexural stress, σ, is relatively close to σ_{fs} there is some chance that fracture will occur.

Mechanisms of Plastic Deformation

12.48 *Cite one reason why ceramic materials are, in general, harder yet more brittle than metals.*

Answer

Crystalline ceramics are harder yet more brittle than metals because they (ceramics) have fewer slip systems, and, therefore, dislocation motion is highly restricted.

Miscellaneous Mechanical Considerations

12.49 *The modulus of elasticity for spinel ($MgAl_2O_4$) having 5 vol% porosity is 240 GPa (35 × 10^6 psi).*

(a) Compute the modulus of elasticity for the nonporous material.

(b) Compute the modulus of elasticity for 15 vol% porosity.

<u>Solution</u>

(a) This portion of the problem requests that we compute the modulus of elasticity for nonporous spinel given that E = 240 GPa for a material having 5 vol% porosity. Thus, we solve Equation 12.9 for E_0 (the modulus of elasticity of the nonporous material) using P = 0.05, as follows:

$$E_0 = \frac{E}{1 - 1.9P + 0.9P^2}$$

$$= \frac{240\text{ GPa}}{1 - (1.9)(0.05) + (0.9)(0.05)^2} = 265 \text{ GPa} \quad (38.6 \times 10^6 \text{ psi})$$

(b) Now we are asked to determine the value of E at P = 15 vol% (i.e., 0.15). Using Equation 12.9 the following results:

$$E = E_0(1 - 1.9P + 0.9P^2)$$

$$= (265\text{ GPa})\left[1 - (1.9)(0.15) + (0.09)(0.15)^2\right] = 195 \text{ GPa} \quad (28.4 \times 10^6 \text{ psi})$$

12.50 *The modulus of elasticity for titanium carbide (TiC) having 5 vol% porosity is 310 GPa (45 × 10^6 psi).*

(a) Compute the modulus of elasticity for the nonporous material.

(b) At what volume percent porosity will the modulus of elasticity be 240 GPa (35 × 10^6 psi)?

Solution

(a) This portion of the problem requests that we compute the modulus of elasticity for nonporous TiC given that E = 310 GPa (45 × 10^6 psi) for a material having 5 vol% porosity. Thus, we solve Equation 12.9 for E_0 (the modulus of elasticity of the nonporous material) using P = 0.05, as follows:

$$E_0 = \frac{E}{1 - 1.9P + 0.9P^2}$$

$$= \frac{310 \text{ GPa}}{1 - (1.9)(0.05) + (0.9)(0.05)^2} = 342 \text{ GPa} \quad (49.6 \times 10^6 \text{ psi})$$

(b) Now we are asked to compute the volume percent porosity at which the elastic modulus of TiC is 240 MPa (35 × 10^6 psi). Since from part (a), E_0 = 342 GPa, and using Equation 12.9, we may write the following:

$$\frac{E}{E_0} = \frac{240 \text{ GPa}}{342 \text{ GPa}} = 0.702 = 1 - 1.9P + 0.9P^2$$

Or, after rearrangement the following expression results:

$$0.9P^2 - 1.9P + 0.298 = 0$$

Now, solving for the value of P using the quadratic equation solution yields

$$P = \frac{1.9 \pm \sqrt{(-1.9)^2 - (4)(0.9)(0.298)}}{(2)(0.9)}$$

The positive and negative roots are as follows:

$$P^+ = 1.94$$

$$P^- = 0.171$$

Obviously, only the negative root is physically meaningful, and therefore the value of the porosity to give the desired modulus of elasticity is 17.1 vol%.

12.51 *Using the data in Table 12.5, do the following:*

(a) Determine the flexural strength for nonporous MgO, assuming a value of 3.75 for n in Equation 12.10.

(b) Compute the volume fraction porosity at which the flexural strength for MgO is 74 MPa (10,700 psi).

Solution

(a) This part of the problem asks us to determine the flexural strength of nonporous MgO assuming that the value of *n* in Equation 12.10 is 3.75. Taking natural logarithms of both sides of Equation 12.10 yields

$$\ln \sigma_{fs} = \ln \sigma_0 - nP$$

In Table 12.5 it is noted that for MgO and for $P = 0.05$, $\sigma_{fs} = 105$ MPa. For the nonporous material (i.e., when $P = 0$), then $\ln \sigma_0 = \ln \sigma_{fs}$. Solving for $\ln \sigma_0$ from the above equation and using these data gives

$$\ln \sigma_0 = \ln \sigma_{fs} + nP$$

$$= \ln(105 \text{ MPa}) + (3.75)(0.05)$$

$$= 4.841$$

which means that

$$\sigma_0 = e^{4.841} = 127 \text{ MPa} \quad (18{,}100 \text{ psi})$$

(b) Now we are asked to compute the volume percent porosity to yield a σ_{fs} of 74 MPa (10,700 psi). Taking the natural logarithms of both sides of Equation 12.10 and solving for *P* leads to

$$P = \frac{\ln \sigma_0 - \ln \sigma_{fs}}{n}$$

and incorporating values for σ_0 and *n* yields the following value for *P:*

$$P = \frac{\ln (127 \text{ MPa}) - \ln (74 \text{ MPa})}{3.75}$$

$$= 0.144 \text{ or } 14.4 \text{ vol\%}$$

12.52 *The flexural strength and associated volume fraction porosity for two specimens of the same ceramic material are as follows:*

σ_{fs} ***(MPa)***	***P***
70	*0.10*
60	*0.15*

(a) Compute the flexural strength for a completely nonporous specimen of this material.

(b) Compute the flexural strength for a 0.20 volume fraction porosity.

Solution

(a) Given the flexural strengths at two different volume fraction porosities, we are asked to determine the flexural strength for a nonporous material. Taking the natural logarithm of both sides of Equation 12.10 yields the following expression:

$$\ln \sigma_{fs} = \ln \sigma_0 - nP$$

Using the data provided in the problem statement, two simultaneous equations may be written in the above form as

$$\ln (70 \text{ MPa}) = \ln \sigma_0 - (0.10)n$$

$$\ln (60 \text{ MPa}) = \ln \sigma_0 - (0.15)n$$

Solving for n and σ_0 leads to the following values:

$n = 3.08$

$\sigma_0 = 95.3$ MPa.

For the nonporous material, $P = 0$, and, from Equation 12.10, $\sigma_0 = \sigma_{fs}$. Thus, σ_{fs} for $P = 0$ is 95.3 MPa.

(b) Now, we are asked for σ_{fs} at $P = 0.20$ for this same material. From Equation 12.10

$$\sigma_{fs} = \sigma_0 \exp(-nP)$$

$$= (95.3 \text{ MPa}) \exp\left[-(3.08)(0.20)\right]$$

$$= 51.5 \text{ MPa}$$

DESIGN PROBLEMS

Crystal Structures

12.D1 *Gallium arsenide (GaAs) and indium arsenide (InAs) both have the zinc blende crystal structure and are soluble in each other at all concentrations. Determine the concentration in weight percent of InAs that must be added to GaAs to yield a unit cell edge length of 0.5820 nm. The densities of GaAs and InAs are 5.316 and 5.668 g/cm^3, respectively.*

Solution

This problem asks that we determine the concentration (in weight percent) of InAs that must be added to GaAs to yield a unit cell edge length of 0.5820 nm. The densities of GaAs and InAs were given in the problem statement as 5.316 and 5.668 g/cm^3, respectively. We will solve this problem using the following steps:

Step 1

First consider a form of Equation 12.1 that applies to this alloy; this expression will include expressions for average atomic weight (A_ave) and average density (ρ_ave).

Step 2

Compute the volume of a unit cell of this alloy from the unit cell edge length provided in the problem statement.

Step 3

Incorporate expressions for A_ave and ρ_ave for this alloy (Equations 4.11a and 4.10a, respectively) into a modified form of Equation 12.1.

Step 4

From the expression developed in Step 3, solve for the value of the concentration of either GaAs or InAs.

Step 1

The form of Equation 12.1 that applies to this situation is as follows:

$$\rho_\text{ave} = \frac{n' A_\text{ave}}{V_C N_\text{A}} \tag{12.D1a}$$

For the zinc blende crystal structure, the number of formula units per unit cell (n') is 4.

Step 2

Because the zinc blende crystal structure is cubic, the unit cell volume V_C is equal to

$$V_C = a^3$$

in which *a* is the unit cell edge length, which in this case is 0.5820 nm. Thus

$$V_C = a^3 = (0.5820 \text{ nm})^3/\text{unit cell}$$

$$= (5.820 \times 10^{-8} \text{ cm})^3 = 1.971 \times 10^{-22} \text{ cm}^3/\text{unit cell}$$

Step 3

At this point we want to develop an expression for A_{ave} using Equation 4.11a. For our problem, this equation takes the form:

$$A_{\text{ave}} = \frac{100}{\dfrac{C_{\text{InAs}}}{A_{\text{InAs}}} + \dfrac{C_{\text{GaAs}}}{A_{\text{GaAs}}}}$$

$$= \frac{100}{\dfrac{C_{\text{InAs}}}{A_{\text{InAs}}} + \dfrac{(100 - C_{\text{InAs}})}{A_{\text{GaAs}}}}$$

In these expressions

C_{InAs} = the concentration (in weight percent) of InAs

C_{GaAs} = the concentration (in weight percent) of GaAs

A_{InAs} = the molecular weight of InAs = A_{In} + A_{As} = 114.82 g/mol + 74.92 g/mol = 189.74 g/mol

A_{GaAs} = the molecular weight of GaAs = A_{Ga} + A_{As} = 69.72 g/mol + 74.92 g/mol = 144.64 g/mol

Note: in the preceding equation, we have expressed alloy composition in weight percent InAs, which is possible since

$$C_{\text{GaAs}} + C_{\text{InAs}} = 100$$

Therefore, we may write an expression for A_{ave} as follows:

$$A_{\text{ave}} = \frac{100}{\dfrac{C_{\text{InAs}}}{189.74 \text{ g/mol}} + \dfrac{(100 - C_{\text{InAs}})}{144.64 \text{ g/mol}}}$$

We use an analogous procedure for the average alloy density using Equation 4.10a, which for our problem is written as follows:

$$\rho_{\text{ave}} = \frac{100}{\dfrac{C_{\text{InAs}}}{\rho_{\text{InAs}}} + \dfrac{(100 - C_{\text{InAs}})}{\rho_{\text{GaAs}}}}$$

$$= \frac{100}{\dfrac{C_{\text{InAs}}}{5.668\ \text{g/cm}^3} + \dfrac{(100 - C_{\text{InAs}})}{5.316\ \text{g/cm}^3}}$$

The densities for InAs and GaAs were given in the problem statement as follows:

ρ_{InAs} = 5.668 g/cm^3

ρ_{GaAs} = 5.316 g/cm^3

The final part of this step is to incorporate the above expressions for A_{ave} and ρ_{ave} into Equation 12.D1a. Let us first rearrange this expression such that V_C is the dependent variable and then include the average molecular weight and density expressions; thus,

$$V_C = \frac{n' A_{\text{ave}}}{\rho_{\text{ave}} N_{\text{A}}}$$

$$= 1.971 \times 10^{-22}\ \text{cm}^3\text{/unit cell}$$

$$= \frac{(4\ \text{fu/unit cell})\left[\dfrac{100}{\dfrac{C_{\text{InAs}}}{189.74\ \text{g/mol}} + \dfrac{(100 - C_{\text{InAs}})}{144.64\ \text{g/mol}}}\right]}{\left[\dfrac{100}{\dfrac{C_{\text{InAs}}}{5.668\ \text{g/cm}^3} + \dfrac{(100 - C_{\text{InAs}})}{5.316\ \text{g/cm}^3}}\right](6.022 \times 10^{23}\ \text{fu/mol})}$$

Step 4

It is now possible (albeit somewhat difficult) to solve for C_{InAs} from this expression; this yields a value of

$$C_{\text{InAs}} = 46.1\ \text{wt\%}$$

Stress–Strain Behavior

12.D2 *It is necessary to select a ceramic material to be stressed using a three-point loading scheme (Figure 12.30). The specimen must have a circular cross section, a radius of 3.8 mm (0.15 in.) and must not experience fracture or a deflection of more than 0.021 mm (8.5 × 10^{-4} in.) at its center when a load of 445 N (100 lb_f) is applied. If the distance between support points is 50.8 mm (2 in.), which of the materials in Table 12.5 are candidates? The magnitude of the centerpoint deflection may be computed using Equation 12.11.*

Solution

This problem asks for us to determine which of the ceramic materials in Table 12.5, when fabricated into cylindrical specimens and stressed in three-point loading, will not fracture when a load of 445 N (100 lb_f) is applied, and also will not experience a center-point deflection of more than 0.021 mm (8.5 × 10^{-4} in.).

The first of these criteria is met by those materials that have flexural strengths greater than the stress calculated using Equation 12.7b. According to this expression

$$\sigma_{fs} = \frac{FL}{\pi R^3}$$

$$= \frac{(445\text{ N})(50.8 \times 10^{-3}\text{ m})}{(\pi)(3.8 \times 10^{-3}\text{m})^3} = 131 \times 10^6\text{ N/m}^2 = 131\text{ MPa}\ \ (18{,}900\text{ psi})$$

Of the materials in Table 12.5, the following have flexural strengths greater than this 131 MPa: Si_3N_4, ZrO_2, SiC, Al_2O_3, glass-ceramic, mullite, and spinel.

For the second criterion we must solve for the magnitude of the modulus of elasticity, *E*, from Equation 12.11. Incorporating the expression for the cross-sectional moment of inertia that appears in Figure 12.30—namely

$$I = \frac{\pi R^4}{4}$$

leads to the following form of Equation 12.11:

$$\Delta y = \frac{FL^3}{48EI}$$

$$= \frac{FL^3}{(48E)\left(\dfrac{\pi R^4}{4}\right)}$$

$$= \frac{FL^3}{12\pi E R^4}$$

Solving for *E* from this expression yields

$$E = \frac{FL^3}{12\pi R^4 \Delta y}$$

And upon incorporation of specified values of *F*, *L*, *R*, and Δ*y* leads to the following value for *E:*

$$E = \frac{(445\ \text{N})(50.8 \times 10^{-3}\ \text{m})^3}{(12)(\pi)(3.8 \times 10^{-3}\ \text{m})^4 (0.021 \times 10^{-3}\ \text{m})}$$

$$= 3.53 \times 10^{11}\ \text{N/m}^2 = 353 \times 10^9\ \text{N/m}^2 = 353\ \text{GPa} \quad (49.3 \times 10^6\ \text{psi})$$

Of those materials that satisfy the first criterion, only Al_2O_3 has a modulus of elasticity greater than 353 GPa (Table 12.5), and, therefore, is a possible candidate.

FUNDAMENTALS OF ENGINEERING QUESTIONS AND PROBLEMS

12.1FE *Which of the following are the most common coordination numbers for ceramic materials?*

(A) 2 and 3 *(C) 6, 8, and 12*

(B) 6 and 12 *(D) 4, 6, and 8*

<u>Answer</u>

The correct answer is D. For ceramic materials, the most common coordination numbers are 4, 6, and 8.

12.2FE *An AX ceramic compound has the rock salt crystal structure. If the radii of the A and X ions are 0.137 and 0.241 nm, respectively, and the respective atomic weights are 22.7 and 91.4 g/mol, what is the density (in g/cm*^{3}*) of this material?*

(A) 0.438 g/cm^3 *(C) 1.75 g/cm*^{3}

(B) 0.571 g/cm^3 *(D) 3.50 g/cm*^{3}

Solution

The density of a ceramic may be calculated using Equation 12.1—that is

$$\rho = \frac{n'\left(\sum A_C + \sum A_A\right)}{V_C N_A}$$

For the rock salt crystal structure, 4 formula units are associated with each unit cell (i.e., *n'* = 4). In addition, for this crystal structure, the anions and cations touch each other along the edge of the unit cell; thus the unit cell edge length, *a*, is equal to twice the sum of the cation and anion radii—that is

$$a = 2(r_C + r_A)$$

Since the unit cell has cubic symmetry,

$$V_C = a^3 = [2(r_C + r_A)]^3 = 8(r_C + r_A)^3$$

Making this substitution into Equation 12.1 above leads to the following:

$$\rho = \frac{n'\left(\sum A_{Na} + \sum A_{Cl}\right)}{V_C N_A} = \frac{n'\left(\sum A_{Na} + \sum A_{Cl}\right)}{8(r_{Na} + r_{Cl})^3 N_A}$$

In formula unit—i.e., "CA" unit, there is one C ion and one A ion, which means that

$$\sum A_C = A_C = 22.7 \text{ g/mol}$$

$$\sum A_A = A_A = 91.4 \text{ g/mol}$$

Now, incorporation of atomic weight values and ionic radii for C and A into the above equation leads to the following value for the density:

$$\rho = \frac{(4 \text{ formula units/unit cell})(22.7 \text{ g/mol} + 91.4 \text{ g/mol})}{8[(1.37 \times 10^{-8} \text{ cm}) + (2.41 \times 10^{-8} \text{ cm})]^3 (6.022 \times 10^{23} \text{ formula units/mol})}$$

$$= 1.75 \text{ g/cm}^3$$

which is answer C.

CHAPTER 12

STRUCTURES AND PROPERTIES OF CERAMICS

PROBLEM SOLUTIONS

Crystal Structures

12.1 *For a ceramic compound, what are the two characteristics of the component ions that determine the crystal structure?*

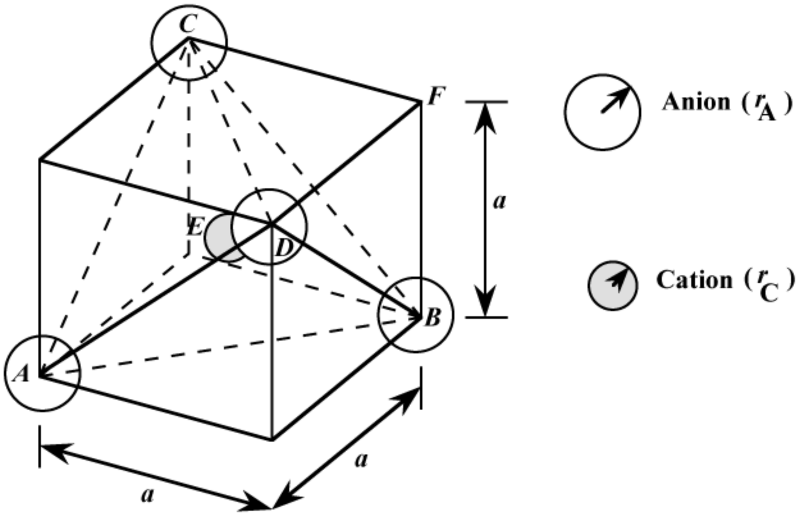
Answer

The two characteristics of component ions that determine the crystal structure of a ceramic compound are: (1) the magnitude of the electrical charge on each ion, and (2) the relative sizes of the cations and anions.

12.2 *Show that the minimum cation-to-anion radius ratio for a coordination number of 4 is 0.225.*

Solution

In this problem we are asked to show that the minimum cation-to-anion radius ratio for a coordination number of four is 0.225. If lines are drawn from the centers of the anions, then a tetrahedron is formed. The tetrahedron may be inscribed within a cube as shown below.



The spheres at the apexes of the tetrahedron are drawn at the corners of the cube, and designated as positions *A*, *B*, *C*, and *D*. (These are reduced in size for the sake of clarity.) The cation resides at the center of the cube, which is designated as point *E*. Let us now express the cation and anion radii in terms of the cube edge length, designated as *a*. The spheres located at positions *A* and *B* touch each other along the bottom face diagonal. Thus,

$$\overline{AB} = 2r_A$$

But

$$(\overline{AB})^2 = a^2 + a^2 = 2a^2$$

Or, combining the above two equations:

$$\overline{AB} = a\sqrt{2} = 2r_A \qquad \text{(S.12.2a)}$$

Which leads to the following:

$$a = \frac{2r_A}{\sqrt{2}} \qquad \text{(S.12.2b)}$$

There will also be an anion located at the corner, point *F* (not drawn), and the cube diagonal $\overline{AEF}$ will be related to the ionic radii as

$$\overline{AEF} = 2(r_A + r_C) \qquad \text{(S.12.2c)}$$

(The line *AEF* has not been drawn to avoid confusion.) From the triangle *ABF*

$$(\overline{AB})^2 + (\overline{FB})^2 = (\overline{AEF})^2 \qquad \text{(S.12.2d)}$$

But, the length of line $\overline{FB}$ is equal to

$$\overline{FB} = a = \frac{2r_A}{\sqrt{2}} \qquad \text{(S.12.2e)}$$

and, as noted above (Equation S.12.2a), the length of line $\overline{AB}$is as follows:

$$\overline{AB} = 2r_A$$

Thus, combining Equations S.12.2a, S.12.2.c, and S.12.2e with Equation S.12.2d leads to the following:

$$(2r_A)^2 + \left(\frac{2r_A}{\sqrt{2}}\right)^2 = \left[2(r_A + r_C)\right]^2$$

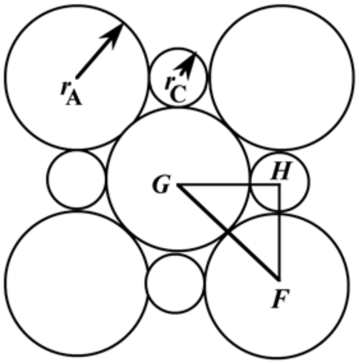
Solving for the r_C/r_A ratio from this expression yields

$$\frac{r_C}{r_A} = \frac{\sqrt{6} - 2}{2} = 0.225$$

12.3 *Show that the minimum cation-to-anion radius ratio for a coordination number of 6 is 0.414. [Hint: Use the NaCl crystal structure (Figure 12.2), and assume that anions and cations are just touching along cube edges and across face diagonals.]*

Solution

This problem asks us to show that the minimum cation-to-anion radius ratio for a coordination number of 6 is 0.414 (using the rock salt crystal structure). Below is shown one of the faces of the rock salt crystal structure in which anions and cations just touch along the edges, and also the face diagonals.



From triangle *FGH*,

$$\overline{GF} = 2r_A$$

Whereas

$$\overline{FH} = \overline{GH} = r_A + r_C$$

Since *FGH* is a right triangle, it is the case that

$$(\overline{GH})^2 + (\overline{FH})^2 = (\overline{GF})^2$$

Upon substitution into this equation, expressions for $\overline{GF}$, $\overline{FH}$, and $\overline{GH}$ cite above gives the following:

$$(r_A + r_C)^2 + (r_A + r_C)^2 = (2r_A)^2$$

which leads to

$$r_A + r_C = \frac{2r_A}{\sqrt{2}}$$

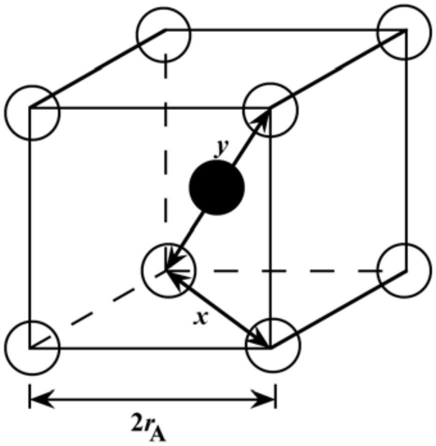
Or, solving for r_C/r_A

$$\frac{r_C}{r_A} = \left(\frac{2}{\sqrt{2}} - 1\right) = 0.414$$

12.4 *Demonstrate that the minimum cation-to-anion radius ratio for a coordination number of 8 is 0.732.*

Solution

This problem asks us to show that the minimum cation-to-anion radius ratio for a coordination number of 8 is 0.732. From the following sketch of a cubic unit cell, it may be noted that the atom represented by the dark circle has eight nearest-neighbor atoms—denoted by the open circles at the corners of the unit cell.



From this unit cell it is the case that the unit cell edge length is $2r_A$. Furthermore, from the base of the unit cell

$$x^2 = (2r_A)^2 + (2r_A)^2 = 8r_A^2$$

which means that

$$x = 2r_A\sqrt{2}$$

Now from the triangle that involves *x*, *y*, and the unit cell edge, the following may be written:

$$x^2 + (2r_A)^2 = y^2 = (2r_A + 2r_C)^2$$

Or, upon substitution for the expression for *x* given above

$$(2r_A\sqrt{2})^2 + 4r_A^2 = (2r_A + 2r_C)^2$$

This equation reduces to the following:

$$2r_A(\sqrt{3} - 1) = 2r_C$$

Or, solving for the r_C-$r_A$ration yields

$$\frac{r_C}{r_A} = \sqrt{3} - 1 = 0.732$$

12.5 *On the basis of ionic charge and ionic radii given in Table 12.3, predict crystal structures for the following materials:*

(a) CaO

(b) MnS

(c) KBr

(d) CsBr

Justify your selections.

Solution

This problem calls for us to predict crystal structures for several ceramic materials on the basis of ionic charge and ionic radii.

(a) For CaO, using data from Table 12.3

$$\frac{r_{\mathrm{Ca}^{2+}}}{r_{\mathrm{O}^{2-}}} = \frac{0.100 \text{ nm}}{0.140 \text{ nm}} = 0.714$$

Now, from Table 12.2, the coordination number for each cation (Ca^{2+}) is six, and, using Table 12.4, the predicted crystal structure is *sodium chloride.*

(b) For MnS, using data from Table 12.3

$$\frac{r_{\mathrm{Mn}^{2+}}}{r_{\mathrm{S}^{2-}}} = \frac{0.067 \text{ nm}}{0.184 \text{ nm}} = 0.364$$

The coordination number is four (Table 12.2), and the predicted crystal structure is *zinc blende* (Table 12.4).

(c) For KBr, using data from Table 12.3

$$\frac{r_{\mathrm{K}^{+}}}{r_{\mathrm{Br}^{-}}} = \frac{0.138 \text{ nm}}{0.196 \text{ nm}} = 0.704$$

The coordination number is six (Table 12.2), and the predicted crystal structure is *sodium chloride* (Table 12.4).

(d) For CsBr, using data from Table 12.3

$$\frac{r_{\mathrm{Cs}^{+}}}{r_{\mathrm{Br}^{-}}} = \frac{0.170 \text{ nm}}{0.196 \text{ nm}} = 0.867$$

The coordination number is eight (Table 12.2), and the predicted crystal structure is cesium chloride (Table 12.4).

12.6 *Which of the cations in Table 12.3 would you predict to form fluorides having the cesium chloride crystal structure? Justify your choices.*

Solution

We are asked to cite the cations in Table 12.3 which would form fluorides having the cesium chloride crystal structure. First of all, the possibilities would include only the monovalent cations Cs^+, K^+, and Na^+. Furthermore, the coordination number for each cation must be 8, which means that $0.732 < r_C/r_A < 1.0$ (Table 12.2). From Table 12.3 the r_C/r_A ratios for these three cations and the F^- ion are as follows:

$$\frac{r_{Cs^+}}{r_{F^-}} = \frac{0.170 \text{ nm}}{0.133 \text{ nm}} = 1.28$$

$$\frac{r_{K^+}}{r_{F^-}} = \frac{0.138 \text{ nm}}{0.133 \text{ nm}} = 1.04$$

$$\frac{r_{Na^+}}{r_{F^-}} = \frac{0.102 \text{ nm}}{0.133 \text{ nm}} = 0.77$$

Thus, on the basis of the $0.732 < r_C/r_A < 1.0$ criterion, only sodium fluoride will form the CsCl crystal structure.

12.7 *Using the Molecule Definition Utility found in both "Metallic Crystal Structures and Crystallography" and "Ceramic Crystal Structures" modules of VMSE, located on the book's web site [www.wiley.com/college/callister (Student Companion Site)], generate (and print out) a three-dimensional unit cell for lead oxide, PbO, given the following: (1) The unit cell is tetragonal with a = 0.397 nm and c = 0.502 nm, (2) oxygen atoms are located at the following point coordinates:*

0 0 0	*0 0 1*
1 0 0	*1 0 1*
0 1 0	*0 1 1*
$\frac{1}{2}\ \frac{1}{2}\ 0$	$\frac{1}{2}\ \frac{1}{2}\ 1$

and (3) Pb atoms are located at the following point coordinates:

$\frac{1}{2}\ 0\ 0.763$	$0\ \frac{1}{2}\ 0.237$
$\frac{1}{2}\ 1\ 0.763$	$1\ \frac{1}{2}\ 0.237$

Solution

First of all, open the "Molecular Definition Utility"; it may be found in either of "Metallic Crystal Structures and Crystallography" or "Ceramic Crystal Structures" modules. After opening either of these modules, then open the "Molecule Definition Utility" submodule. Detailed instructions are provided for each step; therefore, our instructions will be general in nature.

Three steps are provided for generating crystal structures: Step 1—Define atom types; Step 2—Position atoms; Step 3—Define bonds between atoms.

In Step 1 each atom/ion type is given a name, a color, and a size—size may be specified in terms of nanometers; they each atom type is registered.

For Step 2 positions of all atoms/ions of each type are specified. In the problem statement point coordinate indices are provided (see Section 3.8); these need to be converted into lattice positions—i.e., multiplied by the appropriate *a* or *c* lattice parameter. Therefore, these atom positions are entered in nanometers—relative to the three X, Y, and Z axes. After entering the lattice position for each ion, that ion is displayed by clicking on the "Register Atom Position" button.

The X, Y, and Z lattice position entries for the 10 sets of point coordinates for the oxygen ions are as follows:

0, 0, and 0	0, 0, and 0.502
0.397, 0, and 0	0.397, 0, and 0.502
0, 0.397, and 0	0, 0.397, and 0.502

0.397, 0.397, and 0	0.397, 0.397, and 0.502
0.1985, 0.1985, and 0	0.1985, 0.1985, and 0.502

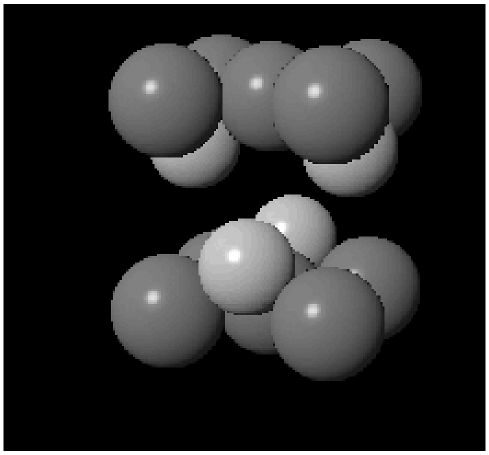
Likewise, for the lead ions, X, Y, and Z lattice position entries for the four sets of points coordinates are the following:

0.1985, 0, and 0.383	0, 0.1985, and 0.1190
0.1985, 0.397, and 0.383	0.397, 0.1985, and 0.1190

Step 3 allows the user to define the nature of the bonds between atoms. For the ceramic and metallic crystal structures, interatomic bonds are not normally displayed.

At any time during this process, the image may be rotated by using mouse click-and-drag.

For this problem the image should appear something like the one shown below:



Here the darker spheres represent oxygen ions, while lead ions are depicted by the lighter balls.

[Note: Unfortunately, with this version of the Molecular Definition Utility, it is not possible to save either the data or the image that you have generated. You may use screen capture (or screen shot) software to record and store your image.]

12.8 *The zinc blende crystal structure is one that may be generated from close-packed planes of anions.*

(a) Will the stacking sequence for this structure be FCC or HCP? Why?

(b) Will cations fill tetrahedral or octahedral positions? Why?

(c) What fraction of the positions will be occupied?

Solution

This question is concerned with the zinc blende crystal structure in terms of close-packed planes of anions.

(a) The stacking sequence of close-packed planes of anions for the zinc blende crystal structure will be the same as FCC (and not HCP) because the anion packing is FCC (Table 12.4).

(b) The cations will fill tetrahedral positions since the coordination number for cations is four (Table 12.4).

(c) Only one-half of the tetrahedral positions will be occupied because there are two tetrahedral sites per anion, and yet only one cation per anion.

12.9 *The corundum crystal structure, found for Al_2O_3, consists of an HCP arrangement of O^{2-} ions; the Al^{3+} ions occupy octahedral positions.*

(a) What fraction of the available octahedral positions are filled with Al^{3+} ions?

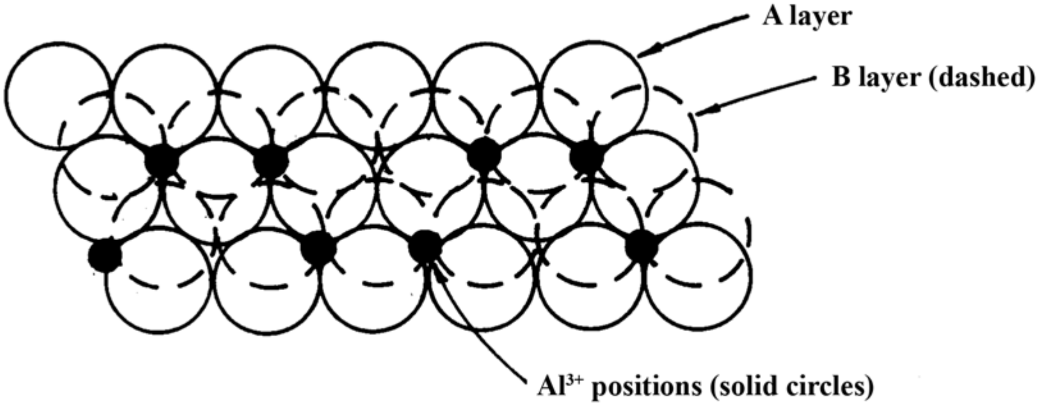
(b) Sketch two close-packed O^{2-} planes stacked in an AB sequence, and note octahedral positions that will be filled with the Al^{3+} ions.

Solution

This question is concerned with the corundum crystal structure in terms of close-packed planes of anions.

(a) For this crystal structure, two-thirds of the octahedral positions will be filled with Al^{3+} ions since there is one octahedral site per O^{2-} ion, and the ratio of Al^{3+} to O^{2-} ions is two-to-three.

(b) Two close-packed O^{2-} planes and the octahedral positions between these planes that will be filled with Al^{3+} ions are sketched below.



12.10 *Beryllium oxide (BeO) may form a crystal structure that consists of an HCP arrangement of* O^{2-} *ions. If the ionic radius of* Be^{2+} *is 0.035 nm, then*

(a) Which type of interstitial site will the Be^{2+} *ions occupy?*

(b) What fraction of these available interstitial sites will be occupied by Be^{2+} *ions?*

Solution

(a) This portion of the problem asks that we specify which type of interstitial site the Be^{2+} ions occupy in BeO if the ionic radius of Be^{2+} is 0.035 nm and the O^{2-} ions form an HCP arrangement. Since, from Table 12.3, $r_{O^{2-}}$ = 0.140 nm, then

$$\frac{r_{Be^{2+}}}{r_{O^{2-}}} = \frac{0.035\text{ nm}}{0.140\text{ nm}} = 0.250$$

Inasmuch as r_C/r_A is between 0.225 and 0.414, the coordination number for Be^{2+} is 4 (Table 12.2); therefore, tetrahedral interstitial positions are occupied.

(b) We are now asked what fraction of these available interstitial sites are occupied by Be^{2+} ions. Since there are two tetrahedral sites per O^{2-} ion, and the ratio of Be^{2+} to O^{2-} is 1:1, one-half of these sites are occupied with Be^{2+} ions.

12.11 *Iron titanate, $FeTiO_3$, forms in the ilmenite crystal structure that consists of an HCP arrangement of O^{2-} ions.*

(a) Which type of interstitial site will the Fe^{2+} ions occupy? Why?

(b) Which type of interstitial site will the Ti^{4+} ions occupy? Why?

(c) What fraction of the total tetrahedral sites will be occupied?

(d) What fraction of the total octahedral sites will be occupied?

Solution

(a) We are first of all asked to cite, for $FeTiO_3$, which type of interstitial site the Fe^{2+} ions will occupy. From Table 12.3, the cation-anion radius ratio is

$$\frac{r_{Fe^{2+}}}{r_{O^{2-}}} = \frac{0.077 \text{ nm}}{0.140 \text{ nm}} = 0.550$$

Since this ratio is between 0.414 and 0.732, the Fe^{2+} ions will occupy octahedral sites (Table 12.2).

(b) Similarly, for the Ti^{4+} ions, the titanium-oxygen ionic radius ratio is as follows:

$$\frac{r_{Ti^{4+}}}{r_{O^{2-}}} = \frac{0.061 \text{ nm}}{0.140 \text{ nm}} = 0.436$$

Since this ratio is between 0.414 and 0.732, the Ti^{4+} ions will also occupy octahedral sites.

(c) Since both Fe^{2+} and Ti^{4+} ions occupy octahedral sites, no tetrahedral sites will be occupied.

(d) For every $FeTiO_3$ formula unit, there are three O^{2-} ions, and, therefore, three octahedral sites; since there is one ion each of Fe^{2+} and Ti^{4+}per formula unit, two-thirds of these octahedral sites will be occupied.

12.12 *For each of the following crystal structures, represent the indicated plane in the manner of Figures 3.12 and 3.13, showing both anions and cations:*

(a) (100) plane for the cesium chloride crystal structure

(b) (200) plane for the cesium chloride crystal structure

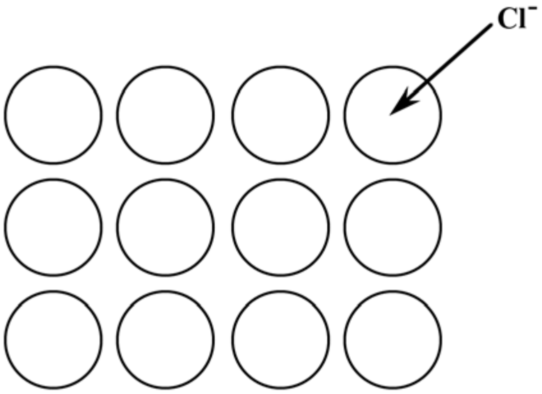
(c) (111) plane for the diamond cubic crystal structure

(d) (110) plane for the fluorite crystal structure

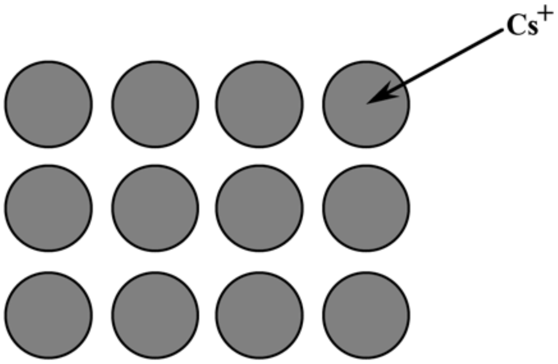
Solution

This problem asks that we represent specific crystallographic planes for various ceramic crystal structures.

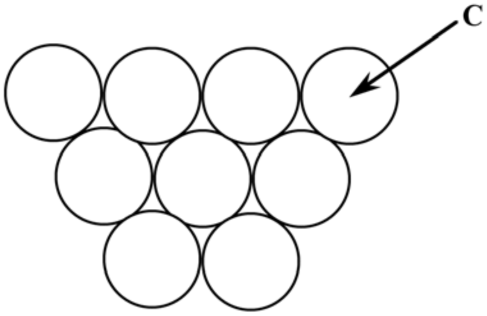
(a) A (100) plane for the cesium chloride crystal structure would appear as



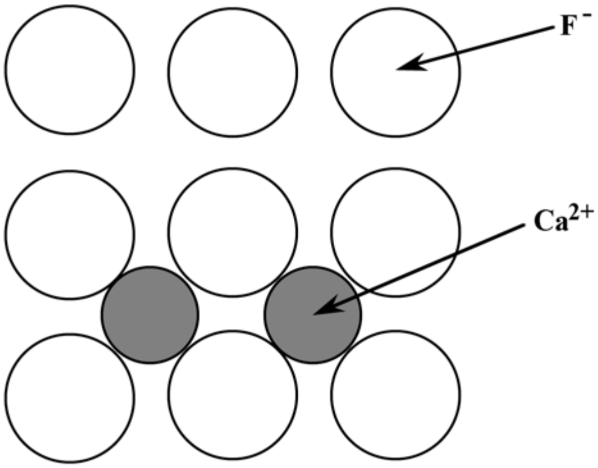
(b) A (200) plane for the cesium chloride crystal structure would appear as



(c) A (111) plane for the diamond cubic crystal structure would appear as



(d) A (110) plane for the fluorite crystal structure would appear as



Ceramic Density Computations

12.13 *Compute the atomic packing factor for the rock salt crystal structure in which r_C/r_A = 0.414.*

Solution

This problem asks that we compute the atomic packing factor for the rock salt crystal structure when r_C/r_A = 0.414. The definition of the atomic packing (APF) is given in Equation 3.3 as follows:

$$\text{APF} = \frac{V_S}{V_C}$$

where V_S and V_C are, respectively sphere volume of ions within the unit cell and unit cell volume. With regard to the sphere volume, there are four cation and four anion spheres per unit cell (because the rock salt crystal structure consists of two interpenetrating FCC networks). Thus,

$$V_S = (4)\left(\frac{4}{3}\pi r_A^3\right) + (4)\left(\frac{4}{3}\pi r_C^3\right)$$

But, since r_C/r_A = 0.414, then the above equation may be rewritten as follows:

$$V_S = \frac{16}{3}\pi r_A^3 \left[1 + (0.414)^3\right] = (17.94)\ r_A^3$$

Now, for r_C/r_A = 0.414 the corner anions in Table 12.2 just touch one another along the cubic unit cell edges such that

$$V_C = a^3 = \left[2(r_A + r_C)\right]^3$$

$$= \left[2(r_A + 0.414 r_A)\right]^3 = (22.62) r_A^3$$

Thus

$$\text{APF} = \frac{V_S}{V_C} = \frac{(17.94)\ r_A^3}{(22.62)\ r_A^3} = 0.793$$

12.14 *The unit cell for Al_2O_3 has hexagonal symmetry with lattice parameters a = 0.4759 nm and c =1.2989 nm. If the density of this material is 3.99 g/cm^3, calculate its atomic packing factor. For this computation use ionic radii listed in Table 12.3.*

Solution

This problem asks for us to calculate the atomic packing factor for aluminum oxide given values for *a* and *c* lattice parameters, and the density. To begin, the atomic packing (APF) is defined in Equation 3.3 as follows:

$$\mathrm{APF} = \frac{V_S}{V_C}$$

where V_S and V_C are, respectively sphere volume of ions within the unit cell and unit cell volume. Let us first begin by determining the value of V_C for Al_2O_3. The first thing we need to do is determine *n'*, the number of formula (Al_2O_3) units in the unit cell, which is one of the parameters in Equation 12.1. However, this necessitates that we calculate the value of V_C, the unit cell volume. The unit cell volume for the HCP crystal was given in Equation 3.7a as follows:

$$V_C = \frac{3a^2c\sqrt{3}}{2} \tag{3.7a}$$

Values for *a* and *c* are given in the problem statement as 0.4759 nm $(\text{or } 4.759 \times 10^{-8}\ \text{cm})$ and 1.2989 nm $(\text{or } 1.2989 \times 10^{-7}\ \text{cm})$, respectively. Thus, the unit cell volume is computed as follows:

$$V_C = \frac{(3)(4.759 \times 10^{-8}\ \text{cm})^2(1.2989 \times 10^{-7}\ \text{cm})(\sqrt{3})}{2}$$

$$= 7.64 \times 10^{-22}\ \text{cm}^3$$

Now, solving for *n'* (Equation 12.1) leads to the following expression:

$$n' = \frac{\rho N_A V_C}{\sum A_{\mathrm{Al}} + \sum A_{\mathrm{O}}}$$

Here

$\sum A_{\mathrm{Al}}$= the sum of the atomic weights of all aluminum ions in Al_2O_3= $2A_{\mathrm{Al}}$ = (2)(26.98 g/mol)

$\sum A_{\mathrm{O}}$ = the sum of the atomic weights of all oxygen ions in Al_2O_3 = $3A_{\mathrm{O}}$ = (3)(16.00 g/mol)

ρ = the density of Al_2O_3, given in the problem statement as 3.99 g/cm^3

N_A = Avogardo's number = 6.022×10^{23} formula units/mol

Thus the value of *n'* is computed as follows:

$$n' = \frac{(3.99\ \text{g/cm}^3)(6.022 \times 10^{23}\ \text{formula units/mol})(7.64 \times 10^{-22}\ \text{cm}^3/\text{unit cell})}{(2)(26.98\ \text{g/mol}) + (3)(16.00\ \text{g/mol})}$$

= 18.0 formula units/unit cell

Which means there are 18 Al_2O_3 units per unit cell, or 36 Al^{3+} ions and 54 O^{2-} ions. From Table 12.3, the radii of these two ion types are 0.053 and 0.140 nm, respectively. Thus, the total sphere volume in Equation 3.3 (which we denote as V_S), is just

$$V_S = (36)\left(\frac{4}{3}\pi\right)(5.3 \times 10^{-9}\text{cm})^3 + (54)\left(\frac{4}{3}\pi\right)(1.4 \times 10^{-8}\text{cm})^3$$

$$= 6.43 \times 10^{-22}\ \text{cm}^3$$

Finally, the APF is equal to

$$\text{APF} = \frac{V_S}{V_C} = \frac{6.43 \times 10^{-22}\ \text{cm}^3}{7.64 \times 10^{-22}\ \text{cm}^3} = 0.842$$

12.15 *Compute the atomic packing factor for cesium chloride using the ionic radii in Table 12.3 and assuming that the ions touch along the cube diagonals.*

Solution

We are asked in this problem to compute the atomic packing factor for the CsCl crystal structure. This requires that we take the ratio of the sphere volume within the unit cell and the total unit cell volume. From Figure 12.3 there is the equivalence of one Cs and one Cl ion per unit cell; the ionic radii of these two ions are 0.170 nm and 0.181 nm, respectively (Table 12.3). Thus, the sphere volume, V_S, is a function of the atomic radii of Cs and Cl (r_{Cs} and r_{Cl}, respectively) as

$$V_S = \frac{4}{3}(\pi)r_{\mathrm{Cs}}^3 + \frac{4}{3}(\pi)r_{\mathrm{Cl}}^3$$

$$= \frac{4}{3}(\pi)\left(r_{\mathrm{Cs}}^3 + r_{\mathrm{Cl}}^3\right)$$

$$= \frac{4}{3}(\pi)\left[(0.170\ \mathrm{nm})^3 + (0.181\ \mathrm{nm})^3\right] = 0.0454\ \mathrm{nm}^3$$

The unit cell for CsCl is cubic, which means that the unit cell volume, V_C, is equal to

$$V_C = a^3$$

Here a is the unit cell edge length. This a parameter is related to the atomic radii of Cs and Cl according to a modified form of Equation 3.4 (for the BCC crystal structure, the relationship between the atomic radius, R and the unit cell edge length a). This expression for the CsCl crystal structure is as follows:

$$a = \frac{2r_{\mathrm{Cs}^+} + 2r_{\mathrm{Cl}^-}}{\sqrt{3}}$$

Incorporation of values for the ionic radii for both Cs and Cl leads to the following value for a:

$$a = \frac{2(0.170\ \mathrm{nm}) + 2(0.181\ \mathrm{nm})}{\sqrt{3}}$$

$$= 0.405\ \mathrm{nm}$$

Thus, the unit cell volume for CsCl is computed as follows:

$$V_C = a^3$$

$$= (0.405 \text{ nm})^3 = 0.0664 \text{ nm}^3$$

And, finally the atomic packing factor for CsCl is just equal to the following:

$$\text{APF} = \frac{V_S}{V_C} = \frac{0.0454 \text{ nm}^3}{0.0664 \text{ nm}^3} = 0.684$$

12.16 *Calculate the theoretical density of NiO, given that it has the rock salt crystal structure.*

Solution

This density of NiO may be computed using Equation 12.1, which for this problem, is of the form

$$\rho = \frac{n'\left(\sum A_{\text{Ni}} + \sum A_{\text{O}}\right)}{V_C N_{\text{A}}}$$

But because the formula unit is "NiO" then

$$\sum A_{\text{Ni}} = A_{\text{Ni}} = 58.69 \text{ g/mol}$$
$$\sum A_{\text{O}} = A_{\text{O}} = 16.00 \text{ g/mol}$$

This means that, for this problem, Equation 12.1 becomes the following:

$$\rho = \frac{n'\left(A_{\text{Ni}} + A_{\text{O}}\right)}{V_C N_{\text{A}}} \tag{12.1a}$$

Since the crystal structure is rock salt, n' = 4 formula units per unit cell (because the rock salt crystal structure consists of two interpenetrating FCC structures—in this case, one for Ni^{2+} ions; the other for the and O^{2-} ions). At this point it becomes necessary to determine the value of the unit cell volume V_C. Because the unit cell has cubic symmetry, V_C and the unit cell edge length a are related as

$$V_C = a^3$$

From Example Problem 12.3, it may be noted, for the rock salt crystal structure, that a, the unit cell edge length is related to (in this case) the ionic radii of Ni and O ions ($r_{\text{Ni}^{2+}}$ and $r_{\text{O}^{2-}}$, respectively) as follows:

$$a = 2r_{\text{Ni}^{2+}} + 2r_{\text{O}^{2-}}$$

Which means that

$$V_C = a^3 = \left(2r_{\text{Ni}^{2+}} + 2r_{\text{O}^{2-}}\right)^3$$

The ionic radii of Ni^{2+} and O^{2-} from Table 12.3 are 0.069 nm and 0.140 nm, respectively. Therefore,

$$V_C = a^3 = \left(2r_{\text{Ni}^{2+}} + 2r_{\text{O}^{2-}}\right)^3 = \left[2(0.069 \text{ nm}) + 2(0.140 \text{ nm})\right]^3$$

$$= 0.0730\ \frac{\text{nm}^3}{\text{unit cell}} = 0.0730\ \frac{\text{nm}^3}{\text{unit cell}}\left(\frac{1\text{ cm}}{10^7\text{ nm}}\right)^3$$

$$= 7.30 \times 10^{-23}\ \text{cm}^3/\text{unit cell}$$

Finally, it is possible for us to compute the density of NiO incorporating Avogadro's number and values of the other parameters in Equation 12.1a, as follows:

$$\rho = \frac{(4\text{ formula units/unit cell})(58.69\text{ g/mol} + 16.00\text{ g/mol})}{\left(7.30 \times 10^{-23}\text{ cm}^3/\text{unit cell}\right)\left(6.022 \times 10^{23}\text{ formula units/mol}\right)}$$

$$= 6.80\text{ g/cm}^3$$

12.17 *Iron oxide (FeO) has the rock salt crystal structure and a density of 5.70 g/cm*^{3}.

(a) Determine the unit cell edge length.

(b) How does this result compare with the edge length as determined from the radii in Table 12.3, assuming that the Fe^{2+} *and* O^{2-} *ions just touch each other along the edges?*

Solution

(a) This part of the problem calls for us to determine the unit cell edge length for FeO. The density of FeO is 5.70 g/cm^3 and the crystal structure is rock salt. From Equation 12.1 the density of Fe, is of the form

$$\rho = \frac{n'\left(\sum A_{\text{Fe}} + \sum A_{\text{O}}\right)}{V_C N_{\text{A}}}$$

But because the formula unit is "FeO" then

$$\sum A_{\text{Fe}} = A_{\text{Fe}} = 55.85 \text{ g/mol}$$
$$\sum A_{\text{O}} = A_{\text{O}} = 16.00 \text{ g/mol}$$

This means that, for this problem, Equation 12.1 becomes the following:

$$\rho = \frac{n'\left(A_{\text{Fe}} + A_{\text{O}}\right)}{V_C N_{\text{A}}} \qquad (12.1b)$$

Since the crystal structure is rock salt, n' = 4 formula units per unit cell (because the rock salt crystal structure consists of two interpenetrating FCC structures—in this case, one for Fe^{2+} ions; the other for the and O^{2-} ions). Because the unit cell has cubic symmetry, V_C and the unit cell edge length a are related as

$$V_C = a^3$$

This means that Equation 12.1b takes the form:

$$\rho = \frac{n'\left(A_{\text{Fe}} + A_{\text{O}}\right)}{a^3 N_{\text{A}}}$$

And solving this expression for a, the unit cell edge length (while incorporating atomic weight values—A_{Fe} = 55.85 g/mol and A_{O} = 16.00 g/mol) leads to

$$a = \left[\frac{n'\left(A_{\text{Fe}} + A_{\text{O}}\right)}{\rho N_{\text{A}}}\right]^{1/3}$$

$$= \left[\frac{(4 \text{ formula units/unit cell})(55.85 \text{ g/mol} + 16.00 \text{ g/mol})}{(5.70 \text{ g/cm}^3)(6.022 \times 10^{23} \text{ formula units/mol})} \right]^{1/3}$$

$$= 4.37 \times 10^{-8} \text{ cm} = 0.437 \text{ nm}$$

(b) The edge length is to be determined from the Fe^{2+} and O^{2-} radii for this portion of the problem. From Example Problem 12.3, it may be noted, for the rock salt crystal structure, that *a*, the unit cell edge length is related to (in this case) the ionic radii of Fe and O ions $(r_{\text{Fe}^{2+}}$ and $r_{\text{O}^{2-}}$, respectively) as follows:

$$a = 2r_{\text{Fe}^{2+}} + 2r_{\text{O}^{2-}}$$

From Table 12.3,

$r_{\text{Fe}^{2+}}$ = 0.077 nm

$r_{\text{O}^{2-}}$ = 0.140 nm

Therefore, the unit cell edge length, as determined from ionic radii, is

$$a = 2r_{\text{Fe}^{2+}} + 2r_{\text{O}^{2-}}$$

$$= 2(0.077 \text{ nm}) + 2(0.140 \text{ nm}) = 0.434 \text{ nm}$$

This value is in excellent agreement with the value of *a* determined from part (a)—i.e., 0.437 nm.

12.18 *One crystalline form of silica (SiO_2) has a cubic unit cell, and from x-ray diffraction data it is known that the cell edge length is 0.700 nm. If the measured density is 2.32 g/cm^3, how many Si^{4+} and O^{2-}ions are there per unit cell?*

Solution

We are asked to determine the number of Si^{4+} and O^{2-} ions per unit cell for a crystalline form of silica (SiO_2). For this material, a = 0.700 nm and ρ = 2.32 g/cm^3. Solving for n' from Equation 12.1, we obtain the following:

$$n' = \frac{\rho V_C N_A}{\sum A_{Si} + \sum A_O} \qquad (12.1c)$$

Now if a formula (SiO_2) unit there is 1 Si^{4+} and 2O^{2-} ions. Therefore

$$\sum A_{Si} = A_{Si} = 28.09 \text{ g/mol}$$

$$\sum A_O = 2A_O = 2(16.00 \text{ g/mol}) = 32.00 \text{ g/mol}$$

(The atomic weight values for Si and O came from inside the front cover.)

Also, because the unit cell has cubic symmetry, it is the case that

$$V_C = a^3$$

Here, a is the unit cell edge length—viz., 0.700 nm $(\text{or } 7.00 \times 10^{-8} \text{ cm})$. Now, realizing that the density, ρ, has a value of 2.32 g/cm^3, the value of n' is determined from Equation 12.1c as follows"

$$n' = \frac{\rho V_C N_A}{\sum A_{Si} + \sum A_O}$$

$$= \frac{(2.32 \text{ g/cm}^3)(7.00 \times 10^{-8} \text{ cm})^3(6.022 \times 10^{23} \text{ formula units/mol})}{28.09 \text{ g/mol} + 32.00 \text{ g/mol}}$$

$$= 7.97 \text{ or almost } 8$$

Therefore, there are 8 Si^{4+} ions and 16 O^{2-} ions per SiO_2 unit cell.

12.19 *(a) Using the ionic radii in Table 12.3, compute the theoretical density of CsCl. (Hint: Use a modification of the result of Problem 3.3.)*

(b) The measured density is 3.99 g/cm^3. How do you explain the slight discrepancy between your calculated value and the measured value?

Solution

(a) We are asked to compute the density of CsCl. To solve this problem it is necessary to use Equation 12.1—namely

$$\rho = \frac{n'\left(\sum A_{\mathrm{Cs}} + \sum A_{\mathrm{Cl}}\right)}{V_C N_{\mathrm{A}}} \qquad (12.1\mathrm{d})$$

But because the formula unit is "CsCl" then

$$\sum A_{\mathrm{Cs}} = A_{\mathrm{Cs}} = 132.91\ \mathrm{g/mol}$$

$$\sum A_{\mathrm{Cl}} = A_{\mathrm{Cl}} = 35.45\ \mathrm{g/mol}$$

Now, in order to compute the unit cell volume, V_C, we make use of the result of Problem 3.3. This problem asks for us to confirm, for the BCC crystal structure, the equation that relates the unit cell edge length (a) and the atomic radius (R)—that is

$$a = \frac{4R}{\sqrt{3}} \qquad (3.4)$$

For this demonstration in Problem 3.3, the "4R" in this equation is the length of a cube diagonal. For the CsCl crystal structure, this cube diagonal length is equal to $2r_{\mathrm{Cs}^+} + 2r_{\mathrm{Cl}^-}$ where

r_{Cs^+} = the radius of a Cs ion = 0.170 nm (Table 12.3)

r_{Cl^-} = the radius of a Cl ion = 0.181 nm (Table 12.3)

Thus, the modified form of Equation 3.4 (above) is

$$a = \frac{2r_{\mathrm{Cs}^+} + 2r_{\mathrm{Cl}^-}}{\sqrt{3}}$$

$$= \frac{2(0.170\ \mathrm{nm}) + 2(0.181\ \mathrm{nm})}{\sqrt{3}}$$

$$= 0.405\ \mathrm{nm} = 4.05 \times 10^{-8}\ \mathrm{cm}$$

Since the unit cell volume, $V_C = a^3$, and for the CsCl crystal structure, $n' = 1$ formula unit/unit cell, we solve for the density of CsCl using Equation 12.1d as follows:

$$\rho = \frac{n'(A_{\mathrm{Cs}} + A_{\mathrm{Cl}})}{V_C N_{\mathrm{A}}} = \frac{n'(A_{\mathrm{Cs}} + A_{\mathrm{Cl}})}{a^3 N_{\mathrm{A}}}$$

$$\rho = \frac{\text{(1 formula unit/unit cell)(132.91 g/mol + 35.45 g/mol)}}{(4.05 \times 10^{-8}\ \text{cm})^3\text{/unit cell}(6.022 \times 10^{23}\ \text{formula units/mol})}$$

$$= 4.21\ \text{g/cm}^3$$

(b) This value of the density is greater than the measured density (3.99 g/cm^3). The reason for this discrepancy is that the ionic radii in Table 12.3, used for this computation, were for a coordination number of six, when, in fact, the coordination number of both Cs^+ and Cl^- is eight. The ionic radii should be slightly greater, leading to a larger V_C value, and a lower density.

12.20 *From the data in Table 12.3, compute the theoretical density of* CaF_2*, which has the fluorite structure.*

Solution

This problem asks that we compute the density of CaF_2. In order to solve this problem it is necessary to use Equation 12.1, which for our problem takes the form:

$$\rho = \frac{n'\left(\sum A_{\mathrm{Ca}} + \sum A_{\mathrm{F}}\right)}{V_C N_{\mathrm{A}}} \qquad (12.1\mathrm{e})$$

But because the formula unit is "CaF_2" then

$$\sum A_{\mathrm{Ca}} = A_{\mathrm{Ca}} = 40.08\ \mathrm{g/mol}$$

$$\sum A_{\mathrm{F}} = 2A_{\mathrm{F}} = (2)(19.00\ \mathrm{g/mol}) = 38.00\ \mathrm{g/mol}$$

It is now necessary to determine the unit cell volume, V_C. A unit cell of the fluorite structure is shown in Figure 12.5. It may be seen that there are four CaF_2 units per unit cell (i.e., n' = 4 formula units/unit cell). For each of the eight small cubes (or sub-cells) in the unit cell (as demonstrated in the solution to Problem 12.19), the sub-cell edge length a is equal to

$$a = \frac{2r_{\mathrm{Ca}^{2+}} + 2r_{\mathrm{F}^-}}{\sqrt{3}}$$

and, from Table 12.3

$r_{\mathrm{Ca}^{2+}} = 0.100$ nm

$r_{\mathrm{F}^-} = 0.133$ nm

Therefore,

$$a = \frac{2(0.100\ \mathrm{nm}) + 2(0.133\ \mathrm{nm})}{\sqrt{3}} = 0.269\ \mathrm{nm} = 2.69 \times 10^{-8}\ \mathrm{cm}$$

And the volume of the unit cell is just

$$V_C = (2a)^3 = \left[(2)(2.69 \times 10^{-3}\ \mathrm{cm})\right]^3 = 1.56 \times 10^{-22}\ \mathrm{cm}^3$$

Also, from Figure 12.5, it may be noted that the unit cell is composed of 4 formula units (CaF_2's), which means that n' in Equation 12.1e is 4. Now it is possible to solve for the density of calcium fluoride using Equation 12.1e as follows:

$$\rho = \frac{n'(A_{\mathrm{Ca}} + 2A_{\mathrm{F}})}{V_C N_{\mathrm{A}}}$$

$$= \frac{(4 \text{ formula units/unit cell})[40.08 \text{ g/mol} + (2)(19.00 \text{ g/mol})]}{(1.56 \times 10^{-22} \text{ cm}^3\text{/unit cell})(6.022 \times 10^{23} \text{ formula units/mol})}$$

$$= 3.32 \text{ g/cm}^3$$

The measured density is 3.18 g/cm^3.

12.21 *A hypothetical AX type of ceramic material is known to have a density of 2.10 g/cm*^{3} *and a unit cell of cubic symmetry with a cell edge length of 0.57 nm. The atomic weights of the A and X elements are 28.5 and 30.0 g/mol, respectively. On the basis of this information, which of the following crystal structures is (are) possible for this material: sodium chloride, cesium chloride, or zinc blende? Justify your choice(s).*

Solution

We are asked to specify possible crystal structures for an AX type of ceramic material given its density (2.10 g/cm^3), that the unit cell has cubic symmetry with edge length of 0.57 nm, and the atomic weights of the A and X elements (28.5 and 30.0 g/mol, respectively). Solving for *n'* in Equation 12.1 leads to the following

$$n' = \frac{\rho V_C N_A}{\sum A_C + \sum A_A}$$

$$= \frac{(2.10 \text{ g/cm}^3)\left[(5.70 \times 10^{-8} \text{ cm})^3/\text{unit cell}\right](6.022 \times 10^{23} \text{ formula units/mol})}{(30.0 \text{ g/mol} + 28.5 \text{ g/mol})}$$

= 4.00 formula units/unit cell

Of the three possible crystal structures, only sodium chloride and zinc blende have four formula units per unit cell, and therefore, are possibilities.

12.22 *The unit cell for Fe_3O_4 (FeO-Fe_2O_3) has cubic symmetry with a unit cell edge length of 0.839 nm. If the density of this material is 5.24 g/cm^3, compute its atomic packing factor. For this computation, you will need to use the ionic radii listed in Table 12.3.*

Solution

This problem asks us to compute the atomic packing factor for Fe_3O_4 given its density and unit cell edge length. It is first necessary to determine the number of formula units in the unit cell in order to calculate the sphere volume. Solving for n' from Equation 12.1 leads to

$$n' = \frac{\rho V_C N_A}{\sum A_{Fe} + \sum A_O}$$

A formula unit of Fe_3O_4 consists of 3 iron ions and 4 oxygen ions; inasmuch as the atomic weights of iron and oxygen (A_{Fe} and A_O) are 55.85 g/mol and 16.00 g/mol, respectively (as cited inside the front cover of the book)—therefore,

$$\sum A_{Fe} = (3)(55.85 \text{ g/mol}) = 167.55 \text{ g/mol}$$

$$\sum A_O = (4)(16.00 \text{ g/mol}) = 64.00 \text{ g/mol}$$

In addition, the unit cell volume, V_C, is equal to a^3 where a is the unit cell edge length (0.839 nm as given in the problem statement). Since the density value is 5.24 g/cm^3 (as also provided in the problem statement), we calculate n' using the above equation as follows:

$$n' = \frac{\rho V_C N_A}{\sum A_{Fe} + \sum A_O}$$

$$= \frac{(5.24 \text{ g/cm}^3)\left[(8.39 \times 10^{-8} \text{ cm})^3/\text{unit cell}\right](6.022 \times 10^{23} \text{ formula units/mol})}{(167.55 \text{ g/mol}) + (64.00 \text{ g/mol})}$$

$$= 8.0 \text{ formula units/unit cell}$$

Thus, in each FeO-Fe_2O_3 unit cell there are 8 Fe^{2+}, 16 Fe^{3+}, and 32 O^{2-} ions. From Table 12.3, $r_{Fe^{2+}} = 0.077$ nm, $r_{Fe^{3+}} = 0.069$ nm, and $r_{O^{2-}} = 0.140$ nm. Thus, the total sphere volume in Equation 3.3 (which we denote as V_S), is the sum of the sphere volume of the 8 Fe^{2+}, 16 Fe^{3+}, and 32 O^{2-} ions as follows:

$$V_S = (8)\left(\frac{4}{3}\pi\right)(7.7 \times 10^{-9} \text{cm})^3 + (16)\left(\frac{4}{3}\pi\right)(6.9 \times 10^{-9} \text{cm})^3$$

$$+ (32)\left(\frac{4}{3}\pi\right)(1.40 \times 10^{-8}\ \text{cm})^3$$

$$= 4.05 \times 10^{-22}\ \text{cm}^3$$

And, as noted above, the unit cell volume (V_C) is just a^3, which means that

$$V_C = a^3 = (8.39 \times 10^{-8}\ \text{cm})^3 = 5.90 \times 10^{-22}\ \text{cm}^3$$

Finally, the atomic packing factor (APF) from Equation 3.3 is just

$$\text{APF} = \frac{V_S}{V_C} = \frac{4.05 \times 10^{-22}\ \text{cm}^3}{5.90 \times 10^{-22}\ \text{cm}^3} = 0.686$$

Silicate Ceramics

12.23 *In terms of bonding, explain why silicate materials have relatively low densities.*

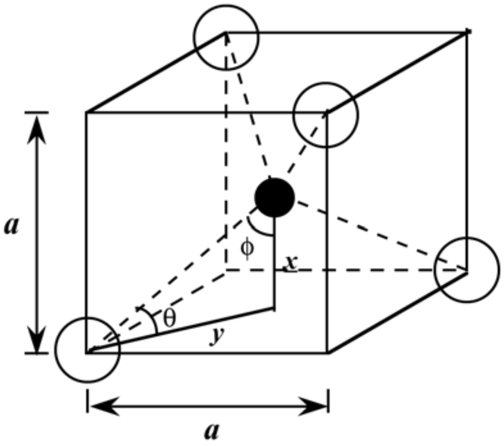
Answer

The silicate materials have relatively low densities because the atomic bonds have a high degree of covalency (Table 12.1), and, therefore, are directional. This limits the packing efficiency of the atoms, and therefore, the magnitude of the density.

12.24 *Determine the angle between covalent bonds in an* SiO_4^{4-} *tetrahedron.*

Solution

Below is shown a SiO_4^{4-} tetrahedron situated within a cube; oxygen atoms are represented by open circles, the Si atom by the dark circle.



Now if we extend the base diagonal (having a length of *y*) from one corner to the other, then

$$(2y)^2 = a^2 + a^2 = 2a^2$$

where *a* is the unit cell edge length. Now, solving the above expression for *y* gives

$$y = \frac{a\sqrt{2}}{2}$$

Furthermore, from he above illustration it may be noted that $x = a/2$, which means that

$$\tan\theta = \frac{x}{y} = \frac{\frac{a}{2}}{\frac{a\sqrt{2}}{2}} = \frac{1}{\sqrt{2}}$$

Now solving the above expression for the angle θ yields the following:

$$\theta = \tan^{-1}\left(\frac{1}{\sqrt{2}}\right) = 35.26°$$

Now, from the illustration shown above, we solve for the value of the angle ϕ realizing that the angle between the *x* and *y* line segments is a right angle (90°); therefore since the total of the angles in a triangle is 180° then

$$\phi = 180° - 90° - \theta$$

$$= 180° - 90° - 35.26° = 54.74°$$

Finally, from the above illustration the bond angle between two silicon atoms (those two atoms located on the base of this unit cell) is just 2ϕ, or $2\phi = (2)(54.74°) = 109.48°$.

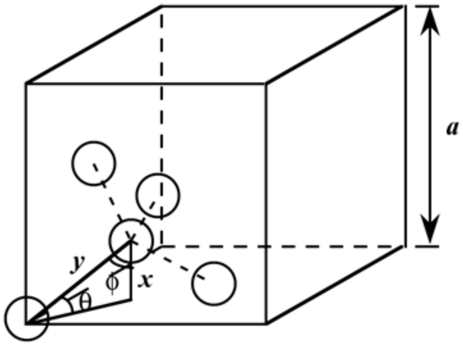
Carbon

12.25 *Compute the theoretical density of diamond, given that the C—C distance and bond angle are 0.154 nm and 109.5°, respectively. How does this value compare with the measured density?*

Solution

This problem asks that we compute the theoretical density of diamond given that the C—C distance and bond angle are 0.154 nm and 109.5°, respectively. To compute the density of diamond it is necessary that we use Equation 12.1. However, in order to do this it is necessary to determine the unit cell edge length (*a*) from the given C—C distance. Once we know the value of *a* it is possible to calculate the unit cell volume (V_C) since, because the unit cell is a cube, $V_C = a^3$.

The drawing below shows the cubic unit cell with those carbon atoms that bond to one another in one-quarter of the unit cell.



From this figure, ϕ is one-half of the bond angle or ϕ = 109.5°/2 = 54.75°; but since the triangle having sides labeled *x* and *y* is a right triangle then

$$\theta + \phi = 90°$$

or that

$$\theta = 90° - 54.75° = 35.25°$$

Also, we are given in the problem statement that y = 0.154 nm, the carbon-carbon bond distance.
Furthermore, it is the case that $x = a/4$, and therefore,

$$x = \frac{a}{4} = y \sin \theta$$

Or

$$a = 4y \sin \theta = (4)(0.154 \text{ nm})(\sin 35.25°) = 0.356 \text{ nm}$$

$$= 3.56 \times 10^{-8}\ \text{cm}$$

As noted above, the unit cell volume, V_C is just a^3, that is

$$V_C = a^3 = (3.56 \times 10^{-8}\ \text{cm})^3 = 4.51 \times 10^{-23}\ \text{cm}^3$$

It is necessary that we use a modified form of Equation 12.1, because there is only one atom type—that is

$$\rho = \frac{n' A_C}{V_C N_A} \tag{12.1f}$$

where A_C is the atomic weight of carbon (12.01 g/mol). The parameter n' in this equation represents the number of carbon atoms per unit cell. The unit cell for diamond, Figure 12.16, consists of a face-centered cubic arrangement of carbon atoms, and, in addition, 4 carbon atoms that are situated within the interior of the unit cell. From Equation 3.2 (Section 3.4) the number of equivalent atoms in a FCC unit cell is 4; which means that n'= 8 when we add in the 4 interior carbon atoms. Therefore, the density of diamond is computed using the above Equation 12.1f, as follows:

$$\rho = \frac{n' A_C}{V_C N_A}$$

$$= \frac{(8\ \text{atoms/unit cell})(12.01\ \text{g/g-atom})}{(4.51 \times 10^{-23}\ \text{cm}^3/\text{unit cell})(6.022 \times 10^{23}\ \text{atoms/g-atom})}$$

$$= 3.54\ \text{g/cm}^3$$

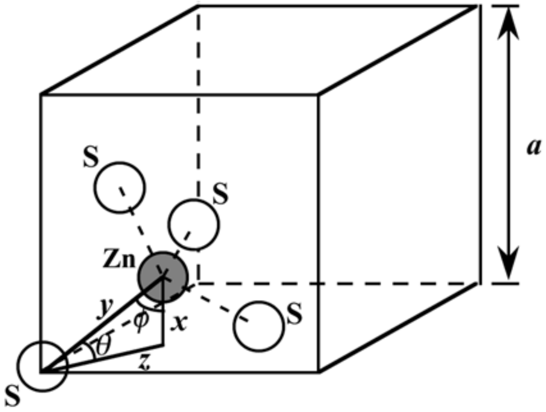
The measured density is 3.51 g/cm^3.

12.26 *Compute the theoretical density of ZnS, given that the Zn—S distance and bond angle are 0.234 nm and 109.5°, respectively. How does this value compare with the measured density?*

Solution

This problem asks that we compute the theoretical density of ZnS given that the Zn—S distance and bond angle are 0.234 nm and 109.5°, respectively. To compute the density of zinc sulfide it is necessary that we use Equation 12.1. However, in order to do this it is necessary to determine the unit cell edge length (a) from the given Zn—S distance. Once we know the value of a it is possible to calculate the unit cell volume (V_C) since, because the unit cell is a cube, $V_C = a^3$.

The drawing below shows the cubic unit cell that shows one Zn atom, which bonds to four sulfur atoms within one-quarter of the unit cell.



From this figure, ϕ is one-half of the bond angle between the Zn atom and the two S atoms in the bottom plane. Thus $\phi = 109.5°/2 = 54.75°$; but since the triangle having sides labeled x, y, and z is a right triangle, and the angle between sides x and z is 90°, □□□□

$$\theta + \phi = 90°$$

or

$$\theta = 90° - 54.75° = 35.25°$$

Also, we are given in the problem statement that $y = 0.234$ nm, the Zn-S bond distance.

Furthermore, it is the case that $x = a/4$, and therefore,

$$x = \frac{a}{4} = y \sin \theta$$

Or

$$a = 4y \sin \theta = (4)(0.234 \text{ nm})(\sin 35.25°) = 0.540 \text{ nm}$$

$$= 5.40 \times 10^{-8} \text{ cm}$$

As noted above, the unit cell volume, V_C is just a^3, that is

$$V_C = a^3 = (5.40 \times 10^{-8} \text{ cm})^3 = 1.575 \times 10^{-22} \text{ cm}^3$$

Now, for this problem, Equation 12.1 reads as follows:

$$\rho = \frac{n'\left(\sum A_{\text{Zn}} + \sum A_{\text{S}}\right)}{V_C N_{\text{A}}} \tag{12.1g}$$

where

$\sum A_{\text{Zn}}$ equals the sum of the atomic weights of all Zn atoms in a formula (ZnS) unit, which is just the atomic weight of Zn (A_{Zn} = 65.41 g/mol) because there is only 1 Zn atom in an ZnS unit. Similarly

$\sum A_{\text{S}}$ equals the sum of the atomic weights of all S atoms in a ZnS unit = A_{S} = 32.06 g/mol.

Now, the parameter n' in this equation represents the number of Zn-S units per unit cell. Because the unit cell for ZnS contains equal numbers of Zn and S atoms, it is necessary only to determine the number of either Zn or S atoms in the unit cell. From Figure 12.4, which represents a unit cell for ZnS, it may be noted that the sulfur atoms form a face-centered cubic structure. From Equation 3.2 (Section 3.4) the number of equivalent atoms in a FCC unit cell is 4, and thus there are 4 ZnS units per unit cell, or that n' = 4. Therefore, the density of ZnS is computed using the above Equation 12.1g, as follows:

$$\rho = \frac{n'\left(\sum A_{\text{Zn}} + \sum A_{\text{S}}\right)}{V_C N_{\text{A}}}$$

$$= \frac{(4 \text{ Zn-S units/unit cell})(65.41 \text{ g/mol} + 32.06 \text{ g/mol})}{(1.575 \times 10^{-22} \text{ cm}^3\text{/unit cell})(6.022 \times 10^{23} \text{ atoms/mol})}$$

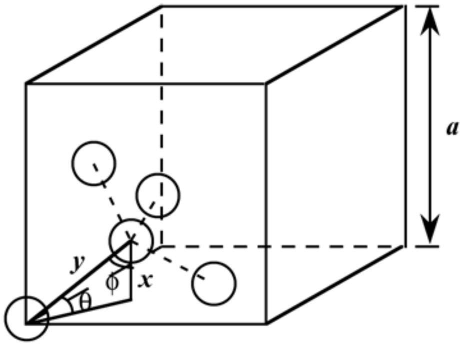
$$= 4.11 \text{ g/cm}^3$$

The measured density is 4.10 g/cm^3.

12.27 *Compute the atomic packing factor for the diamond cubic crystal structure (Figure 12.16). Assume that bonding atoms touch one another, that the angle between adjacent bonds is 109.5°, and that each atom internal to the unit cell is positioned a/4 of the distance away from the two nearest cell faces (a is the unit cell edge length).*

Solution

We are asked in this problem to compute the atomic packing factor for the diamond cubic crystal structure, given that the angle between adjacent bonds is 109.5°. Let us consider he drawing below, which represents the diamond cubic unit cell with those carbon atoms that bond to one another in one-quarter of the unit cell.



Using the above sketch the first thing that we must do is to determine the unit cell volume V_C in terms of the atomic radius *r*. The carbon atom that resides at the intersection between lines *x* and *y* is one-quarter of the distance between from the top and bottom faces, as noted in the problem statement—that is, *x* = *a*/4. Furthermore, from the triangle comprised of sizes denoted *x, y*, and *z* the following relationship exists:

$$\sin\theta = \frac{x}{y}$$

or that $x = y\sin\theta$. And, since *x* = *a*/4 it is the case that

$$x = \frac{a}{4} = y\,\sin\,\theta$$

Or

$$a = 4y\,\sin\,\theta \qquad \text{(S12.27)}$$

Because the two C atoms that are located at the end of the line segment labeled "*y*" touch one another, it the case that *y* = 2*r*. Furthermore, from the above sketch, it may be noted that ϕ is one-half of the bond angle or ϕ = 109.5°/2 = 54.75°; but since this triangle having sides labeled *x, y,* and *z* is a right triangle then

$$\theta + \phi = 90^\circ$$

or that

$$\theta = 90^\circ - 54.75^\circ = 35.25^\circ$$

Thus, we may compute the unit cell edge length using Equation S12.27 as follows:

$$a = 4y\sin\theta$$

$$= (4)(2r)(\sin 35.25^\circ) = 4.62r$$

Furthermore, since the unit cell is cubic, $V_C = a^3$, and therefore

$$V_C = (4.617r)^3 = 98.42\ r^3$$

Now, it is necessary to determine the sphere volume in the unit cell, V_S, in terms of r. For this unit cell (Figure 12.16) there are 4 interior atoms, 6 face atoms, and 8 corner atoms. Thus, from Equation 3.2, the number of equivalent atoms per unit cell is

$$N = N_i + \frac{N_f}{2} + \frac{N_c}{8}$$

$$= 4 + \frac{6}{2} + \frac{8}{8}$$

= 8 atoms/unit cell

Therefore, inasmuch as the volume of a sphere of radius r is equal to

$$V = \frac{4}{3}\pi r^3$$

The total sphere volume within a unit cell V_S is equal to

$$V_S = (8)\left(\frac{4}{3}\pi r^3\right) = 33.51\ r^3$$

Finally, the atomic packing factor is determined using Equation 3.3 as follows:

$$\text{APF} = \frac{V_S}{V_C} = \frac{33.51\ r^3}{98.42\ r^3} = 0.340$$

Imperfections in Ceramics

12.28 *Would you expect Frenkel defects for anions to exist in ionic ceramics in relatively large concentrations? Why or why not?*

Answer

Frenkel defects for anions would not exist in appreciable concentrations because the anion (of an anion vacancy-anion interstitial pair) is quite large and is highly unlikely to exist as an interstitial.

12.29 *Calculate the fraction of lattice sites that are Schottky defects for cesium chloride at its melting temperature (645°C). Assume an energy for defect formation of 1.86 eV.*

Solution

In order to solve this problem it is necessary to use Equation 12.3 and solve for the N_S/N ratio. Rearrangement of Equation 12.3 and substituting values for temperature and the energy of defect formation (Q_S) given in the problem statement leads to

$$\frac{N_s}{N} = \exp\left(-\frac{Q_s}{2kT}\right)$$

$$= \exp\left[-\frac{1.86\text{ eV}}{(2)(8.62 \times 10^{-5}\text{ eV/K})(645 + 273\text{ K})}\right]$$

$$= 7.87 \times 10^{-6}$$

12.30 *Calculate the number of Frenkel defects per cubic meter in silver chloride at 350°C. The energy for defect formation is 1.1 eV, whereas the density for AgCl is 5.50 g/cm^3 at 350°C.*

Solution

Solution of this problem is possible using Equation 12.2. However, we must first determine the value of N, the number of lattice sites per cubic meter, which is possible using a modified form of Equation 4.2, which is given as follows:

$$N = \frac{N_A \rho}{A_{Ag} + A_{Cl}}$$

in which A_{Ag} and A_{Cl} are, respectively, the atomic weights of Ag and Cl (i.e., 107.87 g/mol and 35.45 g/mol). Thus, using the above equation we calculate the value for N

$$N = \frac{(6.022 \times 10^{23} \text{ atoms/mol})(5.50 \text{ g/cm}^3)(10^6 \text{ cm}^3/\text{m}^3)}{107.87 \text{ g/mol} + 35.45 \text{ g/mol}}$$

$$= 2.31 \times 10^{28} \text{ lattice sites/m}^3$$

And, finally the value of N_{fr} is computed using Equation 12.2 as

$$N_{fr} = N \exp\left(-\frac{Q_{fr}}{2kT}\right)$$

$$= (2.31 \times 10^{28} \text{ lattice sites/m}^3) \exp\left[-\frac{1.1 \text{ eV}}{(2)(8.62 \times 10^{-5} \text{ eV/K})(350 + 273 \text{ K})}\right]$$

$$= 8.24 \times 10^{23} \text{ defects/m}^3$$

12.31 *Using the following data that relate to the formation of Schottky defects in some oxide ceramic (having the chemical formula MO), determine the following:*

(a) The energy for defect formation (in eV)

(b) The equilibrium number of Schottky defects per cubic meter at 1000°C

(c) The identity of the oxide (i.e., what is the metal M?)

***T* (°C)**	***ρ* (*g/cm*^{3})**	***N*$_s$ (*m*$^{-3}$)**
750	*3.50*	*5.7 × 10*^{9}
1000	*3.45*	*?*
1500	*3.40*	*5.8 × 10*^{17}

Solution

This problem provides for some oxide ceramic, at temperatures of 750°C and 1500°C, values for density and the number of Schottky defects per cubic meter. The (a) portion of the problem asks that we compute the energy for defect formation. To begin, let us combine a modified form of Equation 4.2—viz.

$$N = \left(\frac{N_A \rho}{A_M + A_O}\right)$$

where A_M and A_O are the atomic weights of the metal M and oxygen, respectively, with Equation 12.3

$$N_s = N \exp\left(-\frac{Q_s}{2kT}\right)$$

which leads to the following:

$$N_s = \left(\frac{N_A \rho}{A_M + A_O}\right) \exp\left(-\frac{Q_s}{2kT}\right)$$

Inasmuch as this is a hypothetical oxide material, we don't know the atomic weight of metal M, nor the value of Q_s in the above equation. Therefore, let us write equations of the above form for two temperatures, T_1 and T_2. These expressions are as follows:

$$N_{s1} = \left(\frac{N_A \rho_1}{A_M + A_O}\right) \exp\left(-\frac{Q_s}{2kT_1}\right) \tag{12.S1a}$$

$$N_{s2} = \left(\frac{N_A \rho_2}{A_M + A_O}\right) \exp\left(-\frac{Q_s}{2kT_2}\right) \tag{12.S1b}$$

Dividing the first of these equations by the second leads to

$$\frac{N_{s1}}{N_{s2}} = \frac{\left(\frac{N_A \rho_1}{A_M + A_O}\right) \exp\left(-\frac{Q_s}{2kT_1}\right)}{\left(\frac{N_A \rho_2}{A_M + A_O}\right) \exp\left(-\frac{Q_s}{2kT_2}\right)}$$

which, after some algebraic manipulation, reduces to the form

$$\frac{N_{s1}}{N_{s2}} = \frac{\rho_1}{\rho_2} \exp\left[-\frac{Q_s}{2k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] \qquad (12.S2)$$

Now, taking natural logarithms of both sides of this equation gives

$$\ln\left(\frac{N_{s1}}{N_{s2}}\right) = \ln\left(\frac{\rho_1}{\rho_2}\right) - \frac{Q_s}{2k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

And solving for Q_s from the above equation leads to the expression

$$Q_s = \frac{-2k\left[\ln\left(\frac{N_{s1}}{N_{s2}}\right) - \ln\left(\frac{\rho_1}{\rho_2}\right)\right]}{\frac{1}{T_1} - \frac{1}{T_2}}$$

Let us take T_1 = 750°C and T_2 = 1500°C, and we may compute the value of Q_s as follows:

$$Q_s = \frac{-(2)(8.62 \times 10^{-5}\ \text{eV/K})\left[\ln\left(\frac{5.7 \times 10^{9}\ \text{m}^{-3}}{5.8 \times 10^{17}\ \text{m}^{-3}}\right) - \ln\left(\frac{3.50\ \text{g/cm}^3}{3.40\ \text{g/cm}^3}\right)\right]}{\frac{1}{750 + 273\ \text{K}} - \frac{1}{1500 + 273\ \text{K}}}$$

$$= 7.70\ \text{eV}$$

(b) It is now possible to solve for N_s at 1000°C using Equation 12.S2 above. This time let's take T_1 = 1000°C and T_2 = 750°C. Thus, solving for N_{s1}, substituting values provided in the problem statement and Q_s determined above yields

$$N_{s1} = \frac{N_{s2}\ \rho_1}{\rho_2} \exp\left[-\frac{Q_s}{2k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]$$

$$= \frac{(5.7 \times 10^{9}\ \mathrm{m}^{-3})(3.45\ \mathrm{g/cm^3})}{3.50\ \mathrm{g/cm^3}} \exp\left[-\frac{7.70\ \mathrm{eV}}{(2)(8.62 \times 10^{-5}\ \mathrm{eV/K})}\left(\frac{1}{1000 + 273\ \mathrm{K}} - \frac{1}{750 + 273\ \mathrm{K}}\right)\right]$$

$$= 2.98 \times 10^{13}\ \mathrm{m}^{-3}$$

(c) And, finally, we want to determine the identity of metal M. This is possible by computing the atomic weight of M (A_M) from Equation 12.S1a. Rearrangement of this expression leads to

$$\left(\frac{N_\mathrm{A}\rho_1}{A_\mathrm{M} + A_\mathrm{O}}\right) = N_{s1}\exp\left(\frac{Q_s}{2kT_1}\right)$$

And, after further algebraic manipulation yields the following equation:

$$\left[\frac{N_\mathrm{A}\rho_1}{N_{s1}\exp\left(\frac{Q_s}{2kT_1}\right)}\right] = A_\mathrm{M} + A_\mathrm{O}$$

And, solving this expression for A_M gives

$$A_\mathrm{M} = \left[\frac{N_\mathrm{A}\rho_1}{N_{s1}\exp\left(\frac{Q_s}{2kT_1}\right)}\right] - A_\mathrm{O}$$

Now, assuming that T_1 = 750°C, the value of A_M is

$$A_\mathrm{M} = \left\{\frac{(6.022 \times 10^{23}\ \mathrm{ions/mol})(3.50\ \mathrm{g/cm^3})(10^{6}\ \mathrm{cm^3/m^3})}{(5.7 \times 10^{9}\ \mathrm{ions/m^3})\exp\left[\frac{7.7\ \mathrm{eV}}{(2)(8.62 \times 10^{-5}\ \mathrm{eV/K})(750 + 273\ \mathrm{K})}\right]}\right\} - 16.00\ \mathrm{g/mol}$$

$$= 24.45\ \mathrm{g/mol}$$

Upon consultation of the periodic table in Figure 2.8, the divalent metal (i.e., that forms M^{2+} ions) that has an atomic weight closest to 24.45 g/mol is magnesium (with an atomic weight of 24.31 g/mol). Thus, this metal oxide is MgO.

12.32 *In your own words, briefly define the term* stoichiometric.

Answer

Stoichiometric means having exactly the ratio of anions to cations as specified by the chemical formula for the compound.

12.33 *If cupric oxide (CuO) is exposed to reducing atmospheres at elevated temperatures, some of the* Cu^{2+} *ions will become* Cu^{+}.

(a) Under these conditions, name one crystalline defect that you would expect to form in order to maintain charge neutrality.

(b) How many Cu^{+} *ions are required for the creation of each defect?*

(c) How would you express the chemical formula for this nonstoichiometric material?

Solution

(a) For a $Cu^{2+}O^{2-}$ compound in which a small fraction of the copper ions exist as Cu^{+}, for each Cu^{+} formed there is one less positive charge introduced (or one more negative charge). In order to maintain charge neutrality, we must either add an additional positive charge or subtract a negative charge. This may be accomplished be either creating Cu^{2+} interstitials or O^{2-} vacancies.

(b) There will be two Cu^{+} ions required for each of these defects.

(c) The chemical formula for this nonstoichiometric material is $\mathbf{Cu_{1+x}O}$ or $\mathbf{CuO_{1-x}}$, where x is some small fraction.

12.34 *Do the Hume-Rothery rules (Section 4.3) also apply to ceramic systems? Explain your answer.*

Answer

For metals, for appreciable solid solubility of one metal in another, the following characteristics of the metals must be the same or similar:

1. *Atomic size* (< ±15%)
2. *Crystal structure*
3. *Electronegativity*
4. *Valence*

A similar set of rules exist for one ceramics—that is, in order to have appreciable solid solubility of one ceramic compound in another the following rules must be satisfied:

1. Atomic size factor—similar to that for metallic systems for both cations and anions
2. Valence factor—valences (charges on) anions should be the same; also the same for cations
3. Crystal structures of the two compounds should be the same or similar
4. Other ceramic compounds may form (i.e., solid solubility is limited) when there is a difference in the electronic structure between the cations and/or anions of the two compounds.

12.35 *Which of the following oxides would you expect to form substitutional solid solutions that have complete (i.e., 100%) solubility with MgO? Explain your answers.*

(a) FeO

(b) BaO

(c) PbO

(d) CoO

Answer

In order to have a high degree (or 100% solubility) of one ceramic compound in another ceramic compound, the following criteria must be met: the relative sizes of cations/anions must be similar (< ±15%); the valence (or charges) on the cations and anions of both compounds must be the same; and the crystals structures of the two compounds must the same or similar. Inasmuch as crystal structure information for the compounds in this problem, for the most part, is not provided in the text, we will base our criteria only on the relative ion sizes and charges on the anions and cations. Because all of these ceramics are oxides and the charge on all of the cations is +2, in making solubility determinations, only the relative sizes of the cations will be considered.

(a) For FeO, the ionic radii of the Mg^{2+} and Fe^{2+} (found inside the front cover of the book) are 0.072 nm and 0.077 nm, respectively. Therefore the percentage difference in ionic radii, $\Delta r\%$ is determined as follows:

$$\Delta r\% = \frac{r_{Fe^{2+}} - r_{Mg^{2+}}}{r_{Fe^{2+}}} \times 100$$

$$= \frac{0.077 \text{ nm} - 0.072 \text{ nm}}{0.077 \text{ nm}} \times 100 = 6.5\%$$

which value is with the acceptable range for a high degree of solubility. Furthermore, as Table 12.4 notes, the crystal structures of both MgO and FeO are rock salt; therefore, it is expected that FeO and MgO form high degrees of solid solubility. Experimentally, these two ceramics exhibit 100% solubility.

(b) For BaO, the ionic radii of the Mg^{2+} and Ba^{2+} (found inside the front cover of the book) are 0.072 nm and 0.136 nm, respectively. Therefore the percentage difference in ionic radii, $\Delta r\%$ is determined as follows:

$$\Delta r\% = \frac{r_{Ba^{2+}} - r_{Mg^{2+}}}{r_{Ba^{2+}}} \times 100$$

$$= \frac{0.136 \text{ nm} - 0.072 \text{ nm}}{0.136 \text{ nm}} \times 100 = 47\%$$

This Δ*r*% value is much larger than the ±15% range, and, therefore, BaO is not expected to experience any appreciable solubility in MgO. Experimentally, the solubility of BaO in MgO is very small; this is also the case for the solubility of MgO in BaO.

(c) For PbO, the ionic radii of the Mg^{2+} and Pb^{2+} (found inside the front cover of the book) are 0.072 nm and 0.120 nm, respectively. Therefore the percentage difference in ionic radii, Δ*r*% is determined as follows:

$$\Delta r\% = \frac{r_{Pb^{2+}} - r_{Mg^{2+}}}{r_{Pb^{2+}}} \times 100$$

$$= \frac{0.120\ \text{nm} - 0.072\ \text{nm}}{0.120\ \text{nm}} \times 100 = 40\%$$

This Δ*r*% value is much larger than the ±15% range, and, therefore, PbO is not expected to experience any appreciable solubility in MgO.

(d) For CoO, the ionic radii of the Mg^{2+} and Co^{2+} (found inside the front cover of the book) are 0.072 nm and 0.072 nm, respectively. Therefore the percentage difference in ionic radii, Δ*r*% is determined as follows:

$$\Delta r\% = \frac{r_{Co^{2+}} - r_{Mg^{2+}}}{r_{Co^{2+}}} \times 100$$

$$= \frac{0.072\ \text{nm} - 0.072\ \text{nm}}{0.072\ \text{nm}} \times 100 = 0\%$$

which value is, of course, within the acceptable range for a high degree (probably 100%) of solubility.

12.36 *(a) Suppose that CaO is added as an impurity to* Li_2O*. If the* Ca^{2+} *substitutes for* Li^+*, what kind of vacancies would you expect to form? How many of these vacancies are created for every* Ca^{2+} *added?*

(b) Suppose that CaO is added as an impurity to $CaCl_2$*. If the* O^{2-} *substitutes for* Cl^-*, what kind of vacancies would you expect to form? How many of these vacancies are created for every* O^{2-} *added*?

Solution

(a) For Ca^{2+} substituting for Li^+ in Li_2O, lithium vacancies would be created. For each Ca^{2+} substituting for Li^+, one positive charge is added; in order to maintain charge neutrality, a single positive charge may be removed. Positive charges are eliminated by creating lithium vacancies, and for every Ca^{2+} ion added, a single lithium vacancy is formed.

(b) For O^{2-} substituting for Cl^- in $CaCl_2$, chlorine vacancies would be created. For each O^{2-} substituting for a Cl^-, one negative charge is added; negative charges are eliminated by creating chlorine vacancies. In order to maintain charge neutrality, one O^{2-} ion will lead to the formation of one chlorine vacancy.

12.37 *What point defects are possible for* Al_2O_3 *as an impurity in MgO? How many* Al^{3+} *ions must be added to form each of these defects?*

Solution

For every Al^{3+} ion that substitutes for Mg^{2+} in MgO, a single positive charge is added. Thus, in order to maintain charge neutrality, either a positive charge must be removed or a negative charge must be added.

Negative charges are added by creating O^{2-} interstitials, which are not likely to form.

Positive charges may be removed by forming Mg^{2+} vacancies, and one magnesium vacancy would be formed for every two Al^{3+} ions added.

Ceramic Phase Diagrams

12.38 *For the ZrO_2–CaO system (Figure 12.24), write all eutectic and eutectoid reactions for cooling.*

Solution

There is only one eutectic for the portion of the ZrO_2-CaO system shown in Figure 12.24, which, upon cooling, is

$$\textbf{Liquid} \rightarrow \textbf{cubic } \mathbf{ZrO_2} + \mathbf{CaZrO_3}$$

There are two eutectoids, which reactions are as follows:

$$\textbf{tetragonal} \rightarrow \textbf{monoclinic } \mathbf{ZrO_2} + \textbf{cubic } \mathbf{ZrO_2}$$

$$\textbf{cubic} \rightarrow \textbf{monoclinic } \mathbf{ZrO_2} + \mathbf{CaZr_4O_9}$$

12.39 *From Figure 12.23, the phase diagram for the MgO–*Al_2O_3 *system, it may be noted that the spinel solid solution exists over a range of compositions, which means that it is nonstoichiometric at compositions other than 50 mol% MgO–50 mol%* Al_2O_3.

(a) The maximum nonstoichiometry on the Al_2O_3*-rich side of the spinel phase field exists at about 2000°C (3630°F), corresponding to approximately 82 mol% (92 wt%)* Al_2O_3*. Determine the type of vacancy defect that is produced and the percentage of vacancies that exist at this composition.*

(b) The maximum nonstoichiometry on the MgO-rich side of the spinel phase field exists at about 2000°C (3630°F), corresponding to approximately 39 mol% (62 wt%) Al_2O_3*. Determine the type of vacancy defect that is produced and the percentage of vacancies that exist at this composition.*

Solution

(a) For this portion of the problem we are to determine the type of vacancy defect that is produced on the Al_2O_3-rich side of the spinel phase field (Figure 12.23) and the percentage of these vacancies at the maximum nonstoichiometry (82 mol% Al_2O_3). On the alumina-rich side of this phase field, there is an excess of Al^{3+} ions, which means that some of the Al^{3+} ions substitute for Mg^{2+} ions. In order to maintain charge neutrality, Mg^{2+} vacancies are formed, and for every Mg^{2+} vacancy formed, two Al^{3+} ions substitute for three Mg^{2+} ions.

Now, we will calculate the percentage of Mg^{2+} vacancies that exist at 82 mol% Al_2O_3. Let us arbitrarily choose as our basis 50 MgO-Al_2O_3 units of the stoichiometric material, which consists of 50 Mg^{2+} ions and 100 Al^{3+} ions. Furthermore, let us designate the number of Mg^{2+} vacancies as x, which means that $2x$ Al^{3+} ions have been added and $3x$ Mg^{2+} ions have been removed (two of which are filled with Al^{3+} ions). Using our 50 MgO-Al_2O_3 unit basis, the number of moles of Al_2O_3 in the nonstoichiometric material is $(100 + 2x)/2$; similarly the number of moles of MgO is $(50 - 3x)$. Thus, the expression for the mol% of Al_2O_3 is just

$$\text{mol\% Al}_2\text{O}_3 = \left[\frac{\dfrac{100 + 2x}{2}}{\dfrac{100 + 2x}{2} + (50 - 3x)}\right] \times 100$$

If we solve for x when the mol% of Al_2O_3 = 82, then $x = 12.1$. Thus, adding $2x$ or (2)(12.1) = 24.2 Al^{3+} ions to the original material consisting of 100 Al^{3+} and 50 Mg^{2+} ions will produce 12.1 Mg^{2+} vacancies. Therefore, the percentage of vacancies is just

$$\text{\% vacancies} = \frac{12.1}{100 + 50} \times 100 = 8.1\%$$

(b) Now, we are asked to make the same determinations for the MgO-rich side of the spinel phase field, for 39 mol% Al_2O_3. In this case, Mg^{2+} ions are substituting for Al^{3+} ions. Since the Mg^{2+} ion has a lower charge than the Al^{3+} ion, in order to maintain charge neutrality, negative charges must be eliminated, which may be accomplished by introducing O^{2-} vacancies. For every 2 Mg^{2+} ions that substitute for 2 Al^{3+} ions, one O^{2-} vacancy is formed.

Now, we will calculate the percentage of O^{2-} vacancies that exist at 39 mol% Al_2O_3. Let us arbitrarily choose as our basis 50 MgO-Al_2O_3 units of the stoichiometric material, which consists of 50 Mg^{2+} ions 100 Al^{3+} ions. Furthermore, let us designate the number of O^{2-} vacancies as *y*, which means that 2*y* Mg^{2+} ions have been added and 2*y* Al^{3+} ions have been removed. Using our 50 MgO- Al_2O_3 unit basis, the number of moles of Al_2O_3 in the nonstoichiometric material is (100 – 2*y*)/2; similarly the number of moles of MgO is (50 + 2*y*). Thus, the expression for the mol% of Al_2O_3 is just

$$\text{mol\% } Al_2O_3 = \left[\frac{\dfrac{100 - 2y}{2}}{\dfrac{100 - 2y}{2} + (50 + 2y)}\right] \times 100$$

If we solve for *y* when the mol% of Al_2O_3 = 39, then $y = 7.91$. Thus, 7.91 O^{2-} vacancies are produced in the original material that had 200 O^{2-} ions. Therefore, the percentage of vacancies is just

$$\text{\% vacancies} = \frac{7.91}{200} \times 100 = 3.96\%$$

12.40 *When kaolinite clay [$Al_2(Si_2O_5)(OH)_4$] is heated to a sufficiently high temperature, chemical water is driven off.*

(a) Under these circumstances, what is the composition of the remaining product (in weight percent Al_2O_3)?

(b) What are the liquidus and solidus temperatures of this material?

Solution

(a) The chemical formula for kaolinite clay may also be written as Al_2O_3–$2SiO_2$-$2H_2O$. Thus, if we remove the chemical water, the formula becomes Al_2O_3–$2SiO_2$. The formula weight for Al_2O_3 is just (2)(26.98 g/mol) + (3)(16.00 g/mol) = 101.96 g/mol; and for SiO_2 the formula weight is 28.09 g/mol + (2)(16.00 g/mol) = 60.09 g/mol. Thus, the composition of this product, in terms of the concentration of Al_2O_3, $C_{Al_2O_3}$, in weight percent is just

$$C_{Al_2O_3} = \frac{101.96 \text{ g/mol}}{101.96 \text{ g/mol} + (2)(60.09 \text{ g/mol})} \times 100 = 45.9 \text{ wt\%}$$

(b) The liquidus and solidus temperatures for this material as determined from the SiO_2–Al_2O_3 phase diagram, Figure 12.25, are 1825°C and 1587°C, respectively.

Brittle Fracture of Ceramics

12.41 *Briefly answer the following:*

(a) Why may there be significant scatter in the fracture strength for some given ceramic material?

(b) Why does the fracture strength increase with decreasing specimen size?

Answer

(a) There may be significant scatter in the fracture strength for some given ceramic material because the fracture strength depends on the probability of the existence of a flaw that is capable of initiating a crack; this probability varies from specimen to specimen of the same material.

(b) The fracture strength increases with decreasing specimen size because as specimen size decreases, the probably of the existence of a flaw of that is capable of initiating a crack diminishes.

12.42 *The tensile strength of brittle materials may be determined using a variation of Equation 8.1. Compute the critical crack tip radius for a glass specimen that experiences tensile fracture at an applied stress of 70 MPa (10,000 psi). Assume a critical surface crack length of 10^{-2} mm and a theoretical fracture strength of E/10, where E is the modulus of elasticity.*

Solution

We are asked for the critical crack tip radius for a glass. From Equation 8.1

$$\sigma_m = 2\sigma_0\left(\frac{a}{\rho_t}\right)^{1/2}$$

Fracture will occur when σ_m reaches the fracture strength of the material, which is given as $E/10$; thus

$$\frac{E}{10} = 2\sigma_0\left(\frac{a}{\rho_t}\right)^{1/2}$$

Or, solving for ρ_t

$$\rho_t = \frac{400\, a\sigma_0^2}{E^2}$$

From Table 12.5, for glass E = 69 GPa (or 69 × 10^3 MPa)—thus, we compute the value of ρ_t as follows:

$$\rho_t = \frac{(400)(1 \times 10^{-2}\text{ mm})(70\text{ MPa})^2}{(69 \times 10^3\text{ MPa})^2}$$

$$= 4.1 \times 10^{-6}\text{ mm} = 4.1\text{ nm}$$

12.43 *The fracture strength of glass may be increased by etching away a thin surface layer. It is believed that the etching may alter surface crack geometry (i.e., reduce the crack length and increase the tip radius). Compute the ratio of the etched and original crack-tip radii for a fourfold increase in fracture strength if half of the crack length is removed.*

Solution

This problem asks that we compute the crack tip radius ratio before and after etching. Let

$$\rho_t = \textbf{original crack tip radius, and}$$
$$\rho'_t = \textbf{etched crack tip radius}$$

Also, as given in the problem statement

$$\sigma'_f = \sigma_f$$

$$a' = \frac{a}{2}$$

$$\sigma'_0 = 4\sigma_0$$

When we incorporate the above relationships into two expressions of Equation 8.1 as follows:

$$\sigma_f = 2\sigma_0\left(\frac{a}{\rho_t}\right)^{1/2} = \sigma'_f = 2\sigma'_0\left(\frac{a'}{\rho'_t}\right)^{1/2}$$

We now solve for the $\frac{\rho'_t}{\rho_t}$ ratio, which yields the following:

$$\frac{\rho'_t}{\rho_t} = \left(\frac{\sigma'_0}{\sigma_0}\right)^2\left(\frac{a'}{a}\right) = \left(\frac{4\sigma_0}{\sigma_0}\right)^2\left(\frac{a/2}{a}\right) = \mathbf{8}$$

which is the solution requested in the problem statement.

Stress–Strain Behavior

12.44 *A three-point bending test is performed on a spinel ($MgAl_2O_4$) specimen having a rectangular cross section of height d = 3.8 mm (0.15 in.) and width b = 9 mm (0.35 in.); the distance between support points is 25 mm (1.0 in.).*

(a) Compute the flexural strength if the load at fracture is 350 N (80 lb_f).

(b) The point of maximum deflection Δy occurs at the center of the specimen and is described by

$$\Delta y = \frac{FL^3}{48EI} \tag{12.11}$$

where E is the modulus of elasticity and I is the cross-sectional moment of inertia. Compute Δy at a load of 310 N (70 lb_f).

Solution

(a) For this portion of the problem we are asked to compute the flexural strength for a spinel specimen that is subjected to a three-point bending test. The flexural strength for a rectangular cross-section (Equation 12.7a) is just

$$\sigma_{fs} = \frac{3F_f L}{2bd^2}$$

for a rectangular cross-section. Incorporating values for the parameters in this equation that are provided in the problem statement, gives the following flexural strength:

$$\sigma_{fs} = \frac{(3)(350\text{ N})(25 \times 10^{-3}\text{m})}{(2)(9.0 \times 10^{-3}\text{m})(3.8 \times 10^{-3}\text{m})^2} = 101 \text{ MPa} \quad (15{,}200 \text{ psi})$$

(b) We are now asked to compute the maximum deflection using Equation 12.11. From Table 12.5, the elastic modulus (*E*) for spinel is 260 GPa (38 × 10^6 psi). Also, the moment of inertia for a rectangular cross section (Figure 12.30) is just

$$I = \frac{bd^3}{12}$$

Incorporating this expression for *I* into Equation 12.11 and also the value for *E*, and values of *F*, *L*, *b*, and *d* given in the problem statement [310 N, 25 mm (25 × 10^{-3} m), 9 mm (9 × 10^{-3} m), and 3.8 mm (3.8 10^{-3} m), respectively] the value of Δ*y* is computed as follows:

$$\Delta y = \frac{FL^3}{48E\left(\frac{bd^3}{12}\right)} = \frac{FL^3}{4Ebd^3}$$

$$= \frac{(310\ \mathrm{N})(25 \times 10^{-3}\ \mathrm{m})^3}{(4)(260 \times 10^9\ \mathrm{N/m^2})(9.0 \times 10^{-3}\ \mathrm{m})(3.8 \times 10^{-3}\ \mathrm{m})^3}$$

$$= 9.4 \times 10^{-6}\ \mathrm{m} = 9.4 \times 10^{-3}\ \mathrm{mm} \quad (3.9 \times 10^{-4}\ \mathrm{in.})$$

12.45 *A circular specimen of MgO is loaded using a three-point bending mode. Compute the minimum possible radius of the specimen without fracture, given that the applied load is 5560 N (1250 lb$_f$), the flexural strength is 105 MPa (15,000 psi), and the separation between load points is 45 mm (1.75 in.).*

Solution

We are asked to calculate the maximum radius of a circular specimen of MgO that is loaded using three-point bending. Solving for the specimen radius, *R*, from Equation 12.7b leads to the following:

$$R = \left[\frac{F_f L}{\sigma_{fs}\pi}\right]^{1/3}$$

which, when substituting the parameters stipulated in the problem statement, yields

$$R = \left[\frac{(5560\ N)(45 \times 10^{-3}\,\mathrm{m})}{(105 \times 10^{6}\,\mathrm{N/m^2})(\pi)}\right]^{1/3}$$

$$= 9.1 \times 10^{-3}\ \mathrm{m} = 9.1\ \mathrm{mm} \quad (0.36\ \mathrm{in.})$$

Thus, the minimum allowable specimen radius is 9.1 mm (0.36 in.)

12.46 *A three-point bending test was performed on an aluminum oxide specimen having a circular cross section of radius 5.0 mm (0.20 in.); the specimen fractured at a load of 3000 N (675 lb_f) when the distance between the support points was 40 mm (1.6 in.). Another test is to be performed on a specimen of this same material, but one that has a square cross section of 15 mm (0.6 in.) length on each edge. At what load would you expect this specimen to fracture if the support point separation is maintained at 40 mm (1.6 in.)?*

Solution

For this problem, the load is given at which a circular specimen of aluminum oxide fractures when subjected to a three-point bending test; we are then are asked to determine the load at which a specimen of the same material having a square cross-section fractures. It is first necessary to compute the flexural strength of the cylindrical specimen from Equation 12.7b; then, using this value, calculate the value of F_f in Equation 12.7a (for the specimen having a square cross-section). From Equation 12.7b, and using the first set of data provided in the problem statement, we compute the flexural strength as follows:

$$\sigma_{fs} = \frac{F_f L}{\pi R^3}$$

$$= \frac{(3000\ \text{N})(40 \times 10^{-3}\ \text{m})}{(\pi)(5.0 \times 10^{-3}\ \text{m})^3} = 306 \times 10^6\ \text{N/m}^2 = 306\ \text{MPa}\quad (42{,}970\ \text{psi})$$

Now, solving for F_f for the second specimen using Equation 12.7a, realizing that $b = d = 15$ mm (15×10^{-3} m), yields

$$F_f = \frac{2\sigma_{fs} d^3}{3L}$$

$$= \frac{(2)(306 \times 10^6\ \text{N/m}^2)(15 \times 10^{-3}\ \text{m})^3}{(3)(40 \times 10^{-3}\ \text{m})} = 17{,}200\ \text{N}\quad (3870\ \text{lb}_\text{f})$$

12.47 *(a) A three-point transverse bending test is conducted on a cylindrical specimen of aluminum oxide having a reported flexural strength of 300 MPa (43,500 psi). If the specimen radius is 5.0 mm (0.20 in.) and the support point separation distance is 15.0 mm (0.61 in.), would you expect the specimen to fracture when a load of 7500 N (1690 lb$_f$) is applied? Justify your answer.*

(b) Would you be 100% certain of the answer in part (a)? Why or why not?

Solution

(a) This portion of the problem asks that we determine whether or not a cylindrical specimen of aluminum oxide having a flexural strength of 300 MPa and a radius of 5.0 mm will fracture when subjected to a load of 7500 N in a three-point bending test; the support point separation is given as 15.0 mm. Using Equation 12.7b we will calculate the value of σ, in this case the flexural stress; if this value is greater than the flexural strength, σ_{fs} (300 MPa), then fracture is expected to occur. Employment of Equation 12.7b to compute the flexural stress yields

$$\sigma = \frac{FL}{\pi R^3} = \frac{(7500\ \mathrm{N})(15 \times 10^{-3}\ \mathrm{m})}{(\pi)(5 \times 10^{-3}\ \mathrm{m})^3}$$

$$= 286.5 \times 10^6\ \mathrm{N/m^2} = 286.5\ \mathrm{MPa} \quad (40{,}300\ \mathrm{psi})$$

Since this value (286.5 MPa) is less than the given value of σ_{fs} (300 MPa), then fracture is not predicted.

(b) However, the certainty of this prediction is not 100% because there is always some variability in the flexural strength for ceramic materials, and since this value of the flexural stress, σ, is relatively close to σ_{fs} there is some chance that fracture will occur.

Mechanisms of Plastic Deformation

12.48 *Cite one reason why ceramic materials are, in general, harder yet more brittle than metals.*

Answer

Crystalline ceramics are harder yet more brittle than metals because they (ceramics) have fewer slip systems, and, therefore, dislocation motion is highly restricted.

Miscellaneous Mechanical Considerations

12.49 *The modulus of elasticity for spinel ($MgAl_2O_4$) having 5 vol% porosity is 240 GPa (35 × 10^6 psi).*

(a) Compute the modulus of elasticity for the nonporous material.

(b) Compute the modulus of elasticity for 15 vol% porosity.

Solution

(a) This portion of the problem requests that we compute the modulus of elasticity for nonporous spinel given that E = 240 GPa for a material having 5 vol% porosity. Thus, we solve Equation 12.9 for E_0 (the modulus of elasticity of the nonporous material) using P = 0.05, as follows:

$$E_0 = \frac{E}{1 - 1.9P + 0.9P^2}$$

$$= \frac{240 \text{ GPa}}{1 - (1.9)(0.05) + (0.9)(0.05)^2} = 265 \text{ GPa} \quad (38.6 \times 10^6 \text{ psi})$$

(b) Now we are asked to determine the value of E at P = 15 vol% (i.e., 0.15). Using Equation 12.9 the following results:

$$E = E_0(1 - 1.9P + 0.9P^2)$$

$$= (265 \text{ GPa})\left[1 - (1.9)(0.15) + (0.09)(0.15)^2\right] = 195 \text{ GPa} \quad (28.4 \times 10^6 \text{ psi})$$

12.50 *The modulus of elasticity for titanium carbide (TiC) having 5 vol% porosity is 310 GPa (45 × 10^6 psi).*

(a) Compute the modulus of elasticity for the nonporous material.

(b) At what volume percent porosity will the modulus of elasticity be 240 GPa (35 × 10^6 psi)?

Solution

(a) This portion of the problem requests that we compute the modulus of elasticity for nonporous TiC given that E = 310 GPa (45 × 10^6 psi) for a material having 5 vol% porosity. Thus, we solve Equation 12.9 for E_0 (the modulus of elasticity of the nonporous material) using P = 0.05, as follows:

$$E_0 = \frac{E}{1 - 1.9P + 0.9P^2}$$

$$= \frac{310\ \text{GPa}}{1 - (1.9)(0.05) + (0.9)(0.05)^2} = 342\ \text{GPa}\quad \left(49.6 \times 10^6\ \text{psi}\right)$$

(b) Now we are asked to compute the volume percent porosity at which the elastic modulus of TiC is 240 MPa (35 × 10^6 psi). Since from part (a), E_0 = 342 GPa, and using Equation 12.9, we may write the following:

$$\frac{E}{E_0} = \frac{240\ \text{GPa}}{342\ \text{GPa}} = 0.702 = 1 - 1.9P + 0.9P^2$$

Or, after rearrangement the following expression results:

$$0.9P^2 - 1.9P + 0.298 = 0$$

Now, solving for the value of P using the quadratic equation solution yields

$$P = \frac{1.9 \pm \sqrt{(-1.9)^2 - (4)(0.9)(0.298)}}{(2)(0.9)}$$

The positive and negative roots are as follows:

$P^+ = 1.94$

$P^- = 0.171$

Obviously, only the negative root is physically meaningful, and therefore the value of the porosity to give the desired modulus of elasticity is 17.1 vol%.

12.51 *Using the data in Table 12.5, do the following:*

(a) Determine the flexural strength for nonporous MgO, assuming a value of 3.75 for n in Equation 12.10.

(b) Compute the volume fraction porosity at which the flexural strength for MgO is 74 MPa (10,700 psi).

Solution

(a) This part of the problem asks us to determine the flexural strength of nonporous MgO assuming that the value of *n* in Equation 12.10 is 3.75. Taking natural logarithms of both sides of Equation 12.10 yields

$$\ln \sigma_{fs} = \ln \sigma_0 - nP$$

In Table 12.5 it is noted that for MgO and for $P = 0.05$, $\sigma_{fs} = 105$ MPa. For the nonporous material (i.e., when $P = 0$), then $\ln \sigma_0 = \ln \sigma_{fs}$. Solving for $\ln \sigma_0$ from the above equation and using these data gives

$$\ln \sigma_0 = \ln \sigma_{fs} + nP$$

$$= \ln(105 \text{ MPa}) + (3.75)(0.05)$$

$$= 4.841$$

which means that

$$\sigma_0 = e^{4.841} = 127 \text{ MPa} \quad (18{,}100 \text{ psi})$$

(b) Now we are asked to compute the volume percent porosity to yield a σ_{fs} of 74 MPa (10,700 psi). Taking the natural logarithms of both sides of Equation 12.10 and solving for *P* leads to

$$P = \frac{\ln \sigma_0 - \ln \sigma_{fs}}{n}$$

and incorporating values for σ_0 and *n* yields the following value for *P:*

$$P = \frac{\ln (127 \text{ MPa}) - \ln (74 \text{ MPa})}{3.75}$$

$$= 0.144 \text{ or } 14.4 \text{ vol\%}$$

12.52 *The flexural strength and associated volume fraction porosity for two specimens of the same ceramic material are as follows:*

σ_{fs} ***(MPa)***	***P***
70	*0.10*
60	*0.15*

(a) Compute the flexural strength for a completely nonporous specimen of this material.

(b) Compute the flexural strength for a 0.20 volume fraction porosity.

Solution

(a) Given the flexural strengths at two different volume fraction porosities, we are asked to determine the flexural strength for a nonporous material. Taking the natural logarithm of both sides of Equation 12.10 yields the following expression:

$$\ln \sigma_{fs} = \ln \sigma_0 - nP$$

Using the data provided in the problem statement, two simultaneous equations may be written in the above form as

$$\ln (70 \text{ MPa}) = \ln \sigma_0 - (0.10)n$$

$$\ln (60 \text{ MPa}) = \ln \sigma_0 - (0.15)n$$

Solving for n and σ_0 leads to the following values:

$n = 3.08$

$\sigma_0 = 95.3$ MPa.

For the nonporous material, $P = 0$, and, from Equation 12.10, $\sigma_0 = \sigma_{fs}$. Thus, σ_{fs} for $P = 0$ is 95.3 MPa.

(b) Now, we are asked for σ_{fs} at $P = 0.20$ for this same material. From Equation 12.10

$$\sigma_{fs} = \sigma_0 \exp(-nP)$$

$$= (95.3 \text{ MPa}) \exp\left[-(3.08)(0.20)\right]$$

$$= 51.5 \text{ MPa}$$

DESIGN PROBLEMS

Crystal Structures

12.D1 *Gallium arsenide (GaAs) and indium arsenide (InAs) both have the zinc blende crystal structure and are soluble in each other at all concentrations. Determine the concentration in weight percent of InAs that must be added to GaAs to yield a unit cell edge length of 0.5820 nm. The densities of GaAs and InAs are 5.316 and 5.668 g/cm^3, respectively.*

Solution

This problem asks that we determine the concentration (in weight percent) of InAs that must be added to GaAs to yield a unit cell edge length of 0.5820 nm. The densities of GaAs and InAs were given in the problem statement as 5.316 and 5.668 g/cm^3, respectively. We will solve this problem using the following steps:

Step 1

First consider a form of Equation 12.1 that applies to this alloy; this expression will include expressions for average atomic weight (A_{ave}) and average density (ρ_{ave}).

Step 2

Compute the volume of a unit cell of this alloy from the unit cell edge length provided in the problem statement.

Step 3

Incorporate expressions for A_{ave} and ρ_{ave} for this alloy (Equations 4.11a and 4.10a, respectively) into a modified form of Equation 12.1.

Step 4

From the expression developed in Step 3, solve for the value of the concentration of either GaAs or InAs.

Step 1

The form of Equation 12.1 that applies to this situation is as follows:

$$\rho_{\text{ave}} = \frac{n' A_{\text{ave}}}{V_C N_{\text{A}}} \tag{12.D1a}$$

For the zinc blende crystal structure, the number of formula units per unit cell (n') is 4.

Step 2

Because the zinc blende crystal structure is cubic, the unit cell volume V_C is equal to

$$V_C = a^3$$

in which *a* is the unit cell edge length, which in this case is 0.5820 nm. Thus

$$V_C = a^3 = (0.5820\ \text{nm})^3/\text{unit cell}$$

$$= (5.820 \times 10^{-8}\ \text{cm})^3 = 1.971 \times 10^{-22}\ \text{cm}^3/\text{unit cell}$$

Step 3

At this point we want to develop an expression for A_{ave} using Equation 4.11a. For our problem, this equation takes the form:

$$A_{\text{ave}} = \frac{100}{\dfrac{C_{\text{InAs}}}{A_{\text{InAs}}} + \dfrac{C_{\text{GaAs}}}{A_{\text{GaAs}}}}$$

$$= \frac{100}{\dfrac{C_{\text{InAs}}}{A_{\text{InAs}}} + \dfrac{(100 - C_{\text{InAs}})}{A_{\text{GaAs}}}}$$

In these expressions

C_{InAs} = the concentration (in weight percent) of InAs

C_{GaAs} = the concentration (in weight percent) of GaAs

A_{InAs} = the molecular weight of InAs = A_{In} + A_{As} = 114.82 g/mol + 74.92 g/mol = 189.74 g/mol

A_{GaAs} = the molecular weight of GaAs = A_{Ga} + A_{As} = 69.72 g/mol + 74.92 g/mol = 144.64 g/mol

Note: in the preceding equation, we have expressed alloy composition in weight percent InAs, which is possible since

$$C_{\text{GaAs}} + C_{\text{InAs}} = 100$$

Therefore, we may write an expression for A_{ave} as follows:

$$A_{\text{ave}} = \frac{100}{\dfrac{C_{\text{InAs}}}{189.74\ \text{g/mol}} + \dfrac{(100 - C_{\text{InAs}})}{144.64\ \text{g/mol}}}$$

We use an analogous procedure for the average alloy density using Equation 4.10a, which for our problem is written as follows:

$$\rho_{\text{ave}} = \frac{100}{\dfrac{C_{\text{InAs}}}{\rho_{\text{InAs}}} + \dfrac{(100 - C_{\text{InAs}})}{\rho_{\text{GaAs}}}}$$

$$= \frac{100}{\dfrac{C_{\text{InAs}}}{5.668\ \text{g/cm}^3} + \dfrac{(100 - C_{\text{InAs}})}{5.316\ \text{g/cm}^3}}$$

The densities for InAs and GaAs were given in the problem statement as follows:

ρ_{InAs} = 5.668 g/cm^3

ρ_{GaAs} = 5.316 g/cm^3

The final part of this step is to incorporate the above expressions for A_{ave} and ρ_{ave} into Equation 12.D1a. Let us first rearrange this expression such that V_C is the dependent variable and then include the average molecular weight and density expressions; thus,

$$V_C = \frac{n'A_{\text{ave}}}{\rho_{\text{ave}} N_{\text{A}}}$$

$$= 1.971 \times 10^{-22}\ \text{cm}^3/\text{unit cell}$$

$$= \frac{(4\ \text{fu/unit cell})\left[\dfrac{100}{\dfrac{C_{\text{InAs}}}{189.74\ \text{g/mol}} + \dfrac{(100 - C_{\text{InAs}})}{144.64\ \text{g/mol}}}\right]}{\left[\dfrac{100}{\dfrac{C_{\text{InAs}}}{5.668\ \text{g/cm}^3} + \dfrac{(100 - C_{\text{InAs}})}{5.316\ \text{g/cm}^3}}\right](6.022 \times 10^{23}\ \text{fu/mol})}$$

Step 4

It is now possible (albeit somewhat difficult) to solve for C_{InAs} from this expression; this yields a value of

$$C_{\text{InAs}} = 46.1\ \text{wt\%}$$

Stress–Strain Behavior

12.D2 *It is necessary to select a ceramic material to be stressed using a three-point loading scheme (Figure 12.30). The specimen must have a circular cross section, a radius of 3.8 mm (0.15 in.) and must not experience fracture or a deflection of more than 0.021 mm (8.5 × 10^{-4} in.) at its center when a load of 445 N (100 lb_f) is applied. If the distance between support points is 50.8 mm (2 in.), which of the materials in Table 12.5 are candidates? The magnitude of the centerpoint deflection may be computed using Equation 12.11.*

Solution

This problem asks for us to determine which of the ceramic materials in Table 12.5, when fabricated into cylindrical specimens and stressed in three-point loading, will not fracture when a load of 445 N (100 lb_f) is applied, and also will not experience a center-point deflection of more than 0.021 mm (8.5 × 10^{-4} in.).

The first of these criteria is met by those materials that have flexural strengths greater than the stress calculated using Equation 12.7b. According to this expression

$$\sigma_{fs} = \frac{FL}{\pi R^3}$$

$$= \frac{(445\ \text{N})(50.8 \times 10^{-3}\ \text{m})}{(\pi)(3.8 \times 10^{-3}\ \text{m})^3} = 131 \times 10^6\ \text{N/m}^2 = 131\ \text{MPa}\ \ (18{,}900\ \text{psi})$$

Of the materials in Table 12.5, the following have flexural strengths greater than this 131 MPa: Si_3N_4, ZrO_2, SiC, Al_2O_3, glass-ceramic, mullite, and spinel.

For the second criterion we must solve for the magnitude of the modulus of elasticity, *E*, from Equation 12.11. Incorporating the expression for the cross-sectional moment of inertia that appears in Figure 12.30—namely

$$I = \frac{\pi R^4}{4}$$

leads to the following form of Equation 12.11:

$$\Delta y = \frac{FL^3}{48EI}$$

$$= \frac{FL^3}{(48E)\left(\dfrac{\pi R^4}{4}\right)}$$

$$= \frac{FL^3}{12\pi E R^4}$$

Solving for E from this expression yields

$$E = \frac{FL^3}{12\,\pi\,R^4\,\Delta y}$$

And upon incorporation of specified values of F, L, R, and Δy leads to the following value for E:

$$E = \frac{(445\ \mathrm{N})\left(50.8 \times 10^{-3}\ \mathrm{m}\right)^3}{(12)(\pi)\left(3.8 \times 10^{-3}\ \mathrm{m}\right)^4\left(0.021 \times 10^{-3}\ \mathrm{m}\right)}$$

$$= 3.53 \times 10^{11}\ \mathrm{N/m^2} = 353 \times 10^9\ \mathrm{N/m^2} = 353\ \mathrm{GPa}\quad (49.3 \times 10^6\ \mathrm{psi})$$

Of those materials that satisfy the first criterion, only Al_2O_3 has a modulus of elasticity greater than 353 GPa (Table 12.5), and, therefore, is a possible candidate.

FUNDAMENTALS OF ENGINEERING QUESTIONS AND PROBLEMS

12.1FE *Which of the following are the most common coordination numbers for ceramic materials?*

(A) 2 and 3	*(C) 6, 8, and 12*
(B) 6 and 12	*(D) 4, 6, and 8*

Answer

The correct answer is D. For ceramic materials, the most common coordination numbers are 4, 6, and 8.

12.2FE *An AX ceramic compound has the rock salt crystal structure. If the radii of the A and X ions are 0.137 and 0.241 nm, respectively, and the respective atomic weights are 22.7 and 91.4 g/mol, what is the density (in g/cm^3) of this material?*

(A) 0.438 g/cm^3 *(C) 1.75 g/cm^3*

(B) 0.571 g/cm^3 *(D) 3.50 g/cm^3*

Solution

The density of a ceramic may be calculated using Equation 12.1—that is

$$\rho = \frac{n'\left(\sum A_C + \sum A_A\right)}{V_C N_A}$$

For the rock salt crystal structure, 4 formula units are associated with each unit cell (i.e., $n' = 4$). In addition, for this crystal structure, the anions and cations touch each other along the edge of the unit cell; thus the unit cell edge length, *a*, is equal to twice the sum of the cation and anion radii—that is

$$a = 2(r_C + r_A)$$

Since the unit cell has cubic symmetry,

$$V_C = a^3 = [2(r_C + r_A)]^3 = 8(r_C + r_A)^3$$

Making this substitution into Equation 12.1 above leads to the following:

$$\rho = \frac{n'\left(\sum A_{Na} + \sum A_{Cl}\right)}{V_C N_A} = \frac{n'\left(\sum A_{Na} + \sum A_{Cl}\right)}{8(r_{Na} + r_{Cl})^3 N_A}$$

In formula unit—i.e., "CA" unit, there is one C ion and one A ion, which means that

$$\sum A_C = A_C = 22.7 \text{ g/mol}$$

$$\sum A_A = A_A = 91.4 \text{ g/mol}$$

Now, incorporation of atomic weight values and ionic radii for C and A into the above equation leads to the following value for the density:

$$\rho = \frac{(4 \text{ formula units/unit cell})(22.7 \text{ g/mol} + 91.4 \text{ g/mol})}{8[(1.37 \times 10^{-8} \text{ cm}) + (2.41 \times 10^{-8} \text{ cm})]^3 (6.022 \times 10^{23} \text{ formula units/mol})}$$

$$= 1.75 \text{ g/cm}^3$$

which is answer C.

CHAPTER 13

APPLICATIONS AND PROCESSING OF CERAMICS

PROBLEM SOLUTIONS

Glasses

Glass–Ceramics

13.1 *Cite the two desirable characteristics of glasses.*

Answer

Two desirable characteristics of glasses are *optical transparency* and *ease of fabrication*.

13.2 *(a) What is crystallization?*

(b) Cite two properties that may be improved by crystallization.

Answer

(a) Crystallization is the process whereby a glass material transforms to a crystalline solid, usually as a result of a heat treatment.

(b) Two properties that may be improved by crystallization are (1) a lower coefficient of thermal expansion, and (2) higher strengths.

Refractories

13.3 *For refractory ceramic materials, cite three characteristics that improve with and two characteristics that are adversely affected by increasing porosity.*

Answer

For refractory ceramic materials, three characteristics that improve with increasing porosity are (1) decreased thermal expansion and contraction upon thermal cycling, (2) improved thermal insulation, and (3) improved resistance to thermal shock. Two characteristics that are adversely affected are (1) load-bearing capacity and (2) resistance to attack by corrosive materials.

13.4 *Find the maximum temperature to which the following two magnesia–alumina refractory materials may be heated before a liquid phase will appear.*

(a) A spinel-bonded magnesia material of composition 88.5 wt% MgO–11.5 wt% Al_2O_3.

(b) A magnesia–alumina spinel of composition 25 wt% MgO–75 wt% Al_2O_3. *Consult Figure 12.23.*

Solution

(a) From Figure 12.23, for a spinel-bonded magnesia material (88.5 wt%MgO-11.5 wt% Al_2O_3), the maximum temperature without a liquid phase corresponds to the temperature at the MgO(ss)-[MgO(ss) + Liquid] boundary for this composition, which is approximately 2220°C (4030°F).

(b) The maximum temperature without the formation of a liquid phase for a magnesia-alumina spinel (25 wt%MgO-75 wt% Al_2O_3) lies at the phase boundary between $MgAl_2O_4$(ss)-($MgAl_2O_4$ + Liquid) phase fields (just slightly to the right of the congruent melting point at which the two phase boundaries become tangent); this temperature is approximately 2070°C (3760°F).

13.5 *Upon consideration of the SiO_2–Al_2O_3 phase diagram in Figure 12.25, for each pair of the following list of compositions, which would you judge to be the more desirable refractory? Justify your choices.*

(a) 99.8 wt% SiO_2–0.2 wt% Al_2O_3 and 99.0 wt% SiO_2–1.0 wt% Al_2O_3

(b) 70 wt% Al_2O_3–30 wt% SiO_2 and 74 wt% Al_2O_3–26 wt% SiO_2

(c) 90 wt% Al_2O_3–10 wt% SiO_2 and 95 wt% Al_2O_3–5 wt% SiO_2

Answer

For each section of this problem two SiO_2-Al_2O_3 compositions are given; we are to decide, on the basis of the SiO_2-Al_2O_3 phase diagram (Figure 12.25), which is the more desirable refractory and then justify the choice.

(a) The 99.8 wt% SiO_2-0.2 wt% Al_2O_3 will be more desirable because the liquidus temperature will be greater for this composition; therefore, at any temperature within the cristobalite + liquid region on the phase diagram, there will be a lower fraction of the liquid phase present than for the 99.0 wt% SiO_2-1.0 wt% Al_2O_3 composition, and, thus, the mechanical integrity will be greater.

(b) The 74 wt% Al_2O_3-26 wt% SiO_2 composition will be more desirable because, for this composition, a liquid phase does not form until about 1750°C [i.e., the temperature at which a vertical line at 74 wt% Al_2O_3 crosses the boundary between the mullite and (mullite + liquid) phase regions]; for the 70 wt% Al_2O_3-30 wt% SiO_2 material, a liquid phase forms at a much lower temperature—1587°C.

(c) The 95 wt% Al_2O_3-5 wt% SiO_2 composition will be more desirable because the liquidus temperature will be greater for this composition. Therefore, at any temperature within the alumina + liquid region on the phase diagram, there will be a lower fraction of the liquid phase present than for the 90 wt% Al_2O_3-10 wt% SiO_2 composition, and, thus, the mechanical integrity of the 95 wt% Al_2O_3-5 wt% SiO_2 material will be greater.

13.6 *Compute the mass fractions of liquid in the following fireclay refractory materials at 1600°C (2910°F):*

(a) 25 wt% Al_2O_3*–75 wt%* SiO_2

(b) 45 wt% Al_2O_3*–55 wt%* SiO_2

Solution

This problem calls for us to compute the mass fractions of liquid for two fireclay refractory materials at 1600°C. In order to solve this problem it is necessary that we use the SiO_2-Al_2O_3 phase diagram (Figure 12.25). The mass fraction of liquid, W_L, as determined using the lever rule and tie line at 1600°C, is just

$$W_L = \frac{C_{\text{mullite}} - C_0}{C_{\text{mullite}} - C_L}$$

where C_{mullite} = 72 wt% Al_2O_3 and C_L = 8 wt% Al_2O_3, as determined using the tie-line; also, C_0 is the composition (in weight percent Al_2O_3) of the refractory material.

(a) For the 25 wt% Al_2O_3-75 wt% SiO_2 composition, C_0 = 25 wt% Al_2O_3, and

$$W_L = \frac{72 - 25}{72 - 8} = 0.73$$

(b) For the 45 wt% Al_2O_3-55 wt% SiO_2 composition, C_0 = 45 wt% Al_2O_3, and

$$W_L = \frac{72 - 45}{72 - 8} = 0.42$$

13.7 *For the MgO–*Al_2O_3 *system, what is the maximum temperature that is possible without the formation of a liquid phase? At what composition or over what range of compositions will this maximum temperature be achieved?*

Answer

This problem asks that we specify, for the MgO-Al_2O_3 system, Figure 12.23, the maximum temperature without the formation of a liquid phase; it is approximately 2800°C which is possible for pure MgO.

Cements

13.8 *Compare the manner in which the aggregate particles become bonded together in clay-based mixtures during firing and in cements during setting.*

Answer

For clay-based aggregates, a liquid phase forms during firing, which infiltrates the pores among the unmelted particles; upon cooling, this liquid becomes a glass, that serves as the bonding phase.

With cements, the bonding process is a chemical, hydration reaction between the water that has been added and the various cement constituents. The cement particles are bonded together by reactions that occur at the particle surfaces.

Fabrication and Processing of Glasses and Glass–Ceramics

13.9 *Soda and lime are added to a glass batch in the form of soda ash (Na_2CO_3) and lime-stone ($CaCO_3$). During heating, these two ingredients decompose to give off carbon dioxide (CO_2), the resulting products being soda and lime. Compute the weight of soda ash and limestone that must be added to 125 lb_m of quartz (SiO_2) to yield a glass of composition 78 wt% SiO_2, 17 wt% Na_2O, and 5 wt% CaO.*

Solution

We are asked to compute the weight of soda ash and limestone that must be added to 125 lb_m of SiO_2 to yield a glass composition of 78 wt% SiO_2, 17 wt% Na_2O, and 5 wt% CaO. Let x = the weight of Na_2O and y = the weight of CaO. Then, employment of Equation 4.3b, we may write the following expressions for the concentrations of Na_2O ($C_{\text{Na}_2\text{O}}$) and CaO (C_{CaO}):

$$C_{\text{Na}_2\text{O}} = 17 \text{ wt\%} = \frac{x}{125 + x + y} \times 100$$

$$C_{\text{CaO}} = 5 \text{ wt\%} = \frac{y}{125 + x + y} \times 100$$

Solving for x and y from these two expressions yields x = 27.2 lb_m Na_2O and y = 8.0 lb_m CaO.

Now, in order to compute the weights of Na_2CO_3 and $CaCO_3$, we must employ molecular weights. The molecular weights of Na_2CO_3 ($MW_{\text{Na}_2\text{CO}_3}$) and Na_2O ($MW_{\text{Na}_2\text{O}}$) are as follows:

$$MW_{\text{Na}_2\text{CO}_3} = 2(A_{\text{Na}}) + A_{\text{C}} + 3(A_{\text{O}})$$

$$= 2(22.99 \text{ g/mol}) + 12.01 \text{ g/mol} + 3(16.00 \text{ g/mol}) = 105.99 \text{ g/mol}$$

$$MW_{\text{Na}_2\text{O}} = 2(A_{\text{Na}}) + A_{\text{O}}$$

$$= 2(22.99 \text{ g/mol}) + 16.00 \text{ g/mol} = 61.98 \text{ g/mol}$$

And, finally, the mass of Na_2CO_3 ($m_{\text{Na}_2\text{CO}_3}$) is equal to

$$m_{\text{Na}_2\text{CO}_3} = (27.2 \text{ lb}_\text{m})\left(\frac{MW_{\text{Na}_2\text{CO}_3}}{MW_{\text{Na}_2O}}\right)$$

$$= (27.2\ \text{lb}_\text{m})\left(\frac{105.99\ \text{g/mol}}{61.98\ \text{g/mol}}\right) = 46.5\ \text{lb}_\text{m}$$

Likewise, the molecular weights of $CaCO_3$ (MW_{CaCO_3}) and CaO (MW_{CaO}) are as follows:

$$MW_{CaCO_3} = A_{Ca} + A_C + 3(A_O)$$

$$= 40.08\ \text{g/mol} + 12.01\ \text{g/mol} + (3)(16.00\ \text{g/mol}) = 100.09\ \text{g/mol}$$

$$MW_{CaO} = A_{Ca} + A_O$$

$$= 40.08\ \text{g/mol} + 16.00\ \text{g/mol} = 56.08\ \text{g/mol}$$

Such that the mass of $CaCO_3$ (m_{CaCO_3}) is equal to

$$m_{CaCO_3} = (8.0\ \text{lb}_\text{m})\left(\frac{MW_{CaCO_3}}{MW_{CaO}}\right)$$

$$= (8.0\ \text{lb}_\text{m})\left(\frac{100.09\ \text{g/mol}}{56.08\ \text{g/mol}}\right) = 14.3\ \text{lb}_\text{m}$$

13.10 *What is the distinction between* glass transition temperature *and* melting temperature*?*

Answer

The glass transition temperature is, for a noncrystalline ceramic, that temperature at which there is a change of slope for the specific volume versus temperature curve (Figure 13.11).

The melting temperature is, for a crystalline material, that temperature at which there is a sudden and discontinuous decrease in the specific-volume-versus-temperature curve.

13.11 *Compare the temperatures at which soda–lime, borosilicate, 96% silica, and fused silica may be annealed.*

Answer

The annealing point is that temperature at which the viscosity of the glass is 10^{12} Pa-s (10^{13} P). From Figure 13.12, these temperatures for the several glasses are as follows:

Glass	Annealing Temperature
Soda-lime	500°C (930°F)
Borosilicate	570°C (1060°F)
96% Silica	930°C (1705°F)
Fused silica	1170°C (2140°F)

13.12 *Compare the softening points for 96% silica, borosilicate, and soda–lime glasses.*

Answer

The softening point of a glass is that temperature at which the viscosity is 4×10^6 Pa-s; from Figure 13.12, these temperatures for the 96% silica, borosilicate, and soda-lime glasses are 1520°C (2770°F), 830°C (1525°F), and 700°C (1290°F), respectively.

13.13 *The viscosity η of a glass varies with temperature according to the relationship*

$$\eta = A\exp\left(\frac{Q_{vis}}{RT}\right)$$

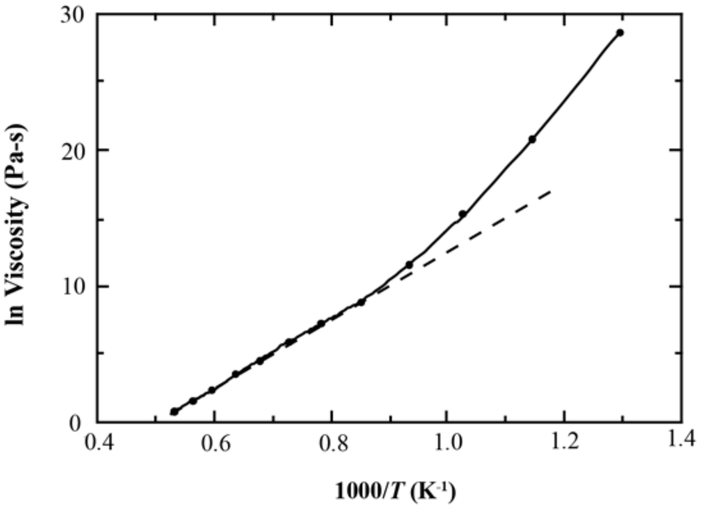
where Q_{vis} *is the energy of activation for viscous flow, A is a temperature-independent constant, and R and T are, respectively, the gas constant and the absolute temperature. A plot of ln η versus l/T should be nearly linear and have a slope of* Q_{vis}/R. *Using the data in Figure 13.12,*

(a) make such a plot for the soda-lime glass, and

(b) determine the activation energy between temperatures of 900°C and 1600°C.

Solution

(a) Below is shown the logarithm viscosity versus reciprocal of temperature plot for the soda-lime glass, using the data in Figure 13.12. The dashed line has been drawn through the data points corresponding to temperatures between 900 and 1600ºC (as stipulated in the problem statement).



(b) In order to determine the activation energy, Q_{vis}, it first becomes necessary to take natural logarithms of both sides of the equation given in the problem statement. Carrying out this mathematical operation leads to the following:

$$\ln\eta = \ln A + \frac{Q_{vis}}{RT}$$

Here R is the gas constant. Thus, from a plot of ln η vs. $1/T$ (for T in K) the slope of the resulting straight line is equal to

$$\text{slope} = \frac{Q_{\text{vis}}}{R}$$

Or, solving for Q_{vis} gives

$$Q_{\text{vis}} = R(\text{slope})$$

Furthermore, from this plot the slope may be expressed by the following expression:

$$\text{slope} = \frac{\Delta \ln \eta}{\Delta\left(\frac{1}{T}\right)}$$

Which is to say that Q_{vis} may be determined from the plot shown above as follows:

$$Q_{\text{vis}} = R\left[\frac{\Delta \ln \eta}{\Delta\left(\frac{1}{T}\right)}\right]$$

Furthermore, it is possible to express $\Delta \ln \eta$ as

$$\Delta \ln \eta = \ln \eta_1 - \ln \eta_2$$

And, likewise for $\Delta\left(\frac{1}{T}\right)$:

$$\Delta\left(\frac{1}{T}\right) = \frac{1}{T_1} - \frac{1}{T_2}$$

From the straight-line segment that has been sketched in the above plot, it is possible to compute Q_{vis} from two points on the line—i.e., two values of $\ln \eta$ (which we denote as $\ln \eta_1$ and $\ln \eta_2$) and their corresponding $1/T$ values ($1/T_1$ and $1/T_2$); that is

$$Q_{\text{vis}} = R\left[\frac{\Delta \ln \eta}{\Delta\left(\frac{1}{T}\right)}\right] = R\left(\frac{\ln \eta_1 - \ln \eta_2}{\frac{1}{T_1} - \frac{1}{T_2}}\right) \qquad \text{(S13.13a)}$$

From the above plot, let us select the following points on the straight line:

$$\frac{1}{T_1} = 0.60 \times 10^{-3}\ \text{K}^{-1};\ \ln \eta_1 = 2.2$$

$$\frac{1}{T_2} = 1.10 \times 10^{-3}\ \text{K}^{-1};\ \ln \eta_2 = 15.0$$

Using these data it is possible to compute the value of Q_{vis} using Equation S13.13a as follows:

$$Q_{\text{vis}} = R\left(\frac{\ln \eta_1 - \ln \eta_2}{\dfrac{1}{T_1} - \dfrac{1}{T_2}}\right)$$

$$= (8.31\ \text{J/mol-K})\left(\frac{2.2 - 15.0}{0.6 \times 10^{-3}\,\text{K}^{-1} - 1.10 \times 10^{-3}\ \text{K}^{-1}}\right)$$

= 212,700 J/mol

13.14 *For many viscous materials, the viscosity η may be defined in terms of the expression*

$$\eta = \frac{\sigma}{d\varepsilon/dt}$$

where σ and $d\varepsilon/dt$ are, respectively, the tensile stress and the strain rate. A cylindrical specimen of a borosilicate glass of diameter 4 mm (0.16 in.) and length 125 mm (4.9 in.) is subjected to a tensile force of 2 N (0.45 lb_f) along its axis. If its deformation is to be less than 2.5 mm (0.10 in.) over a week's time, using Figure 13.12, determine the maximum temperature to which the specimen may be heated.

Solution

This problem calls for us to determine the maximum temperature to which a cylindrical specimen of borosilicate glass may be heated in order that its deformation be less than 2.5 mm over a week's time. Let us first compute the applied stress using Equation 6.1, which for a cylinder of cross-sectional diameter *d* is as follows:

$$\sigma = \frac{F}{A_0} = \frac{F}{\pi\left(\frac{d_0}{2}\right)^2}$$

$$= \frac{2\text{ N}}{\pi\left(\frac{4\times10^{-3}\text{ m}}{2}\right)^2} = 1.59\times10^5\text{ N/m}^2 = 1.59\times10^5\text{ Pa}$$

We now want to compute the value of $d\varepsilon/dt$ for this problem. From Equation 6.2 strain ε is defined as

$$\varepsilon = \frac{\Delta l}{l_0}$$

in which

Δl = the specimen elongation in the direction of the applied stress

l_0 = the original specimen length

Insertion of this expression for ε into the equation above that defines η yields the following:

$$\frac{d\varepsilon}{dt} = \frac{d\left(\frac{\Delta l}{l_0}\right)}{dt}$$

And upon entering values of the parameters given in the problem statement into this equation leads to

$$\frac{d\varepsilon}{dt} = \frac{\frac{2.5\text{ mm}}{125\text{ mm}}}{(1\text{ wk})(7\text{ days/week})(24\text{ h/day})(3600\text{ s/h})} = 3.31\times10^{-8}\text{ s}^{-1}$$

Inasmuch as we have computed values for σ and $d\varepsilon/dt$, it is now possible to compute the viscosity using the equation provided in the problem statement as follows:

$$\eta = \frac{\sigma}{d\varepsilon/dt} = \frac{1.59 \times 10^5 \text{ Pa}}{3.31 \times 10^{-8}\ s^{-1}} = 4.8 \times 10^{12} \text{ Pa-s}$$

From Figure 13.12, the temperature at which the viscosity of the borosilicate glass has a value of 4.8×10^{12} Pa-s is about 540°C (1005°F).

13.15 *(a) Explain why residual thermal stresses are introduced into a glass piece when it is cooled.*

(b) Are thermal stresses introduced upon heating? Why or why not?

Answer

(a) Residual thermal stresses are introduced into a glass piece when it is cooled because surface and interior regions cool at different rates, and, therefore, contract different amounts; because the material will experience very little, if any deformation, stresses are established.

(b) Yes, thermal stresses will be introduced because of thermal expansion upon heating for the same reason as for thermal contraction upon cooling.

13.16 *Borosilicate glasses and fused silica are resistant to thermal shock. Why is this so?*

Answer

Borosilicate glasses and fused silica are resistant to thermal shock because they have relatively low coefficients of thermal expansion; therefore, upon heating or cooling, the difference in the degree of expansion or contraction across a cross-section of a ware that is constructed from these materials will be relatively low.

13.17 *In your own words, briefly describe what happens as a glass piece is thermally tempered.*

Thermal tempering of glasses is described in Section 13.10.

13.18 *Glass pieces may also be strengthened by chemical tempering. With this procedure, the glass surface is put in a state of compression by exchanging some of the cations near the surface with other cations having a larger diameter. Suggest one type of cation that, by replacing* Na^+, *will induce chemical tempering in a soda–lime glass.*

Answer

Chemical tempering will be accomplished by substitution, for Na^+ another monovalent cation with a slightly larger radius. From Table 12.3, both K^+ and Cs^+ fill these criteria, having ionic radii of 0.138 and 0.170 nm, respectively, which are larger than the ionic radius of Na^+ (0.102 nm). In fact, soda-lime glasses are tempered by a K^+-Na^+ ion exchange.

Fabrication and Processing of Clay Products

13.19 *Cite the two desirable characteristics of clay minerals relative to fabrication processes.*

<u>Answer</u>

Two desirable characteristics of clay minerals relative to fabrication processes are as follows: (1) they become hydroplastic (and therefore formable) when mixed with water; and (2) during firing, clays melt over a range of temperatures, which allows some fusion and bonding of the ware without complete melting and a loss of mechanical integrity and shape.

13.20 *From a molecular perspective, briefly explain the mechanism by which clay minerals become hydroplastic when water is added.*

Answer

Clays become hydroplastic when water is added because the water molecules occupy regions between the layered molecular sheets; these water molecules essentially eliminate the secondary molecular bonds between adjacent sheets, and also form a thin film around the clay particles. The net result is that the clay particles are relatively free to move past one another, which is manifested as the hydroplasticity phenomenon.

13.21 *(a) What are the three main components of a whiteware ceramic such as porcelain? (b) What role does each component play in the forming and firing procedures?*

Answer

(a) The three components of a whiteware ceramic are clay, quartz, and a flux (such as feldspar).

(b) With regard to the role that each component plays:

Quartz acts as a filler material.

Clay facilitates the forming operation since, when mixed with water, the mass may be made to become either hydroplastic or form a slip. Also, since clays melt over a range of temperatures, the shape of the piece being fired will be maintained.

The flux facilitates the formation of a glass having a relatively low melting temperature.

13.22 *(a) Why is it so important to control the rate of drying of a ceramic body that has been hydroplastically formed or slip cast?*

(b) Cite three factors that influence the rate of drying, and explain how each affects the rate.

Answer

(a) It is important to control the rate of drying inasmuch as if the rate of drying is too rapid, there will be nonuniform shrinkage between surface and interior regions, such that warping and/or cracking of the ceramic ware may result.

(b) Three factors that affect the rate of drying are temperature, humidity, and rate of air flow. The rate of drying is enhanced by increasing both the temperature and rate of air flow, and by decreasing the humidity of the air.

13.23 *Cite one reason why drying shrinkage is greater for slip cast or hydroplastic products that have smaller clay particles.*

Answer

The reason that drying shrinkage is greater for products having smaller clay particles is because there is more particle surface area, and, consequently, more water will surround a given volume of particles. The drying shrinkage will thus be greater as this water is removed, and as the interparticle separation decreases.

13.24 *(a) Name three factors that influence the degree to which vitrification occurs in clay-based ceramic wares.*

(b) Explain how density, firing distortion, strength, corrosion resistance, and thermal conductivity are affected by the extent of vitrification.

Answer

(a) Three factors that influence the degree to which vitrification occurs in clay-based ceramic wares are: (1) composition (especially the amount of flux present); (2) the temperature of firing; and (3) the time at the firing temperature.

(b) Density will increase with degree of vitrification since the total remaining pore volume decreases.

Firing distortion will increase with degree of vitrification since more liquid phase will be present at the firing temperature.

Strength will also increase with degree of vitrification inasmuch as more of the liquid phase forms, which fills in a greater fraction of pore volume. Upon cooling, the liquid forms a glass matrix of relatively high strength.

Corrosion resistance normally increases also, especially at service temperatures below that at which the glass phase begins to soften. The rate of corrosion is dependent on the amount of surface area exposed to the corrosive medium; hence, decreasing the total surface area by filling in some of the surface pores, diminishes the corrosion rate.

Thermal conductivity will increase with degree of vitrification. The glass phase has a higher conductivity than the pores that it has filled.

Powder Pressing

13.25 *Some ceramic materials are fabricated by hot isostatic pressing. Cite some of the limitations and difficulties associated with this technique.*

Answer

The principal disadvantage of hot-isostatic pressing is that it is expensive. The pressure is applied on a pre-formed green piece by a gas. Thus, the process is slow, and the equipment required to supply the gas and withstand the elevated temperature and pressure is costly.

DESIGN PROBLEM

13.D1 *Some modern kitchen cookware is made of ceramic materials.*

(a) List at least three important characteristics required of a material to be used for this application.

(b) Compare the relative properties and cost of three ceramic materials.

(c) On the basis of this comparison, select the material most suitable for the cookware.

Answer

(a) Important characteristics that are required of a ceramic material to be used for kitchen cookware are the following: (1) it must have a high resistance to thermal shock (Section 19.5) in order to withstand relatively rapid changes in temperature; (2) it must have a relatively high thermal conductivity; (3) it must be relatively strong and tough in order to endure normal kitchen use; and (4) it must be nontoxic.

(b) Possible materials worth considering are a common soda-lime glass, a borosilicate (Pyrex) glass, and a glass ceramic. These materials and some of their characteristics are discussed in this chapter. Using Equation 19.9 a comparison of the resistance to thermal shock may be made. The student will need to obtain cost information.

(c) It is left to the student to make this determination and justify the decision.

FUNDAMENTALS OF ENGINEERING QUESTIONS AND PROBLEMS

13.1FE *As the porosity of a refractory ceramic brick increases,*

(A) strength decreases, chemical resistance decreases, and thermal insulation increases

(B) strength increases, chemical resistance increases, and thermal insulation decreases

(C) strength decreases, chemical resistance increases, and thermal insulation decreases

(D) strength increases, chemical resistance increases, and thermal insulation increases

<u>Answer</u>

The correct answer is A. As the porosity of refractory ceramic bricks increases, strength decreases, chemical resistance decreases, and thermal insulation increases.

13.2FE *Which of the following are the two primary constituents of clays?*

(A) Alumina (Al_2O_3) and limestone ($CaCO_3$)

(B) Limestone ($CaCO_3$) and cupric oxide (CuO)

(C) Silica (SiO_2) and limestone ($CaCO_3$)

(D) Alumina (Al_2O_3) and silica (SiO_2)

Answer

The correct answer is D. The two primary constituents of clays are *alumina* (Al_2O_3) and *silica* (SiO_2).

CHAPTER 14

POLYMER STRUCTURES

PROBLEM SOLUTIONS

Hydrocarbon Molecules

Polymer Molecules

The Chemistry of Polymer Molecules

14.1 *On the basis of the structures presented in this chapter, sketch repeat unit structures for the following polymers*

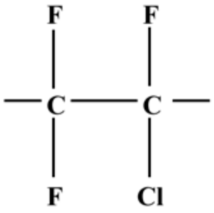
(a) polychlorotrifluoroethylene

(b) poly(vinyl alcohol)

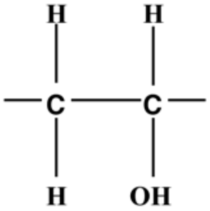
Solution

Repeat unit structures called for are sketched below.

(a) Polychlorotrifluoroethylene



(b) Poly(vinyl alcohol)



Molecular Weight

14.2 *Compute repeat unit molecular weights for the following:*

(a) polytetrafluoroethylene

(b) poly(methyl methacrylate)

(c) nylon 6,6

(d) poly(ethylene terephthalate)

Solution

(a) For polytetrafluoroethylene, each repeat unit consists of two carbon atoms and four fluorine atoms (Table 14.3). If A_C and A_F represent the atomic weights of carbon and fluorine, respectively, then

$$m = 2(A_C) + 4(A_F)$$

$$= (2)(12.01 \text{ g/mol}) + (4)(19.00 \text{ g/mol}) = 100.02 \text{ g/mol}$$

(b) For poly(methyl methacrylate), from Table 14.3, each repeat unit has five carbon atoms, eight hydrogen atoms, and two oxygen atoms. Thus,

$$m = 5(A_C) + 8(A_H) + 2(A_O)$$

$$= (5)(12.01 \text{ g/mol}) + (8)(1.008 \text{ g/mol}) + (2)(16.00 \text{ g/mol}) = 100.11 \text{ g/mol}$$

(c) For nylon 6,6, from Table 14.3, each repeat unit has twelve carbon atoms, twenty-two hydrogen atoms, two nitrogen atoms, and two oxygen atoms. Thus,

$$m = 12(A_C) + 22(A_H) + 2(A_N) + 2(A_O)$$

$$= (12)(12.01 \text{ g/mol}) + (22)(1.008 \text{ g/mol}) + (2)(14.01 \text{ g/mol}) + (2)(16.00 \text{ g/mol})$$

$$= 226.32 \text{ g/mol}$$

(d) For poly(ethylene terephthalate), from Table 14.3, each repeat unit has ten carbon atoms, eight hydrogen atoms, and four oxygen atoms. Thus,

$$m = 10(A_C) + 8(A_H) + 4(A_O)$$

$$= (10)(12.01 \text{ g/mol}) + (8)(1.008 \text{ g/mol}) + (4)(16.00 \text{ g/mol}) = 192.16 \text{ g/mol}$$

14.3 *The number-average molecular weight of a polystyrene is 500,000 g/mol. Compute the degree of polymerization.*

Solution

We are asked to compute the degree of polymerization for polystyrene, given that the number-average molecular weight is 500,000 g/mol. The repeat unit for polystyrene (Table 14.3) has eight carbon atoms and eight hydrogen atoms. Therefore, the repeat unit molecular weight of polystyrene is just

$$m = 8(A_{\mathrm{C}}) + 8(A_{\mathrm{H}})$$

$$= (8)(12.01 \text{ g/mol}) + (8)(1.008 \text{ g/mol}) = 104.14 \text{ g/mol}$$

Now it is possible to compute the degree of polymerization using Equation 14.6 as follows:

$$DP = \frac{\bar{M}_n}{m} = \frac{500{,}000 \text{ g/mol}}{104.14 \text{ g/mol}} = 4800$$

14.4 *(a) Compute the repeat unit molecular weight of polypropylene.*

(b) Compute the number-average molecular weight for a polypropylene for which the degree of polymerization is 15,000.

Solution

(a) The repeat unit molecular weight of polypropylene is called for in this portion of the problem. For polypropylene, from Table 14.3, each repeat unit has three carbon atoms and six hydrogen atoms. Thus,

$$m = 3(A_{\mathrm{C}}) + 6(A_{\mathrm{H}})$$

$$= (3)(12.01\ \mathrm{g/mol}) + (6)(1.008\ \mathrm{g/mol}) = 42.08\ \mathrm{g/mol}$$

(b) Because the degree of polymerization is 15,000, the number-average molecular weight may be computed using Equation 14.6, as follows:

$$\overline{M}_n = (DP)m = (15{,}000)(42.08\ \mathrm{g/mol}) = 631{,}200\ \mathrm{g/mol}$$

14.5 *The following table lists molecular weight data for a polytetrafluoroethylene material. Compute the following:*

(a) the number-average molecular weight

(b) the weight-average molecular weight

(c) the degree of polymerization.

Molecular Weight Range (g/mol)	x_i	w_i
10,000–20,000	*0.03*	*0.01*
20,000–30,000	*0.09*	*0.04*
30,000–40,000	*0.15*	*0.11*
40,000–50,000	*0.25*	*0.23*
50,000–60,000	*0.22*	*0.24*
60,000–70,000	*0.14*	*0.18*
70,000–80,000	*0.08*	*0.12*
80,000–90,000	*0.04*	*0.07*

Solution

(a) From the tabulated data, we are asked to compute $\bar{M}_n$, the number-average molecular weight. This is carried out below.

Molecular wt Range	Mean M_i	x_i	x_iM_i
10,000-20,000	15,000	0.03	450
20,000-30,000	25,000	0.09	2250
30,000-40,000	35,000	0.15	5250
40,000-50,000	45,000	0.25	11,250
50,000-60,000	55,000	0.22	12,100
60,000-70,000	65,000	0.14	9100
70,000-80,000	75,000	0.08	6000
80,000-90,000	85,000	0.04	3400

$$\bar{M}_n = \sum x_i M_i = \mathbf{49{,}800\ g/mol}$$

(b) From the tabulated data, we are asked to compute $\bar{M}_w$, the weight-average molecular weight. This computation is carried out below.

Molecular wt. Range	Mean M_i	w_i	w_iM_i
10,000-20,000	15,000	0.01	150
20,000-30,000	25,000	0.04	1000
30,000-40,000	35,000	0.11	3850
40,000-50,000	45,000	0.23	10,350
50,000-60,000	55,000	0.24	13,200
60,000-70,000	65,000	0.18	11,700
70,000-80,000	75,000	0.12	9000
80,000-90,000	85,000	0.07	5950

$$\bar{M}_w = \sum w_i M_i = 55{,}200 \text{ g/mol}$$

(c) Now we are asked to compute the degree of polymerization, which is possible using Equation 14.6. The polytetrafluoroethylene the repeat unit consists of 2 carbon atoms and 4 fluorine atoms; therefore, its repeat unit molecular weight is equal to

$$m = 2(A_C) + 4(A_F)$$

$$= (2)(12.01 \text{ g/mol}) + (4)(19.00 \text{ g/mol}) = 100.02 \text{ g/mol}$$

Thus, using Equation 14.6 we compute the degree of polymerization as follows:

$$DP = \frac{\bar{M}_n}{m} = \frac{49{,}800 \text{ g/mol}}{100.02 \text{ g/mol}} = 498$$

14.6 *Molecular weight data for some polymer are tabulated here. Compute the following:*

(a) the number-average molecular weight

(b) the weight-average molecular weight.

(c) If it is known that this material's degree of polymerization is 477, which one of the polymers listed in Table 14.3 is this polymer? Why?

Molecular Weight Range g/mol	x_i	w_i
8,000–20,000	*0.05*	*0.02*
20,000–32,000	*0.15*	*0.08*
32,000–44,000	*0.21*	*0.17*
44,000–56,000	*0.28*	*0.29*
56,000–68,000	*0.18*	*0.23*
68,000–80,000	*0.10*	*0.16*
80,000–92,000	*0.03*	*0.05*

Solution

(a) From the tabulated data, we are asked to compute $\bar{M}_n$, the number-average molecular weight. This is carried out below.

Molecular wt. Range	Mean M_i	x_i	x_iM_i
8,000-20,000	14,000	0.05	700
20,000-32,000	26,000	0.15	3900
32,000-44,000	38,000	0.21	7980
44,000-56,000	50,000	0.28	14,000
56,000-68,000	62,000	0.18	11,160
68,000-80,000	74,000	0.10	7400
80,000-92,000	86,000	0.03	2580

$$\bar{M}_n = \sum x_i M_i = 47{,}720 \text{ g/mol}$$

(b) From the tabulated data, we are asked to compute $\bar{M}_w$, the weight-average molecular weight. This determination is performed as follows:

Molecular wt. Range	Mean M_i	w_i	w_iM_i
8,000-20,000	14,000	0.02	280
20,000-32,000	26,000	0.08	2080
32,000-44,000	38,000	0.17	6460
44,000-56,000	50,000	0.29	14,500
56,000-68,000	62,000	0.23	14,260
68,000-80,000	74,000	0.16	11,840
80,000-92,000	86,000	0.05	4300

$$\bar{M}_w = \sum w_i M_i = 53{,}720 \text{ g/mol}$$

(c) We are now asked if the degree of polymerization is 477, to determine which of the polymers in Table 14.3 is this material. It is first necessary to compute *m* in Equation 14.6 as follows:

$$m = \frac{\bar{M}_n}{DP} = \frac{47{,}720 \text{ g/mol}}{477} = 100.04 \text{ g/mol}$$

The repeat unit molecular weights of the polymers listed in Table 14.3 are as follows:

Polyethylene—28.05 g/mol
Poly(vinyl chloride)—62.49 g/mol
Polytetrafluoroethylene—100.02 g/mol
Polypropylene—42.08 g/mol
Polystyrene—104.14 g/mol
Poly(methyl methacrylate)—100.11 g/mol
Phenol-formaldehyde—133.16 g/mol
Nylon 6,6—226.32 g/mol
PET—192.16 g/mol
Polycarbonate—254.27 g/mol

Therefore, polytetrafluoroethylene is the material since its repeat unit molecular weight (100.02 g/mol) is closest to that calculated above (100.04 g/mol).

14.7 *Is it possible to have a poly(vinyl chloride) homopolymer with the following molecular weight data, and a degree of polymerization of 1120? Why or why not?*

Molecular Weight Range (g/mol)	w_i	x_i
8,000–20,000	*0.02*	*0.05*
20,000–32,000	*0.08*	*0.15*
32,000–44,000	*0.17*	*0.21*
44,000–56,000	*0.29*	*0.28*
56,000–68,000	*0.23*	*0.18*
68,000–80,000	*0.16*	*0.10*
80,000–92,000	*0.05*	*0.03*

Solution

This problem asks if it is possible to have a poly(vinyl chloride) homopolymer with the given molecular weight data and a degree of polymerization of 1120. The appropriate data are given below along with a computation of the number-average molecular weight.

Molecular wt. Range	Mean M_i	x_i	x_iM_i
8,000-20,000	14,000	0.05	700
20,000-32,000	26,000	0.15	3900
32,000-44,000	38,000	0.21	7980
44,000-56,000	50,000	0.28	14,000
56,000-68,000	62,000	0.18	11,160
68,000-80,000	74,000	0.10	7440
80,000-92,000	86,000	0.03	2580

$$\boldsymbol{\bar{M}_w = \sum x_i M_i = 47{,}720\ \mathrm{g/mol}}$$

For PVC, from Table 14.3, each repeat unit has two carbon atoms, three hydrogen atoms, and one chlorine atom. Thus, the repeat unit molecular weight for PVC is computed as follows:

$$m = 2(A_\mathrm{C}) + 3(A_\mathrm{H}) + (A_\mathrm{Cl})$$

$$= (2)(12.01 \text{ g/mol}) + (3)(1.008 \text{ g/mol}) + (35.45 \text{ g/mol}) = 62.49 \text{ g/mol}$$

Now, we will compute the degree of polymerization using Equation 14.6 as follows:

$$DP = \frac{\bar{M}_n}{m} = \frac{47{,}720 \text{ g/mol}}{62.49 \text{ g/mol}} = 764$$

Thus, such a homopolymer is *not possible* since the calculated degree of polymerization is 764 not 1120.

14.8 *High-density polyethylene may be chlorinated by inducing the random substitution of chlorine atoms for hydrogen.*

(a) Determine the concentration of Cl (in wt%) that must be added if this substitution occurs for 8% of all the original hydrogen atoms.

(b) In what ways does this chlorinated polyethylene differ from poly(vinyl chloride)?

Solution

(a) For chlorinated polyethylene, we are asked to determine the weight percent of chlorine added for 8% Cl substitution of all original hydrogen atoms. Consider 50 carbon atoms; for polyethylene there are 100 possible side-bonding sites. Ninety-two are occupied by hydrogen and eight are occupied by Cl. Thus, the mass of these 50 carbon atoms, m_C, is just

$$m_C = 50(A_C) = (50)(12.01 \text{ g/mol}) = 600.5 \text{ g}$$

Likewise, for hydrogen and chlorine,

$$m_H = 92(A_H) = (92)(1.008 \text{ g/mol}) = 92.74 \text{ g}$$

$$m_{Cl} = 8(A_{Cl}) = (8)(35.45 \text{ g/mol}) = 283.60 \text{ g}$$

Thus, the concentration of chlorine, C_{Cl}, is determined using Equation 4.3b as follows:

$$C_{Cl} = \frac{m_{Cl}}{m_C + m_H + m_{Cl}} \times 100$$

$$= \frac{283.60 \text{ g}}{600.5 \text{ g} + 92.74 \text{ g} + 283.60 \text{ g}} \times 100 = 29.0 \text{ wt\%}$$

(b) Chlorinated polyethylene differs from poly(vinyl chloride), in that, for PVC, (1) 25% of the side-bonding sites are substituted with Cl, and (2) the substitution is probably much less random.

Molecular Shape

14.9 *For a linear, freely rotating polymer molecule, the total chain length L depends on the bond length between chain atoms d, the total number of bonds in the molecule N, and the angle between adjacent backbone chain atoms θ, as follows:*

$$L = Nd \sin\left(\frac{\theta}{2}\right) \tag{14.11}$$

Furthermore, the average end-to-end distance for a series of polymer molecules r in Figure 14.6 is equal to

$$r = d\sqrt{N} \tag{14.12}$$

A linear polyethylene has a number-average molecular weight of 300,000 g/mol; compute average values of L and r for this material.

Solution

This problem first of all asks for us to calculate, using Equation 14.11, the average total chain length, *L*, for a linear polyethylene polymer having a number-average molecular weight of 300,000 g/mol. It is necessary to calculate the number-average degree of polymerization, *DP*, using Equation 14.6. For polyethylene, from Table 14.3, each repeat unit has two carbon atoms and four hydrogen atoms. Thus,

$$m = 2(A_C) + 4(A_H)$$

$$= (2)(12.01 \text{ g/mol}) + (4)(1.008 \text{ g/mol}) = 28.05 \text{ g/mol}$$

and

$$DP = \frac{\bar{M}_n}{m} = \frac{300{,}000 \text{ g/mol}}{28.05 \text{ g/mol}} = 10{,}695$$

which is the number of repeat units along an average chain. Since there are two carbon atoms per repeat unit, there are two C—C chain bonds per repeat unit, which means that the total number of chain bonds in the molecule, *N*, is just (2)(10,695) = 21,390 bonds. Furthermore, assume that for single carbon-carbon bonds, *d* = 0.154 nm and θ = 109° (Section 14.4); therefore, from Equation 14.11

$$L = Nd \sin\left(\frac{\theta}{2}\right)$$

$$= (21{,}390)(0.154 \text{ nm})\left[\sin\left(\frac{109°}{2}\right)\right] = 2682 \text{ nm}$$

It is now possible to calculate the average chain end-to-end distance, *r*, using Equation 14.12 as follows:

$$r = d\sqrt{N} = (0.154 \text{ nm})\sqrt{21,390} = 22.5 \text{ nm}$$

14.10 *Using the definitions for total chain molecule length L (Equation 14.11) and average chain end-to-end distance r (Equation 14.12), determine the following for a linear polytetrafluoroethylene:*

(a) the number-average molecular weight for L = 2000 nm

(b) the number-average molecular weight for r = 15 nm

Solution

(a) This portion of the problem asks for us to calculate the number-average molecular weight for a linear polytetrafluoroethylene for which L in Equation 14.11 is 2000 nm. It is first necessary to compute the value of N using this equation, where, for the C—C chain bond, d = 0.154 nm, and θ = 109° (Section 14.4). Thus, solving Equation 14.11 for N yields:

$$N = \frac{L}{d\sin\left(\frac{\theta}{2}\right)}$$

$$= \frac{2000\text{ nm}}{(0.154\text{ nm})\sin\left(\frac{109°}{2}\right)} = 15{,}900$$

Since there are two C—C bonds per PTFE repeat unit, there is an average of N/2 or 15,900/2 = 7950 repeat units per chain, which is also the degree of polymerization, DP. In order to compute the value of $\bar{M}_n$ using Equation 14.6, we must first determine m for PTFE. Each PTFE repeat unit consists of two carbon atoms and four fluorine atoms, thus

$$m = 2(A_C) + 4(A_F)$$

$$= (2)(12.01\text{ g/mol}) + (4)(19.00\text{ g/mol}) = 100.02\text{ g/mol}$$

Therefore, using Equation 14.6 and solving for $\bar{M}_n$ yields

$$\bar{M}_n = (DP)m$$

$$= (7950)(100.02\text{ g/mol}) = 795{,}000\text{ g/mol}$$

(b) Next, we are to determine the number-average molecular weight for r = 15 nm. Solving for N from Equation 14.12 leads to

$$N = \frac{r^2}{d^2} = \frac{(15\text{ nm})^2}{(0.154\text{ nm})^2} = 9490$$

which is the total number of bonds per average molecule. Since there are two C—C bonds per repeat unit, then $DP = N/2 = 9490/2 = 4745$. Now, using Equation 14.6, we calculate the number-average molecular weight as follows:

$$\bar{M}_n = (DP)m = (4745)(100.02\text{ g/mol}) = 474{,}600\text{ g/mol}$$

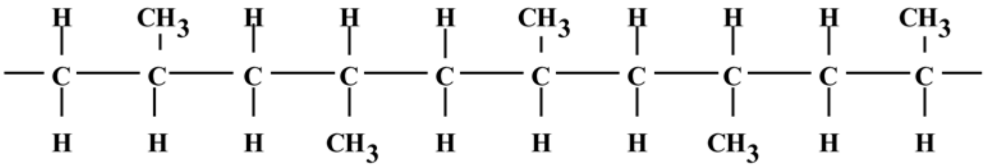
Molecular Configurations

14.11 *Sketch portions of a linear polypropylene molecule that are (a) syndiotactic, (b) atactic, and (c) isotactic. Use two-dimensional schematics per footnote 9 of this chapter.*

Solution

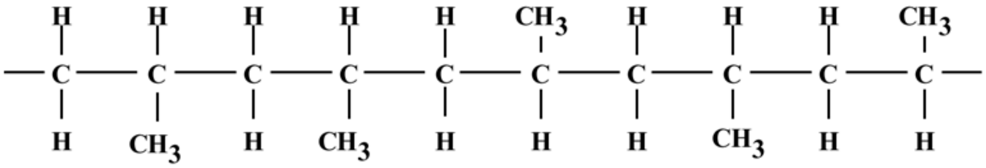
We are asked to sketch portions of a linear polypropylene molecule for different configurations (using two-dimensional schematic sketches). These sketches are as follows:

(a) Syndiotactic polypropylene:



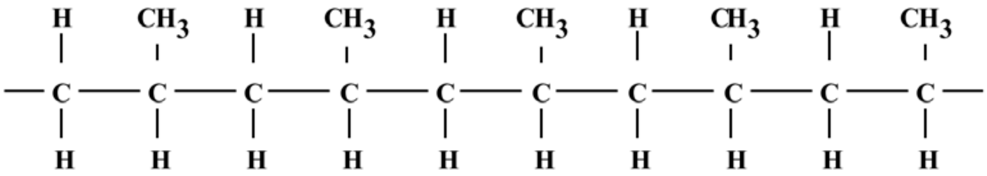
$$\begin{array}{cccccccccc} \mathrm{H} & \mathrm{CH_3} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{CH_3} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{CH_3} \\ | & | & | & | & | & | & | & | & | & | \\ -\mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- \\ | & | & | & | & | & | & | & | & | & | \\ \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{CH_3} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{CH_3} & \mathrm{H} & \mathrm{H} \end{array}$$

(b) Atactic polypropylene:



$$\begin{array}{cccccccccc} \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{CH_3} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{CH_3} \\ | & | & | & | & | & | & | & | & | & | \\ -\mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- \\ | & | & | & | & | & | & | & | & | & | \\ \mathrm{H} & \mathrm{CH_3} & \mathrm{H} & \mathrm{CH_3} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{CH_3} & \mathrm{H} & \mathrm{H} \end{array}$$

(c) Isotactic polypropylene:



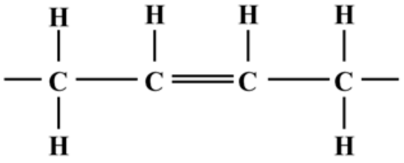
$$\begin{array}{cccccccccc} \mathrm{H} & \mathrm{CH_3} & \mathrm{H} & \mathrm{CH_3} & \mathrm{H} & \mathrm{CH_3} & \mathrm{H} & \mathrm{CH_3} & \mathrm{H} & \mathrm{CH_3} \\ | & | & | & | & | & | & | & | & | & | \\ -\mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- \\ | & | & | & | & | & | & | & | & | & | \\ \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} \end{array}$$

14.12 *Sketch cis and trans structures for (a) polybutadiene and (b) polychloroprene. Use two-dimensional schematics per footnote 12 of this chapter.*

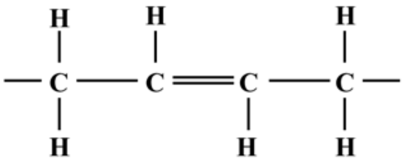
Solution

This problem asks for us to sketch cis and trans structures for butadiene and chloroprene.

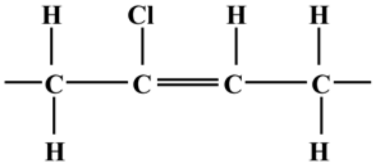
(a) The structure for *cis* polybutadiene (Table 14.5) is



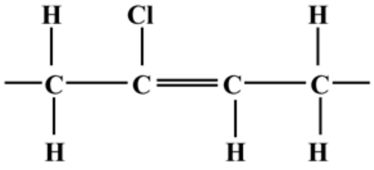
The structure of *trans* butadiene is



(b) The structure of *cis* chloroprene (Table 14.5) is



The structure of *trans* chloroprene is



Thermoplastic and Thermosetting Polymers

14.13 *Compare thermoplastic and thermosetting polymers (a) on the basis of mechanical characteristics upon heating and (b) according to possible molecular structures.*

Answer

(a) Thermoplastic polymers soften when heated and harden when cooled, whereas thermosetting polymers, harden upon heating, while further heating will not lead to softening.

(b) Thermoplastic polymers have linear and branched structures, while for thermosetting polymers, the structures will normally be network or crosslinked.

14.14 *(a) Is it possible to grind up and reuse phenol-formaldehyde? Why or why not?*

(b) Is it possible to grind up and reuse polypropylene? Why or why not?

Answer

(a) It is *not possible* to grind up and reuse phenol-formaldehyde because it is a network thermoset polymer and, therefore, is not amenable to remolding.

(b) Yes, it is *possible* to grind up and reuse polypropylene since it is a thermoplastic polymer, will soften when reheated, and, thus, may be remolded.

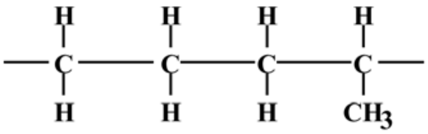
Copolymers

14.15 *Sketch the repeat structure for each of the following alternating copolymers: (a) poly(ethylene-propylene), (b) poly(butadiene-styrene), and (c) poly(isobutylene-isoprene).*

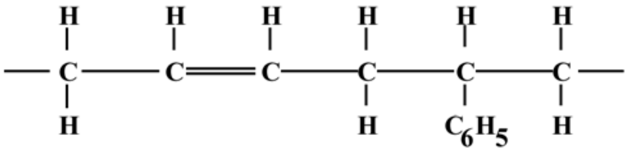
Solution

This problem asks for sketches of the repeat unit structures for several alternating copolymers. These sketches are as follows:

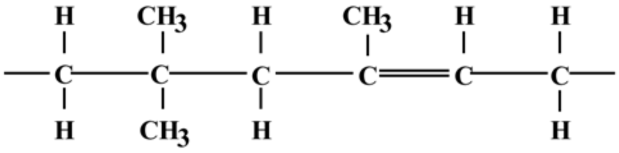
(a) For poly(ethylene-propylene):



(b) For poly(butadiene-styrene):



(c) For poly(isobutylene-isoprene):



14.16 *The number-average molecular weight of a poly(acrylonitrile-butadiene) alternating copolymer is 1,000,000 g/mol; determine the average number of acrylonitrile and butadiene repeat units per molecule.*

Solution

For a poly(acrylonitrile-butadiene) alternating copolymer with a number-average molecular weight of 1,000,000 g/mol, we are asked to determine the average number of acrylonitrile and butadiene repeat units per molecule.

Since it is an alternating copolymer, the number of both types of repeat units will be the same. Therefore, consider them as a single repeat unit, and determine the number-average degree of polymerization. For the acrylonitrile repeat unit, there are three carbon atoms, three hydrogen atoms, and one nitrogen atom, while the butadiene repeat consists of four carbon atoms and six hydrogen atoms. Therefore, the acrylonitrile-butadiene combined repeat unit weight is just

$$m = 7(A_{\mathrm{C}}) + 9(A_{\mathrm{H}}) + 1(A_{\mathrm{N}})$$

$$= (7)(12.01 \text{ g/mol}) + (9)(1.008 \text{ g/mol}) + (14.01 \text{ g/mol}) = 107.15 \text{ g/mol}$$

From Equation 14.6, the degree of polymerization is just

$$DP = \frac{\bar{M}_n}{m} = \frac{1{,}000{,}000 \text{ g/mol}}{107.15 \text{ g/mol}} = 9333$$

Thus, there is an average of 9333 of both repeat unit types per molecule.

14.17 *Calculate the number-average molecular weight of a random poly(isobutylene-isoprene) copolymer in which the fraction of isobutylene repeat units is 0.25; assume that this concentration corresponds to a degree of polymerization of 1500.*

Solution

This problem asks for us to calculate the number-average molecular weight of a random poly(isobutylene-isoprene) copolymer. The isobutylene repeat unit consists of four carbon atoms and eight hydrogen atoms (Table 14.5). Therefore, its repeat unit molecular weight (m_{Ib}) is

$$m_{\mathrm{Ib}} = 4(A_{\mathrm{C}}) + 8(A_{\mathrm{H}})$$

$$= (4)(12.01 \text{ g/mol}) + (8)(1.008 \text{ g/mol}) = 56.10 \text{ g/mol}$$

The isoprene repeat unit is composed of five carbon and eight hydrogen atoms (Table 14.5). Thus, its repeat unit molecular weight (m_{Ip}) is

$$m_{\mathrm{Ip}} = 5(A_{\mathrm{C}}) + 8(A_{\mathrm{H}})$$

$$= (5)(12.01 \text{ g/mol}) + (8)(1.008 \text{ g/mol}) = 68.11 \text{ g/mol}$$

From Equation 14.7, the average repeat unit molecular weight is just

$$\bar{m} = f_{\mathrm{Ib}} m_{\mathrm{Ib}} + f_{\mathrm{Ip}} m_{\mathrm{Ip}}$$

$$= (0.25)(56.10 \text{ g/mol}) + (1 - 0.25)(68.11 \text{ g/mol}) = 65.11 \text{ g/mol}$$

Since DP = 1500 (as given in the problem statement), $\bar{M}_n$ may be computed using Equation 14.6 as follows:

$$\bar{M}_n = \bar{m}(DP) = (65.11 \text{ g/mol})(1500) = 97{,}700 \text{ g/mol}$$

14.18 *An alternating copolymer is known to have a number-average molecular weight of 100,000 g/mol and a degree of polymerization of 2210. If one of the repeat units is ethylene, which of styrene, propylene, tetrafluoroethylene, and vinyl chloride is the other repeat unit? Why?*

Solution

For an alternating copolymer that has a number-average molecular weight of 100,000 g/mol and a degree of polymerization of 2210, we are to determine one of the repeat unit types if the other type is ethylene. It is first necessary to calculate $\bar{m}$ using Equation 14.6 as follows:

$$\bar{m} = \frac{\bar{M}_n}{DP} = \frac{100{,}000 \text{ g/mol}}{2210} = 42.25 \text{ g/mol}$$

Since this is an alternating copolymer we know that chain fraction of each repeat unit type is 0.5; that is $f_e = f_x = 0.5$, f_e and f_x being, respectively, the chain fractions of the ethylene and unknown repeat units. Also, the repeat unit for ethylene contains 2 carbon atoms and 4 hydrogen atoms; hence, the molecular weight for the ethylene repeat unit is

$$m_e = 2(A_\text{C}) + 4(A_\text{H})$$

$$= 2(12.01 \text{ g/mol}) + 4(1.008 \text{ g/mol}) = 28.05 \text{ g/mol}$$

The modified form of Equation 14.7 for this problem reads as follows:

$$\bar{m} = f_e m_e + f_x m_x$$

in which m_x represents the repeat unit weight of the unknown repeat unit type. Rearranging this expression such that m_x is the dependent variable leads to the following:

$$m_x = \frac{\bar{m} - f_e m_e}{f_x}$$

From above we know that

$f_e = f_x = 0.5$

$m_e = 28.05$ g/mol

$\bar{m} = 42.25$ g/mol

Insertion of these values into the above equation leads to the following value for m_x:

$$m_x = \frac{\bar{m} - f_e m_e}{f_x}$$

$$= \frac{45.25\text{ g/mol} - (0.5)(28.05\text{ g/mol})}{0.5} = 62.45\text{ g/mol}$$

Finally, it is necessary to calculate the repeat unit molecular weights for each of the possible other repeat unit types. These are calculated below:

$m_{\text{styrene}} = 8(A_{\text{C}}) + 8(A_{\text{H}}) = 8(12.01\text{ g/mol}) + 8(1.008\text{ g/mol}) = 104.16\text{ g/mol}$
$m_{\text{propylene}} = 3(A_{\text{C}}) + 6(A_{\text{H}}) = 3(12.01\text{ g/mol}) + 6(1.008\text{ g/mol}) = 42.08\text{ g/mol}$
$m_{\text{TFE}} = 2(A_{\text{C}}) + 4(A_{\text{F}}) = 2(12.01\text{ g/mol}) + 4(19.00\text{ g/mol}) = 100.02\text{ g/mol}$
$m_{\text{VC}} = 2(A_{\text{C}}) + 3(A_{\text{H}}) + (A_{\text{Cl}}) = 2(12.01\text{ g/mol}) + 3(1.008\text{ g/mol}) + 35.45\text{ g/mol} = 62.49\text{ g/mol}$

Therefore, *vinyl chloride* is the other repeat unit type since its m value is almost the same as the calculated m_x.

14.19 *(a) Determine the ratio of butadiene to acrylonitrile repeat units in a copolymer having a number-average molecular weight of 250,000 g/mol and a degree of polymerization of 4640.*

(b) Which type(s) of copolymer(s) will this copolymer be, considering the following possibilities: random, alternating, graft, and block? Why?

Solution

(a) This portion of the problem asks us to determine the ratio of butadiene to acrylonitrile repeat units in a copolymer having a weight-average molecular weight of 250,000 g/mol and a degree of polymerization of 4640. It first becomes necessary to calculate the average repeat unit molecular weight of the copolymer, $\bar{m}$, using Equation 14.6 as follows:

$$\bar{m} = \frac{\bar{M}_n}{DP} = \frac{250{,}000\ \text{g/mol}}{4640} = 53.88\ \text{g/mol}$$

If we designate f_b as the chain fraction of butadiene repeat units, since the copolymer consists of only two repeat unit types, the chain fraction of acrylonitrile repeat units f_a is just $1 - f_b$. Now, Equation 14.7 for this copolymer may be written in the form

$$\bar{m} = f_b m_b + f_a m_a = f_b m_b + (1 - f_b) m_a$$

in which m_b and m_a are the repeat unit molecular weights for butadiene and acrylonitrile, respectively. Values of these repeat unit molecular weights are calculated (using the repeat unit structures in Table 14.5) as follows:

$$m_b = 4(A_{\text{C}}) + 6(A_{\text{H}}) = 4(12.01\ \text{g/mol}) + 6(1.008\ \text{g/mol}) = 54.09\ \text{g/mol}$$

$$m_a = 3(A_{\text{C}}) + 3(A_{\text{H}}) + (A_{\text{N}}) = 3(12.01\ \text{g/mol}) + 3(1.008\ \text{g/mol}) + (14.01\ \text{g/mol})$$

$$= 53.06\ \text{g/mol}$$

Solving for f_b in the above expression for $\bar{m}$ yields

$$f_b = \frac{\bar{m} - m_a}{m_b - m_a}$$

And since values for $\bar{m}$, m_a, and m_b are noted above, we determine the value of f_b as follows:

$$f_b = \frac{53.88\ \text{g/mol} - 53.06\ \text{g/mol}}{54.09\ \text{g/mol} - 53.06\ \text{g/mol}} = 0.80$$

Furthermore, $f_a = 1 - f_b = 1 - 0.80 = 0.20$; which means that the ratio is

$$\frac{f_b}{f_a} = \frac{0.80}{0.20} = 4.0$$

(b) Of the possible copolymers, the only one for which there is a restriction on the ratio of repeat unit types is alternating; the ratio must be 1:1. Therefore, on the basis of the result in part (a), the possibilities for this copolymer are *random*, *graft*, and *block*.

14.20 *Crosslinked copolymers consisting of 35 wt% ethylene and 65 wt% propylene may have elastic properties similar to those for natural rubber. For a copolymer of this composition, determine the fraction of both repeat unit types.*

Solution

For a copolymer consisting of 35 wt% ethylene and 65 wt% propylene, we are asked to determine the fraction of both repeat unit types.

In 100 g of this material, there are 35 g of ethylene and 65 g of propylene. The ethylene (C_2H_4) molecular weight is

$$m(\text{ethylene}) = 2(A_{\text{C}}) + 4(A_{\text{H}})$$

$$= (2)(12.01 \text{ g/mol}) + (4)(1.008 \text{ g/mol}) = 28.05 \text{ g/mol}$$

The propylene (C_3H_6) molecular weight is

$$m(\text{propylene}) = 3(A_{\text{C}}) + 6(A_{\text{H}})$$

$$= (3)(12.01 \text{ g/mol}) + (6)(1.008 \text{ g/mol}) = 42.08 \text{ g/mol}$$

We now determine the number of moles of each repeat unit type. In 100 g of this material, the number of moles of ethylene [n_m(ethylene)] is computed as follows:

$$n_m(\text{ethylene}) = \frac{35 \text{ g}}{28.05 \text{ g/mol}} = 1.25 \text{ mol}$$

Furthermore, for propylene

$$n_m(\text{propylene}) = \frac{65 \text{ g}}{42.08 \text{ g/mol}} = 1.54 \text{ mol}$$

Thus, the fraction of the ethylene repeat unit, f(ethylene), is determined as follows:

$$f(\text{ethylene}) = \frac{n_m(\text{ethylene})}{n_m(\text{ethylene}) + n_m(\text{propylene})}$$

$$= \frac{1.25 \text{ mol}}{1.25 \text{ mol} + 1.54 \text{ mol}} = 0.45$$

Likewise, for propylene

$$f(\text{propylene}) = \frac{n_m(\text{propylene})}{n_m(\text{ethylene}) + n_m(\text{propylene})}$$

$$= \frac{1.54\ \text{mol}}{1.25\ \text{mol}\ +\ 1.54\ \text{mol}} = 0.55$$

14.21 *A random poly(styrene-butadiene) copolymer has a number-average molecular weight of 350,000 g/mol and a degree of polymerization of 5000. Compute the fraction of styrene and butadiene repeat units in this copolymer.*

Solution

For a random poly(styrene-butadiene) copolymer in which $\bar{M}_n$ = 350,000 g/mol and DP = 5000, we are asked to compute the fractions of styrene and butadiene repeat units.

From Table 14.5, the styrene repeat unit has eight carbon and eight hydrogen atoms. Thus, the styrene repeat unit molecular weight m_{st} is computed as follows:

$$m_{st} = (8)(12.01 \text{ g/mol}) + (8)(1.008 \text{ g/mol}) = 104.14 \text{ g/mol}$$

Also, from Table 14.5, the butadiene repeat unit has four carbon and six hydrogen atoms; thus the value of m_{bu} is

$$m_{bu} = (4)(12.01 \text{ g/mol}) + (6)(1.008 \text{ g/mol}) = 54.09 \text{ g/mol}$$

For this problem Equation 14.7 takes the form

$$\bar{m} = f_{st}m_{st} + f_{bu}m_{bu}$$

Now since $f_{st} + f_{bu} = 1$, then

$$f_{bu} = 1 - f_{st}$$

and the above equation for $\bar{m}$ takes the form

$$\bar{m} = f_{st}m_{st} + (1 - f_{st})m_{bu}$$

And upon insertion of the above values for m_{st} and m_{bu} the above equation becomes

$$\bar{m} = f_{st}(104.14 \text{ g/mol}) + (1 - f_{st})(54.09 \text{ g/mol})$$

Now from the definition of DP, Equation 14.6,

$$DP = \frac{\bar{M}_n}{\bar{m}}$$

insertion of the above expression for $\bar{m}$ leads to

$$5000 = \frac{350{,}000 \text{ g/mol}}{f_{st}(104.14 \text{ g/mol}) + (1 - f_{st})(54.09 \text{ g/mol})}$$

Solving for f_{st} yields $f_{st} = 0.32$.

And, consequently

$$f_{bu} = 1 - f_{st}$$

$$= 1 - 0.32 = 0.68$$

Polymer Crystallinity

14.22 *Explain briefly why the tendency of a polymer to crystallize decreases with increasing molecular weight.*

Answer

The tendency of a polymer to crystallize decreases with increasing molecular weight because as the chains become longer it is more difficult for all regions along adjacent chains to align so as to produce the ordered atomic array.

14.23 *For each of the following pairs of polymers, do the following: (1) State whether it is possible to determine whether one polymer is more likely to crystallize than the other; (2) if it is possible, note which is the more likely and then cite reason(s) for your choice; and (3) if it is not possible to decide, then state why.*

(a) Linear and atactic poly(vinyl chloride); linear and isotactic polypropylene

(b) Linear and syndiotactic polypropylene; crosslinked cis-polyisoprene

(c) Network phenol-formaldehyde; linear and isotactic polystyrene

(d) Block poly(acrylonitrile-isoprene) copolymer; graft poly(chloroprene-isobutylene) copolymer

Solution

(a) No, it is not possible to decide for these two polymers. On the basis of tacticity, the isotactic PP is more likely to crystallize than the atactic PVC. On the other hand, with regard to side-group bulkiness, the PVC is more likely to crystallize.

(b) Yes, it is possible to decide for these two copolymers. The linear and syndiotactic polypropylene is more likely to crystallize than crosslinked cis-isoprene because linear polymers are more likely to crystallize than crosslinked ones.

(c) Yes, it is possible to decide for these two polymers. The linear and isotactic polystyrene is more likely to crystallize than network phenol-formaldehyde; network polymers rarely crystallize, whereas isotactic ones crystallize relatively easily.

(d) Yes, it is possible to decide for these two copolymers. The block poly(acrylonitrile-isoprene) copolymer is more likely to crystallize than the graft poly(chloroprene-isobutylene) copolymer. Block copolymers crystallize more easily than graft ones.

14.24 *The density of totally crystalline nylon 6,6 at room temperature is 1.213 g/cm*^{3}. *Also, at room temperature the unit cell for this material is triclinic with the following lattice parameters:*

$$a = 0.497 \text{ nm} \qquad \alpha = 48.4°$$

$$b = 0.547 \text{ nm} \qquad \beta = 76.6°$$

$$c = 1.729 \text{ nm} \qquad \gamma = 62.5°$$

If the volume of a triclinic unit cell, is a function of these lattice parameters as

$$V_{\text{tri}} = abc\sqrt{1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma}$$

determine the number of repeat units per unit cell.

Solution

For this problem we are given the density of nylon 6,6 (1.213 g/cm^3), an expression for the volume of its unit cell, and the lattice parameters, and are asked to determine the number of repeat units per unit cell. This computation necessitates the use of Equation 3.8, in which we solve for n. Before this can be carried out we must first calculate V_C, the unit cell volume, and A the repeat unit molecular weight. For V_C

$$V_C = abc\sqrt{1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma}$$

$$= (0.497 \text{ nm})(0.547 \text{ nm})(1.729 \text{ nm})\sqrt{1 - 0.441 - 0.054 - 0.213 + 2(0.664)(0.232)(0.462)}$$

$$= (0.3098 \text{ nm}^3) = (0.3098 \text{ nm}^3)(10^{-7} \text{ cm/nm})^3$$

$$= 3.098 \times 10^{-22} \text{ cm}^3$$

From Table 14.3, the repeat unit for nylon 6,6 has 12 carbon atoms, 22 hydrogen atoms, 2 oxygen atoms and 2 nitrogen atoms. Therefore, the molecular weight for a repeat unit of nylon 6,6 (MW_{nylon}) is determined as follows:

$$MW_{\text{nylon}} = 12(A_{\text{C}}) + 22(A_{\text{H}}) + 2(A_{\text{O}}) + 2(A_{\text{N}})$$

$$= 12(12.01 \text{ g/mol}) + 22(1.008 \text{ g/mol}) + 2(16.00 \text{ g/mol}) + 2(14.01 \text{ g/mol})$$

$$= 226.32 \text{ g/mol}$$

Finally, solving for n from Equation 3.8 and incorporating values for ρ (1.213 g/cm^3), V_C (3.098×10^{-22} cm^3), and MW_{nylon} (226.32 g/mol) leads to the following value for n:

$$n = \frac{\rho V_C N_A}{MW_{\text{nylon}}}$$

$$= \frac{(1.213 \text{ g/cm}^3)(3.098 \times 10^{-22} \text{ cm}^3\text{/unit cell})(6.022 \times 10^{23} \text{ repeat units/mol})}{226.32 \text{ g/mol}}$$

= 1 repeat unit/unit cell

14.25 *The density and associated percent crystallinity for two poly(ethylene terephthalate) materials are as follows:*

ρ (g/cm³)	*crystallinity (%)*
1.408	*74.3*
1.343	*31.2*

(a) Compute the densities of totally crystalline and totally amorphous poly(ethylene terephthalate).

(b) Determine the percent crystallinity of a specimen having a density of 1.382 g/cm^3.

Solution

(a) We are asked to compute the densities of totally crystalline and totally amorphous poly(ethylene terephthalate) (ρ_c and ρ_a from Equation 14.8). From Equation 14.8 let

$$C = \frac{\%\text{ crystallinity}}{100}$$

such that Equation 14.8 now becomes

$$C = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \tag{14.8a}$$

Rearrangement of this expression leads to the following:

$$\rho_c(C\rho_s - \rho_s) + \rho_c\rho_a - C\rho_s\rho_a = 0$$

in which ρ_c and ρ_a are the variables for which solutions are to be found. Since two values of ρ_s and C are provided in the problem statement, two equations may be constructed as follows:

$$\rho_c(C_1\rho_{s1} - \rho_{s1}) + \rho_c\rho_a - C_1\rho_{s1}\rho_a = 0$$

$$\rho_c(C_2\rho_{s2} - \rho_{s2}) + \rho_c\rho_a - C_2\rho_{s2}\rho_a = 0$$

In which ρ_{s1} = 1.408 g/cm^3, ρ_{s2} = 1.343 g/cm^3, C_1 = 0.743, and C_2 = 0.312. Solving the above two equations for ρ_a and ρ_c leads to the following two expressions:

$$\rho_a = \frac{\rho_{s1}\rho_{s2}(C_1 - C_2)}{C_1\rho_{s1} - C_2\rho_{s2}}$$

$$\rho_c = \frac{\rho_{s1}\rho_{s2}(C_2 - C_1)}{\rho_{s2}(C_2 - 1) - \rho_{s1}(C_1 - 1)}$$

Incorporation of values of ρ_{s1}, ρ_{s2}, C_1, and C_2 cited above leads to the following values of ρ_a and ρ_c:

$$\rho_a = \frac{(1.408\text{ g/cm}^3)(1.343\text{ g/cm}^3)(0.743 - 0.312)}{(0.743)(1.408\text{ g/cm}^3) - (0.312)(1.343\text{ g/cm}^3)} = 1.300\text{ g/cm}^3$$

And

$$\rho_c = \frac{(1.408\text{ g/cm}^3)(1.343\text{ g/cm}^3)(0.312 - 0.743)}{(1.343\text{ g/cm}^3)(0.312 - 1.0) - (1.408\text{ g/cm}^3)(0.743 - 1.0)} = 1.450\text{ g/cm}^3$$

(b) Now we are to determine the % crystallinity for $\rho_s = 1.382\text{ g/cm}^3$. Again, using Equation 14.8

$$\%\text{ crystallinity} = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100$$

$$= \frac{(1.450\text{ g/cm}^3)(1.382\text{ g/cm}^3 - 1.300\text{ g/cm}^3)}{(1.382\text{ g/cm}^3)(1.450\text{ g/cm}^3 - 1.300\text{ g/cm}^3)} \times 100$$

= 57.4%

14.26 *The density and associated percent crystallinity for two polypropylene materials are as follows:*

ρ (g/cm^3)	*crystallinity (%)*
0.904	62.8
0.895	54.4

(a) Compute the densities of totally crystalline and totally amorphous polypropylene.

(b) Determine the density of a specimen having 74.6% crystallinity.

Solution

(a) We are asked to compute the densities of totally crystalline and totally amorphous polypropylene (ρ_c and ρ_a from Equation 14.8). From Equation 14.8 let

$$C = \frac{\%\ \text{crystallinity}}{100}$$

such that Equation 14.8 now becomes

$$C = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \tag{14.8a}$$

Rearrangement of this expression leads to the following:

$$\rho_c(C\rho_s - \rho_s) + \rho_c\rho_a - C\rho_s\rho_a = 0$$

in which ρ_c and ρ_a are the variables for which solutions are to be found. Since two values of ρ_s and C are provided in the problem statement, two equations may be constructed as follows:

$$\rho_c(C_1\rho_{s1} - \rho_{s1}) + \rho_c\rho_a - C_1\rho_{s1}\rho_a = 0$$

$$\rho_c(C_2\rho_{s2} - \rho_{s2}) + \rho_c\rho_a - C_2\rho_{s2}\rho_a = 0$$

In which ρ_{s1} = 0.904 g/cm^3, ρ_{s2} = 0.895 g/cm^3, C_1 = 0.628, and C_2 = 0.544. Solving the above two equations for ρ_a and ρ_c leads to the following two expressions:

$$\rho_a = \frac{\rho_{s1}\rho_{s2}(C_1 - C_2)}{C_1\rho_{s1} - C_2\rho_{s2}}$$

$$\rho_c = \frac{\rho_{s1}\rho_{s2}(C_2 - C_1)}{\rho_{s2}(C_2 - 1) - \rho_{s1}(C_1 - 1)}$$

Incorporation of values of ρ_{s1}, ρ_{s2}, C_1, and C_2 cited above leads to the following values of ρ_a and ρ_c:

$$\rho_a = \frac{(0.904 \text{ g/cm}^3)(0.895 \text{ g/cm}^3)(0.628 - 0.544)}{(0.628)(0.904 \text{ g/cm}^3) - (0.544)(0.895 \text{ g/cm}^3)} = 0.841 \text{ g/cm}^3$$

And

$$\rho_c = \frac{(0.904 \text{ g/cm}^3)(0.895 \text{ g/cm}^3)(0.544 - 0.628)}{(0.895 \text{ g/cm}^3)(0.544 - 1.0) - (0.904 \text{ g/cm}^3)(0.628 - 1.0)} = 0.946 \text{ g/cm}^3$$

(b) Now we are asked to determine the density of a specimen having 74.6% crystallinity. Solving for ρ_s from Equation 14.8a and substitution for ρ_a and ρ_c, which were computed in part (a) yields

$$\rho_s = \frac{-\rho_c \rho_a}{C(\rho_c - \rho_a) - \rho_c}$$

$$= \frac{-(0.946 \text{ g/cm}^3)(0.841 \text{ g/cm}^3)}{(0.746)(0.946 \text{ g/cm}^3 - 0.841 \text{ g/cm}^3) - 0.946 \text{ g/cm}^3}$$

$$= 0.917 \text{ g/cm}^3$$

Diffusion in Polymeric Materials

14.27 *Consider the diffusion of oxygen through a low-density polyethylene (LDPE) sheet 15 mm thick. The pressures of oxygen at the two faces are 2000 kPa and 150 kPa, which are maintained constant. Assuming conditions of steady state, what is the diffusion flux [in [(cm^3 STP)/cm^2-s] at 298 K?*

Solution

This is a permeability problem in which we are asked to compute the diffusion flux of oxygen through a 15-mm thick sheet of low-density polyethylene. In order to solve this problem it is necessary to employ Equation 14.9. The permeability coefficient of O_2 through LDPE is given in Table 14.6 as 2.2×10^{-13} (cm^3 STP)-cm/cm^2-s-Pa. Thus, from Equation 14.9

$$J = -P_M \frac{\Delta P}{\Delta x} = -P_M \frac{P_2 - P_1}{\Delta x}$$

and taking P_1 = 2000 kPa (2,000,000 Pa) and P_2 = 150 kPa (150,000 Pa) we get the following value for the flux:

$$J = \left[-2.2 \times 10^{-13} \frac{(\mathrm{cm^3\ STP})(\mathrm{cm})}{\mathrm{cm^2\text{-}s\text{-}Pa}}\right]\left(\frac{150{,}000\ \mathrm{Pa} - 2{,}000{,}000\ \mathrm{Pa}}{1.5\ \mathrm{cm}}\right)$$

$$= 2.7 \times 10^{-7}\ \frac{(\mathrm{cm^3\ STP})}{\mathrm{cm^2\text{-}s}}$$

14.28 *Carbon dioxide diffuses through a high-density polyethylene (HDPE) sheet 50 mm thick at a rate of* 2.2×10^{-8} *(cm^3 STP)/cm^2-s at 325 K. The pressures of carbon dioxide at the two faces are 4000 kPa and 2500 kPa, which are maintained constant. Assuming conditions of steady state, what is the permeability coefficient at 325 K?*

Solution

This problem asks us to compute the permeability coefficient for carbon dioxide through high-density polyethylene at 325 K given a steady-state permeability situation. It is necessary for us to use Equation 14.9 in to solve this problem. Rearranging this expression and solving for the permeability coefficient gives the following:

$$P_M = \frac{-J\,\Delta x}{\Delta P} = \frac{-J\,\Delta x}{P_2 - P_1}$$

Taking P_1 = 4000 kPa (4,000,000 Pa) and P_2 = 2500 kPa (2,500,000 Pa), we compute the permeability coefficient of CO_2 through HDPE as follows:

$$P_M = \frac{\left[-\ 2.2 \times 10^{-8}\,\dfrac{(\mathrm{cm^3\ STP})}{\mathrm{cm^2\text{-}s}}\right](5\ \mathrm{cm})}{(2{,}500{,}000\ \mathrm{Pa} - 4{,}000{,}000\ \mathrm{Pa})}$$

$$= 0.73 \times 10^{-13}\,\frac{(\mathrm{cm^3\ STP})(\mathrm{cm})}{\mathrm{cm^2\text{-}s\text{-}Pa}}$$

14.29 *The permeability coefficient of a type of small gas molecule in a polymer is dependent on absolute temperature according to the following equation:*

$$P_M = P_{M_0} \exp\left(-\frac{Q_p}{RT}\right)$$

where P_{M_0} *and* Q_p *are constants for a given gas-polymer pair. Consider the diffusion of water through a polystyrene sheet 30 mm thick. The water vapor pressures at the two faces are 20 kPa and 1 kPa, which are maintained constant. Compute the diffusion flux [in (cm*^{3} *STP)/cm*^{2}*-s] at 350 K? For this diffusion system,*

$$P_{M_0} = 9.0 \times 10^{-5} \text{ (cm}^3 \text{ STP)(cm)/cm}^2\text{-s-Pa}$$

$$Q_p = 42{,}300 \text{ J/mol}$$

Assume a condition of steady-state diffusion.

Solution

This problem asks that we compute the diffusion flux at 350 K for water in polystyrene. It is first necessary to compute the value of the permeability coefficient at 350 K. The temperature dependence of P_M is given in the problem statement, as follows:

$$P_M = P_{M_0} \exp\left(-\frac{Q_p}{RT}\right)$$

Incorporating values provided for the constants P_{M_0} and Q_p, we get

$$P_M = \left[9.0 \times 10^{-5} \frac{\text{(cm}^3 \text{ STP)(cm)}}{\text{cm}^2\text{-s-Pa}}\right] \exp\left[-\frac{42{,}300 \text{ J/mol}}{(8.314 \text{ J/mol-K})(350 \text{ K})}\right]$$

$$= 4.4 \times 10^{-11} \frac{\text{(cm}^3 \text{ STP)(cm)}}{\text{cm}^2\text{-s-Pa}}$$

And, using Equation 14.9, the diffusion flux is equal to

$$J = -P_M \frac{\Delta P}{\Delta x} = -P_M \frac{P_2 - P_1}{\Delta x}$$

where

P_1 = 20 kPa = 20,000 Pa

P_2 = 1 kPa = 1,000 Pa

Therefore, we solve for the value of the flux as follows:

$$J = -\left[4.4 \times 10^{-11} \frac{(\text{cm}^3\ \text{STP})(\text{cm})}{\text{cm}^2\text{-s-Pa}}\right]\left(\frac{1{,}000\ \text{Pa} - 20{,}000\ \text{Pa}}{3.0\ \text{cm}}\right)$$

$$= 2.8 \times 10^{-7} \frac{(\text{cm}^3\ \text{STP})}{\text{cm}^2\text{-s}}$$

FUNDAMENTALS OF ENGINEERING QUESTIONS AND PROBLEMS

14.1FE *What type(s) of bonds is (are) found between atoms within hydrocarbon molecules?*
(A) Ionic bonds
(B) Covalent bonds
(C) van der Waals bonds
(D) Metallic bonds

Answer

The correct answer is B. Covalent bonds are found between atoms within hydrocarbon molecules.

14.2FE *How do the densities compare for crystalline and amorphous polymers of the same material that have identical molecular weights?*

(A) Density of crystalline polymer < density of amorphous polymer

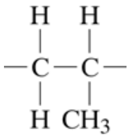
(B) Density of crystalline polymer = density of amorphous polymer

(C) Density of crystalline polymer > density of amorphous polymer

Answer

The correct answer is C. The density of a crystalline polymer is greater than an amorphous polymer of the same material and having the same molecular weight.

14.3FE *What is the name of the polymer represented by the following repeat unit?*



$$-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-$$

(A) Poly(methyl methacrylate)

(B) Polyethylene

(C) Polypropylene

(D) Polystyrene

Answer

The correct answer is C. The repeat unit structure is for polypropylene.

CHAPTER 15

CHARACTERISTICS, APPLICATIONS, AND PROCESSING OF POLYMERS

PROBLEM SOLUTIONS

Stress–Strain Behavior

15.1 *From the stress–strain data for poly(methyl methacrylate) shown in Figure 15.3, determine the modulus of elasticity and tensile strength at room temperature [20°C (68°F)], and compare these values with those given in Table 15.1.*

Solution

From Figure 15.3, the elastic modulus is the slope in the elastic linear, or

$$E = \frac{\Delta(\text{stress})}{\Delta(\text{strain})} = \frac{\sigma_1 - \sigma_2}{\varepsilon_1 - \varepsilon_2}$$

From the plot in Figure 15.3 (20°C curve) let us assign

σ_1 = 30 MPa

σ_2 = 0 MPa

And their corresponding strains are

$\varepsilon_1 = 9 \times 10^{-3}$

$\varepsilon_2 = 0$

Thus, the value of the elastic modulus is determined as follows:

$$E = \frac{\sigma_1 - \sigma_2}{\varepsilon_1 - \varepsilon_2} = \frac{30\ \text{MPa} - 0\ \text{MPa}}{9 \times 10^{-3} - 0} = 3.3\ \text{GPa} \quad (483{,}000\ \text{psi})$$

The value range cited in Table 15.1 is 2.24 to 3.24 GPa (325,000 to 470,000 psi). Thus, the plotted value is a little on the high side.

The tensile strength corresponds to the stress at which the curve ends, which is 52 MPa (7500 psi). This value lies within the range cited in Table 15.1—48.3 to 72.4 MPa (7000 to 10,500 psi).

15.2 *Compute the elastic moduli for the following polymers, whose stress–strain behaviors can be observed in the Tensile Tests module of Virtual Materials Science and Engineering (VMSE):*

(a) high-density polyethylene

(b) nylon

(c) phenol-formaldehyde (Bakelite).

How do these values compare with those presented in Table 15.1 for the same polymers?

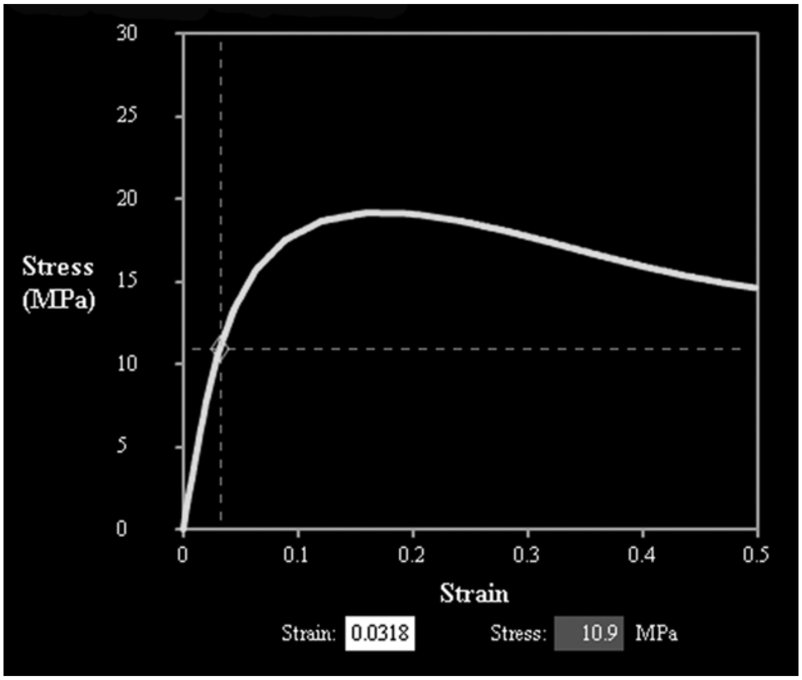
Solution

The elastic modulus is the slope in the linear elastic region (Equation 6.10) as

$$E = \frac{\Delta\sigma}{\Delta\varepsilon} = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1}$$

Since all the stress-strain curves pass through the origin, we make take $\sigma_1 = 0$ and $\varepsilon_1 = 0$. Determinations of σ_2 and ε_2 are possible by moving the cursor to some arbitrary point in the linear region of the curve and then reading corresponding values in the "Stress" and "Strain" windows that are located below the plot.

(a) A screenshot for the high-density polyethylene in the elastic region is shown below.

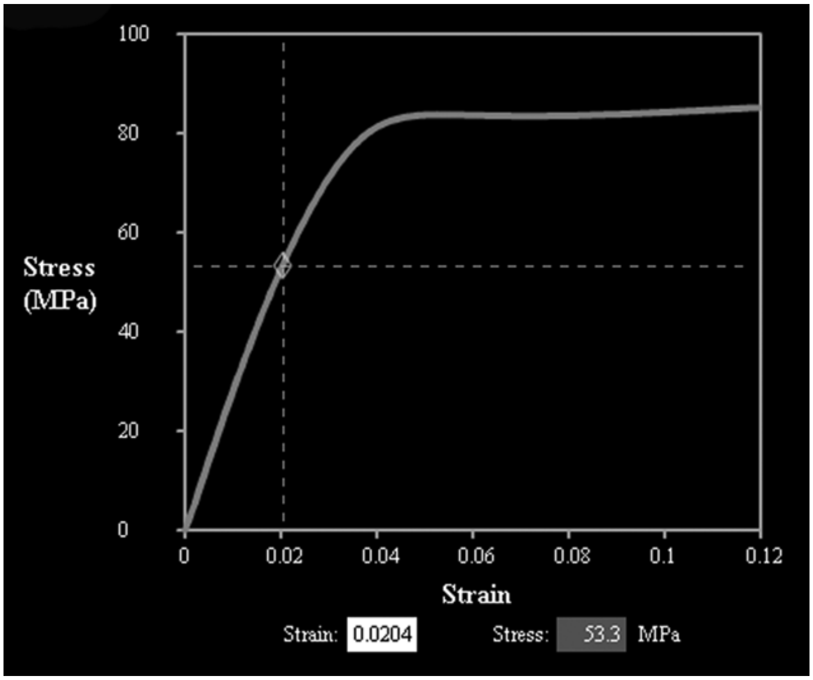


Here the cursor point resides in the elastic region at a stress of 10.9 MPa (which is the value of σ_2) at a strain of 0.0318 (which is the value of ε_2). Thus, the elastic modulus is equal to

$$E = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1} = \frac{10.9\ \text{MPa} - 0\ \text{MPa}}{0.0318 - 0} = 343\ \text{MPa} = 0.343\ \text{GPa}$$

The elastic modulus range for high-density polyethylene given in Table 15.1 is 1.06 to 1.09 GPa, which is significantly higher than this value.

(b) A screenshot for the nylon in the elastic region is shown below.

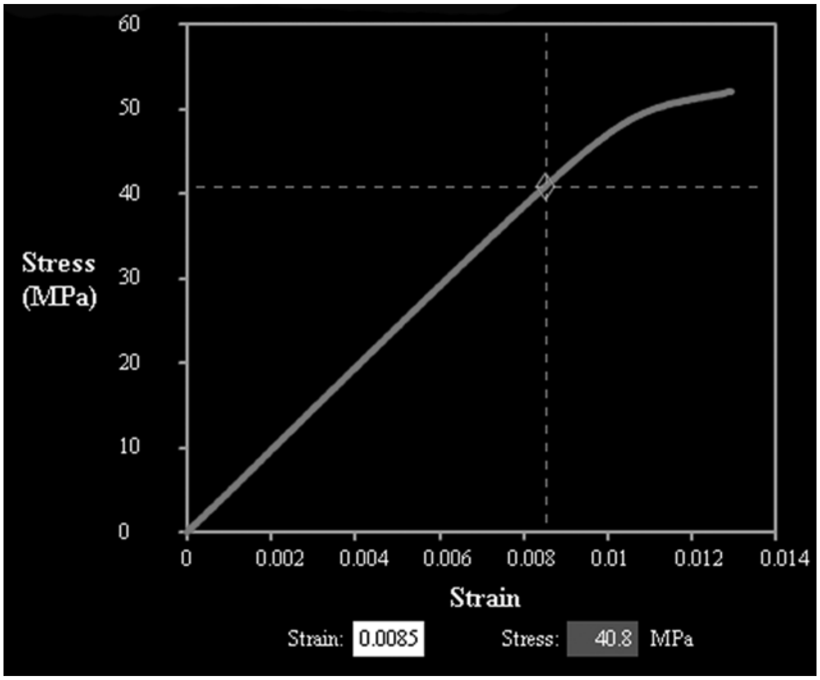


Here the cursor point resides in the elastic region at a stress of 53.3 MPa (which is the value of σ_2) at a strain of 0.0204 (which is the value of ε_2). Thus, the elastic modulus is equal to

$$E = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1} = \frac{53.3\ \text{MPa} - 0\ \text{MPa}}{0.0204 - 0} = 2{,}610\ \text{MPa} = 2.61\ \text{GPa}$$

The elastic modulus range for nylon 6,6 given in Table 15.1 is 1.58 GPa to 3.80 GPa; therefore, the value for the *VMSE* nylon lies within this range.

(c) A screenshot for the Bakelite in the elastic region is shown below.



Strain: 0.0085 Stress: 40.8 MPa

Here the cursor point resides in the elastic region at a stress of 40.8 MPa (which is the value of σ_2) at a strain of 0.0085 (which is the value of ε_2). Thus, the elastic modulus is equal to

$$E = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1} = \frac{\mathbf{40.8\ MPa - 0\ MPa}}{\mathbf{0.0085 - 0}} = \mathbf{4{,}800\ MPa = 4.8\ GPa}$$

The elastic modulus range for the Bakelite given in Table 15.1 is 2.76 GPa to 4.83 GPa; therefore, this value for the *VMSE* Bakelite lies just below the maximum value for this range.

15.3 *For the nylon polymer whose stress–strain behavior can be observed in the Tensile Tests module of Virtual Materials Science and Engineering (VMSE), determine the following:*

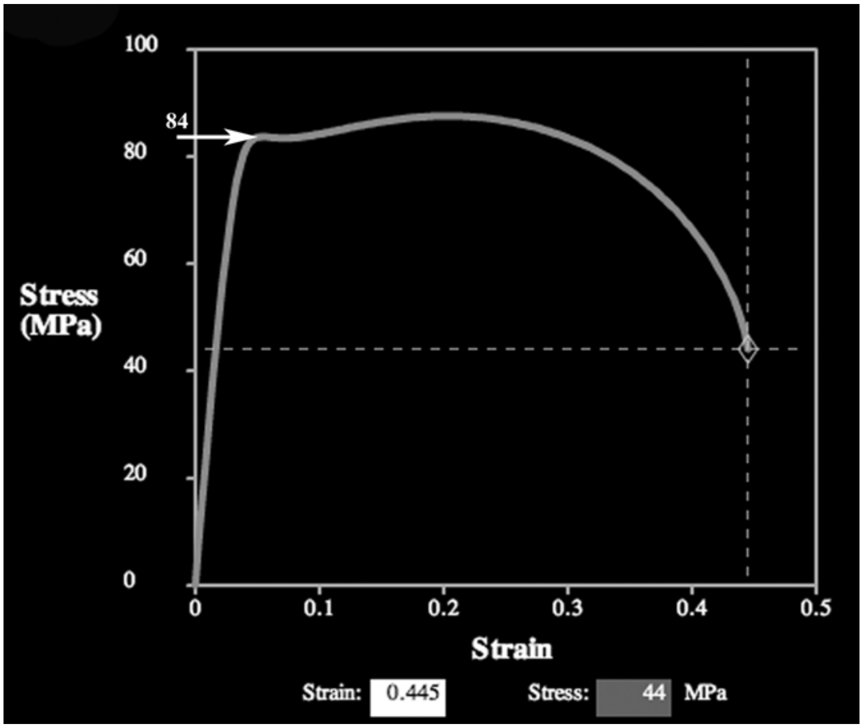
(a) The yield strength

(b) The approximate ductility, in percent elongation

How do these values compare with those for the nylon material presented in Table 15.1?

Solution

A screenshot of the stress-strain curve for nylon (to fracture) is shown below.



(a) The yield strength corresponds to the first maximum (just beyond the initial linear-elastic region) of the stress-strain curve; as noted in this plot, the value is 84 MPa.

(b) The approximate percent elongation corresponds to the strain at fracture ("0.445" as noted in the "Strain" box) multiplied by 100 (i.e., 44.5%) minus the maximum elastic strain (i.e., value of strain at which the linearity of the curve ends multiplied by 100—in this case about 4%); this gives a value of about 40%EL.

For nylon 6,6, the range of values of yield strength presented in Table 15.1 is 44.8 MPa to 82.8 MPa; therefore, the value for the *VMSE* nylon lies slightly above the upper value. The ductility range for nylon 6,6 is 15%EL to 300%EL; therefore, our value (40%EL) lies within this range.

15.4 *For the phenol-formaldehyde (Bakelite) polymer whose stress–strain behavior can be observed in the Tensile Tests module of Virtual Material Science and Engineering (VMSE), determine the following:*

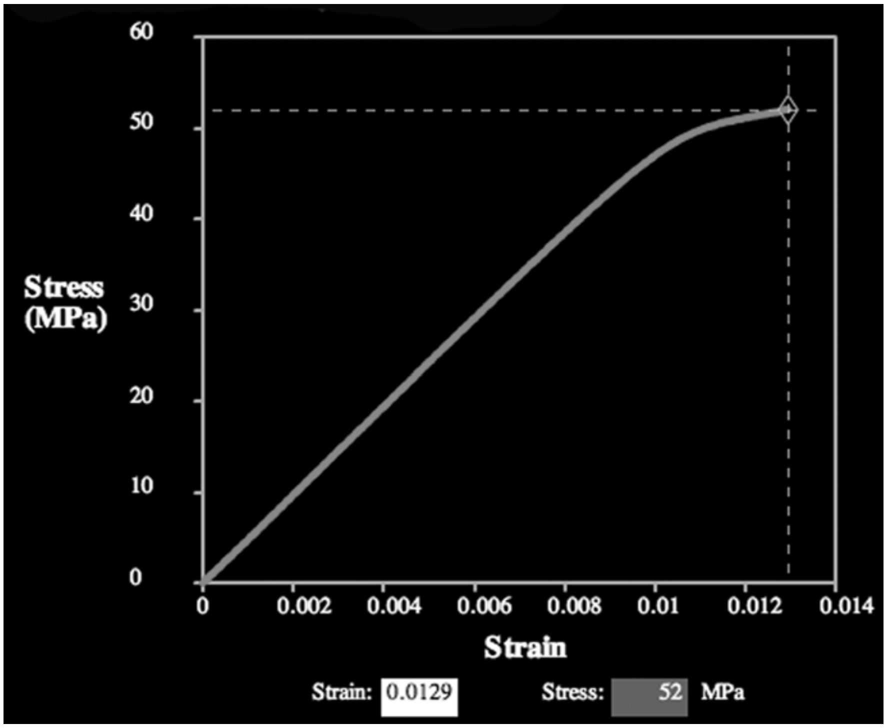
(a) The tensile strength

(b) The approximate ductility, in percent elongation

How do these values compare with those for the phenol-formaldehyde material presented in Table 15.1?

Solution

A screenshot of the stress-strain curve for phenol-formaldehyde (to fracture) is shown below.



(a) The tensile strength corresponds to the stress at which fracture occurs. This reading in the stress window located below this plot at the point of fracture—the tensile strength—is 52 MPa.

(b) The approximate percent elongation corresponds to the strain at fracture ("0.0129" as noted in the "Strain" box) multiplied by 100 (i.e., 1.29%) minus the maximum elastic strain (i.e., value of strain at which the linearity of the curve ends multiplied by 100—in this case about 1%); this gives a value of about 0.29%EL.

For phenol-formaldehyde, the range of values of tensile strength presented in Table 15.1 is 34.5 MPa to 62.1 MPa; therefore, the value for the *VMSE* material (52 MPa) lies within this range. The ductility range for phenol-formaldehyde is 1.5%EL to 2.0%EL; therefore, our value (0.29%EL) lies below the lower limit.

Viscoelastic Deformation

15.5 *In your own words, briefly describe the phenomenon of viscoelasticity.*

The explanation of viscoelasticity is given in Section 15.4.

15.6 *For some viscoelastic polymers that are subjected to stress relaxation tests, the stress decays with time according to*

$$\sigma(t) = \sigma(0)\exp\left(-\frac{t}{\tau}\right) \qquad (15.10)$$

where σ(t) and σ(0) represent the time-dependent and initial (i.e., time = 0) stresses, respectively, and t and τ denote elapsed time and the relaxation time, respectively; τ is a time-independent constant characteristic of the material. A specimen of a viscoelastic polymer whose stress relaxation obeys Equation 15.10 was suddenly pulled in tension to a measured strain of 0.5; the stress necessary to maintain this constant strain was measured as a function of time. Determine $E_r(10)$ *for this material if the initial stress level was 3.5 MPa (500 psi), which dropped to 0.5 MPa (70 psi) after 30 s.*

Solution

In order to determine $\sigma(10)$, it is first necessary to compute τ from the data provided in the problem statement. In order to solve for τ from Equation 15.10 it is first necessary to take natural logarithms of both sides of the equation as follows:

$$\ln\sigma(t) = \ln\sigma(0) - \frac{t}{\tau}$$

And solving this expression for τ leads to the following expression:

$$\tau = \frac{-t}{\ln\sigma(t) - \ln\sigma(0)} = \frac{-t}{\ln\left[\dfrac{\sigma(t)}{\sigma(0)}\right]}$$

The problem statement provides the following values:

$\sigma(0) = 3.5$ MPa

$\sigma(t) = \sigma(30) = 0.5$ MPa

$t = 30$ s

Therefore, the value of τ is equal to

$$\tau = \frac{-t}{\ln\left[\dfrac{\sigma(t)}{\sigma(0)}\right]}$$

$$= \frac{-30\text{ s}}{\ln\left[\dfrac{0.5\text{ MPa}}{3.5\text{ MPa}}\right]} = 15.4\text{ s}$$

Using Equation 15.10 we compute the value of $\sigma(10)$ (that is, the value of σ when $t = 10$ s), as follows:

$$\sigma(10) = \sigma(0)\exp\left(-\frac{10\text{ s}}{\tau}\right)$$

$$= (3.5\text{ MPa})\exp\left(-\frac{10\text{ s}}{15.4\text{ s}}\right) = 1.83\text{ MPa}$$

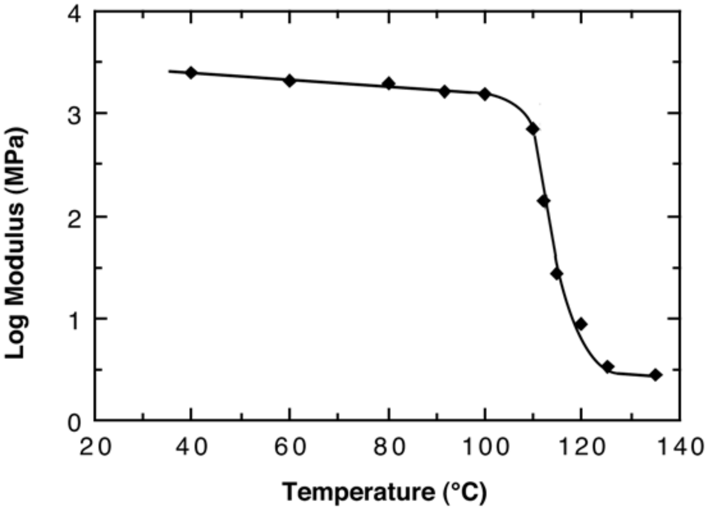
We now compute the value of $E_r(10)$ using Equation 15.1 as follows:

$$E_r(10) = \frac{\sigma(10)}{\varepsilon_0} = \frac{1.83\,\text{MPa}}{0.5} = 3.66\text{ MPa}\ \ (522\text{ psi})$$

15.7 *In Figure 15.28, the logarithm of $E_r(t)$ versus the logarithm of time is plotted for PMMA at a variety of temperatures. Plot log $E_r(10)$ versus temperature and then estimate its T_g.*

Solution

Below is plotted the logarithm of $E_r(10)$ versus temperature.



The glass-transition temperature is that temperature corresponding to the abrupt decrease in log $E_r(10)$, which for this PMMA material is about 115°C.

15.8 *On the basis of the curves in Figure 15.5, sketch schematic strain–time plots for the following polystyrene materials at the specified temperatures:*

(a) Crystalline at 70°C

(b) Amorphous at 180°C

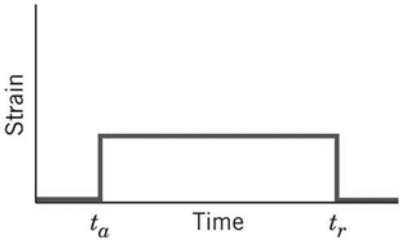
(c) Crosslinked at 180°C

(d) Amorphous at 100°C

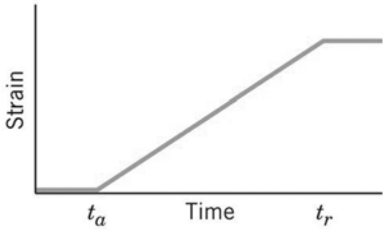
Solution

We are asked to make schematic strain-time plots for various polystyrene materials and at several temperatures.

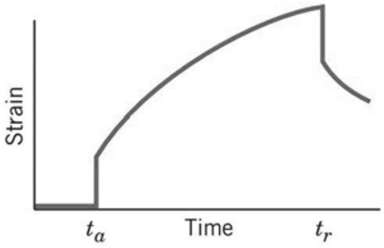
(a) Crystalline polystyrene at 70°C behaves in a glassy manner (Figure 15.8, curve *A*); therefore, the strain-time behavior would be as Figure 15.5*b*—i.e.,



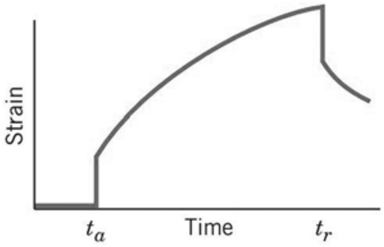
(b) Amorphous polystyrene at 180°C behaves as a viscous liquid (Figure 15.8, curve *C*); therefore, the strain-time behavior will be as Figure 15.5*d*—that is



(c) Crosslinked polystyrene at 180°C behaves as a rubbery material (Figure 15.8, curve *B*); therefore, the strain-time behavior will be as Figure 15.5*c*—i.e.,



(d) Amorphous polystyrene at 100°C behaves as a leathery material (Figure 15.7); therefore, the strain-time behavior will be as Figure 15.5*c*—that is,



15.9 *(a) Contrast the manner in which stress relaxation and viscoelastic creep tests are conducted.*

(b) For each of these tests, cite the experimental parameter of interest and how it is determined.

Answer

(a) Stress relaxation tests are conducted by rapidly straining the material elastically in tension, holding the strain level constant, and then measuring the stress as a function of time. For viscoelastic creep tests, a stress (usually tensile) is applied instantaneously and maintained constant while strain is measured as a function of time.

(b) The experimental parameters of interest from the stress relaxation and viscoelastic creep tests are the relaxation modulus and creep modulus (or creep compliance), respectively. The relaxation modulus is the ratio of stress measured after 10 s and strain (Equation 15.1); creep modulus is the ratio of stress and strain taken at a specific time (Equation 15.2).

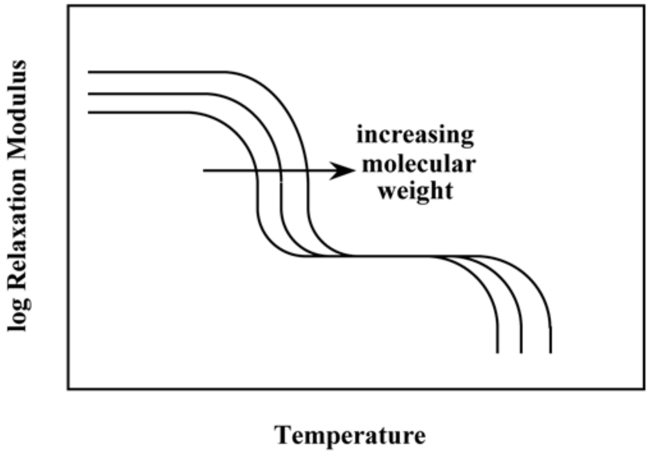
15.10 *Make two schematic plots of the logarithm of relaxation modulus versus temperature for an amorphous polymer (curve C in Figure 15.8).*

(a) On one of these plots demonstrate how the behavior changes with increasing molecular weight.

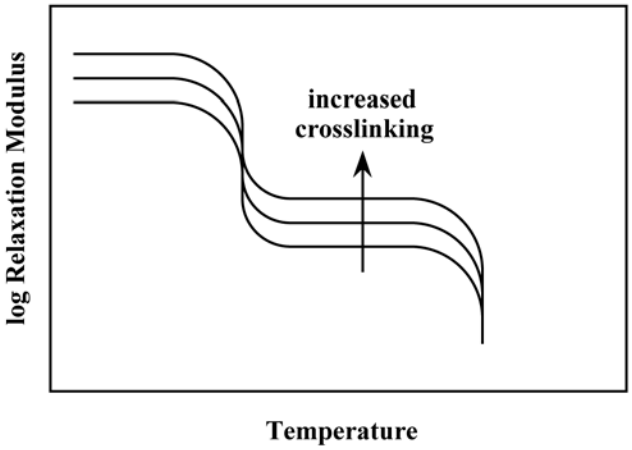
(b) On the other plot, indicate the change in behavior with increasing crosslinking.

Solution

(a) This portion of the problem calls for a plot of log $E_r(10)$ versus temperature demonstrating how the behavior changes with increased molecular weight. Such a plot is given below. Increasing molecular weight increases both glass-transition and melting temperatures.



(b) We are now called upon to make a plot of log $E_r(10)$ versus temperature demonstrating how the behavior changes with increased crosslinking. Such a plot is given below. Increasing the degree of crosslinking will increase the modulus in both glassy and rubbery regions.



Fracture of Polymers

Miscellaneous Mechanical Characteristics

15.11 *For thermoplastic polymers, cite five factors that favor brittle fracture.*

Answer

For thermoplastic polymers, five factors that favor brittle fracture are as follows: (1) a reduction in temperature, (2) an increase in strain rate, (3) the presence of a sharp notch, (4) increased specimen thickness, and (5) modifications of the polymer structure.

15.12 *(a) Compare the fatigue limits for PMMA (Figure 15.11) and the 1045 steel alloy for which fatigue data are given in Figure 8.20.*

(b) Compare the fatigue strengths at 10^6 cycles for nylon 6 (Figure 15.11) and 2014-T6 aluminum alloy (Figure 8.20).

Solution

(a) The fatigue limits for PMMA and the steel alloy are 10 MPa (1450 psi) and 310 MPa (45,000 psi), respectively.

(b) At 10^6 cycles, the fatigue strengths for nylon 6 and 2014-T6 aluminum are 11 MPa (1600 psi) and 210 MPa (30,500 psi), respectively.

Deformation of Semicrystalline Polymers

15.13 *In your own words, describe the mechanisms by which semicrystalline polymers*

(a) elastically deform

(b) plastically deform

(c) by which elastomers elastically deform.

(a) and (b) The mechanisms by which semicrystalline polymers elastically and plastically deform are described in Section 15.7.

(c) The explanation of the mechanism by which elastomers elastically deform is provided in Section 15.9.

Factors That Influence the Mechanical Properties of Semicrystalline Polymers

Deformation of Elastomers

15.14 *Briefly explain how each of the following influences the tensile modulus of a semicrystalline polymer and why:*

(a) molecular weight

(b) degree of crystallinity

(c) deformation by drawing

(d) annealing of an undeformed material

(e) annealing of a drawn material

Answer

(a) The tensile modulus is not directly influenced by a polymer's molecular weight.

(b) Tensile modulus increases with increasing degree of crystallinity for semicrystalline polymers. This is due to enhanced secondary interchain bonding which results from adjacent aligned chain segments as percent crystallinity increases. This enhanced interchain bonding inhibits relative interchain motion.

(c) Deformation by drawing also increases the tensile modulus. The reason for this is that drawing produces a highly oriented molecular structure, and a relatively high degree of interchain secondary bonding.

(d) When an undeformed semicrystalline polymer is annealed below its melting temperature, the tensile modulus increases.

(e) A drawn semicrystalline polymer that is annealed experiences a decrease in tensile modulus as a result of a reduction in chain-induced crystallinity, and a reduction in interchain bonding forces.

15.15 *Briefly explain how each of the following influences the tensile or yield strength of a semicrystalline polymer and why:*

(a) molecular weight

(b) degree of crystallinity

(c) deformation by drawing

(d) annealing of an undeformed material

Answer

(a) The tensile strength of a semicrystalline polymer increases with increasing molecular weight. This effect is explained by increased chain entanglements at higher molecular weights.

(b) Increasing the degree of crystallinity of a semicrystalline polymer leads to an enhancement of the tensile strength. Again, this is due to enhanced interchain bonding and forces; in response to applied stresses, interchain motions are thus inhibited.

(c) Deformation by drawing increases the tensile strength of a semicrystalline polymer. This effect is due to the highly oriented chain structure that is produced by drawing, which gives rise to higher interchain secondary bonding forces.

(d) Annealing an undeformed semicrystalline polymer produces an increase in its tensile strength.

15.16 *Normal butane and isobutane have boiling temperatures of –0.5°C and –12.3°C (31.1°F and 9.9°F), respectively. Briefly explain this behavior on the basis of their molecular structures, as presented in Section 14.2.*

<u>Solution</u>

Normal butane has a higher melting temperature as a result of its molecular structure (Section 14.2). There is more of an opportunity for van der Waals bonds to form between two molecules in close proximity to one another than for isobutane because of the linear nature of each normal butane molecule.

15.17 *The tensile strength and number-average molecular weight for two poly(methyl methacrylate) materials are as follows:*

Tensile Strength (MPa)	***Number-Average Molecular Weight (g/mol)***
50	*30,000*
150	*50,000*

Estimate the tensile strength at a number-average molecular weight of 40,000 g/mol.

Solution

This problem gives us the tensile strengths and associated number-average molecular weights for two poly(methyl methacrylate) materials and then asks that we estimate the tensile strength for $\bar{M}_n$ = 40,000 g/mol. Equation 15.3 cites the dependence of the tensile strength on $\bar{M}_n$--that is

$$TS = TS_\infty - \frac{A}{\bar{M}_n} \tag{15.3}$$

Using data provided in the problem statement, we may set up two simultaneous equations from which it is possible to solve for the two constants TS_∞ and A. These equations are as follows:

$$50 \text{ MPa} = TS_\infty - \frac{A}{30{,}000 \text{ g/mol}}$$

$$150 \text{ MPa} = TS_\infty - \frac{A}{50{,}000 \text{ g/mol}}$$

Values of the two constants are: TS_∞ = 300 MPa and A = 7.50 × 10^6 MPa-g/mol. Substituting these values into Equation 15.3 for $\bar{M}_n$ = 40,000 g/mol leads to

$$TS = TS_\infty - \frac{A}{40{,}000 \text{ g/mol}}$$

$$= 300 \text{ MPa} - \frac{7.50 \times 10^6 \text{ MPa-g/mol}}{40{,}000 \text{ g/mol}}$$

$$= 112.5 \text{ MPa}$$

15.18 *The tensile strength and number-average molecular weight for two polyethylene materials are as follows:*

Tensile Strength (MPa)	***Number-Average Molecular Weight (g/mol)***
90	*20,000*
180	*40,000*

Estimate the number-average molecular weight that is required to give a tensile strength of 140 MPa.

Solution

This problem gives us the tensile strengths and associated number-average molecular weights for two polyethylene materials and then asks that we estimate the $\bar{M}_n$ required for a tensile strength of 140 MPa. Equation 15.3 cites the dependence of the tensile strength on $\bar{M}_n$--that is

$$TS = TS_\infty - \frac{A}{\bar{M}_n} \tag{15.3}$$

Using data provided in the problem statement, we may set up two simultaneous equations from which it is possible to solve for the two constants TS_∞ and A. These equations are as follows:

$$90 \text{ MPa} = TS_\infty - \frac{A}{20{,}000 \text{ g/mol}}$$

$$180 \text{ MPa} = TS_\infty - \frac{A}{40{,}000 \text{ g/mol}}$$

Values of the two constants are: TS_∞ = 270 MPa and A = 3.6 × 10^6 MPa-g/mol. Solving for $\bar{M}_n$ in Equation 15.3 and substituting TS = 140 MPa as well as the above values for TS_∞ and A leads to

$$\bar{M}_n = \frac{A}{TS_\infty - TS}$$

$$= \frac{3.6 \times 10^6 \text{ MPa-g/mol}}{270 \text{ MPa} - 140 \text{ MPa}} = 27{,}700 \text{ g/mol}$$

15.19 *For each of the following pairs of polymers, do the following: (1) state whether it is possible to decide whether one polymer has a higher tensile modulus than the other; (2) if this is possible, note which has the higher tensile modulus and cite the reason(s) for your choice; and (3) if it is not possible to decide, state why.*

(a) Branched and atactic poly(vinyl chloride) with a weight-average molecular weight of 100,000 g/mol; linear and isotactic poly(vinyl chloride) having a weight-average molecular weight of 75,000 g/mol

(b) Random styrene-butadiene copolymer with 5% of possible sites crosslinked; block styrene-butadiene copolymer with 10% of possible sites crosslinked

(c) Branched polyethylene with a number-average molecular weight of 100,000 g/mol; atactic polypropylene with a number-average molecular weight of 150,000 g/mol

Solution

(a) Yes, it is possible. The linear and isotactic poly(vinyl chloride) will display a greater tensile modulus. Linear polymers are more likely to crystallize that branched ones. In addition, polymers having isotactic structures will normally have a higher degree of crystallinity that those having atactic structures. Increasing a polymer's crystallinity leads to an increase in its tensile modulus. In addition, tensile modulus is independent of molecular weight—the atactic/branched material has the higher molecular weight.

(b) Yes, it is possible. The block styrene-butadiene copolymer with 10% of possible sites crosslinked will have the higher modulus. Block copolymers normally have higher degrees of crystallinity than random copolymers of the same material. A higher degree of crystallinity favors larger moduli. In addition, the block copolymer also has a higher degree of crosslinking; increasing the amount of crosslinking also enhances the tensile modulus.

(c) No, it is not possible. Branched polyethylene will tend to have a low degree of crystallinity since branched polymers don't normally crystallize. The atactic polypropylene probably also has a relatively low degree of crystallinity; atactic structures also don't tend to crystallize, and polypropylene has a more complex repeat unit structure than does polyethylene. Tensile modulus increases with degree of crystallinity, and it is not possible to determine which polymer is more crystalline. Furthermore, tensile modulus is independent of molecular weight.

15.20 *For each of the following pairs of polymers, do the following: (1) state whether it is possible to decide whether one polymer has a higher tensile strength than the other; (2) if this is possible, note which has the higher tensile strength and cite the reason(s) for your choice; and (3) if it is not possible to decide, state why.*

(a) Linear and isotactic poly(vinyl chloride) with a weight-average molecular weight of 100,000 g/mol; branched and atactic poly(vinyl chloride) having a weight-average molecular weight of 75,000 g/mol

(b) Graft acrylonitrile-butadiene copolymer with 10% of possible sites crosslinked; alternating acrylonitrile-butadiene copolymer with 5% of possible sites crosslinked

(c) Network polyester; lightly branched polytetrafluoroethylene

Solution

(a) Yes, it is possible. The linear and isotactic material will have the higher tensile strength. Both linearity and isotacticity favor a higher degree of crystallinity than do branching and atacticity; and tensile strength increases with increasing degree of crystallinity. Furthermore, the molecular weight of the linear/isotactic material is higher (100,000 g/mol versus 75,000 g/mol), and tensile strength increases with increasing molecular weight.

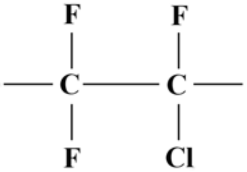
(b) No, it is not possible. Alternating copolymers tend to be more crystalline than graft copolymers, and tensile strength increases with degree of crystallinity. However, the graft material has a higher degree of crosslinking, and tensile strength increases with the percentage of crosslinks.

(c) Yes, it is possible. The network polyester will display a greater tensile strength. Relative chain motion is much more restricted than for the lightly branched polytetrafluoroethylene since there are many more of the strong covalent bonds for the network structure.

15.21 *Would you expect the tensile strength of polychlorotrifluoroethylene to be greater than, the same as, or less than that of a polytetrafluoroethylene specimen having the same molecular weight and degree of crystallinity? Why?*

Solution

The strength of a polychlorotrifluoroethylene having the repeat unit structure



$$-\overset{\displaystyle \mathrm{F}}{\underset{\displaystyle \mathrm{F}}{\mathrm{C}}}-\overset{\displaystyle \mathrm{F}}{\underset{\displaystyle \mathrm{Cl}}{\mathrm{C}}}-$$

will be greater than for a polytetrafluoroethylene having the same molecular weight and degree of crystallinity. The replacement of one fluorine atom within the PTFE repeat unit with a chlorine atom leads to a higher interchain attraction, and, thus, a stronger polymer. Furthermore, poly(vinyl chloride) is stronger than polyethylene (Table 15.1) for the same reason.

15.22 *For each of the following pairs of polymers, plot and label schematic stress–strain curves on the same graph [i.e., make separate plots for parts (a) to (c)].*

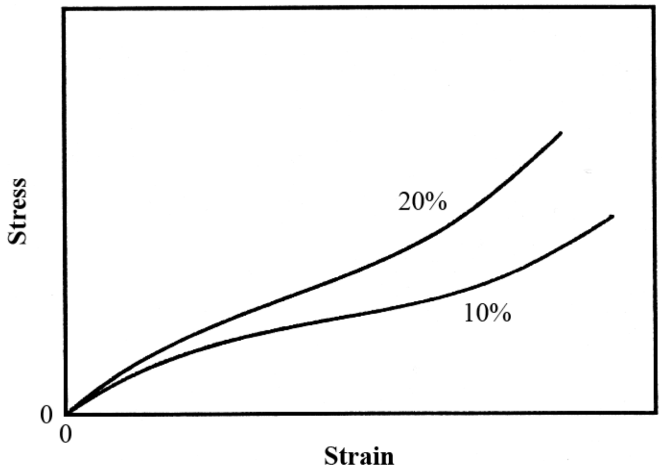
(a) Polyisoprene having a number-average molecular weight of 100,000 g/mol and 10% of available sites crosslinked; polyisoprene having a number-average molecular weight of 100,000 g/mol and 20% of available sites crosslinked

(b) Syndiotactic polypropylene having a weight-average molecular weight of 100,000 g/mol; atactic polypropylene having a weight-average molecular weight of 75,000 g/mol

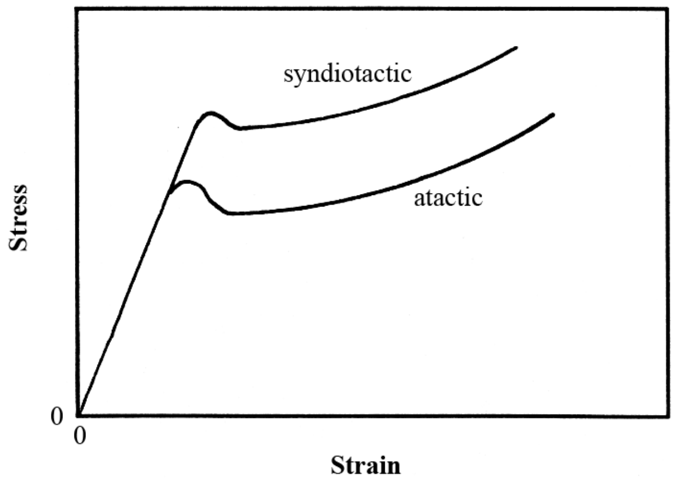
(c) Branched polyethylene having a number-average molecular weight of 90,000 g/mol; heavily crosslinked polyethylene having a number-average molecular weight of 90,000 g/mol

Solution

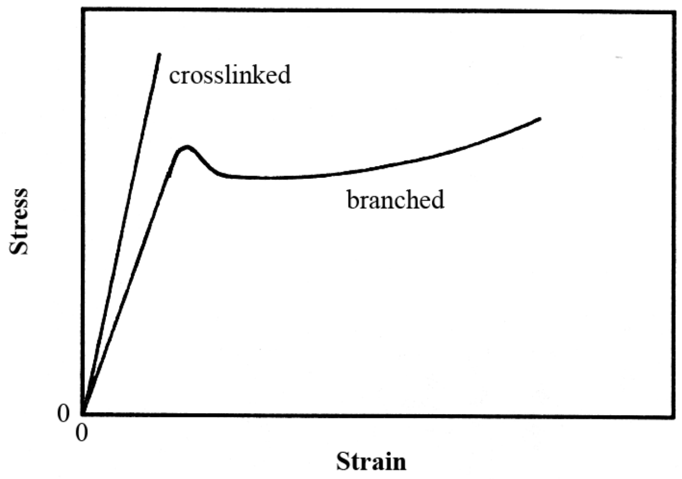
(a) Shown below are the stress-strain curves for the two polyisoprene materials, both of which have a molecular weight of 100,000 g/mol. These two materials are elastomers and will have curves similar to curve *C* in Figure 15.1. However, the curve for the material having the greater number of crosslinks (20%) will have a higher elastic modulus at all strains.



(b) Shown below are the stress-strain curves for the two polypropylene materials. These materials will most probably display the stress-strain behavior of a normal plastic, curve *B* in Figure 15.1. However, the syndiotactic polypropylene has a higher molecular weight and will also undoubtedly have a higher degree of crystallinity; therefore, it will have a higher strength.



(c) Shown below are the stress-strain curves for the two polyethylene materials. The branched polyethylene will display the behavior of a normal plastic, curve *B* in Figure 15.1. On the other hand, the heavily crosslinked polyethylene will be stiffer, stronger, and more brittle (curve *A* of Figure 15.1).



15.23 *List the two molecular characteristics that are essential for elastomers.*

Answer

Two molecular characteristics essential for elastomers are: (1) they must be amorphous, having chains that are extensively coiled and kinked in the unstressed state; and (2) there must be some crosslinking.

15.24 *Which of the following would you expect to be elastomers and which thermosetting polymers at room temperature? Justify each choice.*

(a) Linear and highly crystalline polyethylene

(b) Phenol-formaldehyde

(c) Heavily crosslinked polyisoprene having a glass transition temperature of 50°C (122°F)

(d) Lightly crosslinked polyisoprene having a glass transition temperature of –60°C (– 76°F)

(e) Linear and partially amorphous poly(vinyl chloride)

Solution

(a) Linear and crystalline polyethylene would be neither an elastomer nor a thermoset since it is a linear polymer.

(b) Phenol-formaldehyde having a network structure would be a thermosetting polymer since it has a network structure. It would not be an elastomer since it does not have a crosslinked chain structure.

(c) Heavily crosslinked polyisoprene having a glass transition temperature of 50°C would be a thermosetting polymer because it is heavily crosslinked. It would not be an elastomer since it is heavily crosslinked and room temperature is below its T_g.

(d) Lightly crosslinked polyisoprene having a glass transition temperature of –60°C is both an elastomer and a thermoset. It is an elastomer because it is lightly crosslinked and has a T_g below room temperature. It is a thermoset because it is crosslinked.

(e) Linear and partially amorphous poly(vinyl chloride) is neither an elastomer nor a thermoset. In order to be either it must have some crosslinking.

15.25 *Fifteen kilograms of polychloroprene is vulcanized with 5.2 kg of sulfur. What fraction of the possible crosslink sites is bonded to sulfur crosslinks, assuming that, on the average, 5.5 sulfur atoms participate in each crosslink?*

Solution

This problem asks that we compute the fraction of possible crosslink sites in 15 kg of polychloroprene when 5.2 kg of S is added, assuming that, on the average, 5.5 sulfur atoms participate in each crosslink bond. Given the butadiene repeat unit in Table 14.5, (which is composed of 4 carbon atoms, 5 hydrogen atoms, and 1 chlorine atom) we may calculate its molecular weight as follows:

$$A(\text{chloroprene}) = 4(A_{\text{C}}) + 5(A_{\text{H}}) + A_{\text{Cl}}$$

$$= (4)(12.01 \text{ g/mol}) + 5(1.008 \text{ g/mol}) + 35.45 \text{ g/mol} = 88.53 \text{ g/mol}$$

Which means that for 15 kg of chloroprene there are the following number of moles of chloroprene, n_{chloro}:

$$n_{\text{chloro}} = \frac{15{,}000 \text{ g}}{88.53 \text{ g/mol}} = 169.4 \text{ mol}$$

For the vulcanization of polychloroprene, there are two possible crosslink sites per repeat unit—one for each of the two carbon atoms that are doubly bonded. Furthermore, each of these crosslinks forms a bridge between two repeat units. Therefore, we can say that there is the equivalent of one crosslink per repeat unit. Let us now calculate the number of moles of sulfur (n_{sulfur}) that react with the chloroprene, by taking the mole ratio of sulfur to chloroprene, and then dividing this ratio by 5.5 atoms per crosslink; this yields the fraction of possible sites that are crosslinked. Now, the amount of sulfur added is 5.2 kg (5200 g), which means that

$$n_{\text{sulfur}} = \frac{5200 \text{ g}}{32.06 \text{ g/mol}} = 162.2 \text{ mol}$$

And, finally, we determine the fraction of sites crosslinked as follows:

$$\text{fraction sites crosslinked} = \frac{\dfrac{n_{\text{sulfur}}}{n_{\text{chloro}}}}{5.5} = \frac{\dfrac{162.2 \text{ mol}}{169.4 \text{ mol}}}{5.5} = 0.174$$

15.26 *Compute the weight percent sulfur that must be added to completely crosslink an alternating acrylonitrile-butadiene copolymer, assuming that four sulfur atoms participate in each crosslink.*

Solution

For an alternating acrylonitrile-butadiene copolymer, we are asked to compute the weight percent sulfur necessary for complete crosslinking, assuming that, on the average, four sulfur atoms participate in each crosslink. The acrylonitrile and butadiene repeat units are shown in Table 14.5, from which it may be noted that there are two possible crosslink sites on each butadiene repeat unit (one site at each of the two carbon atoms that are doubly bonded), and no possible sites for acrylonitrile; also, because it is an alternating copolymer, the ratio of butadiene to acrylonitrile repeat units is 1:1. Thus, for each pair of combined butadiene-acrylonitrile repeat units which crosslink, eight sulfur atoms are required, or, for complete crosslinking, the sulfur-to-(acrylonitrile-butadiene) ratio is 4:1.

Now, let us consider as our basis, one mole of the combined acrylonitrile-butadiene repeat units. In order for complete crosslinking, four moles of sulfur are required. Thus, for us to convert this composition to weight percent, it is necessary to convert moles to mass. The acrylonitrile repeat unit consists of three carbon atoms, three hydrogen atoms, and one nitrogen atom; the butadiene repeat unit is composed of four carbon atoms and six hydrogen atoms. This gives a molecular weight for the combined repeat unit of

$$m(\text{acrylonitrile-butadiene}) = 3(A_C) + 3(A_H) + A_N + 4(A_C) + 6(A_H)$$

$$= 7(12.01\text{ g/mol}) + 9(1.008\text{ g/mol}) + 14.007\text{ g/mol} = 107.15\text{ g/mol}$$

Or, in one mole of this combined repeat unit, there are 107.15 g. Furthermore, for complete crosslinking 4.0 mol of sulfur is required, which amounts to (4.0 mol)(32.06 g/mol) = 128.24 g. Thus, the concentration of S in weight percent C_S (using Equation 4.3a) is just

$$C_S = \frac{128.24\text{ g}}{128.24\text{ g} + 107.15\text{ g}} \times 100 = 54.5\text{ wt\%}$$

15.27 *The vulcanization of polyisoprene is accomplished with sulfur atoms according to Equation 15.4. If 45.3 wt% sulfur is combined with polyisoprene, how many crosslinks will be associated with each isoprene repeat unit if it is assumed that, on the average, five sulfur atoms participate in each crosslink?*

Solution

This problem asks for us to determine how many crosslinks form per isoprene repeat unit when 45.3 wt% sulfur is added, assuming that, on the average, five sulfur atoms participate in each crosslink. If we arbitrarily consider 100 g of the vulcanized material, 45.3 g will be sulfur and 54.7 g will be polyisoprene. Next, let us find how many moles of sulfur and isoprene correspond to these masses. The atomic weight of sulfur is 32.06 g/mol, and thus,

$$\text{\# moles S} = \frac{45.3\text{ g}}{32.06\text{ g/mol}} = 1.41\ \text{ mol}$$

Now, in each isoprene repeat unit there are five carbon atoms and eight hydrogen atoms. Thus, the molecular weight of a mole of isoprene units is

$$A(\text{isoprene}) = 5A_\text{C} \ + \ 8A_\text{H}$$

$$= (5)(12.01\text{ g/mol}) + (8)(1.008\text{ g/mol}) = 68.11\text{ g/mol}$$

Or, in 54.7 g of polyisoprene, the number of moles of isoprene is equal to

$$\text{\# moles isoprene} = \frac{54.7\text{ g}}{68.11\text{ g/mol}} = 0.803\ \text{ mol}$$

Therefore, the ratio of moles of S to the number of moles of polyisoprene is

$$\frac{1.41\text{ mol}}{0.803\text{ mol}}:1 = 1.76:1$$

When all possible sites are crosslinked, the ratio of the number of moles of sulfur to the number of moles of isoprene is 5:1; this is because there are two crosslink sites per repeat unit and each crosslink is shared between repeat units on adjacent chains, and there are 5 sulfur atoms per crosslink. Finally, to determine the fraction of sites that are crosslinked, we just divide the actual crosslinked sulfur/isoprene ratio by the completely crosslinked ratio. Or,

$$\text{fraction of repeat unit sites crosslinked} = \frac{1.76/1}{5/1} = 0.352$$

15.28 *For the vulcanization of polyisoprene, compute the weight percent of sulfur that must be added to ensure that 10% of possible sites will be crosslinked; assume that, on the average, 3.5 sulfur atoms are associated with each crosslink.*

Solution

We are asked what weight percent of sulfur must be added to polyisoprene in order to ensure that 10% of possible sites are crosslinked, assuming that, on the average, 3.5 sulfur atoms are associated with each crosslink. Table 14.5 shows the chemical repeat unit for isoprene. For each of these units there are two possible crosslink sites; one site is associated with each of the two carbon atoms that are involved in the chain double bond. Since 10% of the possible sites are crosslinked, for each 100 isoprene repeat units 10 of them are crosslinked; actually there are two crosslink sites per repeat unit, but each crosslink is shared by two chains. Furthermore, on the average we assume that each crosslink is composed of 3.5 sulfur atoms; thus, there must be 3.5 × 10 or 35 sulfur atoms added for every 100 isoprene repeat units. In terms of moles, it is necessary to add 35 moles of sulfur to 100 moles of isoprene. The atomic weight of sulfur is 32.06 g/mol, while the molecular weight of an isoprene repeat unit is

$$A(\text{isoprene}) = 5(A_\text{C}) + 8(A_\text{H})$$

$$= (5)(12.01\text{ g/mol}) + (8)(1.008\text{ g/mol}) = 68.11\text{ g/mol}$$

The mass of sulfur added (m_S) is equal to the number of moles of sulfur (35 mol) times the atomic weight of sulfur (32.06 g/mol) or

$$m_\text{S} = (35\text{ mol})(32.06\text{ g/mol}) = 1122\text{ g}$$

While for isoprene the number of moles (m_ip) is equal to

$$m_\text{ip} = (100\text{ mol})(68.11\text{ g/mol}) = 6811\text{ g}$$

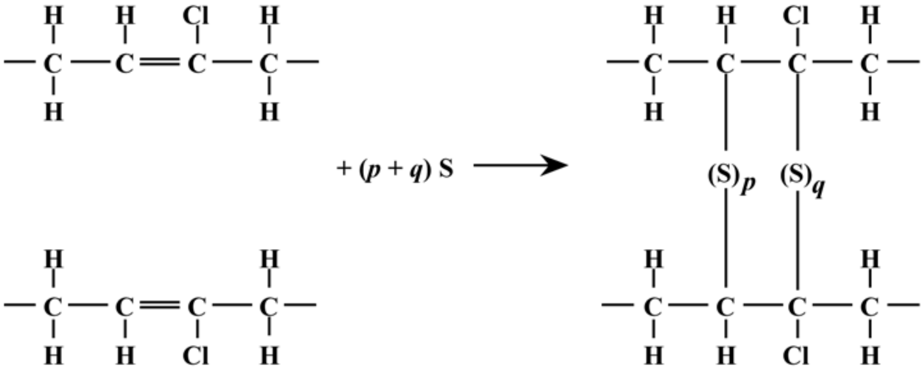
Or, the concentration of sulfur that must be added, in weight percent (Equation 4.3a), is just

$$C_\text{S} = \frac{m_\text{S}}{m_\text{S} + m_\text{ip}} \times 100 = \frac{1122\text{ g}}{1122\text{ g} + 6811\text{ g}} \times 100 = 14.1\text{ wt\%}$$

15.29 *In a manner similar to Equation 15.4, demonstrate how vulcanization may occur in a chloroprene rubber.*

Solution

The reaction by which a chloroprene rubber may become vulcanized is as follows:



Crystallization

15.30 *Determine values for the constants n and k (Equation 10.17) for the crystallization of polypropylene (Figure 15.17) at 150°C.*

Solution

One way to solve this problem is to take two values of percent recrystallization (which is just 100*y*, Equation 10.17) and their corresponding time values, then set up two simultaneous equations, from which *n* and *k* may be determined. In order to expedite this process, we will rearrange and do some algebraic manipulation of Equation 10.17. First of all, we rearrange as follows:

$$1 - y = \exp\left(-kt^n\right)$$

Now taking natural logarithms leads to

$$\ln(1 - y) = -kt^n$$

Or

$$-\ln(1 - y) = kt^n$$

which may also be expressed as

$$\ln\left(\frac{1}{1 - y}\right) = kt^n$$

Now taking natural logarithms again, leads to

$$\ln\left[\ln\left(\frac{1}{1 - y}\right)\right] = \ln k + n \ln t$$

which is the form of the equation that we will now use. From the 150°C curve of Figure 15.17, let us arbitrarily choose two percent crystallized values of 20% and 80% (i.e., y_1 = 0.20 and y_2 = 0.80). The corresponding time values are t_1 = 220 min and t_2 = 470 min (realizing that the time axis is scaled logarithmically). Thus, our two simultaneous equations become

$$\ln\left[\ln\left(\frac{1}{1 - 0.20}\right)\right] = \ln k + n \ln(220)$$

$$\ln\left[\ln\left(\frac{1}{1 - 0.80}\right)\right] = \ln k + n \ln(470)$$

from which we obtain the following values for n and k:

$n = 2.60$

$k = 1.81 \times 10^{-7}$

Melting and Glass Transition Temperatures

15.31 *Which of the following polymers would be suitable for the fabrication of cups to contain hot coffee: polyethylene, polypropylene, poly(vinyl chloride), PET polyester, and polycarbonate. Why?*

Solution

This question asks us to name, which, of five polymers, would be suitable for the fabrication of cups to contain hot coffee. At its glass transition temperature, an amorphous polymer begins to soften. The maximum temperature of hot coffee is probably slightly below 100°C (212°F). Of the polymers listed, only polystyrene and polycarbonate have glass transition temperatures of 100°C or above (Table 15.2), and would be suitable for this application.

15.32 *Of the polymers listed in Table 15.2, which polymer(s) would be best suited for use as ice cube trays? Why?*

Solution

In order for a polymer to be suited for use as an ice cube tray it must have a glass-transition temperature below 0°C. Of those polymers listed in Table 15.2 only low-density and high-density polyethylene, PTFE, and polypropylene would be suitable for this application.

Factors That Influence Melting and Glass Transition Temperatures

15.33 *For each of the following pairs of polymers, plot and label schematic specific volume-versus-temperature curves on the same graph [i.e., make separate plots for parts (a) to (c)].*

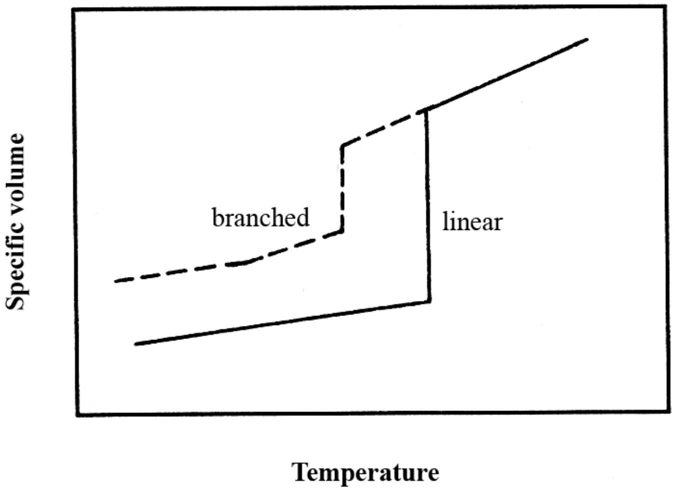
(a) Linear polyethylene with a weight-average molecular weight of 75,000 g/mol; branched polyethylene with a weight-average molecular weight of 50,000 g/mol

(b) Spherulitic poly(vinyl chloride) of 50% crystallinity and having a degree of polymerization of 5000; spherulitic polypropylene of 50% crystallinity and degree of polymerization of 10,000

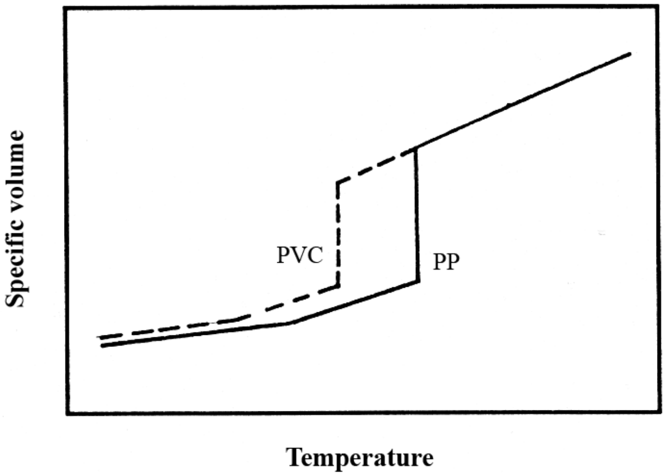
(c) Totally amorphous polystyrene having a degree of polymerization of 7000; totally amorphous polypropylene having a degree of polymerization of 7000

Solution

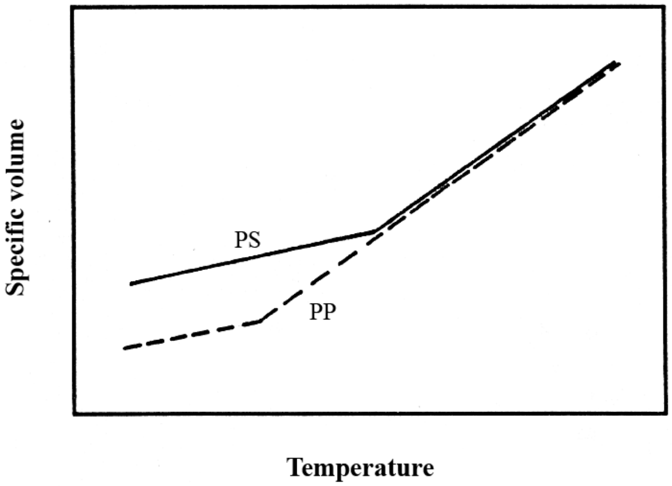
(a) Shown below are specific volume-versus-temperature curves for the two polyethylene materials. The linear polyethylene will be highly crystalline, and, therefore, will exhibit behavior similar to curve *C* in Figure 15.18. The branched polyethylene will be semicrystalline, and, therefore its curve will appear as curve *B* in this same figure. Furthermore, since the linear polyethylene has the greater molecular weight, it will also have the higher melting temperature.



(b) Shown below are specific volume-versus-temperature curves for the poly(vinyl chloride) and polypropylene materials. Since both are 50% crystalline, they will exhibit behavior similar to curve *B* in Figure 15.18. However, since the polypropylene has the greater molecular weight it will have the higher melting temperature. Furthermore, polypropylene will also have the higher glass-transition temperature inasmuch as its CH_3 side group is bulkier than the Cl for PVC.



(c) Shown below are specific volume-versus-temperature curves for the polystyrene and polypropylene materials. Since both are totally amorphous, they will exhibit the behavior similar to curve *A* in Figure 15.18. However, since the polystyrene repeat unit has a bulkier side group than polypropylene (Table 14.3), its chain flexibility will be lower, and, thus, its glass-transition temperature will be higher.



15.34 *For each of the following pairs of polymers, (1) state whether it is possible to determine whether one polymer has a higher melting temperature than the other; (2) if it is possible, note which has the higher melting temperature and then cite reason(s) for your choice; and (3) if it is not possible to decide, then state why.*

(a) Branched polyethylene having a number-average molecular weight of 850,000 g/mol; linear polyethylene having a number-average molecular weight of 850,000 g/mol

(b) Polytetrafluoroethylene having a density of 2.14 g/cm^3 and a weight-average molecular weight of 600,000 g/mol; PTFE having a density of 2.20 g/cm^3 and a weight-average molecular weight of 600,000 g/mol

(c) Linear and syndiotactic poly(vinyl chloride) having a number-average molecular weight of 500,000 g/mol; linear polyethylene having a number-average molecular weight of 225,000 g/mol

(d) Linear and syndiotactic polypropylene having a weight-average molecular weight of 500,000 g/mol; linear and atactic polypropylene having a weight-average molecular weight of 750,000 g/mol

Solution

(a) Yes, it is possible to determine which polymer has the higher melting temperature. The linear polyethylene will most likely have a higher percent crystallinity, and, therefore, a higher melting temperature than the branched polyethylene. The molecular weights of both materials are the same and, thus, molecular weight is not a consideration.

(b) Yes, it is possible to determine which polymer has the higher melting temperature. Of these two polytetrafluoroethylene polymers, the PTFE with the higher density (2.20 g/cm^3) will have the higher percent crystallinity, and, therefore, a higher melting temperature than the lower density PTFE. The molecular weights of both materials are the same and, thus, molecular weight is not a consideration.

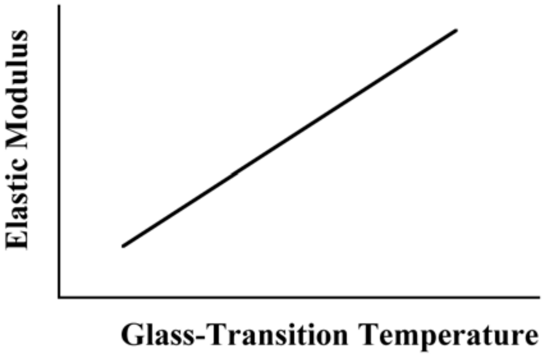
(c) Yes, it is possible to determine which polymer has the higher melting temperature. The linear polyethylene will have the greater melting temperature inasmuch as it will have a higher degree of crystallinity; polymers having a syndiotactic structure do not crystallize as easily as those polymers having identical single-atom side groups. With regard to molecular weight, or rather, degree of polymerization, it is about the same for both materials (8000), and therefore, is not a consideration.

(d) No, it is not possible to determine which of the two polymers has the higher melting temperature. The syndiotactic polypropylene will have a higher degree of crystallinity than the atactic material. On the basis of this effect alone, the syndiotactic PP should have the greater T_m, since melting temperature increases with degree of crystallinity. However, the molecular weight for the syndiotactic polypropylene (500,000 g/mol) is less than for the atactic material (750,000 g/mol); a lowering of molecular weight generally results in a reduction of melting temperature.

15.35 *Make a schematic plot showing how the modulus of elasticity of an amorphous polymer depends on the glass transition temperature. Assume that molecular weight is held constant.*

Solution

For an amorphous polymer, the elastic modulus may be enhanced by increasing the number of crosslinks (while maintaining the molecular weight constant); this will also enhance the glass transition temperature. Thus, the modulus-glass transition temperature behavior would appear something like the following:



Elastomers

Fibers

Miscellaneous Applications

15.36 *Briefly explain the difference in molecular chemistry between silicone polymers and other polymeric materials.*

Answer

The backbone chain of most polymers consists of carbon atoms that are linked together. For the silicone polymers, this backbone chain is composed of silicon and oxygen atoms that alternate positions.

15.37 *List two important characteristics for polymers that are to be used in fiber applications.*

Answer

Two important characteristics for polymers that are to be used in fiber applications are: (1) high molecular weights, and (2) chain configurations/structures that allow for high degrees of crystallinity.

15.38 *Cite five important characteristics for polymers that are to be used in thin-film applications.*

Answer

Five important characteristics for polymers that are to be used in thin-film applications are: (1) low density; (2) high flexibility; (3) high tensile and tear strengths; (4) resistance to moisture/chemical attack; and (5) low gas permeability.

Polymerization

15.39 *Cite the primary differences between addition and condensation polymerization techniques.*

Answer

For addition polymerization, the reactant species have the same chemical composition as the monomer species in the molecular chain. This is not the case for condensation polymerization, wherein there is a chemical reaction between two or more monomer species, producing the repeating unit. There is often a low molecular weight by-product for condensation polymerization; such is not found for addition polymerization.

15.40 *(a) How much ethylene glycol must be added to 20.0 kg of dimethyl terephthalate to produce a linear chain structure of poly(ethylene terephthalate) according to Equations 15.9?*

(b) What is the mass of the resulting polymer?

Solution

(a) This problem asks that we determine how much ethylene glycol must be added to 20.0 kg of dimethyl terephthalate to produce a linear chain structure of poly(ethylene terephthalate) according to Equation 15.9. Since the chemical formulas are provided in this equation we may calculate the molecular weights of each of these materials as follows:

$$MW(\text{ethylene glycol}) = 2(A_\text{C}) + 6(A_\text{H}) + 2(A_\text{O})$$

$$= 2(12.01\text{ g/mol}) + 6(1.008\text{ g/mol}) + 2(16.00\text{ g/mol}) = 62.07\text{ g/mol}$$

$$MW(\text{dimethyl terephthalate}) = 10(A_\text{C}) + 10(A_\text{H}) + 4(A_\text{O})$$

$$= 10(12.01\text{ g/mol}) + 10(1.008\text{ g/mol}) + 4(16.00\text{ g/mol}) = 194.18\text{ g/mol}$$

The 20.0 kg mass of dimethyl terephthalate equals 20,000 g or $\frac{20{,}000\text{ g}}{194.18\text{ g/mol}}$ = 103.0 mol. Since, according to Equation 15.9, each mole of dimethyl terephthalate used requires one mole of ethylene glycol, which is equivalent to (103.0 mol)(62.07 g/mol) = 6393 g = 6.393 kg.

(b) Now we are asked for the mass of the resulting polymer. Inasmuch as 2 moles of methyl alcohol are given off for every repeat unit produced, this corresponds to (2)(103.0 moles) = 206.0 moles. Now the molecular weight of methyl alcohol is as follows:

$$MW(\text{methyl alcohol}) = A_\text{C} + 4(A_\text{H}) + A_\text{O}$$

$$= 12.01\text{ g/mol} + (4)(1.008\text{ g/mol}) + 16.00\text{ g/mol} = 32.04\text{ g/mol}$$

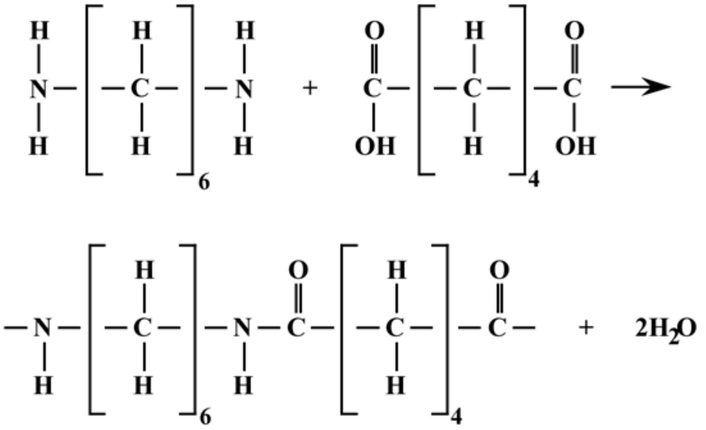
or (206.0 mol)(32.04 g/mol) = 6600 g or 6.600 kg. The mass of poly(ethylene terephthalate) is just the sum of the masses of the two reactant materials [as computed in part (a)] minus the mass of methyl alcohol released, or

$$\text{mass [poly(ethylene terephthalate)]} = 20.0\text{ kg} + 6.393\text{ kg} - 6.600\text{ kg} = 19.793\text{ kg}$$

15.41 *Nylon 6,6 may be formed by means of a condensation polymerization reaction in which hexamethylene diamine [*NH_2*—*$(CH_2)_6$*—*NH_2*] and adipic acid react with one another with the formation of water as a by-product. What masses of hexamethylene diamine and adipic acid are necessary to yield 20 kg of completely linear nylon 6,6? (Note: The chemical equation for this reaction is the answer to Concept Check 15.12.)*

Solution

This problem asks for us to calculate the masses of hexamethylene diamine and adipic acid necessary to yield 20 kg of completely linear nylon 6,6. The chemical equation for this reaction, the answer to Concept Check 15.12, is as follows:



From this equation we may calculate the molecular weights of these molecules.

$$MW(\text{adipic acid}) = 6(A_C) + 10(A_H) + 4(A_O)$$

$$= 6(12.01\text{ g/mol}) + 10(1.008\text{ g/mol}) + 4(16.00\text{ g/mol}) = 146.14\text{ g/mol}$$

$$MW(\text{hexamethylene}) = 6(A_C) + 16(A_H) + 2(A_N)$$

$$= 6(12.01\text{ g/mol}) + 16(1.008\text{ g/mol}) + 2(14.01\text{ g/mol}) = 116.21\text{ g/mol}$$

$$MW(\text{nylon}) = 12(A_C) + 22(A_H) + 2(A_N) + 2(A_O)$$

$$= 12(12.01\text{ g/mol}) + 22(1.008\text{ g/mol}) + 2(14.01\text{ g/mol}) + 2(16.00\text{ g/mol})$$

$$= 226.32 \text{ g/mol}$$

The mass of 20 kg of nylon 6,6 equals 20,000 g or

$$m(\text{nylon}) = \frac{20{,}000 \text{ g}}{226.32 \text{ g/mol}} = 88.37 \text{ mol}$$

Since, according to the chemical equation given above, each mole of nylon 6,6 that is produced requires one mole each of adipic acid and hexamethylene diamine, with two moles of water as the by-product. The masses corresponding to 88.37 moles of adipic acid and hexamethylene diamine are as follows:

$$m(\text{adipic acid}) = (88.37 \text{ mol})(146.14 \text{ g/mol}) = 12{,}914 \text{ g} = 12.914 \text{ kg}$$

$$m(\text{hexamethylene}) = (88.37 \text{ mol})(116.21 \text{ g/mol}) = 10{,}269 \text{ g} = 10.269 \text{ kg}$$

Polymer Additives

15.42 *What is the distinction between dye and pigment colorants?*

Answer

The distinction between dye and pigment colorants is that a dye dissolves within and becomes a part of the polymer structure, whereas a pigment does not dissolve, but remains as a separate phase.

Forming Techniques for Plastics

15.43 *Cite four factors that determine what fabrication technique is used to form polymeric materials.*

Answer

Four factors that determine what fabrication technique is used to form polymeric materials are: (1) whether the polymer is thermoplastic or thermosetting; (2) if thermoplastic, the softening temperature; (3) atmospheric stability; and (4) the geometry and size of the finished product.

15.44 *Contrast compression, injection, and transfer molding techniques that are used to form plastic materials.*

Answer

For compression molding, both heat and pressure are applied after the polymer and necessary additives are situated between the mold members. For transfer molding, the solid materials (normally thermosetting in nature) are first melted in the transfer chamber prior to being forced into the die. And, for injection molding (normally used for thermoplastic materials), the raw materials are impelled by a ram through a heating chamber, and finally into the die cavity.

Fabrication of Fibers and Films

15.45 *Why must fiber materials that are melt-spun and then drawn be thermoplastic? Cite two reasons.*

Answer

Fiber materials that are melt spun must be thermoplastic because: (1) In order to be melt spun, they must be capable of forming a viscous liquid when heated, which is not possible for thermosets. (2) During drawing, mechanical elongation must be possible; inasmuch as thermosetting materials are, in general, hard and relatively brittle, they are not easily elongated.

15.46 *Which of the following polyethylene thin films would have the better mechanical characteristics? (1) Those formed by blowing. (2) Those formed by extrusion and then rolled. Why?*

Answer

Of the two polymers cited, the one that was formed by extrusion and then rolled would have the higher strength. Both blown and extruded materials would have roughly comparable strengths; however the rolling operation would further serve to enhance the strength of the extruded material.

DESIGN QUESTIONS

15.D1 *(a) List several advantages and disadvantages of using transparent polymeric materials for eyeglass lenses.*

(b) Cite four properties (in addition to being transparent) that are important for this application.

(c) Note three polymers that may be candidates for eyeglass lenses, and then tabulate values of the properties noted in part (b) for these three materials.

Answer

(a) Several advantages of using transparent polymeric materials for eyeglass lenses are: they have relatively low densities, and, therefore, are light in weight; they are relatively easy to grind to have the desired contours; they are less likely to shatter than are glass lenses; wraparound lenses for protection during sports activities are possible; and they filter out more ultraviolet radiation than do glass lenses.

The principal disadvantage of these types of lenses is that some are relatively soft and are easily scratched (although antiscratch coatings may be applied). Plastic lenses are not as mechanically stable as glass, and, therefore, are not as precise optically.

(b) Some of the properties that are important for polymer lens materials are as follows: they should be relatively hard in order to resist scratching; they must be impact resistant; they should be shatter resistant; they must have a relatively high index of refraction such that thin lenses may be ground for very nearsighted people; and they should absorb significant proportions of all types of ultraviolet radiation, which radiation can do damage to the eye tissues.

(c) Of those polymers discussed in this chapter and Chapter 14, likely lens candidates are polystyrene, poly(methyl methacrylate), and polycarbonate; these three materials are not easily crystallized, and, therefore, are normally transparent. Upon consultation of their fracture toughnesses (Table B.5 in Appendix B), polycarbonate is the most superior of the three.

Commercially, the two plastic lens materials of choice are polycarbonate and allyl diglycol carbonate (having the trade name CR-39). Polycarbonate is very impact resistant, but not as hard as CR-39. Furthermore, PC comes in both normal and high refractive-index grades.

15.D2 *Write an essay on polymeric materials that are used in the packaging of food products and drinks. Include a list of the general requisite characteristics of materials that are used for these applications. Now cite a specific material that is used for each of three different container types and the rationale for each choice.*

Answer

There are three primary requirements for polymeric materials that are utilized in the packaging of food products and drinks; these are: (1) sufficient strength, to include tensile, tear, and impact strengths; (2) barrier protection--that is, being resistant to permeation by oxygen, water vapor, and carbon dioxide; and (3) be nonreactive with the food/drink contents--such reactions can compromise the integrity of the packaging material, or they can produce toxic by-products.

With regard to strength, poly(ethylene terephthalate) (PET or PETE) and oriented polypropylene (OPP) have high tensile strengths, linear low-density polyethylene (LLDPE) and low-density polyethylene (LDPE) have high tear strengths, while those polymers having the best impact strengths are PET and poly(vinyl chloride) (PVC). Relative to barrier characteristics, ethylene vinyl alcohol (EVOH) and poly(vinylidene chloride) (PVDC) copolymers are relatively impermeable to oxygen and carbon dioxide, whereas high-density polyethylene (HDPE), PVDC, polypropylene, and LDPE are impervious to water vapor.

Most common polymers are relatively nonreactive with food products, and are considered safe; exceptions are acrylonitrile and plasticizers used in PVC materials.

The aesthetics of packaging polymers are also important in the marketing of food and drink products. Some will be colored, many are adorned with printing, others need to be transparent and clear, and many need to be resistant to scuffing.

On the basis of the preceding discussion, examples of polymers that are used for specific applications are as follows:

PET(E) for soda pop containers;
PVC for beer containers;
LDPE and HDPE films for packaging bread and bakery products.

15.D3 *Write an essay on the replacement of metallic automobile components by polymers and composite materials. Address the following issues: (1) Which automotive components (e.g., crankshaft) now use polymers and/or composites? (2) Specifically what materials (e.g., high-density polyethylene) are now being used? (3) What are the reasons for these replacements?*

Answer

The primary reasons that the automotive industry has replaced metallic automobile components with polymer and composite materials are: polymers/composites (1) have lower densities, and afford higher fuel efficiencies; (2) may be produced at lower costs but with comparable mechanical characteristics; (3) in many environments are more corrosion resistant; (4) reduce noise; and (5) are thermally insulating and thus reduce the transference of heat.

These replacements are many and varied. Several are as follows:

Bumper fascia are molded from an elastomer-modified polypropylene.

Overhead consoles are made of poly(phenylene oxide) and recycled polycarbonate.

Rocker arm covers are injection molded of a glass- and mineral-reinforced nylon 6,6 composite.

Torque converter reactors, water outlets, pulleys, and brake pistons, are made from phenolic thermoset composites that are reinforced with glass fibers.

Air intake manifolds are made of a glass-reinforced nylon 6,6.

FUNDAMENTALS OF ENGINEERING QUESTION

15.1FE *Amorphous thermoplastics are formed above their*

(A) glass transition temperatures

(B) softening points

(C) melting temperatures

(D) none of the above

Answer

The correct answer is A. Amorphous thermoplastics are formed above their *glass transition temperatures*.

CHAPTER 16

COMPOSITES

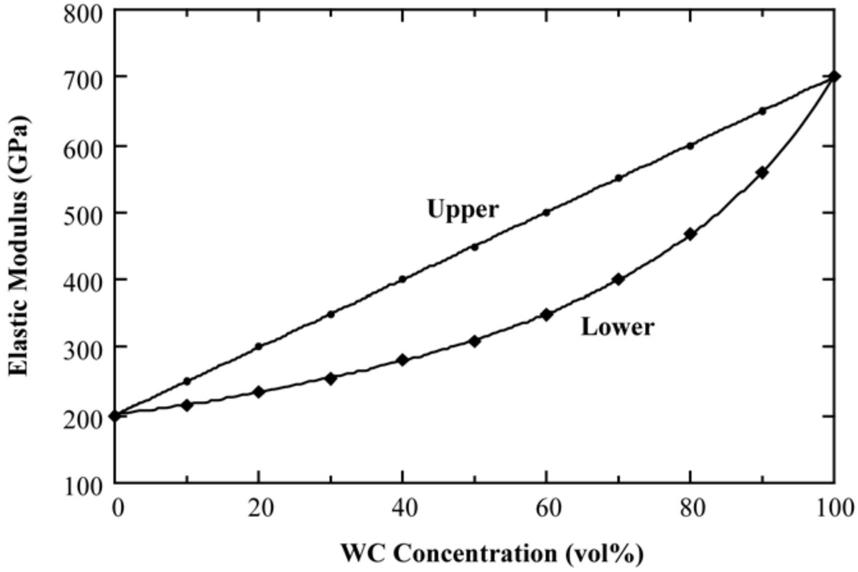
PROBLEM SOLUTIONS

Large-Particle Composites

16.1 *The mechanical properties of cobalt may be improved by incorporating fine particles of tungsten carbide (WC). Given that the moduli of elasticity of these materials are, respectively, 200 GPa (30 × 10^6 psi) and 700 GPa (102 × 10^6 psi), plot the modulus of elasticity versus the volume percent of WC in Co from 0 to 100 vol%, using both upper- and lower-bound expressions.*

Solution

The elastic modulus versus volume percent of WC is shown below; both upper- and lower-bound curves are included. These curves were generated using Equations 16.1 and 16.2, respectively, as well as the moduli of elasticity for cobalt and WC given in the problem statement.



16.2 *Estimate the maximum and minimum thermal conductivity values for a cermet that contains 90 vol% titanium carbide (TiC) particles in a nickel matrix. Assume thermal conductivities of 27 and 67 W/m·K for TiC and Ni, respectively.*

Solution

This problem asks for the maximum and minimum thermal conductivity values for a TiC-Ni cermet. Using a modified form of Equation 16.1 the maximum thermal conductivity k_{max} is calculated as follows:

$$k_{\text{max}} = k_m V_m + k_p V_p = k_{\text{Ni}} V_{\text{Ni}} + k_{\text{TiC}} V_{\text{TiC}}$$

$$= (67 \text{ W/m-K})(0.10) + (27 \text{ W/m-K})(0.90) = 31.0 \text{ W/m-K}$$

Using a modified form of Equation 16.2, the minimum thermal conductivity k_{min} is

$$k_{\text{min}} = \frac{k_{\text{Ni}} k_{\text{TiC}}}{V_{\text{Ni}} k_{\text{TiC}} + V_{\text{TiC}} k_{\text{Ni}}}$$

$$= \frac{(67 \text{ W/m-K})(27 \text{ W/m-K})}{(0.10)(27 \text{ W/m-K}) + (0.90)(67 \text{ W/m-K})}$$

$$= 28.7 \text{ W/m-K}$$

16.3 A *large-particle composite consisting of tungsten particles within a copper matrix is to be prepared. If the volume fractions of tungsten and copper are 0.70 and 0.30, respectively, estimate the upper limit for the specific stiffness of this composite, given the data that follow.*

	Specific Gravity	***Modulus of Elasticity (GPa)***
Copper	*8.9*	*110*
Tungsten	*19.3*	*407*

Solution

There are two approaches that may be applied to solve this problem. The first is to estimate the upper limits for both the elastic modulus [$E_c(u)$] and specific gravity (ρ_c) for the composite, using expressions of the form of Equation 16.1, and then take their ratio. Using this approach

$$E_c(u) = E_{\text{Cu}}V_{\text{Cu}} + E_{\text{W}}V_{\text{W}}$$

$$= (110\text{ GPa})(0.30) + (407\text{ GPa})(0.70)$$

$$= 318\text{ GPa}$$

And for the specific gravity

$$\rho_c = \rho_{\text{Cu}}V_{\text{Cu}} + \rho_{\text{W}}V_{\text{W}}$$

$$= (8.9)(0.30) + (19.3)(0.70) = 16.18$$

Therefore, we compute the specific stiffness as follows:

$$\text{Specific Stiffness} = \frac{E_c(u)}{\rho_c} = \frac{318\text{ GPa}}{16.18} = 19.65\text{ GPa}$$

With the alternate approach, the specific stiffness is calculated, again employing a modification of Equation 16.1, but using the specific stiffness-volume fraction product for both metals, as follows:

$$\text{Specific Stiffness} = \frac{E_{\text{Cu}}}{\rho_{\text{Cu}}}V_{\text{Cu}} + \frac{E_{\text{W}}}{\rho_{\text{W}}}V_{\text{W}}$$

$$= \frac{110\text{ GPa}}{8.9}(0.30) + \frac{407\text{ GPa}}{19.3}(0.70) = 18.47\text{ GPa}$$

16.4 *(a) What is the distinction between cement and concrete?*

(b) Cite three important limitations that restrict the use of concrete as a structural material.

(c) Briefly explain three techniques that are used to strengthen concrete by reinforcement.

Answer

(a) Concrete consists of an aggregate of particles that are bonded together by a cement.

(b) Three limitations of concrete are: (1) it is a relatively weak and brittle material; (2) it experiences relatively large thermal expansions (contractions) with changes in temperature; and (3) it may crack when exposed to freeze-thaw cycles.

(c) Three reinforcement strengthening techniques are: (1) reinforcement with steel wires, rods, etc.; (2) reinforcement with fine fibers of a high modulus material; and (3) introduction of residual compressive stresses by prestressing or posttensioning.

Dispersion-Strengthened Composites

16.5 *Cite one similarity and two differences between precipitation hardening and dispersion strengthening.*

Answer

The similarity between precipitation hardening and dispersion strengthening is the strengthening mechanism--i.e., the precipitates/particles effectively hinder dislocation motion.

The two differences are: (1) the hardening/strengthening effect is not retained at elevated temperatures for precipitation hardening—however, it is retained for dispersion strengthening; and (2) the strength is developed by a heat treatment for precipitation hardening—such is not the case for dispersion strengthening.

Influence of Fiber Length

16.6 *For a glass fiber–epoxy matrix combination, the critical ratio of fiber length to fiber diameter is 40. Using the data in Table 16.4, determine the fiber–matrix bond strength.*

Solution

This problem asks that, for a glass fiber-epoxy matrix combination, to determine the fiber-matrix bond strength if the critical fiber length-fiber diameter ratio is 40. Thus, we are to solve for τ_c in Equation 16.3. Since we are given that σ_f^* = 3.45 GPa from Table 16.4, and that $\frac{l_c}{d}$ = 40, then

$$\tau_c = \frac{\sigma_f^*}{2}\left(\frac{d}{l_c}\right) = \left(\frac{3.45 \times 10^3 \text{ MPa}}{2}\right)\left(\frac{1}{40}\right) = 43.1 \text{ MPa}$$

16.7 *(a) For a fiber-reinforced composite, the efficiency of reinforcement* η *depends on fiber length* l *according to*

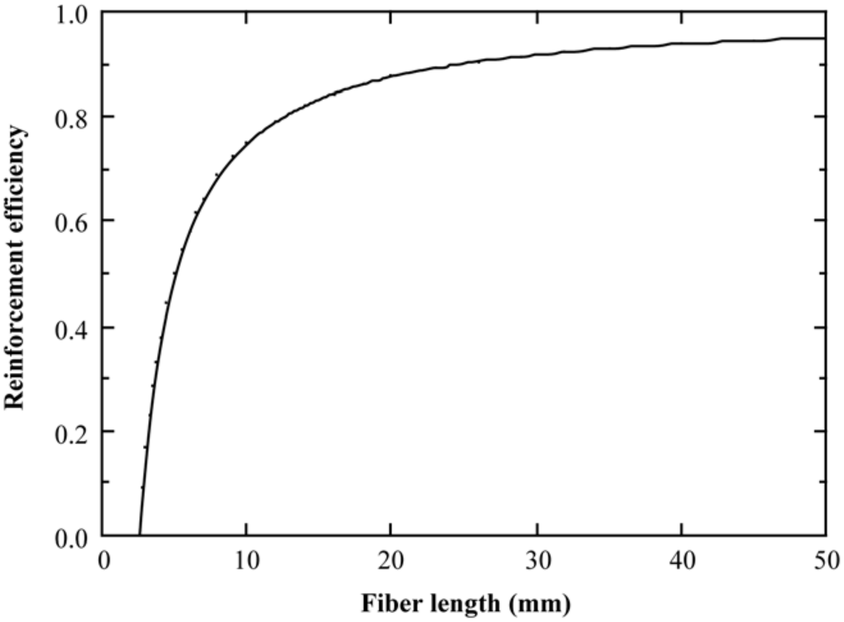
$$\eta = \frac{l - 2x}{l}$$

where x represents the length of the fiber at each end that does not contribute to the load transfer. Make a plot of η *versus l to l =50 mm (2.0 in.), assuming that x =1.25 mm (0.05 in.).*

(b) What length is required for a 0.90 efficiency of reinforcement?

Solution

(a) The plot of reinforcement efficiency versus fiber length is given below.



(b) This portion of the problem asks for the length required for a 0.90 efficiency of reinforcement. Solving for l from the given expression

$$l = \frac{2x}{1 - \eta}$$

Or, when x = 1.25 mm (0.05 in.) and η = 0.90, then

$$l = \frac{(2)(1.25\text{ mm})}{1 - 0.90} = 25\text{ mm} \ \ (1.0\text{ in.})$$

Influence of Fiber Orientation and Concentration

16.8 *A continuous and aligned fiber-reinforced composite is to be produced consisting of 45 vol% aramid fibers and 55 vol% polycarbonate matrix; the mechanical characteristics of these two materials are as follows:*

	***Modulus of Elasticity* [*GPa* (*psi*)]**	***Tensile Strength* [*MPa* (*psi*)]**
Aramid fiber	*131 (19 × 10^6)*	*3600 (520,000)*
Polycarbonate	*2.4 (3.5 × 10^5)*	*65 (9425)*

The stress on the polycarbonate matrix when the aramid fibers fail is 35 MPa (5075 psi).
For this composite, compute the following:

(a) The longitudinal tensile strength

(b) The longitudinal modulus of elasticity

Solution

This problem calls for us to compute the longitudinal tensile strength and elastic modulus of an aramid fiber-reinforced polycarbonate composite.

(a) The longitudinal tensile strength is determined using Equation 16.17 as follows:

$$\sigma_{cl}^{*} = \sigma_m'\left(1 - V_f\right) + \sigma_f^{*}V_f$$

$$= (35\text{ MPa})(1 - 0.45) + (3600)(0.45)$$

$$= 1640\text{ MPa}\ \ (238{,}000\text{ psi})$$

(b) The longitudinal elastic modulus is computed using Equation 16.10a as

$$E_{cl} = E_m V_m + E_f V_f$$

$$= (2.4\text{ GPa})(0.55) + (131\text{ GPa})(0.45)$$

$$= 60.3\text{ GPa}\ \ (8.74 \times 10^6\text{ psi})$$

16.9 *Is it possible to produce a continuous and oriented aramid fiber–epoxy matrix composite having longitudinal and transverse moduli of elasticity of 35 GPa (5 × 10^6 psi) and 5.17 GPa (7.5 × 10^5 psi), respectively? Why or why not? Assume that the elastic modulus of the epoxy is 3.4 GPa (4.93 × 10^5 psi).*

Solution

This problem asks for us to determine if it is possible to produce a continuous and oriented aramid fiber-epoxy matrix composite having longitudinal and transverse moduli of elasticity of 35 GPa and 5.17 GPa, respectively, given that the modulus of elasticity for the epoxy is 3.4 GPa. Also, from Table 16.4 the value of *E* for aramid fibers is 131 GPa. The approach to solve this problem is to calculate values of V_f for both longitudinal and transverse cases using the data and Equations 16.10b and 16.16; if the two V_f values are the same then this composite is possible.

For the longitudinal modulus E_{cl} (using Equation 16.10b),

$$E_{cl} = E_m\left(1 - V_{fl}\right) + E_f V_{fl}$$

$$35 \text{ GPa} = (3.4 \text{ GPa})\left(1 - V_{fl}\right) + (131 \text{ GPa})V_{fl}$$

Solving this expression for V_{fl} (i.e., the volume fraction of fibers for the longitudinal case) yields V_{fl} = 0.248.

Now, repeating this procedure for the transverse modulus E_{ct} (using Equation 16.16) leads to the following:

$$E_{ct} = \frac{E_m E_f}{\left(1 - V_{ft}\right)E_f + V_{ft}E_m}$$

$$5.17 \text{ GPa} = \frac{(3.4 \text{ GPa})(131 \text{ GPa})}{\left(1 - V_{ft}\right)(131 \text{ GPa}) + V_{ft}(3.4 \text{ GPa})}$$

Solving this expression for V_{ft} (i.e., the volume fraction of fibers for the transverse case), leads to V_{ft} = 0.351. Thus, since V_{fl} and V_{ft} are not equal, the proposed composite is *not possible*.

16.10 *For a continuous and oriented fiber-reinforced composite, the moduli of elasticity in the longitudinal and transverse directions are 33.1 and 3.66 GPa (4.8 × 10^6 and 5.3 × 10^5 psi), respectively. If the volume fraction of fibers is 0.30, determine the moduli of elasticity of fiber and matrix phases.*

Solution

This problem asks for us to compute the elastic moduli of fiber and matrix phases for a continuous and oriented fiber-reinforced composite. We can write expressions for the longitudinal and transverse elastic moduli using Equations 16.10b and 16.16, as follows:

For the longitudinal modulus:

$$E_{cl} = E_m(1 - V_f) + E_f V_f$$

$$33.1 \text{ GPa} = E_m(1 - 0.30) + E_f(0.30)$$

While transverse modulus expression is as follows:

$$E_{ct} = \frac{E_m E_f}{(1 - V_f)E_f + V_f E_m}$$

$$3.66 \text{ GPa} = \frac{E_m E_f}{(1 - 0.30)E_f + 0.30 E_m}$$

Solving these two expressions simultaneously for E_m and E_f leads to the following values:

$$E_m = 2.6 \text{ GPa} \ \ (3.77 \times 10^5 \text{ psi})$$

$$E_f = 104 \text{ GPa} \ \ (15 \times 10^6 \text{ psi})$$

16.11 *(a) Verify that Equation 16.11, the expression for the ratio of fiber load to matrix load (F_f/F_m), is valid.*

(b) What is the F_f/F_c ratio in terms of E_f, E_m, and V_f?

Solution

(a) In order to show that the relationship in Equation 16.11 is valid, we begin with Equation 16.4—i.e.,

$$F_c = F_m + F_f$$

which may be manipulated to read as follows:

$$\frac{F_c}{F_m} = 1 + \frac{F_f}{F_m}$$

or, upon rearrangement, takes the form

$$\frac{F_f}{F_m} = \frac{F_c}{F_m} - 1 \qquad \text{(S16.11a)}$$

For elastic deformation, combining Equations 6.1 and 6.5 yields the following expression:

$$\sigma = \frac{F}{A} = \varepsilon E$$

or, after rearranging becomes

$$F = A\varepsilon E \qquad \text{(S16.11b)}$$

Now we may write expressions for F_c and F_m in the form of Equation S16.11b) as follows:

$$F_c = A_c \varepsilon E_c$$

$$F_m = A_m \varepsilon E_m$$

which, when substituted into Equation S16.11a, gives the following expression for F_f/F_m:

$$\frac{F_f}{F_m} = \frac{A_c \varepsilon E_c}{A_m \varepsilon E_m} - 1 \qquad \text{(S16.11c)}$$

But, we may write the following expression as a way of defining V_m:

$$V_m = A_m/A_c$$

which, upon rearrangement gives

$$\frac{A_c}{A_m} = \frac{1}{V_m}$$

which, when substituted into Equation S16.11c leads to

$$\frac{F_f}{F_m} = \frac{E_c}{E_m V_m} - 1 \qquad \text{(S16.11d)}$$

Also, from Equation 16.10a we know that $E_c = E_m V_m + E_f V_f$, which, when substituted for E_c into Equation S16.11d, yields

$$\frac{F_f}{F_m} = \frac{E_m V_m + E_f V_f}{E_m V_m} - 1$$

$$= \frac{E_m V_m + E_f V_f - E_m V_m}{E_m V_m} = \frac{E_f V_f}{E_m V_m}$$

the desired result.

(b) This portion of the problem asks that we establish an expression for F_f/F_c. We determine this ratio in a similar manner. Now, we know from Equation 16.4 that

$$F_c = F_f + F_m \qquad \text{(16.4)}$$

Upon dividing each of the terms in Equation 16.4 by F_c leads to

$$1 = \frac{F_f}{F_c} + \frac{F_m}{F_c}$$

which, upon rearrangement, gives

$$\frac{F_f}{F_c} = 1 - \frac{F_m}{F_c} \qquad \text{(S16.11e)}$$

Now, substitution of the expressions for F_m and F_c of the form of Equation S16.11b into Equation S16.11e, results in the following:

$$\frac{F_f}{F_c} = 1 - \frac{A_m \varepsilon E_m}{A_c \varepsilon E_c} = 1 - \frac{A_m E_m}{A_c E_c} \tag{S16.11f}$$

Now, the volume fraction of fibers is equal to $V_m = A_m/A_c$; upon substitution of this expression for V_m into Equation S16.11f leads to the following:

$$\frac{F_f}{F_c} = 1 - \frac{V_m E_m}{E_c}$$

And, finally substitution of Equation 16.10a for E_c—viz.

$$E_c = E_m V_m + E_f V_f$$

into the above equation leads to the desired result as follows:

$$\frac{F_f}{F_c} = 1 - \frac{V_m E_m}{V_m E_m + V_f E_f}$$

$$= \frac{V_m E_m + V_f E_f - V_m E_m}{V_m E_m + V_f E_f}$$

$$= \frac{V_f E_f}{V_m E_m + V_f E_f}$$

$$= \frac{V_f E_f}{(1 - V_f) E_m + V_f E_f}$$

16.12 *In an aligned and continuous carbon fiber-reinforced nylon 6,6 composite, the fibers are to carry 97% of a load applied in the longitudinal direction.*

(a) Using the data provided, determine the volume fraction of fibers that will be required.

(b) What will be the tensile strength of this composite? Assume that the matrix stress at fiber failure is 50 MPa (7250 psi).

	Modulus of Elasticity [GPa (psi)]	***Tensile Strength [MPa (psi)]***
Carbon fiber	*260 (37 × 10^6)*	*4000 (580,000)*
Nylon 6,6	*2.8 (4.0 × 10^5)*	*76 (11,000)*

Solution

(a) Given some data for an aligned and continuous carbon-fiber-reinforced nylon 6,6 composite, we are asked to compute the volume fraction of fibers that are required such that the fibers carry 97% of a load applied in the longitudinal direction. From Equation 16.11

$$\frac{F_f}{F_m} = \frac{E_f V_f}{E_m V_m} = \frac{E_f V_f}{E_m (1 - V_f)}$$

Now, using values for F_f and F_m from the problem statement

$$\frac{F_f}{F_m} = \frac{0.97}{1 - 0.97} = 32.3$$

And substitution of the values for E_f and E_m given in the problem statement into the first equation above leads to

$$\frac{F_f}{F_m} = 32.3 = \frac{(260 \text{ GPa}) V_f}{(2.8 \text{ GPa})(1 - V_f)}$$

And, solving for V_f yields, $V_f = 0.258$.

(b) We are now asked for the tensile strength of this composite. The computation requires the use of Equation 16.17—viz.,

$$\sigma_{cl}^* = \sigma_m' (1 - V_f) + \sigma_f^* V_f$$

We now substitute into this expression the following values:

$\sigma_m' = \mathbf{50\ MPa}$ (given in the problem statement)

$V_f = 0.258$ (computed above)

$\sigma_f^* = 4000 \text{ MPa}$ (given in the problem statement)

Finally we determine the composite tensile strength as follows:

$$\sigma_{cl}^* = \sigma_m'(1 - V_f) + \sigma_f^* V_f$$

$$= (50 \text{ MPa})(1 - 0.258) + (4000 \text{ MPa})(0.258)$$

= 1070 MPa (155,000 psi)

16.13 *Assume that the composite described in Problem 16.8 has a cross-sectional area of 480 mm*^{2} *(0.75 in.*^{2}*) and is subjected to a longitudinal load of 53,400 N (12,000 lb*$_f$*).*

(a) Calculate the fiber–matrix load ratio.

(b) Calculate the actual loads carried by both fiber and matrix phases.

(c) Compute the magnitude of the stress on each of the fiber and matrix phases.

(d) What strain is experienced by the composite?

Solution

The problem stipulates that the cross-sectional area of a composite, A_c, is 480 mm^2 (0.75 in.^{2}), and the longitudinal load, F_c, is 53,400 N (12,000 lb$_f$) for the composite described in Problem 16.8.

(a) First, we are asked to calculate the F_f/F_m ratio, which requires the use of Equation 16.11—viz.,

$$\frac{F_f}{F_m} = \frac{E_f V_f}{E_m V_m}$$

The following data are found in Problem 16.8:

$V_f = 0.45$

$V_m = 0.55$

$E_f = 131$ GPa

$E_m = 2.4$ GPa

The F_f/F_m ratio may be determined by inserting these values into Equation 16.11 as follows:

$$\frac{F_f}{F_m} = \frac{E_f V_f}{E_m V_m} = \frac{(131 \text{ GPa})(0.45)}{(2.4 \text{ GPa})(0.55)} = 44.7$$

Which means that $F_f = 44.7F_m$.

(b) Now, the actual loads carried by both phases are called for. From Equation 16.4

$$F_f + F_m = F_c = 53{,}400 \text{ N}$$

But, since $F_f = 44.7F_m$ we may write

$$44.7F_m + F_m = 53{,}400 \text{ N}$$

Or that

$$F_m = 1168 \text{ N} \;\; (263 \text{ lb}_f)$$

And using a rearranged form of Equation 16.4 allows for us to solve for the value of F_f as follows:

$$F_f = F_c - F_m = 53{,}400\ \mathrm{N} - 1168\ \mathrm{N} = 52{,}232\ \mathrm{N}\ \ (11{,}737\ \mathrm{lb_f})$$

(c) To compute the stress on each of the phases, it is first necessary to know the cross-sectional areas of both fiber and matrix. These are determined assuming that areas (of fiber and matrix phases) are equal to the product of phase volume fraction and composite cross-sectional area—that is

$$A_f = V_f A_c = (0.45)(480\ \mathrm{mm}^2) = 216\ \mathrm{mm}^2\ \ (0.34\ \mathrm{in.}^2)$$

$$A_m = V_m A_c = (0.55)(480\ \mathrm{mm}^2) = 264\ \mathrm{mm}^2\ \ (0.41\ \mathrm{in.}^2)$$

Now, the stresses of each of the fiber and matrix phases are determined using Equation 6.1 as follows:

$$\sigma_f = \frac{F_f}{A_f} = \frac{52{,}232\ \mathrm{N}}{(216\ \mathrm{mm}^2)(1\ \mathrm{m}/1000\ \mathrm{mm})^2}$$

$$= 242 \times 10^6\ \mathrm{N/m}^2 = 242\ \mathrm{MPa}\ \ (34{,}520\ \mathrm{psi})$$

$$\sigma_m = \frac{F_m}{A_m} = \frac{1168\ \mathrm{N}}{(264\ \mathrm{mm}^2)(1\ \mathrm{m}/1000\ \mathrm{mm})^2}$$

$$= 4.4 \times 10^6\ \mathrm{N/m}^2 = 4.4\ \mathrm{MPa}\ \ (641\ \mathrm{psi})$$

(d) Applying Equation 6.5 to both matrix and fiber phases leads to the following:

$$\varepsilon_m = \frac{\sigma_m}{E_m} = \frac{4.4\ \mathrm{MPa}}{2.4 \times 10^3\ \mathrm{MPa}} = 1.83 \times 10^{-3}$$

$$\varepsilon_f = \frac{\sigma_f}{E_f} = \frac{242\ \mathrm{MPa}}{131 \times 10^3\ \mathrm{MPa}} = 1.84 \times 10^{-3}$$

Therefore, the strains on matrix and fiber phases (as well as the composite itself) are the same (or nearly the same), which they should be according to Equation 16.8.

16.14 *A continuous and aligned fibrous reinforced composite having a cross-sectional area of 970 mm*^{2} *(1.5 in.*^{2}*) is subjected to an external tensile load. If the stresses sustained by the fiber and matrix phases are 215 MPa (31,300 psi) and 5.38 MPa (780 psi), respectively, the force sustained by the fiber phase is 76,800 N (17,265 lb*$_f$*), and the total longitudinal composite strain is 1.56 ×* 10^{-3}*, determine the following:*

(a) The force sustained by the matrix phase

(b) The modulus of elasticity of the composite material in the longitudinal direction

(c) The moduli of elasticity for fiber and matrix phases

Solution

For a continuous and aligned fibrous composite, we are given its cross-sectional area (970 mm^2), the stresses sustained by the fiber and matrix phases (215 MPa and 5.38 MPa), the force sustained by the fiber phase (76,800 N), and the total longitudinal strain (1.56×10^{-3}).

(a) For this portion of the problem we are asked to calculate the force sustained by the matrix phase. It is first necessary to compute the volume fraction of the matrix phase, V_m. This may be accomplished by first determining V_f and then V_m from $V_m = 1 - V_f$. The value of V_f may be calculated since, from the definition of stress (Equation 6.1)—that is

$$\sigma_f = \frac{F_f}{A_f}$$

and realizing $V_f = A_f/A_c$ (or rather, that $A_f = V_f A_c$), then,

$$\sigma_f = \frac{F_f}{A_f} = \frac{F_f}{V_f A_c} \tag{S16.14a}$$

Or, solving for V_f

$$V_f = \frac{F_f}{\sigma_f A_c}$$

The problem statement provides the following data:

$F_f = 76{,}800$ N

$\sigma_f = 215 \text{ MPa} = 215 \times 10^6 \text{ N/m}^2$

$A_c = 970 \text{ mm}^2$

Therefore,

$$V_f = \frac{F_f}{\sigma_f A_c} = \frac{76{,}800 \text{ N}}{(215 \times 10^6 \text{ N/m}^2)(970 \text{ mm}^2)(1 \text{ m}/1000 \text{ mm})^2} = 0.368$$

Also

$$V_m = 1 - V_f = 1 - 0.368 = 0.632$$

And, an expression for σ_m analogous to the one for σ_f given in Equation S16.14a above is as follows:

$$\sigma_m = \frac{F_m}{A_m} = \frac{F_m}{V_m A_c}$$

From which we solve for F_m as follows:

$$F_m = V_m \sigma_m A_c$$

$$= (0.632)\left(5.38 \times 10^6 \text{ N/m}^2\right)\left(0.970 \times 10^{-3} \text{ m}^2\right)$$

$$= 3300 \text{ N} \quad (741 \text{ lb}_\text{f})$$

(b) We are now asked to calculate the modulus of elasticity in the longitudinal direction. This is possible realizing that $E_c = \dfrac{\sigma_c}{\varepsilon}$ (from Equation 6.5), that $\sigma_c = \dfrac{F_c}{A_c}$ (from Equation 6.1) and that $F_c = F_m + F_c$ (Equation 6.4). Combining these three expressions yields the following

$$E_c = \frac{\sigma_c}{\varepsilon}$$

$$= \frac{\dfrac{F_m + F_f}{A_c}}{\varepsilon}$$

$$= \frac{F_m + F_f}{\varepsilon A_c}$$

Now we know values for the parameters in this equation as follows:

F_f = 76,800 N (problem statement)

F_m = 3300 N (computed above)

A_c = 970 mm^2 (problem statement)

$\varepsilon = 1.56 \times 10^{-3}$ (problem statement)

Therefore, we compute the modulus of elasticity for the composite as follows:

$$E_c = \frac{F_m + F_f}{\varepsilon A_c}$$

$$= \frac{3300\ \text{N} + 76,800\ \text{N}}{\left(1.56\ \times 10^{-3}\right)\left(970\ \text{mm}^2\right)\left(1\ \text{m}/1000\ \text{mm}\right)^2}$$

$$= 50.8 \times\ 10^9\ \text{N/m}^2 = 50.8\ \text{GPa}\quad (7.37\ \times\ 10^6\ \text{psi})$$

(c) Finally, it is necessary to determine the moduli of elasticity for the fiber and matrix phases. This is possible assuming Equation 6.5 for the matrix phase—i.e.,

$$E_m = \frac{\sigma_m}{\varepsilon_m}$$

Because this is an isostrain state, it is the case that $\varepsilon_m = \varepsilon_c = 1.56 \times 10^{-3}$. Thus

$$E_m = \frac{\sigma_m}{\varepsilon_c} = \frac{5.38 \times 10^6\ \text{N/m}^2}{1.56 \times 10^{-3}} = 3.45\ \times\ 10^9\ \text{N/m}^2$$

$$= 3.45\ \text{GPa}\ \ (5.0\ \times\ 10^5\ \text{psi})$$

The elastic modulus for the fiber phase may be computed in an analogous manner:

$$E_f = \frac{\sigma_f}{\varepsilon_f} = \frac{\sigma_f}{\varepsilon_c}$$

$$= \frac{215 \times 10^6\ \text{N/m}^2}{1.56 \times 10^{-3}} = 1.38\ \times\ 10^{11}\ \text{N/m}^2$$

$$= 138\ \text{GPa}\ \ (20\ \times\ 10^6\ \text{psi})$$

16.15 *Compute the longitudinal strength of an aligned carbon fiber–epoxy matrix composite having a 0.20 volume fraction of fibers, assuming the following: (1) an average fiber diameter of 6 × 10^{-3} mm (2.4 × 10^{-4} in.), (2) an average fiber length of 8.0 mm (0.31 in.), (3) a fiber fracture strength of 4.5 GPa (6.5 × 10^{5} psi), (4) a fiber–matrix bond strength of 75 MPa (10,900 psi), (5) a matrix stress at composite failure of 6.0 MPa (870 psi), and (6) a matrix tensile strength of 60 MPa (8700 psi).*

Solution

In this problem, for an aligned carbon fiber-epoxy matrix composite, we are given the volume fraction of fibers (0.20), the average fiber diameter (6 × 10^{-3} mm), the average fiber length (8.0 mm), the fiber fracture strength (4.5 GPa), the fiber-matrix bond strength (75 MPa), the matrix stress at composite failure (6.0 MPa), and the matrix tensile strength (60 MPa); and we are asked to compute the longitudinal strength. It is first necessary to compute the value of the critical fiber length using Equation 16.3. If the fiber length is much greater than l_c, then we may determine the longitudinal strength using Equation 16.17; otherwise, use of either Equation 16.18 or Equation 16.19 is necessary. Thus, from Equation 16.3 the value of l_c is

$$l_c = \frac{\sigma_f^* d}{2\tau_c} = \frac{(4.5 \times 10^3\ \text{MPa})(6 \times 10^{-3}\ \text{mm})}{2(75\ \text{MPa})} = 0.18\ \text{mm}$$

Inasmuch as $l >> l_c$ (that is, 8.0 mm >> 0.18 mm), then use of Equation 16.17 is appropriate. Therefore,

$$\sigma_{cl}^* = \sigma_m'(1 - V_f) + \sigma_f^* V_f$$

$$= (6\ \text{MPa})(1 - 0.20) + (4.5 \times 10^3\ \text{MPa})(0.20)$$

$$= 905\ \text{MPa}\ \ (130{,}700\ \text{psi})$$

16.16 *It is desired to produce an aligned carbon fiber–epoxy matrix composite having a longitudinal tensile strength of 500 MPa (72,500 psi). Calculate the volume fraction of fibers necessary if (1) the average fiber diameter and length are 0.01 mm (3.9 × 10^{-4} in.) and 0.5 mm (2 × 10^{-2} in.), respectively; (2) the fiber fracture strength is 4.0 GPa (5.8 × 10^{5} psi); (3) the fiber–matrix bond strength is 25 MPa (3625 psi); and (4) the matrix stress at composite failure is 7.0 MPa (1000 psi).*

Solution

In this problem, for an aligned carbon fiber-epoxy matrix composite, we are given the desired longitudinal tensile strength (500 MPa), the average fiber diameter (1.0 × 10^{-2} mm), the average fiber length (0.5 mm), the fiber fracture strength (4 GPa), the fiber-matrix bond strength (25 MPa), and the matrix stress at composite failure (7.0 MPa); and we are asked to compute the volume fraction of fibers that is required. It is first necessary to compute the value of the critical fiber length using Equation 16.3. If the fiber length is much greater than l_c, then we may determine V_f using Equation 16.17; otherwise, use of either Equation 16.18 or Equation 16.19 is necessary. Thus, the value of the critical fiber length is

$$l_c = \frac{\sigma_f^* d}{2\tau_c} = \frac{(4 \times 10^3 \text{ MPa})(1.0 \times 10^{-2} \text{ mm})}{2(25 \text{ MPa})} = 0.80 \text{ mm}$$

Inasmuch as $l < l_c$ (0.50 mm < 0.80 mm), then use of Equation 16.19 is required. Therefore,

$$\sigma_{cd'}^* = \frac{l\tau_c}{d} V_f + \sigma_m'(1 - V_f)$$

$$500 \text{ MPa} = \frac{(0.5 \times 10^{-3} \text{m})(25 \text{ MPa})}{0.01 \times 10^{-3} \text{m}}(V_f) + (7 \text{ MPa})(1 - V_f)$$

Solving this expression for V_f leads to $V_f = 0.397$.

16.17 *Compute the longitudinal tensile strength of an aligned glass fiber–epoxy matrix composite in which the average fiber diameter and length are 0.015 mm (5.9 × 10^{-4} in.) and 2.0 mm (0.08 in.), respectively, and the volume fraction of fibers is 0.25. Assume that (1) the fiber–matrix bond strength is 100 MPa (14,500 psi), (2) the fracture strength of the fibers is 3500 MPa (5 × 10^5 psi), and (3) the matrix stress at composite failure is 5.5 MPa (800 psi).*

Solution

In this problem, for an aligned glass fiber-epoxy matrix composite, we are asked to compute the longitudinal tensile strength given the following: the average fiber diameter (0.015 mm), the average fiber length (2.0 mm), the volume fraction of fibers (0.25), the fiber fracture strength (3500 MPa), the fiber-matrix bond strength (100 MPa), and the matrix stress at composite failure (5.5 MPa). It is first necessary to compute the value of the critical fiber length using Equation 16.3. If the fiber length is much greater than l_c, then we may determine σ_{cl}^* using Equation 16.17; otherwise, use of either Equations 16.18 or 16.19 is necessary. The critical fiber length is as determined as follows:

$$l_c = \frac{\sigma_f^* d}{2\tau_c} = \frac{(3500\ \text{MPa})(0.015\ \text{mm})}{2(100\ \text{MPa})} = 0.263\ \text{mm}\quad (0.010\ \text{in.})$$

Inasmuch as $l > l_c$ (2.0 mm > 0.263 mm), but since l is not much greater than l_c, then use of Equation 16.18 is necessary. Therefore,

$$\sigma_{cd}^* = \sigma_f^* V_f \left(1 - \frac{l_c}{2l}\right) + \sigma_m'\left(1 - V_f\right)$$

$$= (3500\ \text{MPa})(0.25)\left[1 - \frac{0.263\ \text{mm}}{(2)(2.0\ \text{mm})}\right] + (5.5\ \text{MPa})(1 - 0.25)$$

$$= 822\ \text{MPa}\quad (117{,}800\ \text{psi})$$

16.18 *(a) From the moduli of elasticity data in Table 16.2 for glass fiber-reinforced polycarbonate composites, determine the value of the fiber efficiency parameter for each of 20, 30, and 40 vol% fibers.*

(b) Estimate the modulus of elasticity for 50 vol% glass fibers.

Solution

(a) This portion of the problem calls for computation of values of the fiber efficiency parameter. From Equation 16.20 (in which K is the fiber efficient parameter)

$$E_{cd} = KE_f V_f + E_m V_m$$

Solving this expression for K yields

$$K = \frac{E_{cd} - E_m V_m}{E_f V_f} = \frac{E_{cd} - E_m(1 - V_f)}{E_f V_f}$$

For glass fibers, E_f = 72.5 GPa (Table 16.4); using the data in Table 16.2, and taking an average of the extreme E_m values given (for the unreinforced polycarbonate), E_m = 2.29 GPa (0.333 × 10^6 psi).

Solving for K when V_f = 0.20 yields

$$K = \frac{5.93 \text{ GPa} - (2.29 \text{ GPa})(1 - 0.2)}{(72.5 \text{ GPa})(0.2)} = 0.283$$

For V_f = 0.3

$$K = \frac{8.62 \text{ GPa} - (2.29 \text{ GPa})(1 - 0.3)}{(72.5 \text{ GPa})(0.3)} = 0.323$$

And, for V_f = 0.4

$$K = \frac{11.6 \text{ GPa} - (2.29 \text{ GPa})(1 - 0.4)}{(72.5 \text{ GPa})(0.4)} = 0.353$$

(b) For 50 vol% fibers (V_f = 0.50), we must assume a value for K. Since it is increasing with V_f, let us estimate it to increase by the same amount as going from 0.3 to 0.4—that is, by a value of 0.03. Therefore, let us assume a value for K of 0.383. Now, from Equation 16.20

$$E_{cd} = KE_f V_f + E_m V_m$$

$$= (0.383)(72.5\ \text{GPa})(0.5) + (2.29\ \text{GPa})(0.5)$$

$$= 15.0\ \text{GPa} \quad (2.18 \times 10^6\ \text{psi})$$

The Fiber Phase

The Matrix Phase

16.19 *For a polymer-matrix fiber-reinforced composite:*

(a) List three functions of the matrix phase.

(b) Compare the desired mechanical characteristics of matrix and fiber phases.

(c) Cite two reasons why there must be a strong bond between fiber and matrix at their interface.

Answer

(a) For polymer-matrix fiber-reinforced composites, three functions of the polymer-matrix phase are: (1) to bind the fibers together so that the applied stress is distributed among the fibers; (2) to protect the surface of the fibers from being damaged; and (3) to separate the fibers and inhibit crack propagation.

(b) The matrix phase must be ductile and is usually relatively soft, whereas the fiber phase must be stiff and strong.

(c) There must be a strong interfacial bond between fiber and matrix in order to: (1) maximize the stress transmittance between matrix and fiber phases; and (2) minimize fiber pull-out, and the probability of failure.

16.20 (a) *What is the distinction between matrix and dispersed phases in a composite material?*

(b) Contrast the mechanical characteristics of matrix and dispersed phases for fiber-reinforced composites.

Answer

(a) The matrix phase is a continuous phase that surrounds the noncontinuous dispersed phase.

(b) In general, the matrix phase is relatively weak, has a low elastic modulus, but is quite ductile. On the other hand, the fiber phase is normally quite strong, stiff, and brittle.

Polymer-Matrix Composites

16.21 *(a) Calculate the specific longitudinal strengths of the glass-fiber, carbon-fiber, and aramid-fiber reinforced epoxy composites in Table 16.5 and compare them with those of the following alloys: cold-rolled 17-7PH stainless steel, normalized 1040 plain-carbon steel, 7075-T6 aluminum alloy, cold-worked (H04 temper) C26000 cartridge brass, extruded AZ31B magnesium alloy, and annealed Ti-5Al–2.5Sn titanium alloy.*

(b) Compare the specific moduli of the same three fiber-reinforced epoxy composites with the same metal alloys. Densities (i.e., specific gravities), tensile strengths, and moduli of elasticity for these metal alloys may be found in Tables B.1, B.4, and B.2, respectively, in Appendix B.

Solution

(a) This portion of the problem calls for us to calculate the specific longitudinal strengths of glass-fiber, carbon-fiber, and aramid-fiber reinforced epoxy composites, and then to compare these values with the specific strengths of several metal alloys.

The longitudinal specific strength of the glass-reinforced epoxy material ($V_f = 0.60$) in Table 16.5 is just the ratio of the longitudinal tensile strength and specific gravity as

$$\frac{1020 \text{ MPa}}{2.1} = 486 \text{ MPa}$$

For the carbon-fiber reinforced epoxy

$$\frac{1240 \text{ MPa}}{1.6} = 775 \text{ MPa}$$

And, for the aramid-fiber reinforced epoxy

$$\frac{1380 \text{ MPa}}{1.4} = 986 \text{ MPa}$$

Now, for the metal alloys we use data found in Tables B.1 and B.4 in Appendix B (using the density values from Table B.1 for the specific gravities). For the cold-rolled 17-7PH stainless steel

$$\frac{1380 \text{ MPa}}{7.65} = 180 \text{ MPa}$$

For the normalized 1040 plain carbon steel, the ratio is

$$\frac{590 \text{ MPa}}{7.85} = 75 \text{ MPa}$$

For the 7075-T6 aluminum alloy

$$\frac{572\ \text{MPa}}{2.80} = 204\ \text{MPa}$$

For the C26000 brass (cold worked)

$$\frac{525\ \text{MPa}}{8.53} = 62\ \text{MPa}$$

For the AZ31B (extruded) magnesium alloy

$$\frac{262\ \text{MPa}}{1.77} = 148\ \text{MPa}$$

For the annealed Ti-5Al-2.5Sn titanium alloy

$$\frac{790\ \text{MPa}}{4.48} = 176\ \text{MPa}$$

(b) The longitudinal specific modulus is just the longitudinal tensile modulus-specific gravity ratio. For the glass-fiber reinforced epoxy, this ratio is

$$\frac{45\ \text{GPa}}{2.1} = 21.4\ \text{GPa}$$

For the carbon-fiber reinforced epoxy

$$\frac{145\ \text{GPa}}{1.6} = 90.6\ \text{GPa}$$

And, for the aramid-fiber reinforced epoxy

$$\frac{76\ \text{GPa}}{1.4} = 54.3\ \text{GPa}$$

The specific moduli for the metal alloys (Tables B.1 and B.2) are as follows:

For the cold rolled 17-7PH stainless steel

$$\frac{204\ \text{GPa}}{7.65} = 26.7\ \text{GPa}$$

For the normalized 1040 plain-carbon steel

$$\frac{207\ \text{GPa}}{7.85} = 26.4\ \text{GPa}$$

For the 7075-T6 aluminum alloy

$$\frac{71\ \text{GPa}}{2.80} = 25.4\ \text{GPa}$$

For the cold worked C26000 brass

$$\frac{110\ \text{GPa}}{8.53} = 12.9\ \text{GPa}$$

For the extruded AZ31B magnesium alloy

$$\frac{45\ \text{GPa}}{1.77} = 25.4\ \text{GPa}$$

For the Ti-5Al-2.5Sn titanium alloy

$$\frac{110\ \text{GPa}}{4.48} = 24.6\ \text{GPa}$$

16.22 *(a) List four reasons why glass fibers are most commonly used for reinforcement.*

(b) Why is the surface perfection of glass fibers so important?

(c) What measures are taken to protect the surface of glass fibers?

Answer

(a) The four reasons why glass fibers are most commonly used for reinforcement are listed at the beginning of Section 16.8 under "Glass Fiber-Reinforced Polymer (GFRP) Composites."

(b) The surface perfection of glass fibers is important because surface flaws or cracks act as points of stress concentration, which will dramatically reduce the tensile strength of the material.

(c) Care must be taken not to rub or abrade the surface after the fibers are drawn. As a surface protection, newly drawn fibers are coated with a protective surface film.

16.23 *Cite the distinction between carbon and graphite.*

Answer

"Graphite" is crystalline carbon having the structure shown in Figure 12.16, whereas "carbon" will consist of some noncrystalline material as well as areas of crystal misalignment, per the schematic diagram shown in Figure 13.5.

16.24 *(a) Cite several reasons why fiberglass-reinforced composites are used extensively.*

(b) Cite several limitations of this type of composite.

Answer

(a) Reasons why fiberglass-reinforced composites are utilized extensively are: (1) glass fibers are very inexpensive to produce; (2) these composites have relatively high specific strengths; and (3) they are chemically inert in a wide variety of environments.

(b) Several limitations of these composites are: (1) care must be exercised in handling the fibers inasmuch as they are susceptible to surface damage; (2) they are lacking in stiffness in comparison to other fibrous composites; and (3) they are limited as to maximum temperature use.

Hybrid Composites

16.25 *(a) What is a hybrid composite?*

(b) List two important advantages of hybrid composites over normal fiber composites.

Answer

(a) A hybrid composite is a composite that is reinforced with two or more different fiber materials in a single matrix.

(b) Two advantages of hybrid composites are: (1) better overall property combinations, and (2) failure is not as catastrophic as with single-fiber composites.

16.26 *(a) Write an expression for the modulus of elasticity for a hybrid composite in which all fibers of both types are oriented in the same direction.*

(b) Using this expression, compute the longitudinal modulus of elasticity of a hybrid composite consisting of aramid and glass fibers in volume fractions of 0.25 and 0.35, respectively, within a polyester resin matrix [E_m = 4.0 GPa (6 × 10^5 psi)].

Solution

(a) For a hybrid composite having all fibers aligned in the same direction

$$E_{cl} = E_m V_m + E_{f1} V_{f1} + E_{f2} V_{f2}$$

in which the subscripts *f*1 and *f*2 refer to the two types of fibers.

(b) Now we are asked to compute the longitudinal elastic modulus for a glass- and aramid-fiber hybrid composite. From Table 16.4, the elastic moduli of aramid and glass fibers are, respectively, 131 GPa (19 × 10^6 psi) and 72.5 GPa (10.5 × 10^6 psi). Thus, from the previous expression

$$E_{cl} = (4\ \text{GPa})(1.0 - 0.25 - 0.35) + (131\ \text{GPa})(0.25) + (72.5\ \text{GPa})(0.35)$$

$$= 59.7\ \text{GPa} \quad (8.67 \times 10^6\ \text{psi})$$

16.27 *Derive a generalized expression analogous to Equation 16.16 for the transverse modulus of elasticity of an aligned hybrid composite consisting of two types of continuous fibers.*

Solution

This problem asks that we derive a generalized expression analogous to Equation 16.16 for the transverse modulus of elasticity of an aligned hybrid composite consisting of two types of continuous fibers. Let us denote the subscripts *f*1 and *f*2 for the two fiber types, and *m*, *c*, and *t* subscripts for the matrix, composite, and transverse direction, respectively. For the isostress state, the expressions analogous to Equations 16.12 and 16.13 are as follows:

$$\sigma_c = \sigma_m = \sigma_{f1} = \sigma_{f2}$$

And

$$\varepsilon_c = \varepsilon_m V_m + \varepsilon_{f1} V_{f1} + \varepsilon_{f2} V_{f2}$$

Since, in general, $\varepsilon = \sigma/E$ (Equation 6.5), making substitutions of the form of Equation 6.5 into the previous expression yields the following:

$$\frac{\sigma}{E_{ct}} = \frac{\sigma}{E_m} V_m + \frac{\sigma}{E_{f1}} V_{f1} + \frac{\sigma}{E_{f2}} V_{f2}$$

Now, dividing each of the terms in the previous equation by σ leads to the following equation:

$$\frac{1}{E_{ct}} = \frac{V_m}{E_m} + \frac{V_{f1}}{E_{f1}} + \frac{V_{f2}}{E_{f2}}$$

$$= \frac{V_m E_{f1} E_{f2} + V_{f1} E_m E_{f2} + V_{f2} E_m E_{f1}}{E_m E_{f1} E_{f2}}$$

And, finally, taking the reciprocal of this equation leads to

$$E_{ct} = \frac{E_m E_{f1} E_{f2}}{V_m E_{f1} E_{f2} + V_{f1} E_m E_{f2} + V_{f2} E_m E_{f1}}$$

The desired expression.

Processing of Fiber-Reinforced Composites

16.28 *Briefly describe pultrusion, filament winding, and prepreg production fabrication processes; cite the advantages and disadvantages of each.*

<u>Answer</u>

Pultrusion, filament winding, and prepreg fabrication processes are described in Section 16.13.

For pultrusion, the advantages are: the process may be automated, production rates are relatively high, a wide variety of shapes having constant cross-sections are possible, and very long pieces may be produced. The chief disadvantage is that shapes are limited to those having a constant cross-section.

For filament winding, the advantages are: the process may be automated, a variety of winding patterns are possible, and a high degree of control over winding uniformity and orientation is afforded. The chief disadvantage is that the variety of shapes is somewhat limited.

For prepreg production, the advantages are as follows: resin does not need to be added to the prepreg, the lay-up arrangement relative to the orientation of individual plies is variable, and the lay-up process may be automated. The chief disadvantages of this technique are that final curing is necessary after fabrication, and thermoset prepregs must be stored at subambient temperatures to prevent complete curing.

Laminar Composites

Sandwich Panels

16.29 *Briefly describe laminar composites. What is the prime reason for fabricating these materials?*

Answer

Laminar composites are a series of sheets or panels, each of which has a preferred high-strength direction. These sheets are stacked and then cemented together such that the orientation of the high-strength direction varies from layer to layer.

These composites are constructed in order to have a relatively high strength in virtually all directions within the plane of the laminate.

16.30 *(a) Briefly describe sandwich panels.*

(b) What is the prime reason for fabricating these structural composites?

(c) What are the functions of the faces and the core?

Answer

(a) Sandwich panels consist of two outer face sheets of a high-strength material that are separated by a layer of a less-dense and lower-strength core material.

(b) The prime reason for fabricating these composites is to produce structures having high in-plane strengths, high shear rigidities, and low densities.

(c) The faces function so as to bear the majority of in-plane tensile and compressive stresses. On the other hand, the core separates and provides continuous support for the faces, and also resists shear deformations perpendicular to the faces.

DESIGN PROBLEMS

16.D1 *Composite materials are being used extensively in sports equipment.*

(a) List at least four different sports implements that are made of, or contain, composites.

(b) For one of these implements, write an essay in which you do the following: (1) Cite the materials that are used for matrix and dispersed phases and, if possible, the proportions of each phase; (2) note the nature of the dispersed phase (e.g., continuous fibers); and (3) describe the process by which the implement is fabricated.

Each student will provide his/her own responses to these statements.

Influence of Fiber Orientation and Concentration

16.D2 *It is desired to produce an aligned and continuous fiber-reinforced epoxy composite having a maximum of 40 vol% fibers. In addition, a minimum longitudinal modulus of elasticity of 55 GPa (8 × 10^6 psi) is required, as is a minimum tensile strength of 1200 MPa (175,000 psi). Of E-glass, carbon (PAN standard modulus), and aramid fiber materials, which are possible candidates and why? The epoxy has a modulus of elasticity of 3.1 GPa (4.5 × 10^5 psi) and a tensile strength of 69 MPa (11,000 psi). In addition, assume the following stress levels on the epoxy matrix at fiber failure: E-glass, 70 MPa (10,000 psi); carbon (PAN standard modulus), 30 MPa (4350 psi); and aramid, 50 MPa (7250 psi). Other fiber data are given in Tables B.2 and B.4 in Appendix B. For aramid fibers, use the minimum of the range of strength values provided in Table B.4.*

Solution

In order to solve this problem, we want to make longitudinal elastic modulus and tensile strength computations assuming 40 vol% fibers for the three fiber materials, in order to see which meet the stipulated criteria [i.e., a minimum elastic modulus of 55 GPa (8 × 10^6 psi), and a minimum tensile strength of 1200 MPa (175,000 psi)]. Thus, it becomes necessary to use Equations 16.10b and 16.17 with V_m = 0.60 and V_f = 0.40, E_m = 3.1 GPa, and σ_m^* = 69 MPa.

For glass, E_f = 72.5 GPa (Table B.2) and σ_f^* = 3450 MPa (Table 16.4). Therefore,

$$E_{cl} = E_m(1 - V_f) + E_f V_f$$

$$= (3.1 \text{ GPa})(1 - 0.40) + (72.5 \text{ GPa})(0.40) = 30.9 \text{ GPa} \quad (4.47 \times 10^6 \text{ psi})$$

Because this value is less than the specified minimum (i.e., 55 GPa), glass is not an acceptable candidate.

For carbon (PAN standard-modulus), E_f = 230 GPa (Table B.2) and σ_f^* = 4000 MPa (the average of the range of values in Table B.4); thus, from Equation 16.10b

$$E_{cl} = (3.1 \text{ GPa})(1.00 - 0.40) + (230 \text{ GPa})(0.40) = 93.9 \text{ GPa} \quad (13.6 \times 10^6 \text{ psi})$$

which is greater than the specified minimum. In addition, from Equation 16.17

$$\sigma_{cl}^* = \sigma'_m(1 - V_f) + \sigma_f^* V_f$$

$$= (30 \text{ MPa})(1 - 0.40) + (4000 \text{ MPa})(0.40) = 1620 \text{ MPa} \quad (234{,}600 \text{ psi})$$

This value is greater than the minimum required tensile strength (1200 MPa). Thus, carbon (PAN standard-modulus) is a candidate.

For aramid, E_f = 131 GPa (Table B.2) and σ_f^* = 3850 MPa (the average of the range of values in Table B.4). Thus, the modulus using aramid fibers (Equation 16.10b) is computed as follows:

$$E_{cl} = (3.1 \text{ GPa})(1 - 0.40) + (131 \text{ GPa})(0.40) = 54.3 \text{ GPa} \quad (7.87 \times 10^6 \text{ psi})$$

This value is less than the minimum, which means that the aramid fiber-reinforced composite does not meet the required modulus of elasticity and is not a candidate.

Thus, only the carbon (PAN standard-modulus) fiber-reinforced epoxy composite satisfies both criteria and, therefore, is a candidate for this application.

16.D3 *It is desired to produce a continuous and oriented carbon fiber-reinforced epoxy having a modulus of elasticity of at least 69 GPa (10 × 10^6 psi) in the direction of fiber alignment. The maximum permissible specific gravity is 1.40. Given the data in the following table, is such a composite possible? Why or why not? Assume that composite specific gravity may be determined using a relationship similar to Equation 16.10a.*

	SpecificGravity	***Modulus of Elasticity [GPa (psi)]***
Carbon fiber	*1.80*	*260 (37 × 10^6)*
Epoxy	*1.25*	*2.4 (3.5 × 10^5)*

Solution

This problem asks us to determine whether or not it is possible to produce a continuous and oriented carbon fiber-reinforced epoxy having a modulus of elasticity of at least 69 GPa in the direction of fiber alignment, and a maximum specific gravity of 1.40. We will first calculate the minimum volume fraction of fibers to give the stipulated elastic modulus, and then the maximum volume fraction of fibers possible to yield the maximum permissible specific gravity; if there is an overlap of these two fiber volume fractions then such a composite is possible.

We first use Equation 16.10b to compute the volume fraction of fibers to give a modulus of elasticity of 69 GPa as follows:

$$E_{cl} = E_m(1 - V_f) + E_f V_f$$

$$69 \text{ GPa} = (2.4 \text{ GPa})(1 - V_f) + (260 \text{ GPa})(V_f)$$

Solving for V_f yields $V_f = 0.26$. Therefore, $V_f > 0.26$ to give the minimum desired elastic modulus.

Now, upon consideration of the specific gravity (or density), ρ, we employ the following modified form of Equation 16.10b as follows:

$$\rho_c = \rho_m(1 - V_f) + \rho_f V_f$$

$$1.40 = 1.25(1 - V_f) + 1.80(V_f)$$

And, solving for V_f from this expression gives $V_f = 0.27$. Therefore, it is necessary for $V_f < 0.27$ in order to have a composite specific gravity less than 1.40.

Hence, such a composite *is possible* if $0.26 < V_f < 0.27$

16.D4 *It is desired to fabricate a continuous and aligned glass fiber-reinforced polyester having a tensile strength of at least 1250 MPa (180,000 psi) in the longitudinal direction. The maximum possible specific gravity is 1.80. Using the following data, determine whether such a composite is possible. Justify your decision. Assume a value of 20 MPa for the stress on the matrix at fiber failure.*

	Specific Gravity	***Tensile Strength [MPa (psi)]***
Glass fiber	*2.50*	*3500 (5×10^5)*
Polyester	*1.35*	*50 (7.25×10^3)*

Solution

This problem asks us to determine whether or not it is possible to produce a continuous and oriented glass fiber-reinforced polyester having a tensile strength of at least 1250 MPa in the longitudinal direction, and a maximum specific gravity of 1.80. We will first calculate the minimum volume fraction of fibers to give the stipulated tensile strength, and then the maximum volume fraction of fibers possible to yield the maximum permissible specific gravity; if there is an overlap of these two fiber volume fractions then such a composite is possible.

We first use Equation 16.17 to compute the volume fraction of fibers to give a tensile strength of 1250 MPa as follows:

$$\sigma_{cl}^* = \sigma_m'(1 - V_f) + \sigma_f^* V_f$$

$$1250\text{ MPa} = (20\text{ MPa})(1 - V_f) + (3500\text{ MPa})(V_f)$$

Solving for V_f yields $V_f = 0.353$. Therefore, $V_f > 0.353$ to give the minimum desired tensile strength.

Now, upon consideration of the specific gravity (or density), ρ, we employ the following modified form of Equation 16.10b as follows:

$$\rho_c = \rho_m(1 - V_f) + \rho_f V_f$$

$$1.80 = 1.35(1 - V_f) + 2.50(V_f)$$

And, solving for V_f from this expression gives $V_f = 0.391$. Therefore, it is necessary for $V_f < 0.391$ in order to have a composite specific gravity less than 1.80.

Hence, such a composite *is possible* if $0.353 < V_f < 0.391$.

16.D5 *It is necessary to fabricate an aligned and discontinuous glass fiber–epoxy matrix composite having a longitudinal tensile strength of 1200 MPa (175,000 psi) using a 0.35 volume fraction of fibers. Compute the required fiber fracture strength, assuming that the average fiber diameter and length are 0.015 mm (5.9 × 10^{-4} in.) and 5.0 mm (0.20 in.), respectively. The fiber–matrix bond strength is 80 MPa (11,600 psi), and the matrix stress at composite failure is 6.55 MPa (950 psi).*

Solution

To begin, since the value of σ_f^* is unknown, calculation of the value of l_c in Equation 16.3 is not possible, and, therefore, we are not able to decide which of Equations 16.18 and 16.19 to use. Thus, it is necessary to substitute for l_c in Equation 16.3 into Equation 16.18, solve for the value of σ_f^* then, using this value, solve for l_c from Equation 16.3. If $l > l_c$, we use Equation 16.18, otherwise Equation 16.19 must be used. *Note:* the σ_f^* parameter in Equations 16.18 and 16.3 is the same. Realizing this, and substituting for l_c in Equation 16.3 into Equation 16.18 leads to

$$\sigma_{cd}^* = \sigma_f^* V_f \left(1 - \frac{l_c}{2l}\right) + \sigma_m'(1 - V_f)$$

$$= \sigma_f^* V_f \left[1 - \frac{\sigma_f^* d}{4\tau_c l}\right] + \sigma_m'(1 - V_f)$$

$$= \sigma_f^* V_f - \frac{\sigma_f^{*2} V_f d}{4\tau_c l} + \sigma_m' - \sigma_m' V_f$$

This expression is a quadratic equation in which σ_f^* is the unknown. Rearrangement into a more convenient form leads to the following equation:

$$\sigma_f^{*2}\left(\frac{V_f d}{4\tau_c l}\right) - \sigma_f^*(V_f) + \left[\sigma_{cd}^* - \sigma_m'(1 - V_f)\right] = 0$$

We simplify the form of this equation as follows:

$$a\sigma_f^{*2} + b\sigma_f^* + c = 0$$

Now, the *a* substitution (and its value) are as follows:

$$a = \frac{V_f d}{4 \tau_c l}$$

$$= \frac{(0.35)\left(0.015 \times 10^{-3}\ \text{m}\right)}{(4)(80\ \text{MPa})\left(5 \times 10^{-3}\ \text{m}\right)} = 3.28 \times 10^{-6}\ (\text{MPa})^{-1} \quad \left[2.23 \times 10^{-8}\ (\text{psi})^{-1}\right]$$

Furthermore, for the *b* substitution and value

$$b = -V_f = -0.35$$

And, for *c*

$$c = \sigma^*_{cd} - \sigma'_m\left(1 - V_f\right)$$

$$= 1200\ \text{MPa} - (6.55\ \text{MPa})(1 - 0.35) = 1195.74\ \text{MPa} \quad (174{,}383\ \text{psi})$$

Now solving the above quadratic equation for σ^*_f yields the following:

$$\sigma^*_f = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$= \frac{-(-0.35) \pm \sqrt{(-0.35)^2 - (4)\left[3.28 \times 10^{-6}\ (\text{MPa})^{-1}\right](1195.74\ \text{MPa})}}{(2)\left[3.28 \times 10^{-6}\ (\text{MPa})^{-1}\right]}$$

$$= \frac{0.3500 \pm 0.3268}{6.56 \times 10^{-6}}\ \text{MPa} \quad \left(\frac{0.3500 \pm 0.3270}{4.46 \times 10^{-8}}\ \text{psi}\right)$$

Thus, two roots are possible, as follows:

$$\sigma^*_f(+) = \frac{0.3500 + 0.3268}{6.56 \times 10^{-6}}\ \text{MPa} = 103{,}200\ \text{MPa} \quad (15.2 \times 10^6\ \text{psi})$$

$$\sigma^*_f(-) = \frac{0.3500 - 0.3268}{6.56 \times 10^{-6}}\ \text{MPa} = 3537\ \text{MPa} \quad (515{,}700\ \text{psi})$$

Upon consultation of the magnitudes of σ^*_f for various fibers and whiskers in Table 16.4, only $\sigma^*_f(-)$ is reasonable. Now, using this value, let us calculate the value of l_c using Equation 16.3 in order to ascertain if use of Equation 16.18 in the previous treatment was appropriate. Thus

$$l_c = \frac{\sigma_f^* d}{2\tau_c} = \frac{(3537\ \text{MPa})(0.015\ \text{mm})}{(2)(80\ \text{MPa})} = 0.33\ \text{mm}\ \ (0.0131\ \text{in.})$$

Since $l > l_c$ (5.0 mm > 0.33 mm), our choice of Equation 16.18 was indeed appropriate, and σ_f^* = 3537 MPa (515,700 psi).

16.D6 *A tubular shaft similar to that shown in Figure 16.11 is to be designed that has an outside diameter of 100 mm (4 in.) and a length of 1.25 m (4.1 ft). The mechanical characteristic of prime importance is bending stiffness in terms of the longitudinal modulus of elasticity. Stiffness is to be specified as maximum allowable deflection in bending; when subjected to three-point bending as in Figure 12.30, a load of 1700 N (380* lb_f*) is to produce an elastic deflection of no more than 0.20 mm (0.008 in.) at the midpoint position.*

Continuous fibers that are oriented parallel to the tube axis will be used; possible fiber materials are glass, and carbon in standard-, intermediate-, and high-modulus grades. The matrix material is to be an epoxy resin, and fiber volume fraction is 0.40.

(a) Decide which of the four fiber materials are possible candidates for this application, and for each candidate determine the required inside diameter consistent with the preceding criteria.

(b) For each candidate, determine the required cost, and, on this basis, specify the fiber that would be the least expensive to use.

Elastic modulus, density, and cost data for the fiber and matrix materials are given in Table 16.6.

Solution

(a) This portion of the problem calls for a determination of which of the four fiber types is (are) suitable for a tubular shaft, given that the fibers are to be continuous and oriented with a volume fraction of 0.40. Using Equation 16.10 it is possible to solve for the elastic modulus of the shaft for each of the fiber types. For example, for glass (using moduli data in Table 16.6)

$$E_{cs} = E_m(1 - V_f) + E_f V_f$$

$$= (2.4\text{ GPa})(1.00 - 0.40) + (72.5\text{ GPa})(0.40) = 30.4\text{ GPa}$$

This value for E_{cs} as well as those computed in a like manner for the three carbon fibers are listed in Table 16.D1.

Table 16.D1 Composite Elastic Modulus for Each of Glass and Three Carbon Fiber Types for $V_f = 0.40$

Fiber Type	E_{cs} (GPa)
Glass	30.4
Carbon—standard modulus	93.4
Carbon—intermediate modulus	115
Carbon—high modulus	161

It now becomes necessary to determine, for each fiber type, the inside diameter d_i. Rearrangement of Equation 16.23 such that d_i is the dependent variable leads to the following expression:

$$d_i = \left[d_0^4 - \frac{4FL^3}{3\pi E \Delta y} \right]^{1/4}$$

The d_i values may be computed by substitution into this expression for E the E_{cs} data in Table 16.D1 and also the following data:

F = 1700 N

L = 1.25 m

Δy = 0.20 mm (0.20×10^{-3} m)

d_0 = 100 mm (0.1 m)

These d_i data are tabulated in the second column of Table 16.D2. No entry is included for glass. The elastic modulus for glass fibers is so low that it is not possible to use them for a tube that meets the stipulated criteria; mathematically, the term within brackets in the above equation for d_i is negative, and no real root exists. Thus, only the three carbon types are candidate fiber materials.

Table 16.D2 Inside Tube Diameter, Total Volume, and Fiber, Matrix, and Total Costs for Three Carbon-Fiber Epoxy-Matrix Composites

Fiber Type	Inside Diameter (mm)	Total Volume (cm^3)	Fiber Cost ($)	Matrix Cost ($)	Total Cost ($)
Glass	–	–	–	–	–
Carbon--standard modulus	70.4	4950	213.80	20.30	234.10
Carbon--intermediate modulus	78.9	3700	253.10	15.20	268.30
Carbon--high modulus	86.6	2450	441.00	10.10	451.10

(b) Also included in Table 16.D2 is the total volume of material required for the tubular shaft for each carbon fiber type; Equation 16.24 was utilized for these computations. Since $V_f = 0.40$, 40% this volume is fiber and the other 60% is epoxy matrix. In the manner of Design Example 16.1, the masses and costs of fiber and matrix materials were determined, as well as the total composite cost. These data are also included in Table 16.D2. Here it may be noted that the carbon standard-modulus fiber yields the least expensive composite, followed by the intermediate- and high-modulus materials.

FUNDAMENTALS OF ENGINEERING QUESTIONS AND PROBLEMS

16.1FE *The mechanical properties of some metals may be improved by incorporating fine particles of their oxides. If the moduli of elasticity of the metal and oxide are, respectively, 55 GPa and 430 GPa, what is the upper-bound modulus of elasticity value for a composite that has a composition of 31 vol% of oxide particles?*

(A) 48.8 GPa *(C) 138 GPa*

(B) 75.4 GPa *(D) 171 GPa*

Solution

The upper-bound expression for the elastic modulus of a composite may be computed using Equation 16.1

$$E_c(u) = E_m V_m + E_p V_p$$

where the *m* and *p* subscripts denote matrix and particle phases, respectively. Using data provided in the problem statement the upper-bound elastic modulus for this material is

$$E_c(u) = (55 \text{ GPa})(1 - 0.31) + (430 \text{ GPa})(0.31) = 171 \text{ GPa}$$

which is answer D.

16.2FE *How are continuous fibers typically oriented in fibrous composites?*

(A) Aligned

(B) Partially oriented

(C) Randomly oriented

(D) All of the above

Answer

The correct answer is A. Continuous fibers are typically *aligned* in fibrous composites.

16.3FE *Compared to other ceramic materials, ceramic-matrix composites have better/higher:*

(A) oxidation resistance

(B) stability at elevated temperatures

(C) fracture toughnesses

(D) all of the above

Answer

The correct answer is C. Ceramic-matrix composites have higher *fracture toughnesses* than other ceramic materials.

16.4FE *A continuous and aligned hybrid composite consists of aramid and glass fibers embedded within a polymer resin matrix. Compute the longitudinal modulus of elasticity of this material if the respective volume fractions are 0.24 and 0.28, given the following data:*

Material	***Modulus of Elasticity (GPa)***
Polyester	*2.5*
Aramid fibers	*131*
Glass fibers	*72.5*

(A) 5.06 GPa *(C) 52.9 GPa*

(B) 32.6 GPa *(D) 131 GPa*

Solution

The longitudinal modulus of elasticity for a continuous and aligned hybrid composite consisting of fibers 1 and 2 may be determined using Equation 16.10a with a term added for the second fiber material:

$$E_{cl} = E_m V_m + E_{f1} V_{f1} + E_{f2} V_{f2}$$

Therefore, for the composite described in the problem statement

$$E_{cl} = (2.5\ \text{GPa})(1 - 0.24 - 0.28) + (131\ \text{GPa})(0.24) + (72.5\ \text{GPa})(0.28)$$

$$= 52.9\ \text{GPa}$$

which is answer C.

CHAPTER 17

CORROSION AND DEGRADATION OF MATERIALS

PROBLEM SOLUTIONS

Electrochemical Considerations

17.1 *(a) Briefly explain the difference between oxidation and reduction electrochemical reactions.*
(b) Which reaction occurs at the anode and which at the cathode?

Answer

(a) Oxidation is the process by which an atom gives up an electron (or electrons) to become a cation. Reduction is the process by which an atom acquires an extra electron (or electrons) and becomes an anion.

(b) Oxidation occurs at the anode; reduction occurs at the cathode.

17.2 *(a) Write the possible oxidation and reduction half-reactions that occur when magnesium is immersed in each of the following solutions: (i) HCl, (ii) an HCl solution containing dissolved oxygen, and (iii) an HCl solution containing dissolved oxygen and* Fe^{2+} *ions.*

(b) In which of these solutions would you expect the magnesium to oxidize most rapidly? Why?

Solution

(a) This problem asks that we write possible oxidation and reduction half-reactions for magnesium in various solutions.

(i) In HCl, possible reactions are as follows:

$$\mathrm{Mg} \rightarrow \mathrm{Mg}^{2+} + 2e^- \quad \textbf{(oxidation)}$$

$$2\mathrm{H}^+ + 2e^- \rightarrow \mathrm{H}_2 \quad \textbf{(reduction)}$$

(ii) In an HCl solution containing dissolved oxygen, possible reactions are as follows:

$$\mathrm{Mg} \rightarrow \mathrm{Mg}^{2+} + 2e^- \quad \textbf{(oxidation)}$$

$$4\mathrm{H}^+ + \mathrm{O}_2 + 4e^- \rightarrow 2\mathrm{H}_2\mathrm{O} \quad \textbf{(reduction)}$$

(iii) In an HCl solution containing dissolved oxygen and Fe^{2+} ions, possible reactions are

$$\mathrm{Mg} \rightarrow \mathrm{Mg}^{2+} + 2e^- \quad \textbf{(oxidation)}$$

$$4\mathrm{H}^+ + \mathrm{O}_2 + 4e^- \rightarrow 2\mathrm{H}_2\mathrm{O} \quad \textbf{(reduction)}$$

$$\mathrm{Fe}^{2+} + 2e^- \rightarrow \mathrm{Fe} \quad \textbf{(reduction)}$$

(b) The magnesium would probably oxidize most rapidly in the HCl solution containing dissolved oxygen and Fe^{2+} ions because there are two reduction reactions that will consume electrons from the oxidation of magnesium.

17.3 *Demonstrate that (a) the value of F in Equation 17.19 is 96,500 C/mol, and (b) at 25°C (298 K),*

$$\frac{RT}{nF}\ln x = \frac{0.0592}{n}\log x$$

(*Note:* we denote the Faraday constant by an "*F*" rather than with the symbol used in the textbook.)

Solution

(a) The Faraday constant (*F*) is just the product of the charge per electron and Avogadro's number; that is

$$F = eN_A = \left(1.602 \times 10^{-19} \text{ C/electron}\right)\left(6.022 \times 10^{23} \text{ electrons/mol}\right)$$

= 96,472 C/mol

(b) At 25°C (298 K),

$$\frac{RT}{nF}\ln(x) = \frac{(8.31 \text{ J/mol-K})(298 \text{ K})}{(n)(96{,}500 \text{ C/mol})}(2.303)\log(x)$$

$$= \frac{0.0592}{n}\log(x)$$

This gives units in volts since a volt is a J/C.

17.4 *(a) Compute the voltage at 25°C of an electrochemical cell consisting of pure lead immersed in a 5 × 10^{-2} M solution of Pb^{2+} ions and pure tin in a 0.25 M solution of Sn^{2+} ions.*

(b) Write the spontaneous electrochemical reaction.

Solution

(a) We are asked to compute the voltage of a nonstandard Pb-Sn electrochemical cell. Since tin is lower in the standard emf series (Table 17.1), we will begin by assuming that tin is oxidized and lead is reduced, as

$$\mathrm{Sn} + \mathrm{Pb}^{2+} \rightarrow \mathrm{Sn}^{2+} + \mathrm{Pb}$$

such that Equation 17.20 takes the form

$$\Delta V = (V_{\mathrm{Pb}}^{0} - V_{\mathrm{Sn}}^{0}) - \frac{0.0592}{2} \log \frac{[\mathrm{Sn}^{2+}]}{[\mathrm{Pb}^{2+}]}$$

Table 17.1 gives the following standard electrode potentials:

$$V_{\mathrm{Pb}}^{0} = -\ 0.126\ \mathrm{V}$$

$$V_{\mathrm{Sn}}^{0} = -\ 0.136\ \mathrm{V}$$

Therefore, the voltage of this electrochemical cell is computed as follows:

$$\Delta V = (V_{\mathrm{Pb}}^{0} - V_{\mathrm{Sn}}^{0}) - \frac{0.0592}{2} \log \frac{[\mathrm{Sn}^{2+}]}{[\mathrm{Pb}^{2+}]}$$

$$= \left[-0.126\ \mathrm{V} - (-0.136\ \mathrm{V})\right] - \frac{0.0592}{2} \log \left[\frac{0.25\ M}{5 \times 10^{-2}\ M}\right]$$

$$= -\ 0.0107\ \mathrm{V}$$

(b) Since ΔV is negative, the spontaneous cell direction is just the reverse of that above, or

$$\mathrm{Sn}^{2+} + \mathrm{Pb} \rightarrow \mathrm{Sn} + \mathrm{Pb}^{2+}$$

17.5 *An Fe/Fe*$^{2+}$ *concentration cell is constructed in which both electrodes are pure iron. The Fe*$^{2+}$ *concentration for one cell half is 0.5 M and for the other cell half is 2 × 10*$^{-2}$ *M. Is a voltage generated between the two cell halves? If so, what is its magnitude and which electrode will be oxidized? If no voltage is produced, explain this result.*

Solution

This problem calls for us to determine whether or not a voltage is generated in a Fe/Fe^{2+} concentration cell, and, if so, its magnitude. Let us label the Fe cell having a 0.5 *M* Fe^{2+} solution as cell 1, and the other as cell 2. Furthermore, assume that oxidation occurs within cell 2, wherein $[\mathrm{Fe}_2^{2+}]$ = 2 × 10^{-2} *M*. Hence, we write the electrochemical reaction as follows:

$$\mathrm{Fe}_2 + \mathrm{Fe}_1^{2+} \rightarrow \mathrm{Fe}_2^{2+} + \mathrm{Fe}_1$$

and, employing Equation 17.20 leads to

$$\Delta V = -\frac{0.0592}{2}\log\frac{[\mathrm{Fe}_2^{2+}]}{[\mathrm{Fe}_1^{2+}]}$$

$$= -\frac{0.0592}{2}\log\left[\frac{2 \times 10^{-2}\,M}{0.5\,M}\right] = +0.0414\ \mathrm{V}$$

Therefore, a voltage of 0.0414 V is generated when oxidation occurs in cell 2, the one having the lower Fe^{2+} concentration—i.e., 2 × 10^{-2} *M*.

17.6 *An electrochemical cell is composed of pure copper and pure cadmium electrodes immersed in solutions of their respective divalent ions. For a 6.5 × 10^{-2} M concentration of Cd^{2+}, the cadmium electrode is oxidized, yielding a cell potential of 0.775 V. Calculate the concentration of Cu^{2+} ions if the temperature is 25°C.*

Solution

We are asked to calculate the concentration of Cu^{2+} ions in a copper-cadmium electrochemical cell. The electrochemical reaction that occurs within this cell is as follows:

$$\mathrm{Cd} + \mathrm{Cu}^{2+} \rightarrow \mathrm{Cd}^{2+} + \mathrm{Cu}$$

while ΔV = 0.775 V and $[\mathrm{Cd}^{2+}]$ = 6.5 × 10^{-2} *M*. Thus, Equation 17.20 is written in the following form (assuming that n = 2 since 2 electrons are involved in the above reaction):

$$\Delta V = \left(V^0_{\mathrm{Cu}} - V^0_{\mathrm{Cd}}\right) - \frac{0.0592}{2} \log \frac{[\mathrm{Cd}^{2+}]}{[\mathrm{Cu}^{2+}]}$$

Furthermore, this equation may be rewritten as follows:

$$-\frac{\Delta V - \left(V^0_{\mathrm{Cu}} - V^0_{\mathrm{Cd}}\right)}{0.0296} = \log \frac{[\mathrm{Cd}^{2+}]}{[\mathrm{Cu}^{2+}]}$$

Solving this expression for $[\mathrm{Cu}^{2+}]$ yields the following equation:

$$[\mathrm{Cu}^{2+}] = [\mathrm{Cd}^{2+}] \exp\left[+(2.303)\frac{\Delta V - \left(V^0_{\mathrm{Cu}} - V^0_{\mathrm{Cd}}\right)}{0.0296}\right]$$

The standard potentials from Table 17.1 are as follows:

V^0_{Cu} = +0.340 V

V^0_{Cd} = – 0.403 V

Therefore, we compute the concentration of the copper ion as

$$[\mathrm{Cu}^{2+}] = (6.5 \times 10^{-2}\ M) \exp\left[+ (2.303)\, \frac{0.775\ \mathrm{V} - \{0.340\ \mathrm{V} - (-\ 0.403\ \mathrm{V})\}}{0.0296}\right]$$

$$= 0.784\ M$$

17.7 *An electrochemical cell is constructed such that on one side a pure Zn electrode is in contact with a solution containing* Zn^{2+} *ions at a concentration of* 10^{-2} *M. The other cell half consists of a pure Pb electrode immersed in a solution of* Pb^{2+} *ions that has a concentration of* 10^{-4} *M. At what temperature will the potential between the two electrodes be +0.568 V?*

Solution

This problem asks for us to calculate the temperature for a zinc-lead electrochemical cell when the potential between the Zn and Pb electrodes is +0.568 V. On the basis of their relative positions in the standard emf series (Table 17.1), assume that Zn is oxidized and Pb is reduced. Thus, the electrochemical reaction that occurs within this cell is as follows:

$$\mathrm{Pb^{2+} + Zn \rightarrow Pb + Zn^{2+}}$$

Under these circumstances, Equation 17.20 is written in the following form:

$$\Delta V = \left(V_{\mathrm{Pb}}^{0} - V_{\mathrm{Zn}}^{0}\right) - \frac{RT}{nF}\ln\frac{[\mathrm{Zn}^{2+}]}{[\mathrm{Pb}^{2+}]}$$

(*Note:* we denote the Faraday constant by an "*F*" rather than with the symbol used in the textbook.)

Solving this expression for the temperature *T* gives the following:

$$T = -\frac{nF}{R}\left[\frac{\Delta V - \left(V_{\mathrm{Pb}}^{0} - V_{\mathrm{Zn}}^{0}\right)}{\ln\frac{[\mathrm{Zn}^{2+}]}{[\mathrm{Pb}^{2+}]}}\right]$$

The standard potentials Zn and Pb from Table 17.1 are as follows:

$V_{\mathrm{Zn}}^{0} = -0.763$ V

$V_{\mathrm{Pb}}^{0} = -0.126$ V

Also *n* in Equation 17.20 has a value of 2 since twos electrons are involved in the above electrochemical reaction. Therefore, we solve for the temperature as follows:

$$T = -\frac{(2)(96{,}500\ \mathrm{C/mol})}{8.31\ \mathrm{J/mol\text{-}K}}\left[\frac{0.568\ \mathrm{V} - \left\{-\ 0.126\ \mathrm{V} - (-\ 0.763\ \mathrm{V})\right\}}{\ln\left(\frac{10^{-2}\ M}{10^{-4}\ M}\right)}\right]$$

$$= 348\ \mathrm{K} = 75°\mathrm{C}$$

17.8 *For the following pairs of alloys that are coupled in seawater, predict the possibility of corrosion; if corrosion is probable, note which metal/alloy will corrode.*

(a) Aluminum and cast iron

(b) Inconel and nickel

(c) Cadmium and zinc

(d) Brass and titanium

(e) Low-carbon steel and copper

Solution

This problem asks, for several pairs of alloys that are immersed in seawater, to predict whether or not corrosion is possible, and if it is possible, to note which alloy will corrode. In order to make these predictions it is necessary to use the galvanic series, Table 17.2. If both of the alloys in the pair reside within the same set of brackets in this table, then galvanic corrosion is unlikely. However, if the two alloys do not lie within the same set of brackets, then that alloy appearing lower in the table will experience corrosion.

(a) For the aluminum-cast iron couple, corrosion is possible, and aluminum will corrode.

(b) For the Inconel-nickel couple, corrosion is unlikely inasmuch as both alloys appear within the same set of brackets (in both active and passive states).

(c) For the cadmium-zinc couple, corrosion is possible, and zinc will corrode.

(d) For the brass-titanium pair, corrosion is possible, and brass will corrode.

(e) For the low-carbon steel-copper couple, corrosion is possible, and the low-carbon steel will corrode.

17.9 *(a) From the galvanic series (Table 17.2), cite three metals/alloys that may be used to galvanically protect cast iron.*

(b) As Concept Check 17.4(b) notes, galvanic corrosion is prevented by making an electrical contact between the two metals in the couple and a third metal that is anodic to the other two. Using the galvanic series, name one metal that could be used to protect a nickel-steel galvanic couple.

Solution

(a) The following metals and alloys may be used to galvanically protect cast iron: aluminum/aluminum alloys, cadmium, zinc, magnesium/magnesium alloys. These metals/alloys appear below cast iron in the galvanic series, Table 17.2.

(b) The following metals/alloys could be used to protect a nickel-steel galvanic couple: aluminum/aluminum alloys, cadmium, zinc, magnesium/magnesium alloys; all these metal/alloys are anodic to (i.e., lie below) steel in the galvanic series.

Corrosion Rates

17.10 *Demonstrate that the constant K in Equation 17.23 will have values of 534 and 87.6 for the CPR in units of mpy and mm/yr, respectively.*

Solution

This problem is just an exercise in unit conversions. The parameter *K* in Equation 17.23 must convert the units of W, ρ, A, and t, into the unit scheme for the CPR.

For CPR in mpy (mil/yr)

$$K = \frac{W(\text{mg})(1\ \text{g}/1000\ \text{mg})}{\rho\left(\dfrac{\text{g}}{\text{cm}^3}\right)\left(\dfrac{2.54\ \text{cm}}{\text{in.}}\right)^3\left[A(\text{in.}^2)\right]\left(\dfrac{1\ \text{in.}}{1000\ \text{mil}}\right)[t(\text{h})]\left(\dfrac{1\ \text{day}}{24\ \text{h}}\right)\left(\dfrac{1\ \text{yr}}{365\ \text{days}}\right)}$$

$$= 534.6$$

For CPR in mm/yr

$$K = \frac{W(\text{mg})(1\ \text{g}/1000\ \text{mg})}{\rho\left(\dfrac{\text{g}}{\text{cm}^3}\right)\left(\dfrac{1\ \text{cm}}{10\ \text{mm}}\right)^3\left[A(\text{cm}^2)\right]\left(\dfrac{10\ \text{mm}}{\text{cm}}\right)^2[t(\text{h})]\left(\dfrac{1\ \text{day}}{24\ \text{h}}\right)\left(\dfrac{1\ \text{yr}}{365\ \text{days}}\right)}$$

$$= 87.6$$

17.11 *A piece of corroded metal alloy plate was found in a submerged ocean vessel. It was estimated that the original area of the plate was 800 cm*^{2} *and that approximately 7.6 kg had corroded away during the submersion. Assuming a corrosion penetration rate of 4 mm/yr for this alloy in seawater, estimate the time of submersion in years. The density of the alloy is 4.5 g/cm*^{3}.

Solution

This problem calls for us to compute the time of submersion of a metal plate. In order to solve this problem, we must first rearrange Equation 17.23 such that time, *t*, is the dependent variable:

$$t = \frac{KW}{\rho A(\text{CPR})}$$

Thus, using values for the various parameters given in the problem statement yields the following value for *t:*

$$t = \frac{(87.6)\left(7.6\ \text{kg}\right)(10^6\ \text{mg/kg})}{\left(4.5\ \text{g/cm}^3\right)\left(800\ \text{cm}^2\right)(4\ \text{mm/yr})}$$

$$= 4.62\ \times\ 10^4\ \text{h} = 5.27\ \text{yr}$$

17.12 *A thick steel sheet of area 100 in.*^{2} *is exposed to air near the ocean. After a one-year period it was found to experience a weight loss of 485 g due to corrosion. To what rate of corrosion, in both mpy and mm/yr, does this correspond?*

Solution

This problem asks for us to calculate the CPR in both mpy and mm/yr for a thick steel sheet of area 100 in.^{2} which experiences a weight loss of 485 g after one year. Employment of Equation 17.23 (and taking the density of steel to be 7.9 g/cm^3–Table B.1, Appendix B) leads to the following CPR values

$$\text{CPR(mm/yr)} = \frac{KW}{\rho A t}$$

$$= \frac{(87.6)(485\text{ g})(10^3\text{ mg/g})}{(7.9\text{ g/cm}^3)(100\text{ in.}^2)(2.54\text{ cm/in.})^2(24\text{ h/day})(365\text{ day/yr})(1\text{ yr})}$$

$$= 0.952\text{ mm/yr}$$

Now for the CPR in mpy we have

$$\text{CPR(mpy)} = \frac{(534)(485\text{ g})(10^3\text{ mg/g})}{(7.9\text{ g/cm}^3)(100\text{ in.}^2)(24\text{ h/day})(365\text{ day/yr})(1\text{ yr})}$$

$$= 37.4\text{ mpy}$$

17.13 *(a) Demonstrate that the CPR is related to the corrosion current density i (A/cm^2) through the expression*

$$\mathrm{CPR} = \frac{KAi}{n\rho} \tag{17.38}$$

where K is a constant, A is the atomic weight of the metal experiencing corrosion, n is the number of electrons associated with the ionization of each metal atom, and ρ is the density of the metal.

(b) Calculate the value of the constant K for the CPR in mpy and i in μA/cm^2 (10^{-6} A/cm^2).

Solution

Possibly the best way to conduct this demonstration is by using a unit dimensional analysis. The corrosion rate, *r*, in Equation 17.24 has the units (SI) of

$$r = \frac{i}{nF} = \frac{\mathrm{C/m^2\text{-}s}}{(\mathrm{unitless})(\mathrm{C/mol})} = \frac{\mathrm{mol}}{\mathrm{m^2\text{-}s}}$$

(*Note:* we denote the Faraday constant by an "*F*" rather than with the symbol used in the textbook.)

The units of CPR in Equation 17.23 are length/time, or in the SI scheme, m/s. In order to convert the above expression to the units of m/s it is necessary to multiply *r* by the atomic weight *A* and divide by the density *ρ* as follows:

$$\frac{rA}{\rho} = \frac{(\mathrm{mol/m^2\text{-}s})(\mathrm{g/mol})}{\mathrm{g/m^3}} = \mathrm{m/s} \tag{S17.13a}$$

From this dimensional analysis, and since we can convert the units corrosion rate *r* to units of corrosion penetration rate CPR using Equation S17.13a, then it is the case that the CPR is proportional to *r* according to the following expression:

$$\mathrm{CPR} = K_1\left(\frac{rA}{\rho}\right) \tag{S17.13b}$$

Here K_1 is a constant, and the units for the CPR are correct. If we now substitute the expression for *r* in Equation 17.24 into Equation S17.13b, the following expression results:

$$\mathrm{CPR} = K_1\left(\frac{i}{nF}\right)\left(\frac{A}{\rho}\right) = \frac{K_1 iA}{nF\rho} \tag{S17.13c}$$

Inasmuch as both K_1 and *F* in Equation S17.13c are constants, then their ratio is also a constant, and if we designate that constant *K*, then

$$K = \frac{K_1}{F}$$

and Equation S17.13c becomes

$$\mathbf{CPR} = \frac{KAi}{n\rho}$$

Which is Equation 17.38.

(b) Now we will calculate the value of *K* in order to give the CPR in mpy for *i* in μA/cm^2 (10^{-6} A/cm^2). It should be noted that the units of A (in μA/cm^2) are amperes or C/s. Substitution of the units normally used in Equation S17.13c—viz.,

$$\mathbf{CPR} = K_1 \frac{Ai}{nF\rho}$$

leads to the following:

$$= K_1 \ \frac{\mathbf{(g/mol)(C/s\text{-}cm^2)}}{\mathbf{(unitless)(C/mol)(g/cm^3)}} = \mathbf{cm/s}$$

Since we want the CPR in mpy, that *i* is given in μA/cm^2, and realizing that $K = K_1/F$, leads to the following:

$$K = \left(\frac{1}{96{,}500 \ \text{C/mol}}\right)\left(\frac{10^{-6} \ \text{A/cm}^2}{\mu\text{A/cm}^2}\right)\left(\frac{1 \ \text{in.}}{2.54 \ \text{cm}}\right)\left(\frac{10^3 \ \text{mil}}{\text{in.}}\right)\left(\frac{3.1536 \times 10^7 \ \text{s}}{\text{yr}}\right)$$

$$= 0.129$$

17.14 *Using the results of Problem 17.13, compute the corrosion penetration rate, in mpy, for the corrosion of iron in HCl (to form* Fe^{2+} *ions) if the corrosion current density is* 8×10^{-5} *A/cm*^{2}.

Solution

We are asked to compute the CPR in mpy for the corrosion of Fe for a corrosion current density of 8×10^{-5} A/cm^2 (80 μA/cm^2). From Problem 17.13, the value of K in Equation 17.38 is 0.129; furthermore, the density of iron is 7.9 g/cm^3, the atomic weight of iron is 55.85 g/mol, and the value of n is 2 (since 2 electrons are removed from every iron atom to form an Fe^{2+} ion). Therefore, the CPR is computed as follows:

$$\text{CPR} = \frac{KAi}{n\rho}$$

$$= \frac{(0.129)(55.85 \text{ g/mol})(80\ \mu\text{A/cm}^2)}{(2)(7.9 \text{ g/cm}^3)} = 36.5 \text{ mpy}$$

Prediction of Corrosion Rates

17.15 *(a) Cite the major differences between activation and concentration polarizations.*

(b) Under what conditions is activation polarization rate controlling?

(c) Under what conditions is concentration polarization rate controlling?

Answer

(a) Activation polarization is the condition wherein a reaction rate is controlled by one step in a series of steps that takes place at the slowest rate. For corrosion, activation polarization is possible for both oxidation and reduction reactions. Concentration polarization occurs when a reaction rate is limited by diffusion in a solution. For corrosion, concentration polarization is possible only for reduction reactions.

(b) Activation polarization is rate controlling when the reaction rate is low and/or the concentration of active species in the liquid solution is high.

(c) Concentration polarization is rate controlling when the reaction rate is high and/or the concentration of active species in the liquid solution is low.

17.16 (a) *Describe the phenomenon of dynamic equilibrium as it applies to oxidation and reduction electrochemical reactions.*

(b) What is the exchange current density?

Answer

(a) The phenomenon of dynamic equilibrium is the state wherein oxidation and reduction reactions are occurring at the same rate such that there is no net observable reaction.

(b) The exchange current density is just the current density, which is related to both the rates of oxidation and reduction (which are equal) according to Equation 17.26 for the dynamic equilibrium state.

17.17 *Nickel experiences corrosion in an acid solution according to the reaction*

$$Ni + 2H^+ \rightarrow Ni^{2+} + H_2$$

The rates of both oxidation and reduction half-reactions are controlled by activation polarization.

(a) Compute the rate of oxidation of Ni (in mol/cm^2*-s), given the following activation polarization data:*

For Nickel	***For Hydrogen***
$V_{(Ni/Ni^{2+})} = -0.25V$	$V_{(H^+/H_2)} = 0V$
$i_0 = 10^{-8}$ A/cm^2	$i_0 = 6 \times 10^{-7}$ A/cm^2
$\beta = +0.12$	$\beta = -0.10$

(b) Compute the value of the corrosion potential.

Solution

(a) This portion of the problem asks that we compute the rate of oxidation for Ni given that both the oxidation and reduction reactions are controlled by activation polarization, and also given the polarization data for both nickel oxidation and hydrogen reduction. The first thing necessary is to establish relationships of the form of Equation 17.25 for the potentials of both oxidation and reduction reactions. Next we will set these expressions equal to one another, and then solve for the value of i which is really the corrosion current density, i_c. Finally, the corrosion rate may be calculated using Equation 17.24. The two potential expressions are as follows:

For hydrogen reduction

$$V_H = V_{(H^+/H_2)} + \beta_H \log\left(\frac{i}{i_{0_H}}\right)$$

And for Ni oxidation

$$V_{Ni} = V_{(Ni/Ni^{2+})} + \beta_{Ni} \log\left(\frac{i}{i_{0_{Ni}}}\right)$$

Setting $V_H = V_{Ni}$ and solving for log i (i.e., log i_c) leads to the following expression:

$$\log i_c = \left(\frac{1}{\beta_{Ni} - \beta_H}\right)\left[V_{(H^+/H_2)} - V_{(Ni/Ni^{2+})} - \beta_H \log i_{0_H} + \beta_{Ni} \log i_{0_{Ni}}\right]$$

And, incorporating values for the various parameters provided in the problem statement leads to

$$\log i_c = \left[\frac{1}{0.12 - (-0.10)}\right]\left[0 - (-0.25) - (-0.10)\{\log(6 \times 10^{-7})\} + (0.12)\{\log(10^{-8})\}\right]$$

$$= -6.055$$

From which i_c may be determined as follows:

$$i_c = 10^{-6.055} = 8.81 \times 10^{-7} \text{ A/cm}^2$$

$$= 8.81 \times 10^{-7} \text{ C/s-cm}^2$$

Now, from Equation 17.24

$$r = \frac{i_c}{nF}$$

we compute the oxidation rate as follows:

$$r = \frac{8.81 \times 10^{-7} \text{ C/s-cm}^2}{(2)(96{,}500 \text{ C/mol})} = 4.56 \times 10^{-12} \text{ mol/cm}^2\text{-s}$$

(*Note:* in the above discussion we denote the Faraday constant by an "*F*" rather than with the symbol used in the textbook.)

(b) Now we are asked to compute the value of the corrosion potential, V_c. This is possible by using either of the above equations for V_H or V_{Ni} and substituting for i the value determined above for i_c. This is done as follows (using the expression for hydrogen reduction):

$$V_c = V_{(H^+/H_2)} + \beta_H \log\left(\frac{i_c}{i_{0_H}}\right)$$

$$= 0 + (-0.10 \text{ V}) \log\left(\frac{8.81 \times 10^{-7} \text{ A/cm}^2}{6 \times 10^{-7} \text{ A/cm}^2}\right) = -0.0167 \text{ V}$$

17.18 *The corrosion rate is to be determined for some divalent metal M in a solution containing hydrogen ions. The following corrosion data are known about the metal and solution:*

For Metal M	***For Hydrogen***
$V_{(\mathrm{M/M^{2+}})} = -\ 0.90\ \mathrm{V}$	$V_{(\mathrm{H^+/H_2})} = 0\ \mathrm{V}$
$i_0 = 10^{-12}\ A/cm^2$	$i_0 = 10^{-10}\ A/cm^2$
$\beta = +0.10$	$\beta = -0.15$

(a) Assuming that activation polarization controls both oxidation and reduction reactions, determine the rate of corrosion of metal M (in mol/cm^2*-s).*

(b) Compute the corrosion potential for this reaction.

Solution

(a) This portion of the problem asks that we compute the rate of oxidation for a divalent metal M given that both the oxidation and reduction reactions are controlled by activation polarization, and also given the polarization data for both M oxidation and hydrogen reduction. The first thing necessary is to establish relationships of the form of Equation 17.25 for the potentials of both oxidation and reduction reactions. Next we will set these expressions equal to one another, and then solve for the value of i which is the corrosion current density, i_c. Finally, the corrosion rate may be calculated using Equation 17.24. The two potential expressions are as follows:

For hydrogen reduction

$$V_\mathrm{H} = V_{(\mathrm{H^+/H_2})} + \beta_\mathrm{H} \log\left(\frac{i}{i_{0_\mathrm{H}}}\right)$$

And for M oxidation

$$V_\mathrm{M} = V_{(\mathrm{M/M^{2+}})} + \beta_\mathrm{M} \log\left(\frac{i}{i_{0_\mathrm{M}}}\right)$$

Setting $V_\mathrm{H} = V_\mathrm{M}$ and solving for log i (that is, log i_c) leads to the following expression:

$$\log i_c = \left(\frac{1}{\beta_\mathrm{M} - \beta_\mathrm{H}}\right)\left[V_{(\mathrm{H^+/H_2})} - V_{(\mathrm{M/M^{2+}})} - \beta_\mathrm{H} \log i_{0_\mathrm{H}} + \beta_\mathrm{M} \log i_{0_\mathrm{M}}\right]$$

And, incorporating values for the various parameters provided in the problem statement results in the following:

$$\log i_c = \left[\frac{1}{0.10 - (-0.15)}\right]\left[0 - (-0.90) - (-0.15)\left\{\log(10^{-10})\right\} + (0.10)\left\{\log(10^{-12})\right\}\right]$$

$$= -7.20$$

From which i_c may be determined as follows:

$$i_c = 10^{-7.20} = 6.31 \times 10^{-8} \text{ A/cm}^2$$

$$= 6.31 \times 10^{-8} \text{ C/s-cm}^2$$

Now, from Equation 17.24

$$r = \frac{i_c}{nF}$$

we compute the oxidation rate as follows:

$$r = \frac{6.31 \times 10^{-8} \text{ C/s-cm}^2}{(2)(96,500 \text{ C/mol})} = 3.27 \times 10^{-13} \text{ mol/cm}^2\text{-s}$$

(*Note:* in the above discussion, we denote the Faraday constant by an "*F*" rather than with the symbol used in the textbook.)

(b) Now it becomes necessary to compute the value of the corrosion potential, V_c. This is possible by using either of the above equations for V_H or V_M and substituting for i the value determined above for i_c. This is done as follows (using the expression for hydrogen reduction):

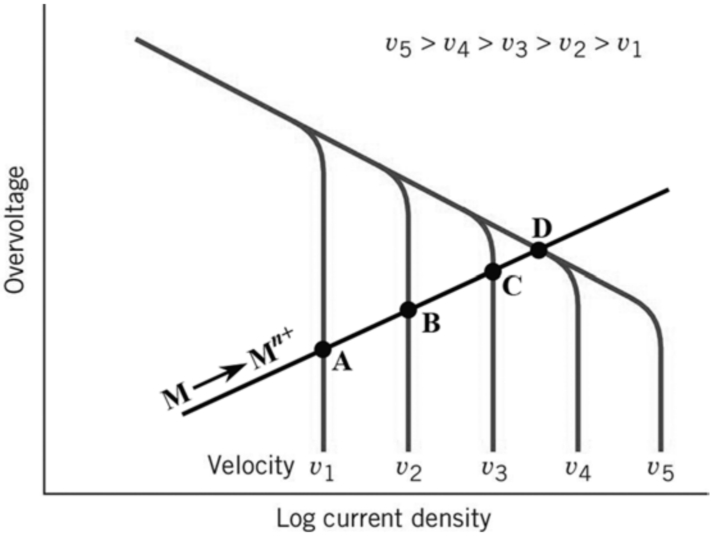
$$V_c = V_{(H^+/H_2)} + \beta_H \log\left(\frac{i_c}{i_{0_H}}\right)$$

$$= 0 + (-0.15 \text{ V}) \log\left(\frac{6.31 \times 10^{-8} \text{ A/cm}^2}{10^{-10} \text{ A/cm}^2}\right) = -0.420 \text{ V}$$

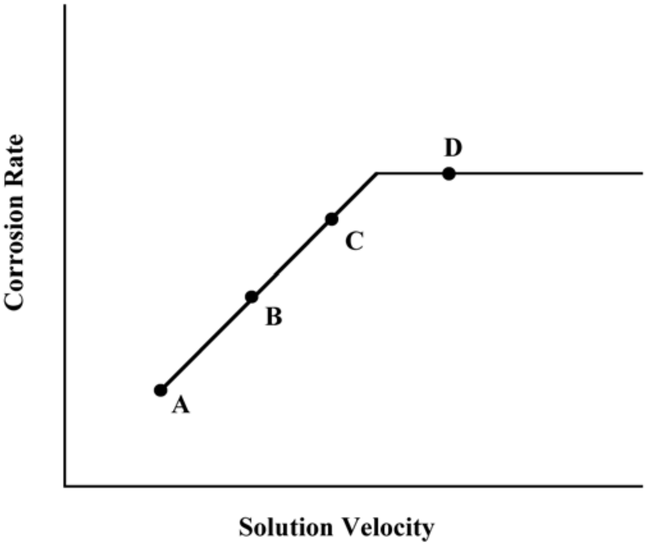
17.19 *The influence of increasing solution velocity on the overvoltage-versus log-current density behavior for a solution that experiences combined activation–concentration polarization is indicated in Figure 17.27. On the basis of this behavior, make a schematic plot of corrosion rate versus solution velocity for the oxidation of a metal; assume that the oxidation reaction is controlled by activation polarization.*

Solution

This problem asks that we make a schematic plot of corrosion rate versus solution velocity. The reduction reaction is controlled by combined activation-concentration polarization for which the overvoltage versus logarithm current density is shown in Figure 17.27. The oxidation of the metal is controlled by activation polarization, such that the electrode kinetic behavior for the combined reactions would appear schematically as shown below.



Thus, the plot of corrosion rate versus solution velocity would be as follows:



The corrosion rate initially increases with increasing solution velocity (for velocities v_1, v_2, and v_3), corresponding to intersections in the concentration polarization regions for the reduction reaction. However, for the higher solution velocities (v_4 and v_5), the metal oxidation line intersects the reduction reaction curve in the linear activation polarization region, and, thus, the reaction becomes independent of solution velocity.

Passivity

17.20 *Briefly describe the phenomenon of passivity. Name two common types of alloy that passivate.*

Answer

Passivity is the loss of chemical reactivity, under particular environmental conditions, of normally active metals and alloys. Stainless steels and aluminum alloys often passivate.

17.21 *Why does chromium in stainless steels make them more corrosion resistant than plain carbon steels in many environments?*

Answer

The chromium in stainless steels causes a very thin and highly adherent surface coating to form over the surface of the alloy, which protects it from further corrosion. For plain carbon steels, rust, instead of this adherent coating, forms.

Forms of Corrosion

17.22 *For each form of corrosion other than uniform, do the following:*

(a) Describe why, where, and the conditions under which the corrosion occurs.

(b) Cite three measures that may be taken to prevent or control it.

For each of the forms of corrosion, the conditions under which it occurs, and measures that may be taken to prevent or control it are outlined in Section 17.7.

17.23 *Briefly explain why cold-worked metals are more susceptible to corrosion than non-cold-worked metals.*

Answer

Cold-worked metals are more susceptible to corrosion than non-cold-worked metals because of the increased dislocation density for the latter. The region in the vicinity of a dislocation that intersects the surface is at a higher energy state, and, therefore, is more readily attacked by a corrosive solution.

17.24 *Briefly explain why, for a small anode-to-cathode area ratio, the corrosion rate will be higher than for a large ratio.*

Answer

For a small anode-to-cathode area ratio, the corrosion rate will be higher than for a large ratio. The reason for this is that for some given current flow associated with the corrosion reaction, for a small area ratio the current density at the anode will be greater than for a large ratio. The corrosion rate is proportional to the current density (i) according to Equation 17.24.

17.25 *For a concentration cell, briefly explain why corrosion occurs at the region having the lower concentration.*

Solution

For a concentration cell, corrosion occurs at that region having the lower concentration. In order to explain this phenomenon let us consider an electrochemical cell consisting of two divalent metal M electrodes each of which is immersed in a solution containing a different concentration of its M^{2+} ion; let us designate the low and high concentrations of M^{2+} as $[M_L^{2+}]$ and $[M_H^{2+}]$, respectively. Now assuming that reduction and oxidation reactions occur in the high- and low-concentration solutions, respectively, let us determine the cell potential in terms of the two $[M^{2+}]$'s; if this potential is positive then we have chosen the solutions in which the reduction and oxidation reactions appropriately.

Thus, the two half-reactions in the form of Equations 17.16 are as follows:

$$M_H^{2+} + 2e^- \rightarrow M \qquad V_M^0$$

$$M \rightarrow M_L^{2+} + 2e^- \qquad -V_M^0$$

Whereas the overall cell reaction is the following:

$$M_H^{2+} + M \rightarrow M + M_L^{2+}$$

From Equation 17.19, this yields a cell potential of

$$\Delta V = V_M^0 - V_M^0 - \frac{RT}{nF}\ln\left(\frac{[M_L^{2+}]}{[M_H^{2+}]}\right)$$

$$= -\frac{RT}{nF}\ln\left(\frac{[M_L^{2+}]}{[M_H^{2+}]}\right)$$

(*Note:* we denote the Faraday constant in the above equations by an "*F*" rather than with the symbol used in the textbook.)

Inasmuch as $[M_L^{2+}] < [M_H^{2+}]$ then the natural logarithm of the $[M^{2+}]$ ratio is negative, which yields a positive value for ΔV. This means that the electrochemical reaction is spontaneous as written, or that oxidation occurs at the electrode having the lower M^{2+} concentration.

Corrosion Prevention

17.26 *(a) What are inhibitors?*

(b) What possible mechanisms account for their effectiveness?

Answer

(a) Inhibitors are substances that, when added to a corrosive environment in relatively low concentrations, decrease the environment's corrosiveness.

(b) Possible mechanisms that account for the effectiveness of inhibitors are: (1) elimination of a chemically active species in the solution; (2) attachment of inhibitor molecules to the corroding surface so as to interfere with either the oxidation or reduction reaction; and (3) the formation of a very thin and protective coating on the corroding surface.

17.27 *Briefly describe the two techniques that are used for galvanic protection.*

Answer

Descriptions of the two techniques used for galvanic protection are as follows:

(1) A sacrificial anode is electrically coupled to the metal piece to be protected, which anode is also situated in the corrosion environment. The sacrificial anode is a metal or alloy that is chemically more reactive in the particular environment. It (the anode) preferentially oxidizes, and, upon giving up electrons to the other metal, protects it from electrochemical corrosion.

(2) An impressed current from an external dc power source provides excess electrons to the metallic structure to be protected.

Oxidation

17.28 *For each of the metals listed in the following table, compute the Pilling–Bedworth ratio. Also, on the basis of this value, specify whether you would expect the oxide scale that forms on the surface to be protective, and then justify your decision. Density data for both the metal and its oxide are also tabulated.*

Metal	***Metal Density (g/cm^3)***	***Metal Oxide***	***Oxide Density (g/cm^3)***
Mg	*1.74*	*MgO*	*3.58*
V	*6.11*	V_2O_5	*3.36*
Zn	*7.13*	*ZnO*	*5.61*

Solution

For this problem we are given, for three metals, their densities, oxide chemical formulas, and oxide densities, and are asked to compute the Pilling-Bedworth ratios, and then to specify whether or not the oxide scales that form will be protective. The form of the equation used to calculate this ratio for some metal is either Equation 17.32 or Equation 17.33. For magnesium, oxidation occurs by the following reaction:

$$\mathbf{Mg} + \frac{1}{2}\mathbf{O_2} \rightarrow \mathbf{MgO}$$

Therefore, we use Equation 17.32 to make the calculation as follows:

$$\mathbf{P-B\ ratio} = \frac{A_{\mathbf{MgO}}\rho_{\mathbf{Mg}}}{A_{\mathbf{Mg}}\rho_{\mathbf{MgO}}}$$

$$= \frac{(40.31\ \mathrm{g/mol})(1.74\ \mathrm{g/cm^3})}{(24.31\ \mathrm{g/mol})(3.58\ \mathrm{g/cm^3})} = 0.81$$

(In this computation we used 24.31 g/mol and 40.31 g/mol, respectively for the atomic weights of Mg and MgO.)

Thus, this would probably be a nonprotective oxide film since the P-B ratio is less than unity; to be protective, this ratio should be between one and two.

The oxidation reaction for V is given by the following reaction:

$$2\mathbf{V} + \frac{5}{2}\mathbf{O_2} \rightarrow \mathbf{V_2O_5}$$

We calculate the P-B ratio using Equation 17.33 as follows:

$$\text{P} - \text{B ratio} = \frac{A_{\text{V}_2\text{O}_5}\rho_{\text{V}}}{(2)A_{\text{V}}\rho_{\text{V}_2\text{O}_5}}$$

$$= \frac{(181.88\ \text{g/mol})(6.11\ \text{g/cm}^3)}{(2)(50.94\ \text{g/mol})(3.36\ \text{g/cm}^3)} = 3.25$$

Hence, the film would be nonprotective since the ratio does not lie between one and two.

Now for Zn, the reaction for its oxidation is as follows:

$$\text{Zn} + \frac{1}{2}\text{O}_2 \rightarrow \text{ZnO}$$

Therefore, the Pilling-Bedworth ratio is determined as follows:

$$\text{P} - \text{B ratio} = \frac{A_{\text{ZnO}}\rho_{\text{Zn}}}{A_{\text{Zn}}\rho_{\text{ZnO}}}$$

$$= \frac{(81.41\ \text{g/mol})(7.13\ \text{g/cm}^3)}{(65.41\ \text{g/mol})(5.61\ \text{g/cm}^3)} = 1.58$$

Thus, the ZnO film would probably be protective since the ratio is between one and two.

17.29 *According to Table 17.3, the oxide coating that forms on silver should be nonprotective, and yet Ag does not oxidize appreciably at room temperature and in air. How do you explain this apparent discrepancy?*

Answer

Silver does not oxidize appreciably at room temperature and in air even though, according to Table 17.3, the oxide coating should be nonprotective. The reason for this is that the oxidation of silver in air is not thermodynamically favorable; therefore, the lack of a reaction is independent of whether or not a protective scale forms.

17.30 *The following table gives weight gain–time data for the oxidation of nickel at an elevated temperature.*

***W* (mg/cm^2)**	***Time (min)***
0.527	*10*
0.857	*30*
1.526	*100*

(a) Determine whether the oxidation kinetics obey a linear, parabolic, or logarithmic rate expression.

(b) Now compute W after a time of 600 min.

Solution

(a) For this part of the problem we are given weight gain-time data for the oxidation of nickel at an elevated temperature, and are asked to determine whether the oxidation kinetics obey a linear, parabolic, or logarithmic rate expression; rate expressions for these three kinetic modes are described by Equations 17.35, 17.34, and 17.36, respectively. (Note: there is an additional data point at $W = 0$ and $t = 0$ since there is no weight gain at time = zero.)

The data are plotted as weight gain versus time in Figure S17.30a.

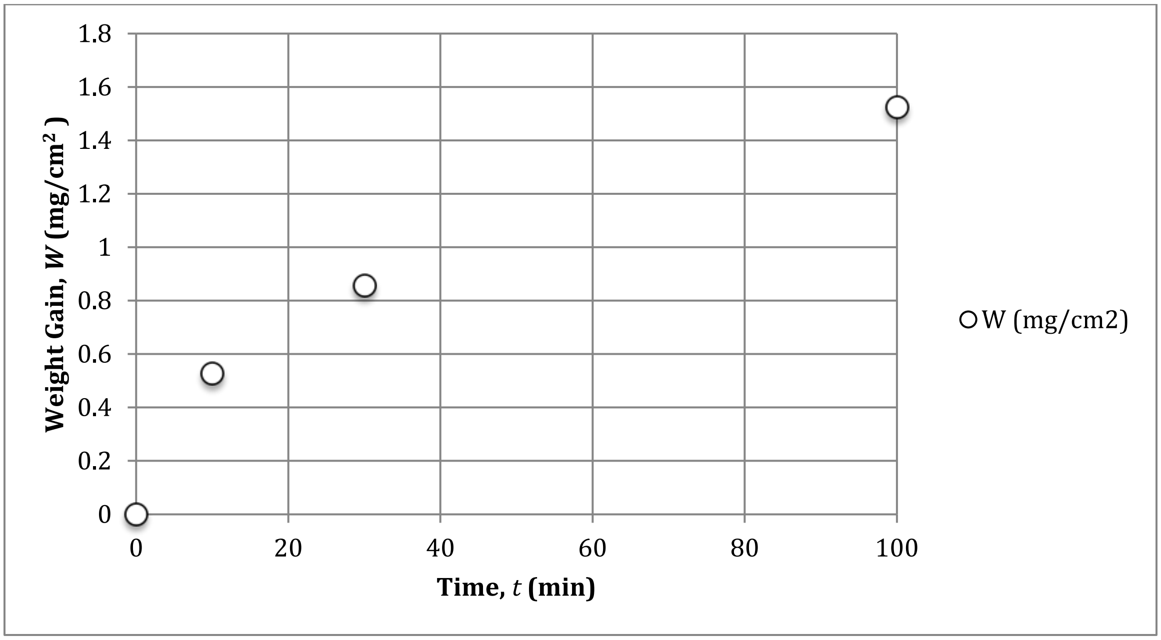


Figure S17.30a. Plot of weight gain versus time for the oxidation of nickel.

We can see by inspection of this plot that the experimental data do not obey a linear model.

Let us now investigate the possibility of logarithmic kinetics—that is Equation 17.36

$$W = K_4 \log(K_5 t + K_6)$$

In order to determine the validity of logarithmic kinetics it is necessary to fit a curve to the data, from which values of the constants K_4, K_5, and K_6 may be determined. This process, sometimes termed “data regression, " can be carried out using a number of computational tools. However, one common technique is to fit the equation by minimizing the sum of the squares of the differences between fitted data and experimental data. For example, for logarithmic kinetics, “best fit” values for the three K_4, K_5, and K_6 constants in Equation 17.36 are as follows:

$K_4 = 1.316$

$K_5 = 0.1299$

$K_6 = 1.019$

The curve incorporating these values into Equation 17.36 is superimposed on the plot of experimental W-versus-t data in Figure S17.30b. As may be noted, the curve fit is reasonable, but does not pass though all of the experimental data points.

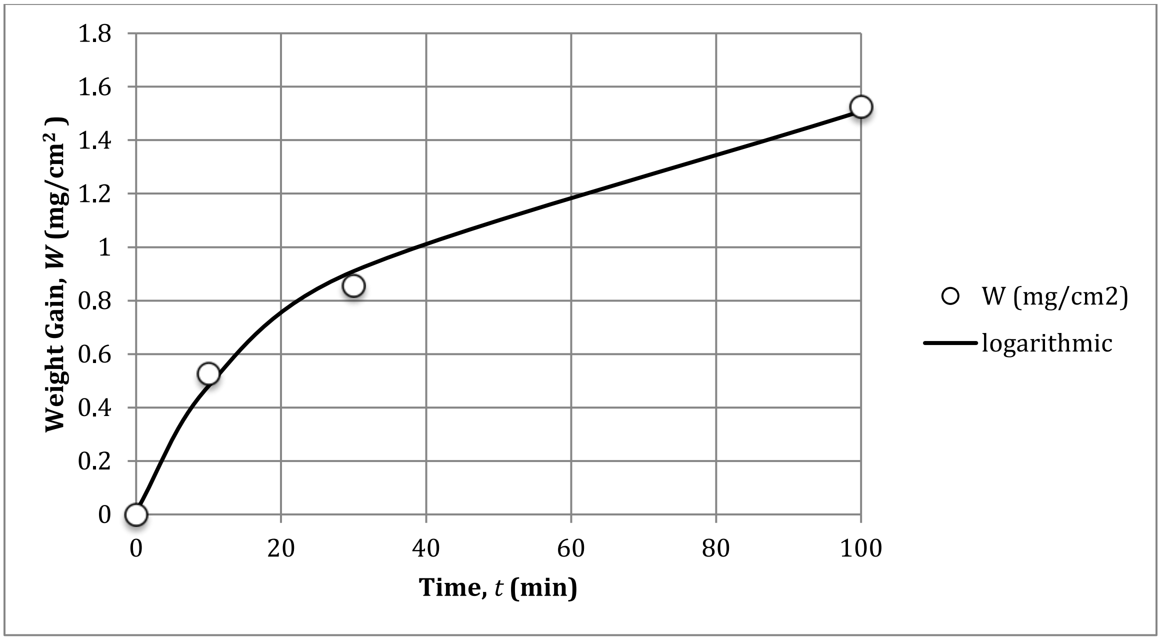


Figure S17.30b. Plot of weight gain versus time; also a curve that has been fitted to the logarithmic rate equation.

Let us now investigate parabolic kinetics in the same manner using Equation 17.34—i.e.,

$$W^2 = K_1 t + K_2$$

Manipulation of this expression such that W is the dependent variable leads to the following expression:

$$W = \sqrt{K_1 t + K_2}$$

Subjection of the experimental data to the "best-fit" linear regression process for logarithmic kinetics produces the following values for the two K_1 and K_2 constants:

$$K_1 = 0.02385$$

$$K_2 = 0.00000$$

When these data are incorporated into Equation 17.34 and then plotted as W versus t, as in Figure S17.30c, it may be noted that the resulting curve passes through all of the experimental data points—i.e., there is a satisfactory fit of these data with the logarithmic rate equation.

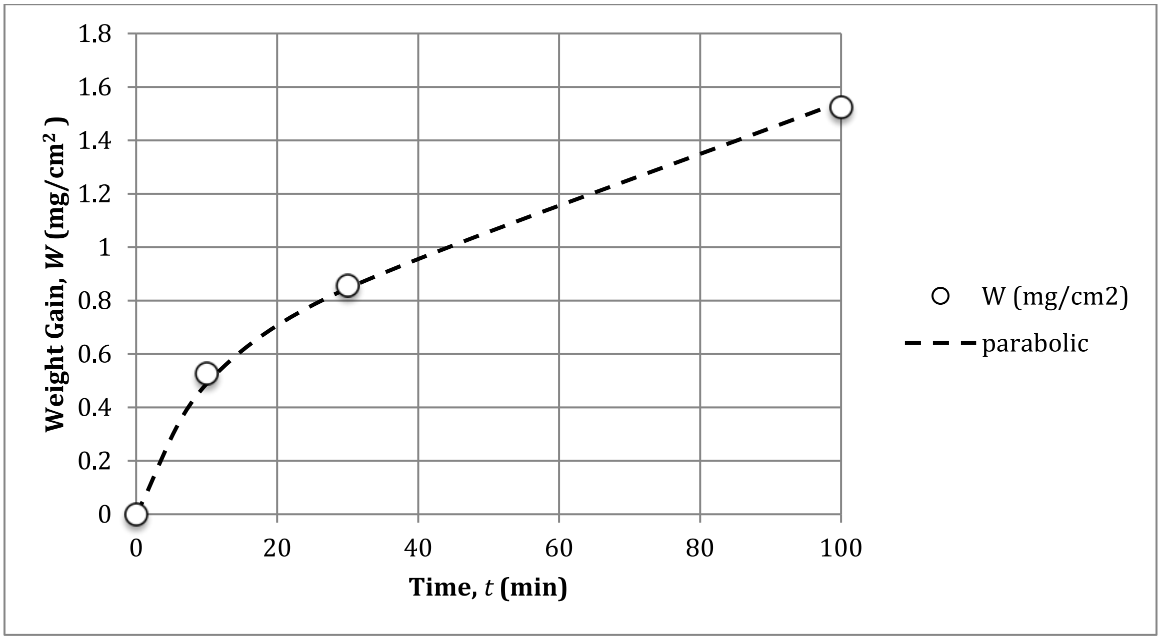


Figure S17.30c. Plot of weight gain versus time; also a curve that has been fitted to the parabolic rate equation.

(b) In order to determine the value of W after 600 min, we use Equation 17.34 with the values of K_1 and K_2 determined in part (a). Thus,

$$W = \sqrt{K_1 t + K_2}$$

$$= \sqrt{(0.0239)(600\text{ min}) + 0.0000}$$

$$= 3.78\text{ mg/cm}^2$$

17.31 *The following table gives weight gain–time data for the oxidation of some metal at an elevated temperature.*

***W* (mg/cm^2)**	***Time (min)***
6.16	*100*
8.59	*250*
12.72	*1000*

(a) Determine whether the oxidation kinetics obey a linear, parabolic, or logarithmic rate expression.

(b) Now compute W after a time of 5000 min.

Solution

(a) For this part of the problem we are given weight gain-time data for the oxidation of some metal at an elevated temperature, and are asked to determine whether the oxidation kinetics obey a linear, parabolic, or logarithmic rate expression; rate expressions for these three kinetic modes are described by Equations 17.35, 17.34, and 17.36, respectively. (Note: there an additional data point at *W* = 0 and *t* = 0 since there is no weight gain at time = zero.)

The data are plotted as weight gain versus time in Figure S17.31a.

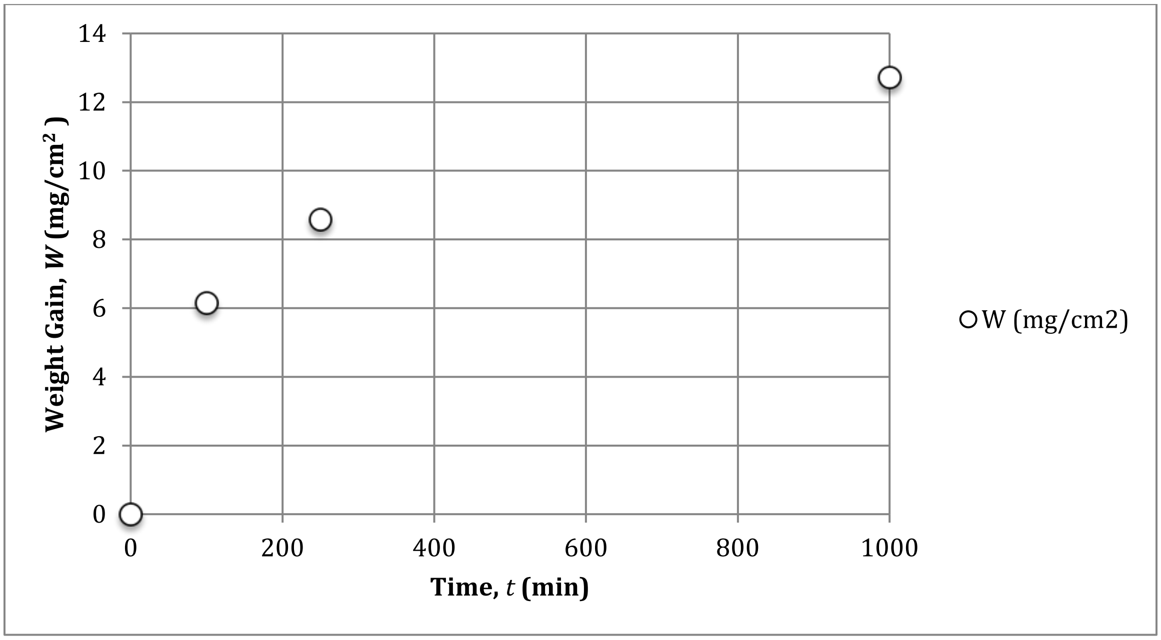


Figure S17.31a. Plot of weight gain versus time for the elevated-temperature oxidation of a metal.

We can see by inspection of this plot that the experimental data do not obey a linear model.

Let us now investigate the possibility of parabolic kinetics—that is Equation 17.34

$$W^2 = K_1 t + K_2$$

Manipulation of this expression such that W is the dependent variable leads to the following expression:

$$W = \sqrt{K_1 t + K_2}$$

In order to determine the validity of parabolic kinetics it is necessary to fit a curve to the data, from which values of the constants K_1 and K_2 may be determined. This process, sometimes termed "data regression, " can be carried out using a number of computational tools. However, one common technique is to fit the equation by minimizing the sum of the squares of the differences between fitted data and experimental data. For example, for parabolic kinetics, "best fit" values of the constants K_1 and K_2 in Equation 17.34 are as follows:

$K_1 = 0.1973$

$K_2 = 0.0000$

The curve incorporating these values of K_1 and K_2 into Equation 17.34 is superimposed on the plot of experimental W-versus-t data in Figure S17.31b. As may be noted, the curve fit is unsatisfactory since this fitted curve doesn't pass through any of the experimental data points.

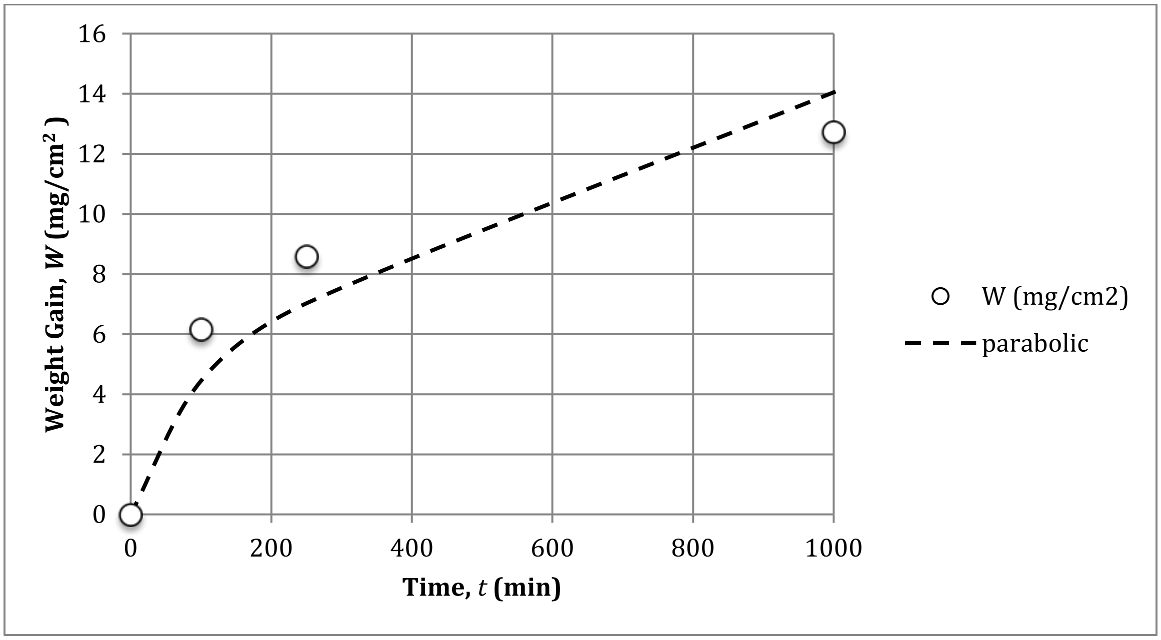


Figure S17.31b. Plot of weight gain versus time; also a curve that has been fitted to the parabolic rate equation.

Let us now investigate logarithmic kinetics in the same manner using Equation 17.36—i.e.,

$$W = K_4 \log \left(K_5 t + K_6\right)$$

Subjection of the experimental data to the "best-fit" linear regression process for logarithmic kinetics produces the following values for the three K_4, K_5, and K_6 constants:

$K_4 = 6.961$
$K_5 = 0.0658$
$K_6 = 1.001$

When these data are incorporated into Equation 17.36 and then plotted as W versus t, as in Figure S17.31c, it may noted that the resulting curve passes through all of the experimental data points—i.e., there is a satisfactory fit of these data with the logarithmic rate equation.

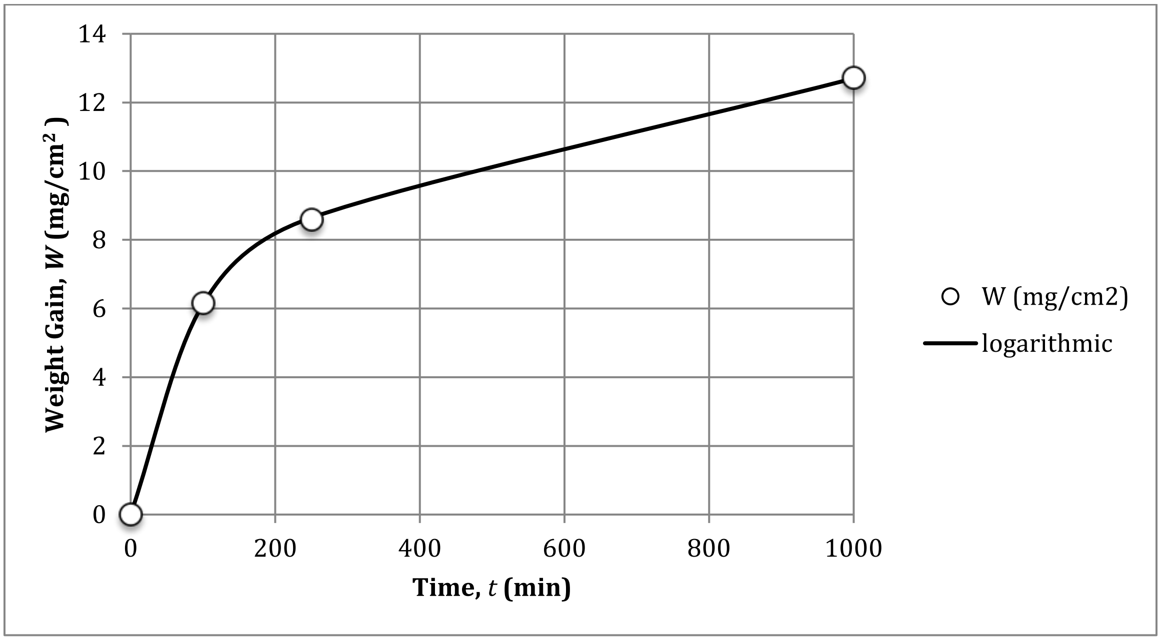


Figure S17.31c. Plot of weight gain versus time; also a curve that has been fitted to the logarithmic rate equation.

(b) In order to determine the value of W after 5000 min, we use Equation 17.36 with the values of K_4, K_5, and K_6 determined in part (a). Thus,

$$W = K_4 \log \left(K_5 t + K_6\right)$$

$$= (6.961) \log \left[(0.0658)(5000 \text{ min}) + (1.001)\right]$$

$$= 17.53 \text{ mg/cm}^2$$

17.32 *The following table gives weight gain–time data for the oxidation of some metal at an elevated temperature.*

***W* (mg/cm^2)**	***Time (min)***
1.54	*10*
23.24	*150*
95.37	*620*

(a) Determine whether the oxidation kinetics obey a linear, parabolic, or logarithmic rate expression.

(b) Now compute W after a time of 1200 min.

Solution

(a) For this part of the problem we are given weight gain-time data for the oxidation of some metal at an elevated temperature, and are asked to determine whether the oxidation kinetics obey a linear, parabolic, or logarithmic rate expression; rate expressions for these three kinetic modes are described by Equations 17.35, 17.34, and 17.36, respectively. (Note: there is an additional data point at $W = 0$ and $t = 0$ since there is no weight gain at time = zero.)

The data are plotted as weight gain versus time in Figure S17.32a.

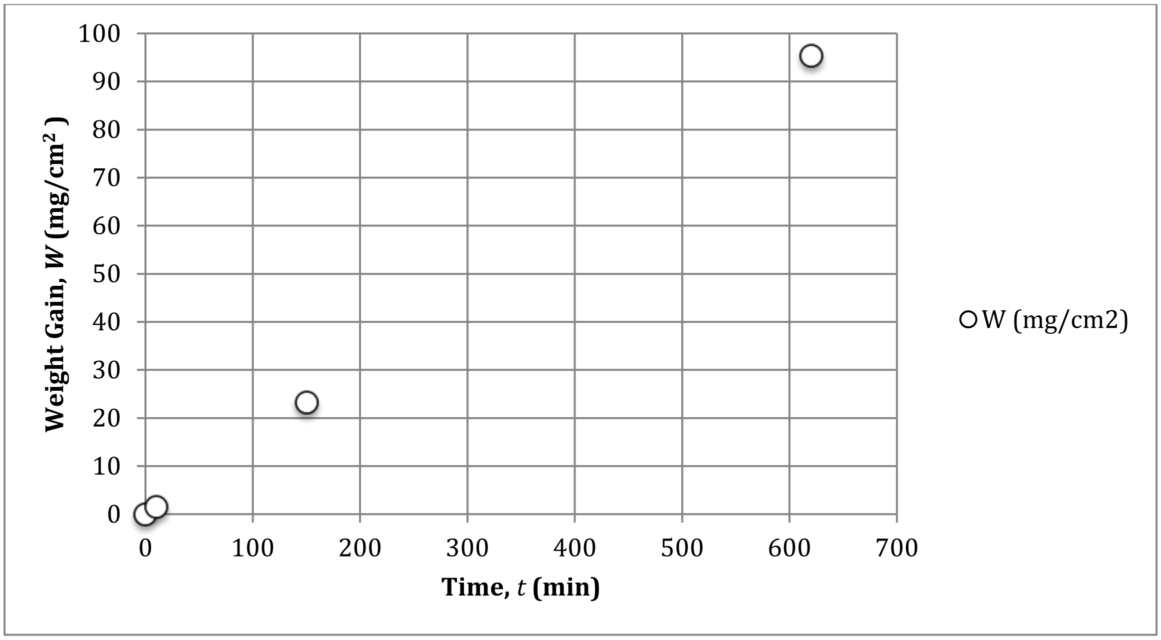


Figure S17.32a. Plot of weight gain versus time for the high-temperature oxidation of a metal.

We can see by inspection of this plot that the experimental data will obey a linear model—that is Equation 17.35.

$$W = K_3 t$$

In order to verify the validity of linear kinetics it is necessary to fit a straight line to data, from which the value of the constant K_3 may be determined. This process, sometimes termed “data regression, " can be carried out using a number of computational tools. However, one common technique is to fit the equation by minimizing the sum of the squares of the differences between fitted data and experimental data. For example, for linear kinetics, the “best fit” values for the K_3 constant in Equation 17.35 is as follows:

$$K_3 = 0.1539$$

When this value is incorporated into Equation 17.35 and then plotted as W versus t, as in Figure S17.32b, it may noted that the resulting curve passes through all of the experimental data points—i.e., there is a satisfactory fit of these data with the linear rate equation.

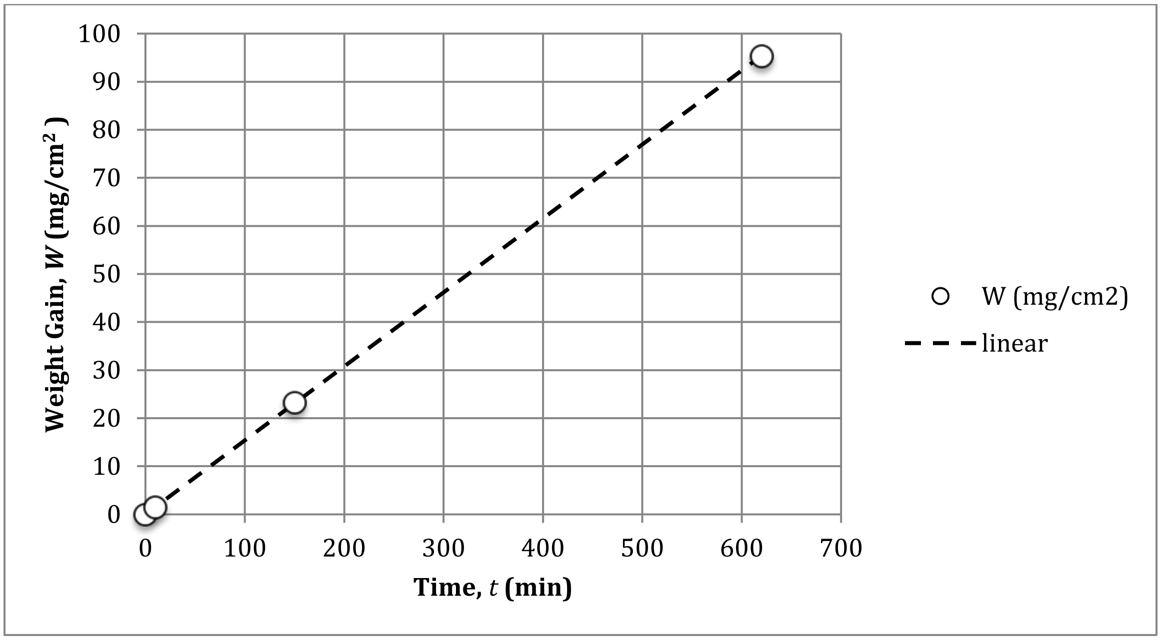


Figure S17.32b. Plot of weight gain versus time; also a curve that has been fitted to the linear rate equation.

(b) In order to determine the value of W after 1200 min, we use Equation 17.35 with the value of K_3 determined in part (a). Thus,

$$W = K_3 t$$

$$= (0.1539)(1200 \text{ min})$$

$$= 184.7 \text{ mg/cm}^2$$

DESIGN PROBLEMS

17.D1 *A brine solution is used as a cooling medium in a steel heat exchanger. The brine is circulated within the heat exchanger and contains some dissolved oxygen. Suggest three methods other than cathodic protection for reducing corrosion of the steel by the brine. Explain the rationale for each suggestion.*

Solution

Possible methods that may be used to reduce corrosion of the heat exchanger by the brine solution are as follows:

(1) Reduce the temperature of the brine; normally, the rate of a corrosion reaction increases with increasing temperature.

(2) Change the composition of the brine; the corrosion rate is often quite dependent on the composition of the corrosion environment.

(3) Remove as much dissolved oxygen as possible. Under some circumstances, the dissolved oxygen may form bubbles, which can lead to erosion-corrosion damage.

(4) Minimize the number of bends and/or changes in pipe contours in order to minimize erosion-corrosion.

(5) Add inhibitors.

(6) Avoid connections between different metal alloys.

17.D2 *Suggest an appropriate material for each of the following applications, and, if necessary, recommend corrosion prevention measures that should be taken. Justify your suggestions.*

(a) Laboratory bottles to contain relatively dilute solutions of nitric acid

(b) Barrels to contain benzene

(c) Pipe to transport hot alkaline (basic) solutions

(d) Underground tanks to store large quantities of high-purity water

(e) Architectural trim for high-rise buildings

Solution

This question asks that we suggest appropriate materials, and if necessary, recommend corrosion prevention measures that should be taken for several specific applications. These are as follows:

(a) Laboratory bottles to contain relatively dilute solutions of nitric acid. Probably the best material for this application would be polytetrafluoroethylene (PTFE). The reasons for this are: (1) it is flexible and will not easily break if dropped; and (2) PTFE is resistant to this type of acid, as noted in Table 17.4.

(b) Barrels to contain benzene. Poly(ethylene terephthalate) (PET) or an epoxy would be suited for this application, since both are resistant to degradation by benzene (C_6H_6, Table 17.4), and are less expensive than the other two satisfactory materials listed in Table 17.4 (PTFE and PEEK); (material costs are tabulated in Appendix C).

(c) Pipe to transport hot alkaline (basic) solutions. The best material for this application would probably be a nickel alloy (Section 11.3). Polymeric materials listed in Table 17.4 would not be suitable inasmuch as the solutions are hot.

(d) Underground tanks to store large quantities of high-purity water. The outside of the tanks should probably be some type of low-carbon steel that is cathodically protected (Sections 17.8 and 17.9). Inside the steel shell should be coated with an inert polymeric material; polytetrafluoroethylene or some other fluorocarbon would probably be the material of choice (Table 17.4).

(e) Architectural trim for high-rise buildings. The most likely candidate for this application would probably be an aluminum alloy. Aluminum and its alloys are relatively corrosion resistant in normal atmospheres (Section 17.8), retain their lustrous appearance, and are relatively inexpensive (Appendix C).

17.D3 *Each student (or group of students) is to find a real-life corrosion problem that has not been solved, conduct a thorough investigation as to the cause(s) and type(s) of corrosion, and propose possible solutions for the problem, indicating which of the solutions is best and why. Submit a report that addresses these issues.*

Each student or group of students is to submit their own report on a corrosion problem investigation that was conducted.

FUNDAMENTALS OF ENGINEERING QUESTIONS AND PROBLEMS

17.1FE *Which of the following is (are) reduction reaction(s)?*

(A) $Fe^{2+} \rightarrow Fe^{3+} + e^-$

(B) $Al^{3+} + 3e^- \rightarrow Al$

(C) $H_2 \rightarrow 2H^+ + 2e^-$

(D) *Both A and C*

Solution

The correct answer is B. Reduction of an atom involves the gain of electrons; thus the reduction reaction is as follows:

$$\mathrm{Al}^{3+} + 3e^- \rightarrow \mathrm{Al}$$

17.2FE *An electrochemical cell is composed of pure nickel and pure iron electrodes immersed in solutions of their divalent ions. If the concentrations of* Ni^{2+} *and* Fe^{2+} *ions are 0.002 M and 0.40 M, respectively, what voltage is generated at 25°C? (The respective standard reduction potentials for Ni and Fe are –0.250 V and –0.440 V.)*

(A) –0.76 V *(C) +0.12 V*

(B) –0.26 V *(D) +0.76 V*

Solution

It is first necessary to make an assumption as to which of Ni and Fe is oxidized and which is reduced. Since Fe has the more negative standard potential, let's assume that Fe is oxidized. This being the case, the electrochemical reaction is as follows:

$$\begin{array}{r}
\mathrm{Fe} \rightarrow \mathrm{Fe}^{2+} + 2e^- \\
\mathrm{Ni}^{2+} + 2e^- \rightarrow \mathrm{Ni} \\
\hline
\mathrm{Ni}^{2+} + \mathrm{Fe} \rightarrow \mathrm{Ni} + \mathrm{Fe}^{2+}
\end{array}$$

This choice will be substantiated or refuted on the basis of the sign of the ΔV that results (i.e., if $\Delta V > 0$, then the reaction will occur as written; if ΔV is negative then the reaction will occur in the reverse direction).

The cell potential between these two metal electrodes may be calculated using Equation 17.20, as follows:

$$\Delta V = (V^0_{\mathrm{Ni}} - V^0_{\mathrm{Fe}}) - \frac{0.0592}{2}\log\frac{[\mathrm{Fe}^{2+}]}{[\mathrm{Ni}^{2+}]}$$

Incorporation of values for V^0_{Ni}, V^0_{Fe}, $[\mathrm{Ni}^{2+}]$, and $[\mathrm{Fe}^{2+}]$ given in the problem statement leads to the following:

$$\Delta V = [-0.250\ \mathrm{V} - (-0.440\ \mathrm{V})] - \frac{0.0592}{2}\log\frac{[0.40M]}{[0.002M]}$$

$$= +\ 0.12\ \mathrm{V}$$

Since this value of ΔV is positive, the electrochemical reaction is as written above, and the correct answer is C.

17.3FE *Which of the following describes crevice corrosion?*

(A) Corrosion that occurs preferentially along grain boundaries

(B) Corrosion that results from the combined action of an applied tensile stress and a corrosive environment

(C) Localized corrosion that may be initiated at a surface defect

(D) Corrosion that is produced by a difference in concentration of ions or dissolved gases in the electrolyte

Solution

The correct answer is D. Crevice corrosion results *from a difference in concentration of ions or dissolved gases in the electrolyte.*

17.4FE *Polymer deterioration by swelling may be reduced by which of the following?*

(A) Increasing degree of crosslinking, increasing molecular weight, and increasing degree of crystallinity

(B) Decreasing degree of crosslinking, decreasing molecular weight, and decreasing degree of crystallinity

(C) Increasing degree of crosslinking, increasing molecular weight, and decreasing degree of crystallinity

(D) Decreasing degree of crosslinking, increasing molecular weight, and increasing degree of crystallinity

Answer

The correct answer is A. Polymer deterioration by swelling may be reduced by *increasing the degree of crosslinking*, *increasing the molecular weight*, and *increasing the degree of crystallinity*.

CHAPTER 18

ELECTRICAL PROPERTIES

PROBLEM SOLUTIONS

Ohm's Law

Electrical Conductivity

18.1 *(a) Compute the electrical conductivity of a cylindrical silicon specimen 7.0 mm (0.28 in.) diameter and 57 mm (2.25 in.) in length in which a current of 0.25 A passes in an axial direction. A voltage of 24 V is measured across two probes that are separated by 45 mm (1.75 in.).*

(b) Compute the resistance over the entire 57 mm (2.25 in.) of the specimen.

Solution

This problem calls for us to compute the electrical conductivity and resistance of a silicon specimen.

(a) We use Equations 18.4 and 18.3 for the conductivity, as follows:

$$\sigma = \frac{1}{\rho}$$

$$= \frac{1}{\frac{VA}{Il}} = \frac{Il}{VA}$$

$$= \frac{Il}{V\pi\left(\frac{d}{2}\right)^2}$$

Since the cross-sectional area of a cylinder having a diameter *d* is

$$A = \pi\left(\frac{d}{2}\right)^2$$

Now, incorporation of values for the several parameters provided in the problem statement, leads to the following:

$$\sigma = \frac{Il}{V\pi\left(\frac{d}{2}\right)^2}$$

$$= \frac{(0.25\ \text{A})(45 \times 10^{-3}\ \text{m})}{(24\ \text{V})(\pi)\left(\frac{7.0 \times 10^{-3}\ \text{m}}{2}\right)^2} = 12.2\ (\Omega\text{-m})^{-1}$$

(b) The resistance, *R*, over the entire specimen length may be computed by combining and rearranging Equations 18.2 and 18.4 as follows:

$$R = \frac{l\rho}{A}$$

$$= \frac{l\left(\frac{1}{\sigma}\right)}{A} = \frac{l}{\sigma A}$$

$$= \frac{l}{\sigma\pi\left(\frac{d}{2}\right)^2}$$

The value of *R* may be computed upon entering values given in the problem statement into the preceding expression:

$$R = \frac{l}{\sigma\pi\left(\frac{d}{2}\right)^2}$$

$$= \frac{57 \times 10^{-3}\ \text{m}}{\left[12.2\ (\Omega\text{-m})^{-1}\right](\pi)\left(\frac{7.0 \times 10^{-3}\ \text{m}}{2}\right)^2} = 121.4\ \Omega$$

18.2 *An aluminum wire 10 m long must experience a voltage drop of less than 1.0 V when a current of 5 A passes through it. Using the data in Table 18.1, compute the minimum diameter of the wire.*

Solution

For this problem, given that an aluminum wire 10 m long must experience a voltage drop of less than 1.0 V when a current of 5 A passes through it, we are to compute the minimum diameter of the wire. Combining Equations 18.3 and 18.4 and solving for the cross-sectional area *A* leads to

$$A = \frac{\rho I l}{V}$$

$$= \frac{\left(\frac{1}{\sigma}\right) I l}{V} = \frac{I l}{\sigma V}$$

From Table 18.1, for aluminum, the conductivity, $\sigma = 3.8 \times 10^7$ (Ω-m)$^{-1}$. Furthermore, inasmuch as $A = \pi\left(\frac{d}{2}\right)^2$ for a cylindrical wire, then we may rewrite the previous equation as follows:

$$\pi\left(\frac{d}{2}\right)^2 = \frac{I l}{\sigma V}$$

And, solving for the diameter *d* yields the following expression:

$$d = \sqrt{\frac{4 I l}{\pi \sigma V}}$$

When values for the several parameters given in the problem statement are incorporated into this expression, we obtain the following value for *d:*

$$d = \sqrt{\frac{(4)(5\text{ A})(10\text{ m})}{(\pi)\left[3.8 \times 10^7\ (\Omega\text{-m})^{-1}\right](1.0\text{ V})}}$$

$$= 1.29 \times 10^{-3}\text{ m} = 1.29\text{ mm}$$

18.3 *A plain carbon steel wire 3 mm in diameter is to offer a resistance of no more than 20 Ω. Using the data in Table 18.1, compute the maximum wire length.*

Solution

This problem asks that we compute, for a plain carbon steel wire of 3 mm diameter, the maximum length such that the resistance will not exceed 20 Ω. From Table 18.1 for a plain carbon steel $\sigma = 0.6 \times 10^{7}$ (Ω-m)$^{-1}$. If d is the wire diameter then, combining Equations 18.2 and 18.4 and then solving for the length l leads to the following:

$$l = \frac{RA}{\rho}$$

$$= \frac{RA}{\frac{1}{\sigma}} = R\sigma A$$

$$= R\sigma\pi\left(\frac{d}{2}\right)^{2}$$

Upon inserting values for R and d given in the problem statement and the value of σ taken from Table 18.1 yields the following value for the wire length:

$$l = R\sigma\pi\left(\frac{d}{2}\right)^{2}$$

$$= (20\ \Omega)\left[0.6 \times 10^{7}\ (\Omega\text{-m})^{-1}\right](\pi)\left(\frac{3 \times 10^{-3}\ \text{m}}{2}\right)^{2} = 848\ \text{m}$$

18.4 *Demonstrate that the two Ohm's law expressions, Equations 18.1 and 18.5, are equivalent.*

Solution

Let us demonstrate, by appropriate substitution and algebraic manipulation, that Equation 18.5 may be made to take the form of Equation 18.1. Now, Equation 18.5 is just

$$J = \sigma E$$

(In this equation we represent the electric field with an "*E*".) But, by definition, *J* is just the current density, the current per unit cross-sectional area, or $J = \frac{I}{A}$. Also, the electric field is defined by $E = \frac{V}{l}$ (Equation 18.6). Substitution of these expressions for *J* and *E* into Equation 18.5 leads to the following:

$$\frac{I}{A} = \sigma \frac{V}{l} \tag{S18.4a}$$

Also, when we combine Equations 18.2 and 18.4, then

$$\sigma = \frac{1}{\rho}$$

$$= \frac{1}{\frac{RA}{l}} = \frac{l}{RA}$$

Then substitution of this expression for σ into Equation S18.4a yields the following:

$$\frac{I}{A} = \left(\frac{l}{RA}\right)\left(\frac{V}{l}\right)$$

Solving for *V* from this expression gives $V = IR$, which is just Equation 18.1.

18.5 *(a) Using the data in Table 18.1, compute the resistance of an aluminum wire 5 mm (0.20 in.) in diameter and 5 m (200 in.) in length.*

(b) What would be the current flow if the potential drop across the ends of the wire is 0.04 V?

(c) What is the current density?

(d) What is the magnitude of the electric field across the ends of the wire?

Solution

(a) In order to compute the resistance of this aluminum wire it is necessary to combine Equations 18.2 and 18.4, and then solve for the resistance in terms of the conductivity; this is done as follows:

$$R = \frac{\rho l}{A}$$

$$= \frac{\left(\frac{1}{\sigma}\right) l}{A} = \frac{l}{\sigma A}$$

$$= \frac{l}{\sigma \pi \left(\frac{d}{2}\right)^2}$$

From Table 18.1, the conductivity of aluminum is 3.8 × 10^7 $(\Omega\text{-m})^{-1}$. Therefore, we solve for the resistance as follows:

$$R = \frac{l}{\sigma \pi \left(\frac{d}{2}\right)^2}$$

$$= \frac{5 \text{ m}}{\left[3.8 \times 10^7 \ (\Omega\text{-m})^{-1}\right](\pi)\left(\frac{5 \ \times 10^{-3} \text{ m}}{2}\right)^2}$$

$$= 6.70 \ \times \ 10^{-3} \ \Omega$$

(b) If V = 0.04 V then, from Equation 18.1, the current, I, is computed as follows:

$$I = \frac{V}{R} = \frac{0.04 \text{ V}}{6.70 \times 10^{-3} \ \Omega} = 6.00 \text{ A}$$

(c) The current density is equal to the current divided by the specimen cross-sectional area as

$$J = \frac{I}{A} = \frac{I}{\pi\left(\frac{d}{2}\right)^2} = \frac{6.00\ \text{A}}{\pi\left(\frac{5\ \times 10^{-3}\ \text{m}}{2}\right)^2} = 3.06\ \times\ 10^5\ \text{A/m}^2$$

(d) The electric field is computed using Equation 18.6 as follows:

$$E = \frac{V}{l} = \frac{0.04\ \text{V}}{5\ \text{m}} = 8.0\ \times\ 10^{-3}\ \text{V/m}$$

Electronic and Ionic Conduction

18.6 *What is the distinction between electronic and ionic conduction?*

Answer

When a current arises from a flow of electrons, the conduction is termed *electronic*; for *ionic conduction*, the current results from the net motion of charged ions.

Energy Band Structures in Solids

18.7 *How does the electron structure of an isolated atom differ from that of a solid material?*

Answer

For an isolated atom, there exist discrete electron energy states (arranged into shells and subshells); each state may be occupied by, at most, two electrons, which must have opposite spins. On the other hand, an electron band structure is found for solid materials; within each band exist closely spaced yet discrete electron states, each of which may be occupied by, at most, two electrons, having opposite spins. The number of electron states in each band will equal the total number of corresponding states contributed by all of the atoms in the solid.

Conduction in Terms of Band and Atomic Bonding Models

18.8 *In terms of electron energy band structure, discuss reasons for the difference in electrical conductivity among metals, semiconductors, and insulators.*

Answer

For metallic materials, there are vacant electron energy states adjacent to the highest filled state; thus, very little energy is required to excite large numbers of electrons into conducting states. These electrons are those that participate in the conduction process, and, because there are so many of them, metals are good electrical conductors.

There are no empty electron states adjacent to and above filled states for semiconductors and insulators, but rather, an energy band gap across which electrons must be excited in order to participate in the conduction process. Thermal excitation of electrons occurs, and the number of electrons excited will be less than for metals, and will depend on the band gap energy. For semiconductors, the band gap is narrower than for insulators; consequently, at a specific temperature more electrons will be excited for semiconductors, giving rise to higher conductivities.

Electron Mobility

18.9 *Briefly state what is meant by the drift velocity and mobility of a free electron.*

Answer

The drift velocity of a free electron is the average electron velocity in the direction of the force imposed by an electric field.

The mobility is the proportionality constant between the drift velocity and the electric field. It is also a measure of the frequency of scattering events (and is inversely proportional to the frequency of scattering).

18.10 *(a) Calculate the drift velocity of electrons in silicon at room temperature and when the magnitude of the electric field is 500 V/m.*

(b) Under these circumstances, how long does it take an electron to traverse a 25-mm (1-in.) length of crystal?

Solution

(a) The drift velocity of electrons in Si may be determined using Equation 18.7. Since the room temperature mobility of electrons is 0.145 $\mathrm{m^2/V\text{-}s}$ (Table 18.3), and the electric field is 500 V/m (as stipulated in the problem statement), the drift velocity is equal to

$$v_d = \mu_e E$$

$$= (0.145\ \mathrm{m^2/V\text{-}s})(500\ \mathrm{V/m}) = 72.5\ \mathrm{m/s}$$

(b) The time, *t*, required to traverse a given length, *l* (= 25 mm), is just the length divided by the drift velocity, as follows:

$$t = \frac{l}{v_d} = \frac{25 \times 10^{-3}\ \mathrm{m}}{72.5\ \mathrm{m/s}} = 3.45 \times 10^{-4}\ \mathrm{s}$$

18.11 *At room temperature the electrical conductivity and the electron mobility for aluminum are 3.8 × 10^7 $(\Omega\cdot m)^{-1}$ and 0.0012 $m^2/V\cdot s$, respectively.*

(a) Compute the number of free electrons per cubic meter for aluminum at room temperature.

(b) What is the number of free electrons per aluminum atom? Assume a density of 2.7 g/cm^3.

Solution

(a) The number of free electrons per cubic meter for aluminum at room temperature may be computed using rearranged form of Equation 18.8 as follows:

$$n = \frac{\sigma}{|e|\,\mu_e}$$

$$= \frac{3.8 \times 10^7\,(\Omega\text{-m})^{-1}}{(1.602 \times 10^{-19}\text{ C})(0.0012\text{ m}^2/\text{V-s})}$$

$$= 1.98 \times 10^{29}\text{ m}^{-3}$$

(b) In order to calculate the number of free electrons per aluminum atom, we must first determine the number of copper atoms per cubic meter, N_{Al}. From Equation 4.2 (and using the atomic weight for Al found inside the front cover—viz. 26.98 g/mol) then the values of N_{Al} is determined as follows:

$$N_{\text{Al}} = \frac{N_A\,\rho'}{A_{\text{Al}}}$$

$$= \frac{(6.022 \times 10^{23}\text{ atoms/mol})(2.7\text{ g/cm}^3)(10^6\text{ cm}^3/\text{m}^3)}{26.98\text{ g/mol}}$$

$$= 6.03 \times 10^{28}\text{ m}^{-3}$$

(*Note*: in the above expression, density is represented by ρ' in order to avoid confusion with resistivity which is designated by ρ.) And, finally, the number of free electrons per aluminum atom (n/N_{Al}) is equal to the following:

$$\frac{n}{N_{\text{Al}}} = \frac{1.98 \times 10^{29}\text{ m}^{-3}}{6.03 \times 10^{28}\text{ m}^{-3}} = 3.28\text{ electrons/Al atom}$$

18.12 *(a) Calculate the number of free electrons per cubic meter for silver, assuming that there are 1.3 free electrons per silver atom. The electrical conductivity and density for Ag are 6.8 × 10^7 (Ω·m)$^{-1}$ and 10.5 g/cm^3, respectively.*

(b) Now compute the electron mobility for Ag.

Solution

(a) This portion of the problem asks that we calculate, for silver, the number of free electrons per cubic meter (n) given that there are 1.3 free electrons per silver atom, that the electrical conductivity is 6.8 × 10^7 (Ω-m)$^{-1}$, and that the density (ρ'_{Ag}) is 10.5 g/cm^3. (Note: in this discussion, the density of silver is represented by ρ'_{Ag} in order to avoid confusion with resistivity, which is designated by ρ.) Since $n = 1.3N_{\text{Ag}}$, and N_{Ag} is defined in Equation 4.2 (and using the atomic weight of Ag found inside the front cover—viz., 107.87 g/mol), we compute the value of n as follows:

$$n = 1.3N_{\text{Ag}} = 1.3\left[\frac{\rho'_{\text{Ag}}N_{\text{A}}}{A_{\text{Ag}}}\right]$$

$$= 1.3\left[\frac{(10.5\ \text{g/cm}^3)(6.022 \times 10^{23}\ \text{atoms/mol})}{107.87\ \text{g/mol}}\right]$$

$$= 7.62 \times 10^{22}\ \text{cm}^{-3}$$

$$= (7.62 \times 10^{22}\ \text{cm}^{-3})\left(\frac{10^2\ \text{cm}}{\text{m}}\right)^3 = 7.62 \times 10^{28}\ \text{m}^{-3}$$

(b) Now we are asked to compute the electron mobility, μ_e. Using Equation 18.8, and incorporating this value of n and the value of σ given in the problem statement, the electron mobility is determined as follows:

$$\mu_e = \frac{\sigma}{n|e|}$$

$$= \frac{6.8 \times 10^7\ (\Omega\text{-m})^{-1}}{(7.62 \times 10^{28}\ \text{m}^{-3})(1.602 \times 10^{-19}\ \text{C})} = 5.57 \times 10^{-3}\ \text{m}^2/\text{V-s}$$

Electrical Resistivity of Metals

18.13 *From Figure 18.39, estimate the value of A in Equation 18.11 for zinc as an impurity in copper–zinc alloys.*

Solution

We want to solve for the parameter A in Equation 18.11 using the data in Figure 18.37. First of all, we rearrange Equation 18.11 as follows:

$$A = \frac{\rho_i}{c_i(1 - c_i)}$$

However, the data plotted in Figure 18.37 is the total resistivity, ρ_{total}, and includes both impurity (ρ_i) and thermal (ρ_t) contributions (Equation 18.9). The value of ρ_t is taken as the resistivity at $c_i = 0$ in Figure 18.39, which has a value of 1.7×10^{-8} (Ω-m); this value must be subtracted from ρ_{total}. Below are tabulated values of A determined at $c_i = 0.10$, 0.20, and 0.30, including other data that were used in the computations. (*Note:* the c_i values were taken from the upper horizontal axis of Figure 18.39, since it is graduated in atom percent zinc.)

c_i	$1 - c_i$	ρ_{total} (Ω-m)	ρ_i (Ω-m)	A (Ω-m)
0.10	0.90	4.0×10^{-8}	2.3×10^{-8}	2.56×10^{-7}
0.20	0.80	5.4×10^{-8}	3.7×10^{-8}	2.31×10^{-7}
0.30	0.70	6.15×10^{-8}	4.45×10^{-8}	2.12×10^{-7}

So, there is a slight decrease of A with increasing c_i.

18.14 *(a) Using the data in Figure 18.8, determine the values of* ρ_0 *and a from Equation 18.10 for pure copper. Take the temperature T to be in degrees Celsius.*

(b) Determine the value of A in Equation 18.11 for nickel as an impurity in copper, using the data in Figure 18.8.

(c) Using the results of parts (a) and (b), estimate the electrical resistivity of copper containing 2.50 at% Ni at 120°C.

Solution

(a) One way to determine the values of ρ_0 and a in Equation 18.10 for pure copper in Figure 18.8, is to set up two simultaneous equations using two resistivity values (labeled ρ_{t1} and ρ_{t2}) taken at two corresponding temperatures (T_1 and T_2). These two equations are as follows:

$$\rho_{t1} = \rho_0 + aT_1$$

$$\rho_{t2} = \rho_0 + aT_2$$

And solving these equations simultaneously leads to the following expressions for a and ρ_0:

$$a = \frac{\rho_{t1} - \rho_{t2}}{T_1 - T_2} \qquad \text{(S18.14a)}$$

$$\rho_0 = \rho_{t1} - T_1\left[\frac{\rho_{t1} - \rho_{t2}}{T_1 - T_2}\right] \qquad \text{(S18.14b)}$$

$$= \rho_{t2} - T_2\left[\frac{\rho_{t1} - \rho_{t2}}{T_1 - T_2}\right]$$

From Figure 18.8, let us take T_1 = –150°C and T_2 = –50°C, which gives the corresponding values of resistivity:

$\rho_{t1} = 0.6 \times 10^{-8}$ (Ω-m)

$\rho_{t2} = 1.25 \times 10^{-8}$ (Ω-m)

We determine the value of a using Equation S18.14a, as follows:

$$a = \frac{\rho_{t1} - \rho_{t2}}{T_1 - T_2}$$

$$= \frac{\left[(0.6 \times 10^{-8}) - (1.25 \times 10^{-8})\right](\Omega\text{-m})}{-150°\text{C} - (-50°\text{C})}$$

$$= 6.5 \times 10^{-11}\ (\Omega\text{-m})/^\circ\text{C}$$

The value of ρ_0 is now determined using Equation S18.14b:

$$\rho_0 = \rho_{t1} - T_1\left[\frac{\rho_{t1} - \rho_{t2}}{T_1 - T_2}\right]$$

$$= (0.6 \times 10^{-8}) - (-150)\,\frac{\left[(0.6 \times 10^{-8}) - (1.25 \times 10^{-8})\right](\Omega\text{-m})}{-150^\circ\text{C} - (-50^\circ\text{C})}$$

$$1.58 \times 10^{-8}\ (\Omega\text{-m})$$

(b) For this part of the problem, we want to calculate A from Equation 18.11:

$$\rho_i = Ac_i(1 - c_i)$$

That is

$$A = \frac{\rho_i}{c_i(1 - c_i)}$$

In Figure 18.8, curves are plotted for three c_i values (0.0112, 0.0216, and 0.0332). Let us find A for each of these c_i's by taking a ρ_{total} from each curve at some temperature (say 0°C) and then subtracting out ρ_i for pure copper at this same temperature (which is 1.7×10^{-8} Ω-m). Below are tabulated values of A determined from these three c_i values, and other data that were used in the computations.

c_i	$1 - c_i$	ρ_{total} (Ω-m)	ρ_i (Ω-m)	A (Ω-m)
0.0112	0.989	3.0×10^{-8}	1.3×10^{-8}	1.17×10^{-6}
0.0216	0.978	4.2×10^{-8}	2.5×10^{-8}	1.18×10^{-6}
0.0332	0.967	5.5×10^{-8}	3.8×10^{-8}	1.18×10^{-6}

The average of these three A values is 1.18×10^{-6} (Ω-m).

(c) We use the results of parts (a) and (b) to estimate the electrical resistivity of copper containing 2.50 at% Ni ($c_i = 0.025$) at 120°C. The total resistivity is just

$$\rho_{\text{total}} = \rho_t + \rho_i$$

Or incorporating the expressions for ρ_t and ρ_i from Equations 18.10 and 18.11, and the values of ρ_0, a, and A determined above, leads to

$$\rho_{\text{total}} = (\rho_0 + aT) + Ac_i(1 - c_i)$$

$$= \left\{1.58 \times 10^{-8}\ (\Omega\text{-m}) + \left[6.5 \times 10^{-11}\ (\Omega\text{-m})/{}^\circ\text{C}\right](120^\circ\text{C})\right\}$$
$$+ \left\{\left[1.18 \times 10^{-6}\ (\Omega\text{-m})\right](0.0250)(1 - 0.0250)\right\}$$

$$= 5.24 \times 10^{-8}\ (\Omega\text{-m})$$

18.15 *Determine the electrical conductivity of a Cu–Ni alloy that has a tensile strength of 275 MPa (40,000 psi). See Figure 7.16.*

Solution

We are asked to determine the electrical conductivity of a Cu-Ni alloy that has a tensile strength of 275 MPa. From Figure 7.16*a*, the composition of an alloy having this tensile strength is about 8 wt% Ni. For this composition, the resistivity is about 14×10^{-8} Ω-m (Figure 18.9). And since the conductivity is the reciprocal of the resistivity, Equation 18.4, we determine the conductivity as follows:

$$\sigma = \frac{1}{\rho} = \frac{1}{14 \times 10^{-8}\ \Omega\text{-m}} = \mathbf{7.14 \times 10^{6}\ (\Omega\text{-m})^{-1}}$$

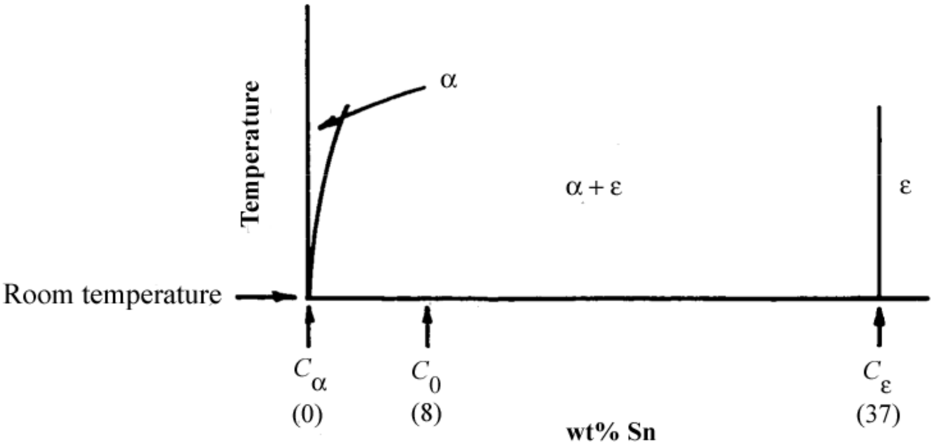
18.16 *Tin bronze has a composition of 89 wt% Cu and 11 wt% Sn and consists of two phases at room temperature: an α phase, which is copper containing a very small amount of tin in solid solution, and an ε phase, which consists of approximately 37 wt% Sn. Compute the room-temperature conductivity of this alloy given the following data:*

Phase	***Electrical Resistivity (Ω·m)***	***Density (g/cm^3)***
α	1.88×10^{-8}	*8.94*
ε	5.32×10^{-7}	*8.25*

Solution

This problem asks for us to compute the room-temperature conductivity of a two-phase Cu-Sn alloy which composition is 89 wt% Cu-11 wt% Sn. It is first necessary for us to determine the volume fractions of the α and ε phases, after which the resistivity (and subsequently, the conductivity) may be calculated using Equation 18.12. Weight fractions of the two phases are first calculated using the phase diagram information provided in the problem.

We may represent a portion of the phase diagram near room temperature as follows:



Applying the lever rule, we calculate the weight-fraction of the α phase, W_α, as follows:

$$W_\alpha = \frac{C_\varepsilon - C_0}{C_\varepsilon - C_\alpha} = \frac{37 - 11}{37 - 0} = 0.703$$

Likewise for the ε phase—its weight fraction is determined as follows:

$$W_\varepsilon = \frac{C_0 - C_\alpha}{C_\varepsilon - C_\alpha} = \frac{11 - 0}{37 - 0} = 0.297$$

We must now convert these mass fractions into volume fractions using the phase densities given in the problem statement. (*Note:* in the following expressions, density is represented by ρ' in order to avoid confusion with resistivity, which is designated by ρ.) Utilization of Equations 9.6a and 9.6b leads to

$$V_\alpha = \frac{\dfrac{W_\alpha}{\rho'_\alpha}}{\dfrac{W_\alpha}{\rho'_\alpha} + \dfrac{W_\varepsilon}{\rho'_\varepsilon}}$$

$$= \frac{\dfrac{0.703}{8.94\ \text{g/cm}^3}}{\dfrac{0.703}{8.94\ \text{g/cm}^3} + \dfrac{0.297}{8.25\ \text{g/cm}^3}}$$

$$= 0.686$$

$$V_\varepsilon = \frac{\dfrac{W_\varepsilon}{\rho'_\varepsilon}}{\dfrac{W_\alpha}{\rho'_\alpha} + \dfrac{W_\varepsilon}{\rho'_\varepsilon}}$$

$$= \frac{\dfrac{0.297}{8.25\ \text{g/cm}^3}}{\dfrac{0.703}{8.94\ \text{g/cm}^3} + \dfrac{0.297}{8.25\ \text{g/cm}^3}}$$

$$= 0.314$$

Now, using Equation 18.12—viz.,

$$\rho = \rho_\alpha V_\alpha + \rho_\varepsilon V_\varepsilon$$

and realizing the following:

$$\rho_\alpha = 1.88 \times 10^{-8}\ (\Omega\text{-m})$$
$$\rho_\varepsilon = 5.32 \times 10^{-7}\ (\Omega\text{-m})$$

leads to computation of the resistivity of this alloy, as follows:

$$\rho = \rho_\alpha V_\alpha + \rho_\varepsilon V_\varepsilon$$

$$= \left(1.88 \times 10^{-8}\ \Omega\text{-m}\right)(0.686) + \left(5.32 \times 10^{-7}\ \Omega\text{-m}\right)(0.314)$$

$$= 1.80 \times 10^{-7}\ \Omega\text{-m}$$

Finally, we calculate the conductivity using Equation 18.4, as follows:

$$\sigma = \frac{1}{\rho} = \frac{1}{1.80 \times 10^{-7}\ \Omega\text{-m}} = 5.56 \times 10^{6}\ (\Omega\text{-m})^{-1}$$

18.17 *A cylindrical metal wire 3 mm (0.12 in.) in diameter is required to carry a current of 12 A with a minimum of 0.01 V drop per foot (300 mm) of wire. Which of the metals and alloys listed in Table 18.1 are possible candidates?*

Solution

We are asked to select which of several metals may be used for a 3 mm diameter wire to carry 12 A, and have a voltage drop less than 0.01 V per foot (300 mm). Using Equations 18.3 and 18.4, let us determine the minimum conductivity required, and then select from Table 18.1, those metals that have conductivities greater than this value. Combining Equations 18.3 and 18.4, the minimum conductivity is just

$$\sigma = \frac{1}{\rho}$$

$$= \frac{1}{\frac{VA}{Il}} = \frac{Il}{VA}$$

$$= \frac{Il}{V\pi\left(\frac{d}{2}\right)^2}$$

$$= \frac{(12\ \mathrm{A})(300 \times 10^{-3}\ \mathrm{m})}{(0.01\ \mathrm{V})\,(\pi)\left(\frac{3 \times 10^{-3}\ \mathrm{m}}{2}\right)^2} = 5.09 \times 10^7\ (\Omega\text{-m})^{-1}$$

Thus, from Table 18.1, only copper, and silver have conductivity values greater than $5.09 \times 10^7\ (\Omega\text{-m})^{-1}$ and, therefore, are candidates.

Intrinsic Semiconduction

18.18 *(a) Using the data presented in Figure 18.16, determine the number of free electrons per atom for intrinsic germanium and silicon at room temperature (298 K). The densities for Ge and Si are 5.32 and 2.33 g/cm*^{3}*, respectively.*

(b) Now explain the difference in these free-electron-per-atom values.

Solution

(a) For this part of the problem, we first read, from Figure 18.16, the number of free electrons (i.e., the intrinsic carrier concentration) at room temperature (298 K). These values are as follows:

n_i(Ge) ≅ 4 × 10^{19} m^{-3}

n_i(Si) ≅ 1 × 10^{17} m^{-3}

Now, the number of atoms per cubic meter for Ge and Si (N_{Ge} and N_{Si}, respectively) may be determined using Equation 4.2, which involves the densities (ρ'_{Ge} and ρ'_{Si}) and atomic weights (A_{Ge} and A_{Si}). (*Note:* here we use ρ' to represent density in order to avoid confusion with resistivity, which is designated by ρ. Also, the atomic weights for Ge and Si, 72.64 and 28.09 g/mol, respectively, are found inside the front cover.) Therefore, the number of Ge atoms per cubic meter is computed using Equation 4.2, as follows:

$$N_{\text{Ge}} = \frac{N_{\text{A}}\rho'_{\text{Ge}}}{A_{\text{Ge}}}$$

$$= \frac{(6.022 \times 10^{23}\ \text{atoms/mol})(5.32\ \text{g/cm}^3)(10^6\ \text{cm}^3/\text{m}^3)}{72.64\ \text{g/mol}}$$

$$= 4.41 \times 10^{28}\ \text{atoms/m}^3$$

Similarly, for Si, the number of atoms per cubic meter is

$$N_{\text{Si}} = \frac{N_{\text{A}}\rho'_{\text{Si}}}{A_{\text{Si}}}$$

$$= \frac{(6.022 \times 10^{23}\ \text{atoms/mol})(2.33\ \text{g/cm}^3)(10^6\ \text{cm}^3/\text{m}^3)}{28.09\ \text{g/mol}}$$

$$= 5.00 \times 10^{28}\ \text{atoms/m}^3$$

Finally, the ratio of the number of free electrons per atom is calculated by dividing n_i by N. For Ge, this ratio is as follows:

$$\frac{n_i(\text{Ge})}{N_{\text{Ge}}} = \frac{\sim 4 \times 10^{19} \text{ electrons/m}^3}{4.41 \times 10^{28} \text{ atoms/m}^3} \cong 9 \times 10^{-10} \text{ electron/atom}$$

Similarly, for Si this ratio is determined as follows:

$$\frac{n_i(\text{Si})}{N_{\text{Si}}} = \frac{\sim 1 \times 10^{17} \text{ electrons/m}^3}{5.00 \times 10^{28} \text{ atoms/m}^3}$$

$$\cong \mathbf{2 \times 10^{-12}} \textbf{ electron/atom}$$

(b) The difference is due to the magnitudes of the band gap energies (Table 18.3). The band gap energy at room temperature for Si (1.11 eV) is larger than for Ge (0.67 eV), and, consequently, the probability of excitation across the band gap for a valence electron is much smaller for Si.

18.19 *For intrinsic semiconductors, the intrinsic carrier concentration* n_i *depends on temperature as follows:*

$$n_i \propto \exp\left(-\frac{E_g}{2kT}\right) \qquad (18.35a)$$

or, taking natural logarithms,

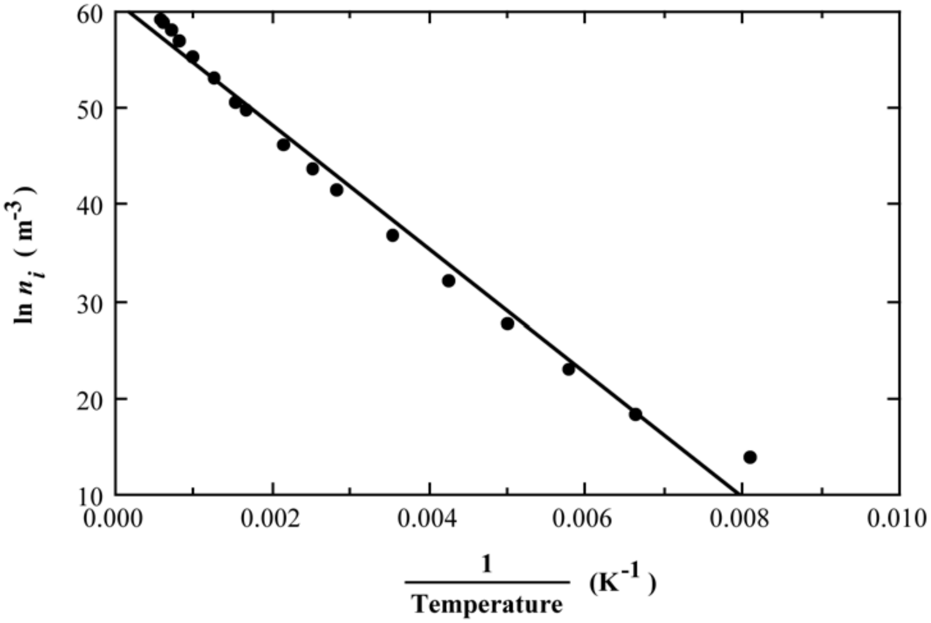
$$\ln n_i \propto -\frac{E_g}{2kT} \qquad (18.35b)$$

Thus, a plot of ln n_i *versus 1/T* $(K)^{-1}$ *should be linear and yield a slope of* $-E_g/2k$*. Using this information and the data presented in Figure 18.16, determine the band gap energies for silicon and germanium and compare these values with those given in Table 18.3.*

Solution

This problem asks that we make plots of ln n_i versus reciprocal temperature for both Si and Ge, using the data presented in Figure 18.16, and then determine the band gap energy for each material realizing that the slope of the resulting line is equal to $-E_g/2k$.

Below is shown such a plot for Si.



The slope of the line is equal to

$$\textbf{Slope} = \frac{\Delta \ln \eta_i}{\Delta\left(\frac{1}{T}\right)} = \frac{\ln \eta_1 - \ln \eta_2}{\frac{1}{T_1} - \frac{1}{T_2}}$$

Let us take $1/T_1$ = 0.001 and $1/T_2$ = 0.007; their corresponding ln η values are ln η_1 = 54.80 and ln η_2 = 16.00. Incorporating these values into the above expression leads to a slope of

$$\textbf{Slope} = \frac{54.80 - 16.00}{0.001 - 0.007} = -6470$$

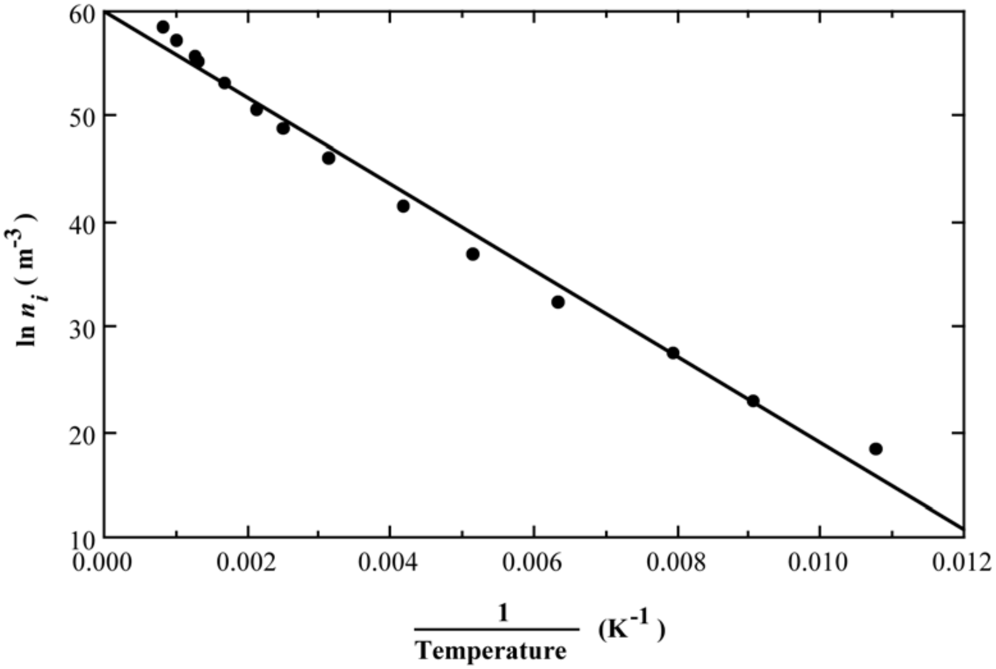
This slope yields an E_g value of

$$E_g = -\,2k\ (\text{Slope})$$

$$= -2\left(8.62 \times 10^{-5}\ \text{eV/K}\right)\left(-6470\right) = 1.115\ \text{eV}$$

The value cited in Table 18.3 is 1.11 eV; thus the agreement is very good.

Now for Ge, an analogous plot is shown below.



We calculate the slope and band gap energy values in the manner outlined above. Let us take $1/T_1 = 0.001$ and $1/T_2 = 0.011$; their corresponding ln η values are ln $\eta_1 = 55.8$ and ln $\eta_2 = 14.8$. Incorporating these values into the above expression leads to a slope of

$$\text{Slope} = \frac{55.8 - 14.8}{0.001 - 0.011} = -4100$$

This slope leads to an E_g value of

$$E_g = -2k\,(\text{Slope})$$

$$E_g = -(2)(8.62 \times 10^{-5}\ \text{eV/K})(-4100)$$

$$= 0.71\ \text{eV}$$

This value is in reasonable agreement with the 0.67 eV cited in Table 18.3.

18.20 *Briefly explain the presence of the factor 2 in the denominator of Equation 18.35a.*

Answer

The factor 2 in Equation 18.35a takes into account the creation of two charge carriers (an electron and a hole) for each valence-band-to-conduction-band intrinsic excitation; both charge carriers participate in the conduction process.

18.21 *At room temperature the electrical conductivity of PbS is 25* $(\Omega \cdot m)^{-1}$*, whereas the electron and hole mobilities are 0.06 and 0.02* $m^2/V \cdot s$*, respectively. Compute the intrinsic carrier concentration for PbS at room temperature.*

Solution

In this problem we are asked to compute the intrinsic carrier concentration for PbS at room temperature. Since the conductivity and both electron and hole mobilities are provided in the problem statement, all we need do is solve for n or p (i.e., n_i) using Equation 18.15. Making the appropriate rearrangement of Equation 18.15 such that n_i is the dependent variable leads to the following:

$$n_i = \frac{\sigma}{|e|(\mu_e + \mu_h)}$$

$$= \frac{25\ (\Omega\text{-m})^{-1}}{(1.602 \times 10^{-19}\ \text{C})(0.06\ +\ 0.02)\ \text{m}^2/\text{V-s}}$$

$$= 1.95\ \times\ 10^{21}\ \text{m}^{-3}$$

18.22 *Is it possible for compound semiconductors to exhibit intrinsic behavior? Explain your answer.*

Answer

Yes, compound semiconductors can exhibit intrinsic behavior. They will be intrinsic even though they are composed of two different elements as long as the electrical behavior is not influenced by the presence of other elements.

18.23 *For each of the following pairs of semiconductors, decide which has the smaller band gap energy, E_g, and then cite the reason for your choice.*

(a) C (diamond) and Ge

(b) AlP and InAs

(c) GaAs and ZnSe

(d) ZnSe and CdTe

(e) CdS and NaCl

Solution

This problem calls for us to decide for each of several pairs of semiconductors, which will have the smaller band gap energy and then cite a reason for the choice.

(a) Germanium will have a smaller band gap energy than C (diamond) since Ge is lower in row IVA of the periodic table (Figure 2.8) than is C. In moving from top to bottom of the periodic table, E_g decreases.

(b) Indium arsenide will have a smaller band gap energy than aluminum phosphide. Both of these semiconductors are III-V compounds, and the positions of both In and As are lower vertically in the periodic table (Figure 2.8) than Al and P.

(c) Gallium arsenide will have a smaller band gap energy than zinc selenide. All four of these elements are in the same row of the periodic table, but Zn and Se are more widely separated horizontally than Ga and As; as the distance of separation increases, so does the band gap.

(d) Cadmium telluride will have a smaller band gap energy than zinc selenide. Both are II-VI compounds, and Cd and Te are both lower vertically in the periodic table than Zn and Se.

(e) Cadmium sulfide will have a smaller band gap energy than sodium chloride since Na and Cl are much more widely separated horizontally in the periodic table than are Cd and S.

Extrinsic Semiconduction

18.24 *Define the following terms as they pertain to semiconducting materials: intrinsic, extrinsic, compound, elemental. Provide an example of each.*

Answer

An intrinsic semiconductor is one in which the electrical characteristics are characteristic of the "pure" material. Examples include high-purity (undoped) Si, GaAs, CdS.

An extrinsic semiconductor is one in which the electrical characteristics are determined by the presence of impurities. Examples include P-doped Ge, B-doped Si, S-doped GaP.

A compound semiconductor is one that is one that is composed of elements in Groups IIIA and VA and Groups IIB and VIA of the periodic table. Examples include GaAs, InP, CdS.

An elemental semiconductor is one composed of a single element. Examples are Si and Ge.

18.25 *An n-type semiconductor is known to have an electron concentration of 5 × 10^{17} m^{-3}. If the electron drift velocity is 350 m/s in an electric field of 1000 V/m, calculate the conductivity of this material.*

Solution

For this problem we are to determine the electrical conductivity of and *n*-type semiconductor, given that $n = 5 \times 10^{17}$ m^{-3} and the electron drift velocity is 350 m/s in an electric field of 1000 V/m. The conductivity of this material may be computed using Equation 18.16. But before this is possible, it is necessary to calculate the value of μ_e using Equation 18.7, as follows:

$$\mu_e = \frac{v_d}{E}$$

$$= \frac{350 \text{ m/s}}{1000 \text{ V/m}} = 0.35 \text{ m}^2/\text{V-s}$$

It is now possible to compute the conductivity using Equation 18.16,

$$\sigma = n|e|\mu_e$$

$$= \left(5 \times 10^{17} \text{ m}^{-3}\right)\left(1.602 \times 10^{-19} \text{C}\right)\left(0.35 \text{ m}^2/\text{V-s}\right)$$

$$= 0.028\ (\Omega\text{-m})^{-1}$$

18.26 *(a) In your own words, explain how donor impurities in semiconductors give rise to free electrons in numbers in excess of those generated by valence band–conduction band excitations.*

(b) Also explain how acceptor impurities give rise to holes in numbers in excess of those generated by valence band–conduction band excitations.

The explanations called for are found in Section 18.11.

18.27 *(a) Explain why no hole is generated by the electron excitation involving a donor impurity atom.*

(b) Explain why no free electron is generated by the electron excitation involving an acceptor impurity atom.

Answer

(a) No hole is generated by an electron excitation involving a donor impurity atom because the excitation comes from a level within the band gap, and thus, no missing electron is created within the normally filled valence band.

(b) No free electron is generated by an electron excitation involving an acceptor impurity atom because the electron is excited from the valence band into the impurity level within the band gap; no free electron is introduced into the conduction band.

18.28 *Predict whether each of the following elements will act as a donor or an acceptor when added to the indicated semiconducting material. Assume that the impurity elements are substitutional.*

Impurity	***Semiconductor***
N	*Si*
B	*Ge*
S	*InSb*
In	*CdS*
As	*ZnTe*

Solution

Nitrogen will act as a donor in Si. Since it (N) is from group VA of the periodic table (Figure 2.8), and an N atom has one more valence electron than an Si atom.

Boron will act as an acceptor in Ge. Since it (B) is from group IIIA of the periodic table, a B atom has one less valence electron than a Ge atom.

Sulfur will act as a donor in InSb. Since S is from group VIA of the periodic table, it will substitute for Sb; an S atom has one more valence electron than an Sb atom.

Indium will act as a donor in CdS. Since In is from group IIIA of the periodic table, it will substitute for Cd; an In atom has one more valence electron than a Cd atom.

Arsenic will act as an acceptor in ZnTe. Since As is from group VA of the periodic table, it will substitute for Te; furthermore, an As atom has one less valence electron than a Te atom.

18.29 *(a) The room-temperature electrical conductivity of a silicon specimen is 500* $(\Omega \cdot m)^{-1}$. *The hole concentration is known to be* 2.0×10^{22} m^{-3}. *Using the electron and hole mobilities for silicon in Table 18.3, compute the electron concentration.*

(b) On the basis of the result in part (a), is the specimen intrinsic, n-type extrinsic, or p-type extrinsic? Why?

Solution

(a) In this problem, for a Si specimen, we are given values for p $(2.0 \times 10^{22} \text{ m}^{-3})$ and $\sigma\,[500\ (\Omega\text{-m})^{-1}]$, while values for μ_h and μ_e (0.05 and 0.145 m^2/V-s, respectively) are found in Table 18.3. In order to solve for n we must use Equation 18.13, which, after rearrangement, leads to the following expression:

$$n = \frac{\sigma - p|e|\mu_h}{|e|\mu_e}$$

Incorporation of values of parameters on the right-hand side of this equation leads to the following value for *n:*

$$n = \frac{500\,(\Omega\text{-m})^{-1} - (2.0 \times 10^{22}\text{ m}^{-3})(1.602 \times 10^{-19}\text{ C})(0.05\text{ m}^2/\text{V-s})}{(1.602 \times 10^{-19}\text{ C})(0.145\text{ m}^2/\text{V-s})}$$

$$= 1.46 \times 10^{22}\text{ m}^{-3}$$

(b) This material is p-type extrinsic (although only slightly) since p $(2.0 \times 10^{22} \text{ m}^{-3})$ is slightly greater than n $(1.46 \times 10^{22} \text{ m}^{-3})$.

18.30 *Germanium to which* 10^{24} m^{-3} *As atoms have been added is an extrinsic semiconductor at room temperature, and virtually all the As atoms may be thought of as being ionized (i.e., one charge carrier exists for each As atom).*

(a) Is this material n-type or p-type?

(b) Calculate the electrical conductivity of this material, assuming electron and hole mobilities of 0.1 and 0.05 m^2*/V-s, respectively.*

Solution

(a) This germanium material to which has been added 10^{24} m^{-3} As atoms is *n*-type since As is a donor in Ge. (Arsenic is from group VA of the periodic table--Ge is from group IVA.)

(b) Since this material is *n*-type extrinsic, Equation 18.16 is valid. Furthermore, each As atom will donate a single electron, or the electron concentration is equal to the As concentration since all of the As atoms are ionized at room temperature; that is $n = 10^{24}$ m^{-3}, and, as given in the problem statement, $\mu_e = 0.1$ m^2/V-s. Thus, the conductivity is equal to

$$\sigma = n|e|\mu_e$$

$$= (10^{24}\ \text{m}^{-3})(1.602 \times 10^{-19}\ \text{C})(0.1\ \text{m}^2/\text{V-s})$$

$$= 1.60 \times 10^{4}\ (\Omega\text{-m})^{-1}$$

18.31 *The following electrical characteristics have been determined for both intrinsic and p-type extrinsic gallium antimonide (GaSb) at room temperature:*

	σ (Ω·m)$^{-1}$	**n (m^{-3})**	**p (m^{-3})**
Intrinsic	8.9×10^4	8.7×10^{23}	8.7×10^{23}
Extrinsic (p-type)	2.3×10^5	7.6×10^{22}	1.0×10^{25}

Calculate electron and hole mobilities.

Solution

In order to solve for the electron and hole mobilities for GaSb, we must write conductivity expressions for the two materials, of the form of Equation 18.13—i.e.,

$$\sigma = n|e|\mu_e + p|e|\mu_h$$

For the intrinsic material, incorporation of values of the relevant constants in the problem statement into Equation 18.13 gives the following:

$$8.9 \times 10^4 \ (\Omega\text{-m})^{-1} = (8.7 \times 10^{23} \text{ m}^{-3})(1.602 \times 10^{-19} \text{ C})\,\mu_e$$
$$+ (8.7 \times 10^{23} \text{ m}^{-3})(1.602 \times 10^{-19} \text{ C})\mu_h$$

which reduces to

$$0.639 = \mu_e + \mu_h \qquad \text{(S18.31)}$$

Whereas, for the extrinsic GaSb, we use Equation 18.17

$$\sigma = p|e|\mu_h$$

$$2.3 \times 10^5 \ (\Omega\text{-m})^{-1} = (1.0 \times 10^{25} \text{ m}^{-3})(1.602 \times 10^{-19} \text{ C})\,\mu_h$$

which simplifies to the following:

$$\mu_h = 0.144 \text{ m}^2/\text{V-s}$$

Thus, we determine the value for μ_e by substitution of this value for μ_h into Equation S18.31 as follows:

$$\mu_e = 0.639 - \mu_h$$

$$= 0.639 \text{ m}^2/\text{V-s} - 0.144 \text{ m}^2/\text{V-s}$$

$$= 0.495 \text{ m}^2/\text{V-s}$$

The Temperature Dependence of Carrier Concentration

18.32 *Calculate the conductivity of intrinsic silicon at 80°C.*

Solution

In order to estimate the electrical conductivity of intrinsic silicon at 80°C, we must employ Equation 18.15. However, before this is possible, it is necessary to determine values for n_i, μ_e, and μ_h. From Figure 18.16, at 80°C (353 K), $n_i = 1.5 \times 10^{18}$ m^{-3}, whereas from the "$<10^{20}$ m^{-3}" curves of Figures 18.19a and 18.19b, at 80ºC (353 K), μ_e = 0.10 m^2/V-s and μ_h = 0.035 m^2/V-s (realizing that the mobility axes of these two plot are scaled logarithmically). Thus, using Equation 18.15 we compute the conductivity at 80°C as follows:

$$\sigma = n_i |e| (\mu_e + \mu_h)$$

$$= (1.5 \times 10^{18}\ \mathrm{m}^{-3})(1.602 \times 10^{-19}\ \mathrm{C})(0.10\ \mathrm{m}^2/\mathrm{V\text{-}s} + 0.035\ \mathrm{m}^2/\mathrm{V\text{-}s})$$

$$= 0.0324\ (\Omega\text{-m})^{-1}$$

18.33 *At temperatures near room temperature, the temperature dependence of the conductivity for intrinsic germanium is found to be given by*

$$\sigma = CT^{-3/2} \exp\left(-\frac{E_g}{2kT}\right) \qquad (18.36)$$

where C is a temperature-independent constant and T is in Kelvins. Using Equation 18.36, calculate the intrinsic electrical conductivity of germanium at 175°C.

Solution

In order to solve this problem it is first necessary to solve for C in Equation 18.36 using the room-temperature (298 K) conductivity for Ge [2.2 $(\Omega\text{-m})^{-1}$] (Table 18.3). This is accomplished by taking natural logarithms of both sides of Equation 18.36 as

$$\ln \sigma = \ln C - \frac{3}{2}\ln T - \frac{E_g}{2kT} \qquad (18.36a)$$

and after rearranging this expression and substitution of values for E_g (0.67 eV, Table 18.3), and the room-temperature conductivity [2.2 $(\Omega\text{-m})^{-1}$], we get the following value for ln *C:*

$$\ln C = \ln \sigma + \frac{3}{2}\ln T + \frac{E_g}{2kT}$$

$$= \ln (2.2) + \frac{3}{2}\ln (298) + \frac{0.67 \text{ eV}}{(2)(8.62 \times 10^{-5} \text{ eV/K})(298 \text{ K})}$$

$$= 22.38$$

Now, using Equation 18.36a, we are able to compute the conductivity at 448 K (175°C) as follows:

$$\ln \sigma = \ln C - \frac{3}{2}\ln T - \frac{E_g}{2kT}$$

$$= 22.38 - \frac{3}{2}\ln (448 \text{ K}) - \frac{0.67 \text{ eV}}{(2)(8.62 \times 10^{-5} \text{ eV/K})(448 \text{ K})}$$

$$= 4.548$$

which leads to

$$\sigma = e^{4.548} = 94.4 \ (\Omega\text{-m})^{-1}$$

18.34 *Using Equation 18.36 and the results of Problem 18.33, determine the temperature at which the electrical conductivity of intrinsic germanium is 40 (Ω·m)$^{-1}$.*

Solution

This problem asks that we determine the temperature at which the electrical conductivity of intrinsic Ge is 40 (Ω-m)$^{-1}$, using Equation 18.36 and the results of Problem 18.33. First of all, taking logarithms of Equation 18.36 leads to the following expression:

$$\ln \sigma = \ln C - \frac{3}{2}\ln T - \frac{E_g}{2kT} \tag{18.36a}$$

From Problem 18.33 the value of ln C was determined to be 22.38. Using this results and that σ = 40 (Ω-m)$^{-1}$, the above equation becomes

$$\ln 40(\Omega\text{-m})^{-1} = 22.38 - \frac{3}{2}\ln T - \frac{0.67 \text{ eV}}{(2)(8.62 \times 10^{-5} \text{ eV/K})(T)}$$

Using an equation solver (root solver) the value of T is determined as T = 400, which value is the temperature in K; this corresponds to T(ºC) = 400 – 273 = 127°C.

18.35 *Estimate the temperature at which GaAs has an electrical conductivity of 1.6 × 10^{-3} (Ω·m)$^{-1}$, assuming the temperature dependence for σ of Equation 18.36. The data shown in Table 18.3 may prove helpful.*

Solution

This problem asks that we estimate the temperature at which GaAs has an electrical conductivity of 1.6 × 10^{-3} (Ω-m)$^{-1}$ assuming that the conductivity has a temperature dependence as shown in Equation 18.36. From the room temperature (298 K) conductivity [3 × 10^{-7} (Ω-m)$^{-1}$] and band gap energy (1.42 eV) of Table 18.3 we determine the value of ln C (Equation 18.36) by taking natural logarithms of both sides of the equation, and after rearrangement the following results:

$$\ln C = \ln \sigma \ + \frac{3}{2}\ln T + \frac{E_g}{2kT}$$

$$= \ln\left[3 \times 10^{-7}\,(\Omega\text{-m})^{-1}\right] + \frac{3}{2}\ln(298\ \text{K}) \ + \frac{1.42\ \text{eV}}{(2)(8.62 \times 10^{-5}\ \text{eV/K})(298\ \text{K})}$$

$$= 21.17$$

Again, taking logarithms of both sides of Equation 18.36 leads to

$$\ln \sigma = \ln C - \frac{3}{2}\ln T - \frac{E_g}{2kT} \qquad (18.36a)$$

Now we substitute this value of C as well as the value of the band gap energy (1.42 eV) into Equation 18.36a in order to determine the value of T for which σ = 1.6 × 10^{-3} (Ω-m)$^{-1}$; thus

$$\ln \sigma = \ln C \ - \frac{3}{2}\ln T - \frac{E_g}{2kT}$$

$$\ln\left[1.6 \times 10^{-3}\,(\Omega\text{-m})^{-1}\right] = 21.17 \ - \frac{3}{2}\ln T \ - \frac{1.42\ \text{eV}}{(2)(8.62 \times 10^{-5}\ \text{eV/K})(T)}$$

Using an equation solver (root solver) the value of T is determined as T = 446, which value is the temperature in K; this corresponds to T(ºC) = 446 – 273 = 173°C.

18.36 *Compare the temperature dependence of the conductivity for metals and intrinsic semiconductors. Briefly explain the difference in behavior.*

Answer

This question asks that we compare and then explain the difference in temperature dependence of the electrical conductivity for metals and intrinsic semiconductors.

For metals, the temperature dependence is described by Equation 18.10 (and converting from resistivity to conductivity using Equation 18.4), as

$$\sigma = \frac{1}{\rho} = \frac{1}{\rho_0 + aT}$$

That is, the electrical conductivity decreases with increasing temperature.

Alternatively, from Equation 18.8, the conductivity of metals is equal to

$$\sigma = n|e|\mu_e$$

As the temperature rises, n will remain virtually constant, whereas the mobility (μ_e) will decrease, because the thermal scattering of free electrons will become more efficient. Since $|e|$ is independent of temperature, the net result will be diminishment in the magnitude of σ.

For intrinsic semiconductors, the temperature-dependence of conductivity is just the opposite of that for metals—i.e., conductivity increases with rising temperature. One explanation is as follows: Equation 18.15 expresses the dependence of conductivity on electron/hole concentrations and electron/hole mobilities—that is,

$$\sigma = n|e|(\mu_e + \mu_h) = p|e|(\mu_e + \mu_h)$$

$$= n_i|e|(\mu_e + \mu_h)$$

Both n and p increase dramatically with rising temperature (Figure 18.16), because more thermal energy becomes available for valence band-conduction band electron excitations. The magnitudes of μ_e and μ_h will diminish somewhat with increasing temperature (per the upper curves of Figures 18.19a and 18.19b), as a consequence of the thermal scattering of electrons and holes. However, this reduction of μ_e and μ_h will be overwhelmed by the increase in n and p, with the net result is that σ increases with temperature.

An alternative explanation is as follows: for an intrinsic semiconductor the temperature dependence is represented by an equation of the form of Equation 18.36. This expression contains two terms that involve temperature—a preexponential one (in this case $T^{-3/2}$) and the other in the exponential. With rising temperature the preexponential term decreases, while the exp ($-E_g/2kT$) parameter increases. With regard to relative magnitudes, the exponential term increases much more rapidly than the preexponential one, such that the electrical conductivity of an intrinsic semiconductor increases with rising temperature.

Factors That Affect Carrier Mobility

18.37 *Calculate the room-temperature electrical conductivity of silicon that has been doped with* 10^{23} m^{-3} *of arsenic atoms.*

Solution

This problem asks that we determine the room-temperature electrical conductivity of silicon that has been doped with 10^{23} m^{-3} of arsenic atoms. Inasmuch as As is a group VA element in the periodic table (Figure 2.8) it acts as a donor in silicon. Thus, this material is *n*-type extrinsic, and it is necessary to use Equation 18.16, with $n = 10^{23}$ m^{-3} since at room temperature all of the As donor impurities are ionized. The electron mobility, from Figure 18.18 at an impurity concentration of 10^{23} m^{-3}, is 0.065 m^2/V-s. Therefore, the conductivity is equal to

$$\sigma = n|e|\mu_e$$

$$= \left(10^{23}\ \mathrm{m}^{-3}\right)\left(1.602 \times 10^{-19}\ \mathrm{C}\right)\left(0.065\ \mathrm{m}^2/\mathrm{V\text{-}s}\right)$$

$$= 1040\ (\Omega\text{-m})^{-1}$$

18.38 *Calculate the room-temperature electrical conductivity of silicon that has been doped with* 2×10^{24} m^{-3} *of boron atoms.*

Solution

Here we are asked to calculate the room-temperature electrical conductivity of silicon that has been doped with 2×10^{24} m^{-3} of boron atoms. Inasmuch as B is a group IIIA element in the periodic table (Figure 2.8) it acts as an acceptor in silicon. Thus, this material is *p*-type extrinsic, and it is necessary to use Equation 18.17, with $p = 2 \times 10^{24}$ m^{-3} since at room temperature all of the B acceptor impurities are ionized. The hole mobility, from Figure 18.18 at an impurity concentration of 2×10^{24} m^{-3}, is 0.0070 m^2/V-s. Therefore, the conductivity is equal to

$$\sigma = p|e|\mu_e$$

$$= (2 \times 10^{24}\ \mathrm{m}^{-3})(1.602 \times 10^{-19}\ \mathrm{C})(0.0070\ \mathrm{m}^2/\mathrm{V\text{-}s})$$

$$= 2240\ (\Omega\text{-m})^{-1}$$

18.39 *Estimate the electrical conductivity at 75°C of silicon that has been doped with* 10^{22} m^{-3} *of phosphorus atoms.*

Solution

In this problem we are to estimate the electrical conductivity, at 75°C, of silicon that has been doped with 10^{22} m^{-3} of phosphorous atoms. Inasmuch as P is a group VA element in the periodic table (Figure 2.8) it acts as a donor in silicon. Thus, this material is *n*-type extrinsic, and it is necessary to use Equation 18.16; *n* in this expression is 10^{22} m^{-3} since at 75°C all of the P donor impurities are ionized. The electron mobility is determined using Figure 18.19a. From the 10^{22} m^{-3} impurity concentration curve and at 75°C (348 K), μ_e = 0.080 m^2/V-s. Therefore, the conductivity is calculated using Equation 18.16 as follows:

$$\sigma = n|e|\mu_e$$

$$= \left(10^{22}\ \mathrm{m}^{-3}\right)\left(1.602 \times 10^{-19}\ \mathrm{C}\right)\left(0.080\ \mathrm{m}^2/\mathrm{V\text{-}s}\right)$$

$$= 128\ (\Omega\text{-m})^{-1}$$

18.40 *Estimate the electrical conductivity at 135°C of silicon that has been doped with* 10^{24} m^{-3} *of aluminum atoms.*

Solution

In this problem we are to estimate the electrical conductivity, at 135°C, of silicon that has been doped with 10^{24} m^{-3} of aluminum atoms. Inasmuch as Al is a group IIIA element in the periodic table (Figure 2.8) it acts as an acceptor in silicon. Thus, this material is *p*-type extrinsic, and it is necessary to use Equation 18.17; *p* in this expression is 10^{24} m^{-3} since at 135°C all of the Al acceptor impurities are ionized. The hole mobility is determined using Figure 18.19b. From the 10^{24} m^{-3} impurity concentration curve and at 135°C (408 K,) μ_h = 0.007 m^2/V-s. Therefore, we compute the conductivity of this material using Equation 18.17 as follows:

$$\sigma = p|e|\mu_h$$

$$= (10^{24}\ \mathrm{m}^{-3})(1.602 \times 10^{-19}\ \mathrm{C})(0.007\ \mathrm{m}^2/\mathrm{V\text{-}s})$$

$$= 1120\ (\Omega\text{-m})^{-1}$$

The Hall Effect

18.41 *A hypothetical metal is known to have an electrical resistivity of 3.3 × 10^{-8} (Ω·m). A current of 25 is passed through a specimen of this metal 15 mm thick. When a magnetic field of 0.95 tesla is simultaneously imposed in a direction perpendicular to that of the current, a Hall voltage of –2.4 × 10^{-7} V is measured. Compute the following:*

(a) the electron mobility for this metal

(b) the number of free electrons per cubic meter.

Solution

(a) This portion of the problem calls for us to determine the electron mobility for some hypothetical metal using the Hall effect. This metal has an electrical resistivity of 3.3 × 10^{-8} (Ω-m), while the specimen thickness is 15 mm, I_x = 25 A and B_z = 0.95 tesla; under these circumstances a Hall voltage of –2.4 × 10^{-7} V is measured. It is first necessary to convert resistivity to conductivity using Equation 18.4 as follows:

$$\sigma = \frac{1}{\rho} = \frac{1}{3.3 \times 10^{-8}\ (\Omega\text{-m})} = 3.0 \times 10^{7}\ (\Omega\text{-m})^{-1}$$

The electron mobility may be determined using Equation 18.20b—that is

$$\mu_e = |R_{\mathrm{H}}|\sigma$$

Now incorporation into this expression the rearranged form of Equation 18.18 wherein R_{H} is the dependent variable—i.e.,

$$R_{\mathrm{H}} = \frac{V_{\mathrm{H}} d}{I_x B_z}$$

leads to the following expression

$$\mu_e = \frac{|V_H| d\sigma}{I_x B_z}$$

And incorporation of values for the variables on the right-hand side of this equation yields a value for the electron mobility as follows:

$$\mu_e = \frac{\left(\left|-2.4 \times 10^{-7}\ V\right|\right)(15 \times 10^{-3}\ \mathrm{m})\left[3.0 \times 10^{7}\ (\Omega\text{-m})^{-1}\right]}{(25\ \mathrm{A})(0.95\ \mathrm{tesla})}$$

$$= 0.00455\ \mathrm{m^2/V\text{-}s}$$

(b) Now we are to calculate the number of free electrons per cubic meter (*n*). From a rearranged form of Equation 18.8 we solve for *n* as follows:

$$n = \frac{\sigma}{|e|\,\mu_e}$$

$$= \frac{3.0 \times 10^7\ (\Omega\text{-m})^{-1}}{\left(1.602 \times 10^{-19}\ \mathrm{C}\right)\left(0.00455\ \mathrm{m^2/V\text{-}s}\right)}$$

$$= 4.12 \times 10^{28}\ \mathrm{m^{-3}}$$

18.42 *A metal alloy is known to have electrical conductivity and electron mobility values of 1.2 × 10^7 (Ω·m)$^{-1}$ and 0.0050 m^2/V·s, respectively. A current of 40 A is passed through a specimen of this alloy that is 35 mm thick. What magnetic field would need to be imposed to yield a Hall voltage of –3.5 × 10^{-7} V?*

Solution

In this problem we are asked to determine the magnetic field required to produce a Hall voltage of –3.5 × 10^{-7} V, given that σ = 1.2 × 10^7 (Ω-m)$^{-1}$, μ_e = 0.0050 m^2/V-s, I_x = 40 A, and d = 35 mm. We now take a rearranged form of Equation 18.20b

$$|R_\mathrm{H}| = \frac{\mu_e}{\sigma}$$

and incorporate into it Equation 18.18 as follows:

$$V_\mathrm{H} = \frac{R_\mathrm{H} I_x B_z}{d}$$

$$= \frac{\mu_e I_x B_z}{\sigma d}$$

We now rearrange this expression such that B_z is the dependent variable, and after inserting values for the remaining parameters that were given in the problem statement, the value of B_z is determined as follows:

$$B_z = \frac{|V_H| \sigma d}{I_x \mu_e}$$

$$= \frac{\left(\left|-3.5 \times 10^{-7}\,\mathrm{V}\right|\right)\left[1.2 \times 10^7\,(\Omega\text{-m})^{-1}\right]\left(35 \times 10^{-3}\,\mathrm{m}\right)}{(40\,\mathrm{A})(0.0050\,\mathrm{m^2/V\text{-}s})}$$

= 0.735 tesla

Semiconducting Devices

18.43 *Briefly describe electron and hole motions in a p–n junction for forward and reverse biases; then explain how these lead to rectification.*

The explanations called for are found in Section 18.15.

18.44 *How is the energy in the reaction described by Equation 18.21 dissipated?*

Answer

The energy generated by the electron-hole annihilation reaction, Equation 18.21, is dissipated as heat.

18.45 *What are the two functions that a transistor may perform in an electronic circuit?*

Answer

In an electronic circuit, a transistor may be used to (1) amplify an electrical signal, and (2) act as a switching device in computers.

18.46 *State the differences in operation and application for junction transistors and MOSFETs.*

The differences in operation and application for junction transistors and MOSFETs are described in Section 18.15.

Conduction in Ionic Materials

18.47 *We noted in Section 12.5 (Figure 12.20) that in FeO (wüstite), the iron ions can exist in both* Fe^{2+} *and* Fe^{3+} *states. The number of each of these ion types depends on temperature and the ambient oxygen pressure. Furthermore, we also noted that in order to retain electroneutrality, one* Fe^{2+} *vacancy will be created for every two* Fe^{3+} *ions that are formed; consequently, in order to reflect the existence of these vacancies the formula for wüstite is often represented as* $Fe_{(1-x)}O$*, where x is some small fraction less than unity.*

In this nonstoichiometric $Fe_{(1-x)}O$ *material, conduction is electronic, and, in fact, it behaves as a p-type semiconductor—that is, the* Fe^{3+} *ions act as electron acceptors, and it is relatively easy to excite an electron from the valence band into an* Fe^{3+} *acceptor state, with the formation of a hole. Determine the electrical conductivity of a specimen of wüstite that has a hole mobility of* 1.0×10^{-5} $m^2/V\cdot s$ *and for which the value of x is 0.040. Assume that the acceptor states are saturated (i.e., one hole exists for every* Fe^{3+} *ion). Wüstite has the sodium chloride crystal structure with a unit cell edge length of 0.437 nm.*

Solution

We are asked in this problem to determine the electrical conductivity for the nonstoichiometric $Fe_{(1-x)}O$, given $x = 0.040$ and that the hole mobility is 1.0×10^{-5} m^2/V-s. It is first necessary to compute the number of vacancies per cubic meter for this material. For this determination let us use as our basis 10 unit cells. For the sodium chloride crystal structure there are four cations and four anions per unit cell. Thus, in ten unit cells of FeO there will normally be forty O^{2-} and forty Fe^{2+} ions. However, when $x = 0.04$, (0.04)(40) = 1.6 of the Fe^{2+} sites will be vacant. (Furthermore, there will be 3.2 Fe^{3+} ions in these ten unit cells inasmuch as two Fe^{3+} ions are created for every vacancy). Therefore, each unit cell will, on the average contain 0.16 vacancies. Now, the number of vacancies per cubic meter is just the number of vacancies per unit cell divided by the unit cell volume; this volume is just the unit cell edge length (0.437 nm) cubed. Thus

$$\frac{\#\text{vacancies}}{\text{m}^3} = \frac{0.16 \text{ vacancies/unit cell}}{(0.437 \times 10^{-9} \text{ m})^3}$$

$$= 1.92 \times 10^{27} \text{ vacancies/m}^3$$

Inasmuch as it is assumed that the vacancies are saturated, the number of holes (p) is also 1.92×10^{27} m^{-3}. It is now possible, using Equation 18.17, to compute the electrical conductivity of this material as

$$\sigma = p|e|\mu_h$$

$$= (1.92 \times 10^{27} \text{ m}^{-3})(1.602 \times 10^{-19} \text{ C})(1.0 \times 10^{-5} \text{ m}^2/\text{V-s}) = 3076\ (\Omega\text{-m})^{-1}$$

18.48 *At temperatures between 540°C (813 K) and 727°C (1000 K), the activation energy and preexponential for the diffusion coefficient of* Na^+ *in NaCl are 173,000 J/mol and 4.0 ×* 10^{-4} m^2/s*, respectively. Compute the mobility for an* Na^+ *ion at 600°C (873 K).*

Solution

For this problem, we are given, for NaCl, the activation energy (173,000 J/mol) and preexponential (4.0 × 10^{-4} m^2/s) for the diffusion coefficient of Na^+ and are asked to compute the mobility for a Na^+ ion at 873 K. The mobility, μ_{Na^+}, may be computed using Equation 18.23; however, this expression also includes the diffusion coefficient D_{Na^+}, which is determined using Equation 5.8 as follows:

$$D_{Na^+} = D_0 \exp\left(-\frac{Q_d}{RT}\right)$$

$$= (4.0 \times 10^{-4}\ \text{m}^2/\text{s}) \exp\left[-\frac{173{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(873\ \text{K})}\right]$$

$$= 1.76 \times 10^{-14}\ \text{m}^2/\text{s}$$

Now solving for μ_{Na^+} using Equation 18.23 (assuming that n_{Na^+} = 1, since the valence of the Na^+ ion is +1) yields the following:

$$\mu_{Na^+} = \frac{n_{Na^+} e D_{Na^+}}{kT}$$

$$= \frac{(1)(1.602 \times 10^{-19}\ \text{C/atom})(1.76 \times 10^{-14}\ \text{m}^2/\text{s})}{(1.38 \times 10^{-23}\ \text{J/atom-K})(873\ \text{K})}$$

$$= 2.34 \times 10^{-13}\ \text{m}^2/\text{V-s}$$

Capacitance

18.49 *A parallel-plate capacitor using a dielectric material having an ε_r of 2.2 has a plate spacing of 2 mm (0.08 in.). If another material having a dielectric constant of 3.7 is used and the capacitance is to be unchanged, what must be the new spacing between the plates?*

Solution

We want to compute the plate spacing of a parallel-plate capacitor as the dielectric constant is increased form 2.2 to 3.7, while maintaining the capacitance constant. Combining Equations 18.26 and 18.27 yields the following expression:

$$C = \varepsilon \frac{A}{l} = \varepsilon_r \varepsilon_0 \frac{A}{l}$$

Now, let us use the subscripts 1 and 2 to denote the initial and final states, respectively. Since $C_1 = C_2$, then we can write the following:

$$\frac{\varepsilon_{r1}\varepsilon_0 A}{l_1} = \frac{\varepsilon_{r2}\varepsilon_0 A}{l_2}$$

And, solving for l_2 leads to the following:

$$l_2 = \frac{\varepsilon_{r2} l_1}{\varepsilon_{r1}} = \frac{(3.7)(2\text{ mm})}{2.2} = 3.36\text{ mm}$$

18.50 *A parallel-plate capacitor with dimensions of 38 mm by 65 mm (1 $\frac{1}{2}$ in. by 2 $\frac{1}{2}$ in.) and a plate separation of 1.3 mm (0.05 in.) must have a minimum capacitance of 70 pF (7×10^{-11} F) when an ac potential of 1000 V is applied at a frequency of 1 MHz. Which of the materials listed in Table 18.5 are possible candidates? Why?*

Solution

This problem asks for us to ascertain which of the materials listed in Table 18.5 are candidates for a parallel-plate capacitor that has dimensions of 38 mm by 65 mm, a plate separation of 1.3 mm so as to have a minimum capacitance of 7×10^{-11} F, when an ac potential of 1000 V is applied at 1 MHz. We first of all combine Equations 18.26 and 18.27 as follows:

$$C = \varepsilon \frac{A}{l} = \varepsilon_r \varepsilon_0 \frac{A}{l}$$

and solving for the dielectric constant ε_r we get

$$\varepsilon_r = \frac{lC}{\varepsilon_0 A}$$

And upon substitution of values given in the problem statement for the parameters on the right-hand side of this equation the following results:

$$\varepsilon_r = \frac{(1.3 \times 10^{-3}\,\mathrm{m})(7 \times 10^{-11}\,\mathrm{F})}{(8.85 \times 10^{-12}\,\mathrm{F/m})(38 \times 10^{-3}\,\mathrm{m})(65 \times 10^{-3}\,\mathrm{m})}$$

$$= 4.16$$

Thus, the minimum value of ε_r to achieve the desired capacitance is 4.16 at 1 MHz. Of those materials listed in Table 18.5, titanate ceramics, mica, steatite, soda-lime glass, porcelain, and phenol-formaldehyde are candidates.

18.51 *Consider a parallel-plate capacitor having an area of 3225 mm*^{2} *(5 in.*^{2}*), a plate separation of 1 mm (0.04 in.), and a material having a dielectric constant of 3.5 positioned between the plates.*

(a) What is the capacitance of this capacitor?

(b) Compute the electric field that must be applied for 2 × 10^{-8} *C to be stored on each plate.*

Solution

(a) We are first asked to compute the capacitance. Combining Equations 18.26 and 18.27 leads to the following expression:

$$C = \varepsilon \frac{A}{l}$$

$$= \frac{\varepsilon_r \varepsilon_0 A}{l}$$

Incorporation of values given in the problem statement for parameters on the right-hand side of this expression, and solving for *C* yields

$$C = \frac{\varepsilon_r \varepsilon_0 A}{l}$$

$$= \frac{(3.5)(8.85 \times 10^{-12}\ \text{F/m})(3225\ \text{mm}^2)(1\ \text{m}^2/10^6\ \text{mm}^2)}{10^{-3}\ \text{m}}$$

$$= 10^{-10}\ \text{F} = 100\ \text{pF}$$

(b) Now we are asked to compute the electric field that must be applied in order for 2 × 10^{-8} C to be stored on each plate. First we need to solve for *V* in Equation 18.24 as

$$V = \frac{Q}{C} = \frac{2 \times 10^{-8}\ \text{C}}{10^{-10}\ \text{F}} = 200\ \text{V}$$

The electric field *E* may now be determined using Equation 18.6, as follows:

$$E = \frac{V}{l} = \frac{200\ \text{V}}{10^{-3}\ \text{m}} = 2.0 \times 10^5\ \text{V/m}$$

18.52 *In your own words, explain the mechanism by which charge-storing capacity is increased by the insertion of a dielectric material within the plates of a capacitor.*

This explanation is found in Section 18.19.

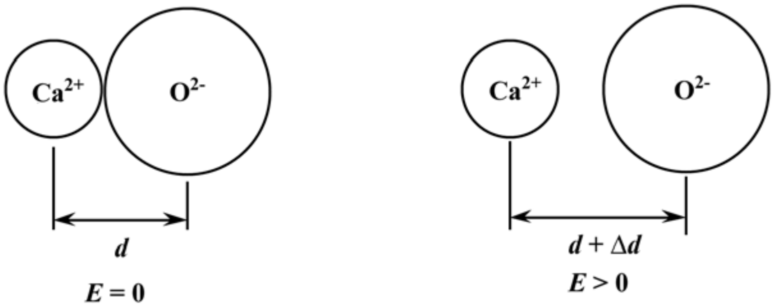
Field Vectors and Polarization

Types of Polarization

18.53 *For CaO, the ionic radii for Ca^{2+} and O^{2-} ions are 0.100 and 0.140 nm, respectively. If an externally applied electric field produces a 5% expansion of the lattice, compute the dipole moment for each Ca^{2+}–O^{2-} pair. Assume that this material is completely unpolarized in the absence of an electric field.*

Solution

Shown below are the relative positions of Ca^{2+} and O^{2-} ions, without and with an electric field present.



Now, the distance *d*, the distance between the centers of the ions in the absence of an electric field is computed in terms of the radii of Ca^{2+} and O^{2-} ions as follows:

$$d = r_{Ca^{2+}} + r_{O^{2-}} = 0.100 \text{ nm} + 0.140 \text{ nm} = 0.240 \text{ nm}$$

The amount of expansion between the ions when the field is applied, Δd is equal to

$$\Delta d = 0.05\, d = (0.05)(0.240 \text{ nm}) = 0.0120 \text{ nm} = 1.20 \times 10^{-11} \text{ m}$$

From Equation 18.28, the dipole moment created, *p*, is just

$$p = q\Delta d$$

$$= 2|e^-|\Delta q$$

The "2" is included in this expression because the charge on each Ca^{2+} ion is 2+, and on each O^{2-} ion is 2–; therefore

$$p = 2|e^-|\Delta q$$

$$= (2)(|1.602 \times 10^{-19} \text{ C}|)(1.20 \times 10^{-11} \text{ m})$$

$$= 3.84 \times 10^{-30} \text{ C-m}$$

18.54 *The polarization P of a dielectric material positioned within a parallel-plate capacitor is to be 4.0 × 10^{-6} C/m^2.*

(a) What must be the dielectric constant if an electric field of 10^5 V/m is applied?

(b) What will be the dielectric displacement D?

Solution

(a) We solve this portion of the problem by computing the value of ε_r using Equation 18.32. Rearranging this equation such that ε_r is the dependent parameter gives the following:

$$\varepsilon_r = \frac{P}{\varepsilon_0 E} + 1$$

When values of the parameters on the right-hand side of this equation are inserted the value of ε_r equal to

$$\varepsilon_r = \frac{4.0 \times 10^{-6}\ \mathrm{C/m^2}}{(8.85 \times 10^{-12}\ \mathrm{F/m})(1 \times 10^5\ \mathrm{V/m})} + 1$$

$$= 5.52$$

(b) The dielectric displacement *D* may be determined using Equation 18.31, as follows:

$$D = \varepsilon_0 E + P$$

$$= (8.85 \times 10^{-12}\ \mathrm{F/m})(1 \times 10^5\ \mathrm{V/m}) + 4.0 \times 10^{-6}\ \mathrm{C/m^2}$$

$$= 4.89 \times 10^{-6}\ \mathrm{C/m^2}$$

18.55 *A charge of 2.0 × 10^{-10} C is to be stored on each plate of a parallel-plate capacitor having an area of 650 mm^2 (1.0 $in.^2$) and a plate separation of 4.0 mm (0.16 in.).*

(a) What voltage is required if a material having a dielectric constant of 3.5 is positioned within the plates?

(b) What voltage would be required if a vacuum were used?

(c) What are the capacitances for parts (a) and (b)?

(d) Compute the dielectric displacement for part (a).

(e) Compute the polarization for part (a).

Solution

(a) For this part of the problem we want to solve for the voltage when $Q = 2.0 \times 10^{-10}$ C, $A = 650$ mm^2, $l = 4.0$ mm, and $\varepsilon_r = 3.5$. Combining Equations 18.24, 18.26, and 18.27 yields

$$C = \frac{Q}{V}$$

$$= \varepsilon \frac{A}{l}$$

$$= \varepsilon_r \varepsilon_0 \frac{A}{l}$$

Or

$$\frac{Q}{V} = \varepsilon_r \varepsilon_0 \frac{A}{l}$$

Now, solving for *V*, and incorporating values provided in the problem statement, leads to the following:

$$V = \frac{Ql}{\varepsilon_r \varepsilon_0 A}$$

$$= \frac{(2.0 \times 10^{-10}\ \mathrm{C})(4.0 \times 10^{-3}\mathrm{m})}{(3.5)(8.85 \times 10^{-12}\ \mathrm{F/m})(650\ \mathrm{mm}^2)(1\ \mathrm{m}^2/10^6\ \mathrm{mm}^2)}$$

$$= 39.7\ \mathrm{V}$$

(b) For this same capacitor, if a vacuum is used, then the value of ε_r in the preceding equation is equal to unity (i.e., 1); now, solving for *V* leads to the following:

$$V = \frac{Ql}{\varepsilon_0 A}$$

$$= \frac{(2.0 \times 10^{-10}\ \mathrm{C})(4.0 \times 10^{-3}\ \mathrm{m})}{(8.85 \times 10^{-12}\ \mathrm{F/m})(650 \times 10^{-6}\ \mathrm{m}^2)}$$

$$= 139\ \mathrm{V}$$

(c) The capacitance for part (a) is computed using Equation 18.24 as follows:

$$C = \frac{Q}{V} = \frac{2.0 \times 10^{-10}\ \mathrm{C}}{39.7\ \mathrm{V}} = 5.04 \times 10^{-12}\ \mathrm{F}$$

While for part (b) the capacitance is

$$C = \frac{Q}{V} = \frac{2.0 \times 10^{-10}\ \mathrm{C}}{139\ \mathrm{V}} = 1.44 \times 10^{-12}\ \mathrm{F}$$

(d) The dielectric displacement may be computed by combining Equations 18.31, 18.32 and 18.6, as follows:

$$D = \varepsilon_0 E + P$$

$$= \varepsilon_0 E + \varepsilon_0(\varepsilon_r - 1)E$$

$$= \varepsilon_0 \varepsilon_r E$$

$$= \frac{\varepsilon_0 \varepsilon_r V}{l}$$

And incorporating values for ε_r and l provided in the problem statement, as well as the value of V computed in part (a) results in the following value for D:

$$D = \frac{(8.85 \times 10^{-12}\ \mathrm{F/m})(3.5)(39.7\ \mathrm{V})}{4.0 \times 10^{-3}\ \mathrm{m}}$$

$$= 3.07 \times 10^{-7}\ \mathrm{C/m^2}$$

(e) The polarization is determined using Equations 18.32 and 18.6 as follows:

$$P = \varepsilon_0(\varepsilon_r - 1)E$$

$$= \varepsilon_0(\varepsilon_r - 1)\frac{V}{l}$$

$$= \frac{(8.85 \times 10^{-12}\,\mathrm{F/m})(3.5 - 1)(39.7\ \mathrm{V})}{4.0 \times 10^{-3}\,\mathrm{m}}$$

$$= 2.20 \times 10^{-7}\ \mathrm{C/m^2}$$

18.56 *(a) For each of the three types of polarization, briefly describe the mechanism by which dipoles are induced and/or oriented by the action of an applied electric field.*

(b) For gaseous argon, solid LiF, liquid H_2O*, and solid Si, what kind(s) of polarization is (are) possible? Why?*

Solution

(a) For electronic polarization, the electric field causes a net displacement of the center of the negatively charged electron cloud relative to the positive nucleus. With ionic polarization, the cations and anions are displaced in opposite directions as a result of the application of an electric field. Orientation polarization is found in substances that possess permanent dipole moments; these dipole moments become aligned in the direction of the electric field.

(b) Only electronic polarization is to be found in gaseous argon; being an inert gas, its atoms will not be ionized nor possess permanent dipole moments.

Both electronic and ionic polarizations will be found in solid LiF, since it is strongly ionic. In all probability, no permanent dipole moments will be found in this material.

Both electronic and orientation polarizations are found in liquid H_2O. The H_2O molecules have permanent dipole moments that are easily oriented in the liquid state.

Only electronic polarization is to be found in solid Si; this material does not have molecules with permanent dipole moments, nor is it an ionic material.

18.57 *(a) Compute the magnitude of the dipole moment associated with each unit cell of $BaTiO_3$, as illustrated in Figure 18.35.*

(b) Compute the maximum polarization that is possible for this material.

Solution

(a) This portion of the problem asks that we compute the magnitude of the dipole moment associated with each unit cell of $BaTiO_3$, which is illustrated in Figure 18.35. The dipole moment p is defined by Equation 18.28 as $p = qd$ in which q is the magnitude of each dipole charge, and d is the distance of separation between the charges. Each Ti^{4+} ion has four units of charge associated with it, and thus $q = (4)(1.602 \times 10^{-19}\ \text{C}) = 6.41 \times 10^{-19}$ C. Furthermore, d is the distance the Ti^{4+} ion has been displaced from the center of the unit cell, which is just 0.006 nm + 0.006 nm = 0.012 nm (Figure 18.35*b*). Hence

$$p = qd = (6.41 \times 10^{-19}\ \text{C})(0.012 \times 10^{-9}\ \text{m})$$

$$= 7.69 \times 10^{-30}\ \text{C-m}$$

(b) Now it becomes necessary to compute the maximum polarization that is possible for this material. The maximum polarization will exist when the dipole moments of all unit cells are aligned in the same direction. Furthermore, it is computed by dividing the above value of p by the volume of each unit cell, which is equal to the product of three unit cell edge lengths, as shown in Figure 18.35. Thus

$$P = \frac{p}{V_C}$$

$$= \frac{7.69 \times 10^{-30}\ \text{C-m}}{(0.403 \times 10^{-9}\ \text{m})(0.398 \times 10^{-9}\ \text{m})(0.398 \times 10^{-9}\ \text{m})}$$

$$= 0.120\ \text{C/m}^2$$

Frequency Dependence of the Dielectric Constant

18.58 *The dielectric constant for a soda–lime glass measured at very high frequencies (on the order of 10^{15} Hz) is approximately 2.3. What fraction of the dielectric constant at relatively low frequencies (1 MHz) is attributed to ionic polarization? Neglect any orientation polarization contributions.*

Solution

For this soda-lime glass, in order to compute the fraction of the dielectric constant at low frequencies that is attributed to ionic polarization, we must determine the ε_r within this low-frequency regime; such is tabulated in Table 18.5, and at 1 MHz its value is 6.9. Thus, this fraction is just

$$\text{fraction} = \frac{\varepsilon_r(\text{low}) - \varepsilon_r(\text{high})}{\varepsilon_r(\text{low})}$$

$$= \frac{6.9 - 2.3}{6.9} = \mathbf{0.67}$$

Ferroelectricity

18.59 *Briefly explain why the ferroelectric behavior of* $BaTiO_3$ *ceases above its ferroelectric Curie temperature.*

Answer

The ferroelectric behavior of $BaTiO_3$ ceases above its ferroelectric Curie temperature because, above the ferroelectric Curie temperature the unit cell transforms from tetragonal geometry to cubic; thus, the Ti^{4+} is situated at the center of the cubic unit cell, there is no charge separation, and no net dipole moment.

DESIGN PROBLEMS

Electrical Resistivity of Metals

18.D1 *A 90 wt% Cu–10 wt% Ni alloy is known to have an electrical resistivity of 1.90 × 10^{-7} Ω-m at room temperature (25°C). Calculate the composition of a copper–nickel alloy that gives a room-temperature resistivity of 2.5 × 10^{-7} Ω•m. The room-temperature resistivity of pure copper may be determined from the data in Table 18.1; assume that copper and nickel form a solid solution.*

Solution

This problem asks that we calculate the composition of a copper-nickel alloy that has a room temperature resistivity of 2.5 × 10^{-7} Ω-m. The first thing to do is, using the 90 Cu-10 Ni resistivity value (1.90 × 10^{-7} Ω-m), determine the impurity contribution, and, from this result, calculate the constant *A* in Equation 18.11. From Equation 18.9 we write the following expression:

$$\rho_{\text{total}(1)} = 1.90 \times 10^{-7}\ (\Omega\text{-m}) = \rho_{i(1)} + \rho_t$$

(*Note:* we have elected to use $\rho_{\text{total}(1)}$ and $\rho_{i(1)}$ to denote the total and impurity contribution conductivities for the 90 wt% Cu-10 wt% Ni alloy.) From Table 18.1, the conductivity for pure copper (σ_t) is 6.0 × 10^7 (Ω-m)$^{-1}$. Using this value we compute the electrical resistivity (which is ρ_t) using Equation 18.4 as follows:

$$\rho_t = \frac{1}{\sigma_t} = \frac{1}{6.0 \times 10^7\ (\Omega\text{-m})^{-1}} = 1.67 \times 10^{-8}\ (\Omega\text{-m})$$

Thus, for the 90 Cu-10 Ni alloy, the impurity contribution to the total conductivity is computed as follows:

$$\rho_{i(1)} = \rho_{\text{total}(1)} - \rho_t = 1.90 \times 10^{-7}\ (\Omega\text{-m}) - 1.67 \times 10^{-8}\ (\Omega\text{-m})$$

$$1.73 \times 10^{-7}\ (\Omega\text{-m})$$

In the problem statement, the impurity (i.e., nickel) concentration is expressed in weight percent. However, Equation 18.11 calls for concentration in atom fraction (i.e., atom percent divided by 100). Consequently, conversion from weight percent to atom fraction is necessary. (Note: we now choose to denote the atom fraction of nickel as c'_{Ni}, and the weight percents of Ni and Cu by C_{Ni} and C_{Cu}, respectively.) Using these notations, the conversion of 90 wt% Cu-10 wt% Ni may be accomplished by using a modified form of Equation 4.6a as follows:

$$c'_{\text{Ni}} = \frac{C'_{\text{Ni}}}{100} = \frac{C_{\text{Ni}}A_{\text{Cu}}}{C_{\text{Ni}}A_{\text{Cu}} + C_{\text{Cu}}A_{\text{Ni}}}$$

Here A_{Ni} and A_{Cu} denote the atomic weights of nickel and copper (which values are 58.69 and 63.55 g/mol, respectively). (Also, we have chosen to denote this value of c'_{Ni} as $c'_{\text{Ni(1)}}$ so as not confuse it with the unknown $c'_{\text{Ni(2)}}$). Therefore we compute the value of $c'_{\text{Ni(1)}}$ as follows:

$$c'_{\text{Ni(1)}} = \frac{(10 \text{ wt\%})(63.55 \text{ g/mol})}{(10 \text{ wt\%})(63.55 \text{ g/mol}) + (90 \text{ wt\%})(58.69 \text{ g/mol})}$$

$$= 0.107$$

We now want to solve for the value of *A* in Equation 18.11. Rearrangement of this expression such that *A* is the dependent variable leads to

$$A = \frac{\rho_{i(1)}}{c'_{\text{Ni(1)}}\left(1 - c'_{\text{Ni(1)}}\right)}$$

and upon incorporation of values of ρ_i and $c'_{\text{Ni(1)}}$ determined above, leads to the computation of the value of *A* as follows:

$$A = \frac{1.73 \times 10^{-7} (\Omega\text{-m})}{(0.107)(1 - 0.107)} = 1.81 \times 10^{-6} \ (\Omega\text{-m})$$

Now it is possible to compute the c'_{Ni} [which we designate $c'_{\text{Ni(2)}}$] to give a room temperature resistivity of 2.5 × 10^{-7} Ω-m and represented by $\rho_{\text{total(2)}}$. The impurity resistivity contribution for this unknown composition $\rho_{i(2)}$ may be determined using a rearranged form of Equation 18.9 as follows:

$$\rho_{i(2)} = \rho_{\text{total(2)}} - \rho_t$$

$$= 2.5 \times 10^{-7} (\Omega\text{-m}) - 1.67 \times 10^{-8} \ (\Omega\text{-m}) = 2.33 \times 10^{-7} \ (\Omega\text{-m})$$

We may represent Equation 18.11 in its expanded form as follows:

$$\rho_i = Ac'_{\text{Ni}} - Ac'^{2}_{\text{Ni}}$$

Or, rearranging this equation, we have

$$Ac'^{2}_{\text{Ni}} - Ac'_{\text{Ni}} + \rho_i = 0$$

Since this is a quadratic equation, we solve for c'_{Ni} using the quadratic equation solution—that is

$$c'_{\mathrm{Ni}} = \frac{A \pm \sqrt{A^2 - 4A\rho_i}}{2A}$$

which, for this problem, takes the form

$$c'_{\mathrm{Ni}(2)} = \frac{A \pm \sqrt{A^2 - 4A\rho_{i_2}}}{2A}$$

Again, incorporating the following values

$A = 1.81 \times 10^{-6}$ (Ω-m)

$\rho_{i(2)} = 2.33 \times 10^{-7}$ (Ω-m)

leads to

$$c'_{\mathrm{Ni}(2)} = \frac{1.81 \times 10^{-6} \pm \sqrt{(1.81 \times 10^{-6})^2 - (4)(1.81 \times 10^{-6})(2.33 \times 10^{-7})}}{(2)(1.81 \times 10^{-6})}$$

$$= \frac{1.81 \times 10^{-6} \pm 1.26 \times 10^{-6}}{3.62 \times 10^{-6}}$$

The two roots for this solution are as follows:

$c'_{\mathrm{Ni}(2)}[+] = 0.848$

$c'_{\mathrm{Ni}(2)}[-] = 0.152$

And, taking the negative root, 0.152, is the concentration of Ni (in at%/100), while the positive root (0.848) is the concentration of Cu. Or, in terms of atom percent,

$$C'_{\mathrm{Ni}(2)} = (0.152)(100) = 15.2 \text{ at\%}$$

$$C'_{\mathrm{Cu}(2)} = (0.848)(100) = 84.8 \text{ at\%}$$

To convert these compositions to weight percent requires that we use Equation 4.7a as follows:

$$C_{\mathrm{Ni}} = \frac{C'_{\mathrm{Ni}(2)} A_{\mathrm{Ni}}}{C'_{\mathrm{Ni}(2)} A_{\mathrm{Ni}} + C'_{\mathrm{Cu}(2)} A_{\mathrm{Cu}}} \text{ x } 100$$

$$= \frac{(15.2 \text{ at\%})(58.69 \text{ g/mol})}{(15.2 \text{ at\%})(58.69 \text{ g/mol}) + (84.8 \text{ at\%})(63.55 \text{ g/mol})} \times 100$$

= 14.2 wt%

18.D2 *Using information contained in Figures 18.8 and 18.39, determine the electrical conductivity of an 85 wt% Cu–15 wt% Zn alloy at –100° C (–150°F).*

Solution

This problem asks that we determine the electrical conductivity of an 85 wt% Cu-15 wt% Zn alloy at –100°C using information contained in Figures 18.8 and 18.39. In order to solve this problem it is necessary to employ Equation 18.9, which is of the form

$$\rho_{\text{total}} = \rho_t + \rho_i$$

since it is assumed that the alloy is undeformed (i.e., that $\rho_d = 0$). Let us first determine the value of ρ_i at room temperature (25°C) which value will be independent of temperature. From Figure 18.8, at 25°C and for pure Cu, $\rho_t(25) = 1.75 \times 10^{-8}$ Ω-m. Now, since the curve in Figure 18.39 was generated also at room temperature, we may take ρ as $\rho_{\text{total}}(25)$ at 85 wt% Cu-15 wt% Zn which has a value of 4.7×10^{-8} Ω-m. Thus, rearranging Equation 18.9 (as presented above)

$$\rho_i = \rho_{\text{total}}(25) - \rho_t(25)$$

$$= 4.7 \times 10^{-8}\ \Omega\text{-m} - 1.75 \times 10^{-8}\ \Omega\text{-m} = 2.95 \times 10^{-8}\ \Omega\text{-m}$$

Finally, we may determine the resistivity at –100°C, $\rho_{\text{total}}(-100)$, by taking the resistivity of pure Cu at –100°C from Figure 18.8, which gives us $\rho_t(-100) = 0.90 \times 10^{-8}$ Ω-m. Therefore

$$\rho_{\text{total}}(-100) = \rho_i + \rho_t(-100)$$

$$= 2.95 \times 10^{-8}\ \Omega\text{-m} + 0.90 \times 10^{-8}\ \Omega\text{-m} = 3.85 \times 10^{-8}\ \Omega\text{-m}$$

And, using Equation 18.4 the conductivity is calculated as follows:

$$\sigma_{\text{total}} = \frac{1}{\rho_{\text{total}}} = \frac{1}{3.85 \times 10^{-8}\ \Omega\text{-m}} = 2.60 \times 10^{7}\ (\Omega\text{-m})^{-1}$$

18.D3 *Is it possible to alloy copper with nickel to achieve a minimum yield strength of 130 MPa (19,000 psi) and yet maintain an electrical conductivity of 4.0 × 10^6 (Ω•m)$^{-1}$? If not, why? If so, what concentration of nickel is required? See Figure 7.16b.*

Solution

To solve this problem, we want to consult Figures 7.16*b* and 18.9 in order to determine the Ni concentration ranges over which the yield strength is greater than 130 MPa (19,000 psi) and the conductivity exceeds 4.0 × 10^6 (Ω-m)$^{-1}$.

From Figure 7.16*b*, a Ni concentration greater than about 23 wt% is necessary for a yield strength in excess of 130 MPa. In Figure 18.9 is plotted the resistivity versus the Ni content. Since conductivity is the reciprocal of resistivity (Equation 18.4), the resistivity must be less than

$$\rho < \frac{1}{4 \times 10^6\ (\Omega\text{-m})^{-1}} = 25 \times 10^{-8}\ (\Omega\text{-m})$$

From Figure 18.9, a Cu-Ni alloy having a concentration less than 17 wt% is necessary to achieve a resistivity of less than 25 × 10^{-8} (Ω-m).

Hence, it is *not* possible to prepare an alloy meeting the criteria; for the stipulated yield strength the required Ni content must be greater than 23 wt%, whereas for the required conductivity, less than 17 wt% Ni is necessary.

Extrinsic Semiconduction

Factors That Affect Carrier Mobility

18.D4 *Specify a donor impurity type and concentration (in weight percent) that will produce an n-type silicon material having a room-temperature electrical conductivity of 200 (Ω·m)$^{-1}$.*

Solution

First of all, those elements which, when added to silicon render it *n*-type, lie one group to the right of silicon in the periodic table; these include the group VA elements (Figure 2.8)—i.e., nitrogen, phosphorus, arsenic, and antimony.

Since this material is extrinsic and *n*-type, $n >> p$, and the electrical conductivity is a function of the hole concentration according to Equation 18.16—that is

$$\sigma = n|e|\mu_e$$

Also, the number of free electrons is about equal to the number of donor impurities, N_d. That is

$$n \sim N_d$$

Furthermore, the room-temperature electron mobility is dependent on impurity concentration as represented in Figure 18.18. One way to solve this problem is to use an iterative approach—i.e., assume some donor impurity concentration (which will also equal the value of *n*), and then determine a "calculated" electron mobility from a rearranged form of Equation 18.16—i.e.,

$$\mu_e = \frac{\sigma}{n\,|e|}$$

Finally, compare this mobility with the "measured" value from Figure 18.18, taken at the assumed *n* (i.e., N_d) value.

Let us begin by assuming that $N_d = 10^{22}$ m^{-3}. Thus, the "calculated" mobility value is

$$\mu_e = \frac{\sigma}{n|e|} = \frac{200\ (\Omega\text{-m})^{-1}}{(10^{22}\ \text{m}^{-3})(1.602 \times 10^{-19}\ \text{C})} = 0.125\ \text{m}^2/\text{V-s}$$

From Figure 18.18, at an impurity concentration of 10^{22} m^{-3} the "measured" electron mobility is 0.10 m^2/V-s, which is slightly lower than the "calculated" value.

For our second choice for n, let us assume a higher impurity concentration, say 10^{23} m^{-3}. At this higher concentration there will be a reduction of both "calculated" and "measured" electron mobilities. The "calculated" mobility is just

$$\mu_e = \frac{\sigma}{n|e|} = \frac{200\ (\Omega\text{-m})^{-1}}{(10^{23}\,\text{m}^{-3})(1.602 \times 10^{-19}\ \text{C})} = 0.0125\ \text{m}^2/\text{V-s}$$

Whereas, Figure 18.18 yields a "measured" μ_e of about 0.06 m^2/V-s, which is higher than the "calculated" value. Therefore, the correct impurity concentration will lie somewhere between 10^{22} and 10^{23} m^{-3} probably closer to the lower of these two values. At 1.3 × 10^{22} m^{-3}, both "measured" and "calculated" μ_e values are about equal (0.095 m^2/V-s).

It next becomes necessary to calculate the concentration of donor impurities in atom percent. This computation first requires the determination of the number of silicon atoms per cubic meter, N_{Si}, using Equation 4.2, which is as follows (using values of 2.33 g/cm^3 and 28.09 g/mol, respectively, for the density and atomic weight of Si):

$$N_{\text{Si}} = \frac{N_A \rho'_{\text{Si}}}{A_{\text{Si}}}$$

$$= \frac{(6.022 \times 10^{23}\ \text{atoms/mol})(2.33\ \text{g/cm}^3)(10^6\ \text{cm}^3/\text{m}^3)}{28.09\ \text{g/mol}}$$

$$= 5.00 \times 10^{28}\ \text{m}^{-3}$$

(*Note:* in the above discussion, the density of silicon is represented by ρ'_{Si} in order to avoid confusion with resistivity, which is designated by ρ.)

The concentration of donor impurities in atom percent (C'_d) is just the ratio of N_d and $(N_d + N_{\text{Si}})$ multiplied by 100 as follows:

$$C'_d = \frac{N_d}{N_d + N_{\text{Si}}} \times 100$$

$$= \frac{1.3 \times 10^{22}\ \text{m}^{-3}}{(1.3 \times 10^{22}\ \text{m}^{-3}) + (5 \times 10^{28}\ \text{m}^{-3})} \times 100 = 2.60 \times 10^{-5}\ \text{at\%}$$

Now, conversion from atom percent to weight percent (C_d) is possible using Equation 4.7a as follows:

$$C_d = \frac{C'_d A_d}{C'_d A_d + C'_{\text{Si}} A_{\text{Si}}} \times 100$$

Here A_d and A_{Si} are the atomic weights of the donor and silicon, respectively. Thus, the concentration in weight percent will depend on the particular donor type. For example, for nitrogen

$$C_{\text{N}} = \frac{C'_{\text{N}} A_{\text{N}}}{C'_{\text{N}} A_{\text{N}} + C'_{\text{Si}} A_{\text{Si}}} \times 100$$

$$= \frac{(2.60 \times 10^{-5} \text{ at\%})(14.01 \text{ g/mol})}{(2.60 \times 10^{-5} \text{ at\%})(14.01 \text{ g/mol}) + (99.999974 \text{ at\%})(28.09 \text{ g/mol})} \times 100$$

$$= 1.30 \times 10^{-5} \text{ wt\%}$$

Similar calculations may be carried out for the other possible donor impurities, which yield the following:

$$C_{\text{P}} = 2.87 \times 10^{-5} \text{ wt\%}$$

$$C_{\text{As}} = 6.93 \times 10^{-5} \text{ wt\%}$$

$$C_{\text{Sb}} = 1.127 \times 10^{-4} \text{ wt\%}$$

18.D5 *One integrated circuit design calls for diffusing boron into very high-purity silicon at an elevated temperature. It is necessary that at a distance 0.2 μm from the surface of the silicon wafer, the room-temperature electrical conductivity be 1000 (Ω•m)*$^{-1}$*. The concentration of B at the surface of the Si is maintained at a constant level of 1.0 × 10*^{25} *m*$^{-3}$*; furthermore, it is assumed that the concentration of B in the original Si material is negligible, and that at room temperature the boron atoms are saturated. Specify the temperature at which this diffusion heat treatment is to take place if the treatment time is to be 1 h. The diffusion coefficient for the diffusion of B in Si is a function of temperature as*

$$D(\mathrm{m^2/s}) = 2.4 \times 10^{-4} \exp\left(-\frac{347{,}000\ \mathrm{J/mol}}{RT}\right)$$

Solution

This problem asks for us to determine the temperature at which boron is to be diffused into high-purity silicon in order to achieve a room-temperature electrical conductivity of 1000 (Ω-m)$^{-1}$ at a distance 0.2 μm from the surface if the B concentration at the surface is maintained at 1.0 × 10^{25} m^{-3}. It is first necessary for us to compute the hole concentration (since B is an acceptor in Si) at this 0.2 μm location.

From Equation 18.17, the conductivity is a function of both the hole concentration (p) and the hole mobility (μ_h). Furthermore, the room-temperature hole mobility is dependent on impurity concentration (Figure 18.18). One way to solve this problem is to use an iterative approach—i.e., assume some boron concentration, N_B (which will also equal the value of p), then determine a "calculated" hole mobility from a rearranged form of Equation 18.17—i.e.,

$$\mu_h = \frac{\sigma}{p|e|}$$

and then compare this mobility with the "measured" value from Figure 18.18, taken at the assumed p (i.e., N_B).

Let us begin by assuming that $N_B = 10^{24}$ m^{-3}. Thus, the "calculated" mobility value is

$$\mu_h = \frac{\sigma}{p|e|} = \frac{1000\ (\Omega\text{-m})^{-1}}{(10^{24}\ \mathrm{m^{-3}})(1.602 \times 10^{-19}\ \mathrm{C})} = 0.00624\ \mathrm{m^2/V\text{-}s}$$

From Figure 18.18, at an impurity concentration of 10^{24} m^{-3} the "measured" hole mobility is 0.01 m^2/V-s, which is higher than the "calculated" value.

For our next choice, let us assume a lower boron concentration, say 10^{23} m^{-3}. At this lower concentration there will be an increase of both "calculated" and "measured" hole mobilities. The "calculated" value is just

$$\mu_h = \frac{\sigma}{p|e|} = \frac{1000\ (\Omega\text{-m})^{-1}}{(10^{23}\ \mathrm{m^{-3}})(1.602 \times 10^{-19}\ \mathrm{C})} = 0.0624\ \mathrm{m^2/V\text{-}s}$$

Whereas, Figure 18.18 yields a "measured" μ_h of 0.024 m^2/V-s at a concentration of 10^{23} m^{-3}, which is lower than the "calculated" value. Therefore, the correct impurity concentration will lie somewhere between 10^{23} and 10^{24} m^{-3}. At 4.0×10^{23} m^{-3}, "measured" and "calculated" values are about equal (0.015 m^2/V-s).

With regard to diffusion, the problem is one involving the nonsteady-state diffusion of B into the Si, wherein we have to solve for temperature. Temperature is incorporated into the diffusion coefficient expression given in the problem statement. But we must first employ the solution to Fick's second law for constant surface composition boundary conditions, Equation 5.5; in this expression C_0 is taken to be zero inasmuch as the problem stipulates that the initial boron concentration may be neglected. Thus, incorporation of the appropriate values into Equation 5.5 yields the following:

$$\frac{C_x - C_0}{C_s - C_0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$\frac{4.0 \times 10^{23}\,\mathrm{m}^{-3} - 0}{1.0 \times 10^{25}\,\mathrm{m}^{-3} - 0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

which reduces to

$$0.9600 = \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

In order to solve this expression for a value $\frac{x}{2\sqrt{Dt}}$ of it is necessary to interpolate using data in Table 5.1 and using a procedure detailed in Example Problem 5.2. Thus

z	erf(z)
1.4	0.9523
z	0.9600
1.5	0.9661

$$\frac{z - 1.4}{1.5 - 1.4} = \frac{0.9600 - 0.9523}{0.9661 - 0.9523}$$

From which, $z = 1.4558$; which is to say that

$$1.4558 = \frac{x}{2\sqrt{Dt}}$$

Inasmuch as there are 3600 s/h (= t) and $x = 0.2$ μm (= 2×10^{-7} m) the above equation becomes

$$1.4558 = \frac{2 \times 10^{-7}\ \mathrm{m}}{2\sqrt{(D)(3600\ \mathrm{s})}}$$

which, when solving for the value of D, leads to the following

$$D = \frac{1}{3600\ \mathrm{s}}\left[\frac{2 \times 10^{-7}\ \mathrm{m}}{(2)(1.4558)}\right]^2 = 1.31 \times 10^{-18}\ \mathrm{m^2/s}$$

Now, equating this value to the expression for D given in the problem statement gives the following:

$$D = 1.31 \times 10^{-18}\ \mathrm{m^2/s} = \left(2.4 \times 10^{-4}\right)\exp\left[-\frac{347{,}000\ \mathrm{J/mol}}{(8.31\ \mathrm{J/mol\text{-}K})(T)}\right]$$

To solve for T, let us take the natural logarithms of both sides of the above equation; this leads to the following expression:

$$\ln\left(1.31 \times 10^{-18}\right) = \ln\left(2.4 \times 10^{-4}\right) - \frac{347{,}000}{8.31T}$$

which reduces to

$$-41.176 = -8.335 - \frac{4.176 \times 10^4}{T}$$

and yields a value for T of 1271 K (998°C).

Semiconductor Devices

18.D6 *One of the procedures in the production of integrated circuits is the formation of a thin insulating layer of* SiO_2 *on the surface of chips (see Figure 18.26). This is accomplished by oxidizing the surface of the silicon by subjecting it to an oxidizing atmosphere (i.e., gaseous oxygen or water vapor) at an elevated temperature. The rate of growth of the oxide film is parabolic—that is, the thickness of the oxide layer (x) is a function of time (t) according to the following equation:*

$$x^2 = Bt \tag{18.37}$$

Here the parameter B is dependent on both temperature and the oxidizing atmosphere.

(a) For an atmosphere of O_2 *at a pressure of 1 atm, the temperature dependence of B (in units of* $\mu m^2/h$*) is as follows:*

$$B = 800 \exp\left(-\frac{1.24\ \text{eV}}{kT}\right) \tag{18.38a}$$

where k is Boltzmann's constant (8.62 × 10^{-5} *eV/atom) and T is in K. Calculate the time required to grow an oxide layer (in an atmosphere of* O_2*) that is 100 nm thick at both 700°C and 1000°C.*

(b) In an atmosphere of H_2O *(1 atm pressure), the expression for B (again in units of* $\mu m^2/h$*) is*

$$B = 215\ \exp\left(-\frac{0.70\ \text{eV}}{kT}\right) \tag{18.38b}$$

Calculate the time required to grow an oxide layer that is 100 nm thick (in an atmosphere of H_2O*) at both 700°C and 1000°C, and compare these times with those computed in part (a).*

Solution

(a) In this portion of the problem we are asked to determine the time required to grow a layer of SiO_2 that is 100 nm (i.e., 0.100 µm) thick on the surface of a silicon chip at 1000°C, in an atmosphere of O_2 (oxygen pressure = 1 atm). Thus, using Equation 18.37, it is necessary to solve for the time *t*. However, before this is possible, we must calculate the value of *B* from Equation 18.38a as follows:

$$B = 800 \exp\left(-\frac{1.24\ \text{eV}}{kT}\right)$$

$$= (800) \exp\left[-\frac{1.24\ \text{eV}}{(8.62 \times 10^{-5}\ \text{eV/atom-K})(1000 + 273\ \text{K})}\right]$$

$$= 0.00990\ \mu\text{m}^2/\text{h}$$

Now, solving for t from Equation 18.37 using the above value for B and realizing that $x = 0.100$ µm, we have

$$t = \frac{x^2}{B} = \frac{(0.100\ \mu\text{m})^2}{0.00990\ \mu\text{m}^2/\text{h}}$$

$$= 1.01\ \text{h}$$

Repeating the computation for B at 700°C leads to the following:

$$B = (800)\exp\left[-\frac{1.24\ \text{eV}}{(8.62\ \times\ 10^{-5}\ \text{eV/atom-K})(700 + 273\ \text{K})}\right]$$

$$= 3.04 \times 10^{-4}\ \mu\text{m}^2/\text{h}$$

And solving for the oxidation time as above

$$t = \frac{x^2}{B} = \frac{(0.100\ \mu\text{m})^2}{3.04\ \times\ 10^{-4}\ \mu\text{m}^2/\text{h}}$$

$$= \mathbf{32.9\ h}$$

(b) This part of the problem asks for us to compute the heating times to form an oxide layer 100 nm thick at the same two temperatures (1000°C and 700°C) when the atmosphere is water vapor (1 atm pressure). At 1000°C, the value of B is determined using Equation 18.38b, as follows:

$$B = 215\exp\left(-\frac{0.70\ \text{eV}}{kT}\right)$$

$$= (215)\exp\left[-\frac{0.70\ \text{eV}}{(8.62\ \times\ 10^{-5}\ \text{eV/atom-K})(1000 + 273\ \text{K})}\right]$$

$$= 0.365\ \mu\text{m}^2/\text{h}$$

And computation of the time t from the rearranged form of Equation 18.37, leads to

$$t = \frac{x^2}{B} = \frac{(0.100\ \mu\text{m})^2}{0.365\ \mu\text{m}^2/\text{h}}$$

$$= 0.0274 \text{ h} = 98.6 \text{ s}$$

And at 700°C, the value of B is computed as follows:

$$B = (215)\exp\left[-\frac{0.70 \text{ eV}}{(8.62 \times 10^{-5} \text{ eV/atom-K})(700 + 273 \text{ K})}\right] = 0.0510\ \mu\text{m}^2/\text{h}$$

Whereas the time required to grow the 100 nm oxide layer is

$$t = \frac{x^2}{B} = \frac{(0.100\ \mu\text{m})^2}{0.0510\ \mu\text{m}^2/\text{h}}$$

$$= 0.196 \text{ h} = 706 \text{ s}$$

From the above computations, it is very apparent (1) that the 100 nm oxide layer forms more rapidly at 1000°C (than at 700°C) in both O_2 and H_2O gaseous atmospheres, and (2) that the oxide layer formation is more rapid in water vapor than in oxygen.

18.D7 *The base semiconducting material used in virtually all modern integrated circuits is silicon. However, silicon has some limitations and restrictions. Write an essay comparing the properties and applications (and/or potential applications) of silicon and gallium arsenide.*

Answer

We are asked to compare silicon and gallium arsenide semiconductors relative to properties and applications.

The following are the characteristics and applications for Si: (1) being an elemental semiconductor, it is cheaper to grow in single-crystalline form; (2) because of its electron band structure, it is best used in transistors; (3) electronic processes are relatively slow due to the low mobilities for electrons and holes (Table 18.3).

For GaAs: (1) it is much more expensive to produce inasmuch as it is a compound semiconductor; (2) because of its electron band structure it is best used in light-emitting diodes and semiconducting lasers; (3) its band gap may be altered by alloying; (4) electronic processes are more rapid than in Si due to the greater mobilities for electrons and holes; (5) absorption of electromagnetic radiation is greater in GaAs, and therefore, thinner layers are required for solar cells.

Conduction in Ionic Materials

18.D8 *Problem 18.47 noted that FeO (wüstite) may behave as a semiconductor by virtue of the transformation of* Fe^{2+} *to* Fe^{3+} *and the creation of* Fe^{2+} *vacancies; the maintenance of electroneutrality requires that for every two* Fe^{3+} *ions, one vacancy is formed. The existence of these vacancies is reflected in the chemical formula of this nonstoichiometric wüstite as* $Fe_{(1-x)}O$*, where x is a small number having a value less than unity. The degree of nonstoichiometry (i.e., the value of x) may be varied by changing temperature and oxygen partial pressure. Compute the value of x that is required to produce an* $Fe_{(1-x)}O$ *material having a p-type electrical conductivity of 1200* $(\Omega\cdot m)^{-1}$*; assume that the hole mobility is* 1.0×10^{-5} $m^2/V\cdot s$*, the crystal structure for FeO is sodium chloride (with a unit cell edge length of 0.437 nm), and the acceptor states are saturated.*

Solution

This problem asks, for the nonstoichiometric $Fe_{(1-x)}O$, given the electrical conductivity [1200 $(\Omega\text{-m})^{-1}$] and hole mobility (1.0×10^{-5} $m^2/V\text{-s}$) that we determine the value of x. It is first necessary to compute the number of holes per unit volume (p) using a rearranged form of Equation 18.17. Thus

$$p = \frac{\sigma}{|e|\,\mu_h}$$

$$= \frac{1200\ (\Omega\text{-m})^{-1}}{(1.602 \times 10^{-19}\ \text{C})(1.0 \times 10^{-5}\ \text{m}^2/\text{V-s})} = 7.49 \times 10^{26}\ \text{holes/m}^3$$

Inasmuch as it is assumed that the acceptor states are saturated, the number of vacancies is also 7.49×10^{26} m^{-3}. Next, it is possible to compute the number of vacancies per unit cell by taking the product of the number of vacancies per cubic meter times the volume of a unit cell. This volume is just the unit cell edge length (0.437 nm) cubed:

$$\frac{\#\ \text{vacancies}}{\text{unit cell}} = (7.49 \times 10^{26}\ \text{m}^{-3})(0.437 \times 10^{-9}\ \text{m})^3 = 0.0625$$

A unit cell for the sodium chloride structure contains the equivalence of four cations and four anions. Thus, if we take as a basis for this problem 10 unit cells, there will be 0.625 vacancies, 40 O^{2-} ions, and 39.375 iron ions (since 0.625 of the iron sites is vacant). (It should also be noted that since two Fe^{3+} ions are created for each vacancy, that of the 39.375 iron ions, 38.125 of them are Fe^{2+} and 1.25 of them are Fe^{3+}). In order to find the value of $(1 - x)$ in the chemical formula, we just take the ratio of the number of total Fe ions (39.375) and the number of total Fe ion sites (40). Thus

$$(1 - x) = \frac{39.375}{40} = 0.984$$

Or the formula for this nonstoichiometric material is $Fe_{0.984}O$.

FUNDAMENTALS OF ENGINEERING QUESTIONS AND PROBLEMS

18.1FE *For a metal that has an electrical conductivity of* $6.1 \times 10^7\ (\Omega\cdot m)^{-1}$*, what is the resistance of a wire that is 4.3 mm in diameter and 8.1 m long?*

(A) $3.93 \times 10^{-5}\ \Omega$

(B) $2.29 \times 10^{-3}\ \Omega$

(C) $9.14 \times 10^{-3}\ \Omega$

(D) $1.46 \times 10^{11}\ \Omega$

Solution

The electrical resistivity (ρ) and resistance (R) are related according to Equation 18.2 as follows:

$$\rho = \frac{RA}{l}$$

Furthermore, the conductivity and resistivity are related to one another by Equation 18.4—that is

$$\sigma = \frac{1}{\rho}$$

Combining these equations, and incorporating the expression for the cross-sectional area, A, of a cylindrical specimen—i.e.,

$$A = \pi\left(\frac{d}{2}\right)^2 = \frac{\pi d^2}{4}$$

leads to the following equation for electrical conductivity:

$$\sigma = \frac{1}{\rho} = \frac{1}{\frac{RA}{l}} = \frac{l}{RA} = \frac{l}{R\left(\frac{\pi d^2}{4}\right)} = \frac{4l}{R\pi d^2}$$

And, solving this expression for the resistance, R, leads to the following:

$$R = \frac{4l}{\sigma \pi d^2}$$

Which for this problem gives a value of

$$R = \frac{(4)(8.1\ \text{m})}{\left[6.1\times10^{7}\ (\Omega\text{-m})^{-1}\right](\pi)(4.3\times10^{-3}\ \text{m})^{2}}$$

$$= 9.14 \times 10^{-3}\ \Omega$$

which is answer C.

18.2FE *What is the typical electrical conductivity value/range for semiconducting materials?*

(A) 10^{7} $(\Omega{\cdot}m)^{-1}$

(B) 10^{-20} *to* 10^{7} $(\Omega{\cdot}m)^{-1}$

(C) 10^{-6} *to* 10^{4} $(\Omega{\cdot}m)^{-1}$

(D) 10^{-20} *to* 10^{-10} $(\Omega{\cdot}m)^{-1}$

Answer

The correct answer is C. Semiconducting materials typically have electrical conductivities in the range of 10^{-6} to 10^{4} $(\Omega\text{-m})^{-1}$.

18.3FE *A two-phase metal alloy is known to be composed of α and β phases that have mass fractions of 0.64 and 0.36, respectively. Using the following room-temperature electrical resistivity and density data, calculate the electrical resistivity of this alloy at room temperature.*

Phase	***Resistivity (Ω·m)***	***Density (g/cm^3)***
α	1.9×10^{-8}	*8.26*
β	5.6×10^{-7}	*8.60*

(A) 2.09×10^{-7} *Ω·m*

(B) 2.14×10^{-7} *Ω·m*

(C) 3.70×10^{-7} *Ω·m*

(D) 5.90×10^{-7} *Ω·m*

Solution

For a two-phase alloy composed of α and β phases, Equation 18.12 may be used to approximate the electrical resistivity (ρ_i) of the alloy—i.e.,

$$\rho_i = \rho_\alpha V_\alpha + \rho_\beta V_\beta$$

Here V_α and V_β denote volume fractions of the two phases, and ρ_α and ρ_β their respective resistivities. It is first necessary to convert the mass fractions into phase volume fractions. The mass fraction of phase α (W_α) may be converted into volume fraction (V_α) using Equations 10.6a:

$$V_\alpha = \frac{\dfrac{W_\alpha}{\rho'_\alpha}}{\dfrac{W_\alpha}{\rho'_\alpha} + \dfrac{W_\beta}{\rho'_\beta}}$$

(*Note:* In this equation we use ρ'_α and ρ'_β to represent phase densities so as not to cause confusion with resistivity, which is designated using ρ). Thus, for the α phase we write

$$V_\alpha = \frac{\dfrac{0.64}{8.26\ \mathrm{g/cm^3}}}{\dfrac{0.64}{8.26\ \mathrm{g/cm^3}} + \dfrac{0.36}{8.60\ \mathrm{g/cm^3}}} = 0.649$$

Similarly, for the *β* phase

$$V_\beta = \frac{\dfrac{W_\beta}{\rho'_\beta}}{\dfrac{W_\alpha}{\rho'_\alpha} + \dfrac{W_\beta}{\rho'_\beta}}$$

$$= \frac{\dfrac{0.36}{8.60\ \text{g/cm}^3}}{\dfrac{0.64}{8.26\ \text{g/cm}^3} + \dfrac{0.36}{8.60\ \text{g/cm}^3}} = 0.351$$

Substitution into Equation 18.12 these volume fractions and the phase resistivities given in the problem statement leads to an alloy resistivity value of

$$\rho_i = \rho_\alpha V_\alpha + \rho_\beta V_\beta$$

$$= (1.9 \times 10^{-8}\ \Omega\text{-m})(0.649) + (5.6 \times 10^{-7}\ \Omega\text{-m})(0.351)$$

$$= 2.09 \times 10^{-7}\ \Omega\text{-m}$$

which is answer A.

18.4FE *For an n-type semiconductor, where is the Fermi level located?*

(A) In the valence band

(B) In the band gap just above the top of valence band

(C) In the middle of the band gap

(D) In the band gap just below the bottom of the conduction band

Answer

The correct answer is D. For an *n*-type semiconductor, the Fermi energy is located *just below the conduction band in the band gap*.

18.5FE *The room-temperature electrical conductivity of a semiconductor specimen is* $2.8 \times 10^4\ (\Omega\cdot\text{m})^{-1}$. *If the electron concentration is* $2.9 \times 10^{22}\ \text{m}^{-3}$ *and electron and hole mobilities are 0.14 and 0.023* $\text{m}^2/\text{V}\cdot\text{s}$, *respectively, calculate the hole concentration.*

(A) $1.24 \times 10^{24}\ \text{m}^{-3}$

(B) $7.42 \times 10^{24}\ \text{m}^{-3}$

(C) $7.60 \times 10^{24}\ \text{m}^{-3}$

(D) $7.78 \times 10^{24}\ \text{m}^{-3}$

Solution

For a semiconducting material, the conductivity is given by Equation 18.13 as follows:

$$\sigma = n|e|\mu_e + p|e|\mu_h$$

where e is the charge on an electron: 1.602×10^{-19} C. Solving this equation for the number of holes p results in the following expression:

$$p = \frac{\sigma - n|e|\mu_e}{|e|\mu_h}$$

And, incorporating into this equation, values of the parameters provided in the problem statement yields the following value for p:

$$p = \frac{2.8 \times 10^4 - (2.9 \times 10^{22}\ \text{m}^{-3})(1.602 \times 10^{-19}\ \text{C})(0.14\ \text{m}^2/\text{V-s})}{(1.602 \times 10^{-19}\ \text{C})(0.023\ \text{m}^2/\text{V-s})}$$

$$= 7.42 \times 10^{24}\ \text{m}^{-3}$$

which is answer B.

CHAPTER 19

THERMAL PROPERTIES

PROBLEM SOLUTIONS

Heat Capacity

19.1 *Estimate the energy required to raise the temperature of 5 kg (11.0 lb_m) of the following materials from 20°C to 150°C (68°F to 300°F): aluminum, brass, aluminum oxide (alumina), and polypropylene.*

Solution

The energy, *E*, required to raise the temperature of a given mass of material, *m*, is the product of the specific heat, the mass of material, and the temperature change, ΔT, as

$$E = c_p m \Delta T$$

The ΔT in this problem is equal to 150°C – 20°C = 130°C (= 130 K), while the mass is 5 kg, and the specific heats are presented in Table 19.1, as follows:

c_p (aluminum) = 900 J/kg-K
c_p (brass) = 375 J/kg-K
c_p (alumina) = 775 J/kg-K
c_p (polypropylene) = 1925 J/kg-K

Thus, energy values for these four materials are determined as follows:

$$E(\text{aluminum}) = (900\ \text{J/kg-K})(5\ \text{kg})(130\ \text{K}) = 5.85 \times 10^5\ \text{J}$$

$$E(\text{brass}) = (375\ \text{J/kg-K})(5\ \text{kg})(130\ \text{K}) = 2.44 \times 10^5\ \text{J}$$

$$E(\text{alumina}) = (775\ \text{J/kg-K})(5\ \text{kg})(130\ \text{K}) = 5.04 \times 10^5\ \text{J}$$

$$E(\text{polypropylene}) = (1925\ \text{J/kg-K})(5\ \text{kg})(130\ \text{K}) = 1.25 \times 10^6\ \text{J}$$

19.2 *To what temperature would 10* lb_m *of a brass specimen at 25°C (77°F) be raised if 65 Btu of heat is supplied?*

Solution

We are asked to determine the temperature to which 10 lb_m of brass initially at 25°C would be raised if 65 Btu of heat is supplied. This is accomplished by utilization of a modified form of Equation 19.1 as follows:

$$\Delta T = \frac{\Delta Q}{m c_p} \tag{S19.2a}$$

Here ΔQ is the amount of heat supplied, m is the mass of the specimen, and c_p is the specific heat. From Table 19.1, for brass, c_p = 375 J/kg-K, which is converted into Customary U.S. units (Btu/lb_m-°F) using data found inside the back cover of this book, as follows:

$$c_p = (375\ \text{J/kg-K})\left(\frac{2.39 \times 10^{-4}\ \text{Btu/lb}_\text{m}\text{-°F}}{1\ \text{J/kg-K}}\right) = 0.090\ \text{Btu/lb}_\text{m}\text{-°F}$$

Thus, we compute the value of ΔT using Equation S19.2a as follows:

$$\Delta T = \frac{65\ \text{Btu}}{(10\ \text{lb}_\text{m})(0.090\ \text{Btu/lb}_\text{m}\text{-°F})} = 72.2\text{°F}$$

and the final temperature, T_f is equal to

$$T_f = T_0 + \Delta T = 77\text{°F} + 72.2\text{°F} = 149.2\text{°F} \quad (65.1\text{°C})$$

19.3 *(a) Determine the room-temperature heat capacities at constant pressure for the following materials: copper, iron, gold, and nickel.*

(b) How do these values compare with one another? How do you explain this?

Solution

(a) This problem asks that we determine the room-temperature heat capacity at constant pressure, C_p, for each of copper, iron, gold, and nickel. All we need do is multiply the c_p values in Table 19.1 by the atomic weights (values are found inside the front cover), taking into account the conversion from grams to kilograms (for the atomic weights)—that is

$$C_p = c_p A \left(\frac{1\text{ kg}}{1000\text{ g}}\right)$$

The parameter labeled A is the atomic weight of the material (in g/mol).

Thus, the C_p for copper is computed as follows:

$$C_p(\text{Cu}) = c_p(\text{Cu}) A_{\text{Cu}} \left(\frac{1\text{ kg}}{1000\text{ g}}\right)$$

$$= (386\text{ J/kg-K})(63.55\text{ g/mol})\left(\frac{1\text{ kg}}{1000\text{ g}}\right) = 24.5\text{ J/mol-K}$$

Likewise for Fe

$$C_p(\text{Fe}) = (448\text{ J/kg-K})(55.85\text{ g/mol})\left(\frac{1\text{ kg}}{1000\text{ g}}\right) = 25.0\text{ J/mol-K}$$

And for Au

$$C_p(\text{Au}) = (128\text{ J/kg-K})(196.97\text{ g/mol})\left(\frac{1\text{ kg}}{1000\text{ g}}\right) = 25.2\text{ J/mol-K}$$

Finally, for Ni

$$C_p(\text{Ni}) = (443\text{ J/kg-K})(58.69\text{ g/mol})\left(\frac{1\text{ kg}}{1000\text{ g}}\right) = 26.0\text{ J/mol-K}$$

(b) These values of C_p are very close to one another because room temperature is considerably above the Debye temperature for these metals; therefore, the values of C_p should be about equal to $3R$ [(3)(8.31 J/mol-K) = 24.9 J/mol-K], which is indeed the case for all four metals.

19.4 *For copper, the heat capacity at constant volume C_v at 20 K is 0.38 J/mol-K and the Debye temperature is 340 K. Estimate the specific heat for the following:*

(a) at 40 K

(b) at 400 K

Solution

(a) For copper, C_v at 20 K may be approximated by Equation 19.2, since this temperature is significantly below the Debye temperature (340 K). The value of C_v at 20 K is given, and thus, we may compute the constant A by rearranging Equation 19.2 as follows:

$$A = \frac{C_v}{T^3} = \frac{0.38 \text{ J/mol-K}}{(20 \text{ K})^3} = 4.75 \times 10^{-5} \text{ J/mol-K}^4$$

Therefore, at 40 K the value of C_v is equal to

$$C_v = AT^3$$

$$= (4.75 \times 10^{-5} \text{ J/mol-K}^4)(40 \text{ K})^3$$

$$= 3.04 \text{ J/mol-K}$$

and the specific heat is computed using the following expression:

$$c_v = \left(\frac{C_v}{A'}\right)\left(\frac{1000 \text{ g}}{1 \text{ kg}}\right) \tag{S19.4a}$$

In this equation, the parameter A' represents the atomic weight of the material. Therefore, the specific heat for copper at 40 K is equal to

$$c_v = \left(\frac{3.04 \text{ J/mol-K}}{63.55 \text{ g/mol}}\right)\left(\frac{1000 \text{ g}}{1 \text{ kg}}\right)$$

$$= 47.8 \text{ J/kg-K}$$

(b) Because 400 K is above the Debye temperature, a good approximation for C_v is as follows:

$$C_v = 3R$$

$$= (3)(8.31 \text{ J/mol-K}) = 24.9 \text{ J/mol-K}$$

We convert this C_v to specific heat using Equation S19.4a as follows:

$$c_v = \left(\frac{C_v}{A'}\right)\left(\frac{1000\ \text{g}}{1\ \text{kg}}\right)$$

$$= \left(\frac{24.9\ \text{J/mol-K}}{63.55\ \text{g/mol}}\right)\left(\frac{1000\ \text{g}}{1\ \text{kg}}\right)$$

$$= 392\ \text{J/kg-K}$$

19.5 *The constant A in Equation 19.2 is* $12\pi^4 R/5\theta_D^3$, *where R is the gas constant and* θ_D *is the Debye temperature (K). Estimate* θ_D *for aluminum, given that the specific heat is 4.60 J/kg-K at 15 K.*

Solution

For aluminum, we want to compute the Debye temperature, θ_D, given the expression for *A* in Equation 19.2 and the heat capacity at 15 K. First of all, let us determine the magnitude of *A* using the following rearranged form of Equation 19.2:

$$A = \frac{C_v}{T^3} \qquad (19.2a)$$

Inasmuch as the specific heat is given in the problem statement, and heat capacity is required in the above expression, it is necessary to convert c_v to C_v, which is possible using the following equation:

$$C_v = c_v A' \left(\frac{1 \text{ kg}}{1000 \text{ g}}\right)$$

Here we use *A'* to represent the atomic weight (so as not to confuse this parameter with the *A* in Equation 9.2). Making the above substitution into Equation 19.2a above yields the following expression for *A*:

$$A = \left[\frac{c_v A' \left(\frac{1 \text{ kg}}{1000 \text{ g}}\right)}{T^3}\right]$$

We now compute the value of *A* using the following values for parameters in this equation:

T = 15 K (given in problem statement)
c_v = 4.60 J/kg-K (given in problem statement)
A' = 26.98 g/mol (from inside the front book cover)

Therefore, the *A* is determined as follows:

$$A = \left[\frac{c_v A' \left(\frac{1 \text{ kg}}{1000 \text{ g}}\right)}{T^3}\right]$$

$$= \left[\frac{(4.60 \text{ J/kg-K})(26.98 \text{ g/mol}) \left(\frac{1 \text{ kg}}{1000 \text{ g}}\right)}{(15 \text{ K})^3}\right]$$

$$= 3.68 \times 10^{-5} \text{ J/mol-K}^4$$

The problem statement cites the following expression for *A:*

$$A = \frac{12\pi^4 R}{5\theta_D^3}$$

From this equation we solve for the Debye temperature, θ_D, as requested as follows:

$$\theta_D = \left(\frac{12\pi^4 R}{5A}\right)^{1/3}$$

$$= \left[\frac{(12)(\pi)^4(8.31 \text{ J/mol-K})}{(5)(3.68 \times 10^{-5} \text{ J/mol-K}^4)}\right]^{1/3} = 375 \text{ K}$$

19.6 *(a) Briefly explain why* C_v *rises with increasing temperature at temperatures near 0 K.*

(b) Briefly explain why C_v *becomes virtually independent of temperature at temperatures far removed from 0 K.*

Answer

(a) The reason that C_v rises with increasing temperature at temperatures near 0 K is because, in this temperature range, the allowed vibrational energy levels of the lattice waves are far apart relative to the available thermal energy, and only a portion of the lattice waves may be excited. As temperature increases, more of the lattice waves may be excited by the available thermal energy, and, hence, the ability of the solid to absorb energy (i.e., the magnitude of the heat capacity) increases.

(b) At temperatures far removed from 0 K, C_v becomes independent of temperature because all of the lattice waves have been excited and the energy required to produce an incremental temperature change is nearly constant.

Thermal Expansion

19.7 *A copper wire 15 m (49.2 ft) long is cooled from 40°C to –9°C (104°F to 15°F). How much change in length does it experience?*

Solution

In order to determine the change in length of the copper wire Δl, we must employ a rearranged form of Equation 19.3b—that is

$$\Delta l = l_0 \alpha_l \Delta T = l_0 \alpha_l (T_f - T_0)$$

Now using the value of α_l for copper taken from Table 19.1 [17.0×10^{-6} $(°\mathrm{C})^{-1}$], we calculate the wire elongation as follows:

$$\Delta l = (15\ \mathrm{m})\left[17.0 \times 10^{-6} (°\mathrm{C})^{-1}\right](-9°\mathrm{C} - 40°\mathrm{C})$$

$$= -1.25 \times 10^{-2}\ \mathrm{m} = -12.5\ \mathrm{mm} \quad (-0.50\ \mathrm{in.})$$

19.8 *A 0.4-m (15.7-in.) rod of a metal elongates 0.48 mm (0.019 in.) on heating from 20°C to 100°C (68°F to 212°F). Determine the value of the linear coefficient of thermal expansion for this material.*

Solution

The linear coefficient of thermal expansion for this material may be determined using a rearranged form of Equation 19.3b as follows:

$$\alpha_l = \frac{\Delta l}{l_0 \Delta T} = \frac{\Delta l}{l_0 (T_f - T_0)}$$

$$= \frac{0.48 \times 10^{-3}\ \mathrm{m}}{(0.4\ \mathrm{m})(100°\mathrm{C} - 20°\mathrm{C})}$$

$$= 15.0 \times 10^{-6}\ (°\mathrm{C})^{-1} \quad \left[8.40 \times 10^{-6}\ (°\mathrm{F})^{-1}\right]$$

19.9 *Briefly explain thermal expansion using the potential energy-versus-interatomic spacing curve.*

The phenomenon of thermal expansion using the potential energy-versus-interatomic spacing curve is explained in Section 19.3.

19.10 *Compute the density for iron at 700°C, given that its room-temperature density is 7.870 g/cm*^{3}*. Assume that the volume coefficient of thermal expansion,* α_v*, is equal to* $3\alpha_l$*.*

Solution

In this problem we are asked to determine the density of iron at 700°C. Let us use as the basis for this determination 1 cm^3 of iron at 20°C that has a mass of 7.870 g. If it is assumed that the mass of iron (7.870 g) remains constant upon heating, then the density at 700°C is just this mass divided by the 700°C volume; this volume will be greater than 1 cm^3, as a result of thermal expansion. Let us compute the volume of this specimen of iron when it is heated to 700°C. A volume expansion expression is given in Equation 19.4—viz.,

$$\frac{\Delta V}{V_0} = \alpha_v \Delta T$$

or, rearranging leads to

$$\Delta V = V_0 \alpha_v \Delta T \tag{19.4a}$$

But since

$$\Delta V = V_f - V_0$$

in which V_f and V_0 represent the final and initial volumes, respectively, we can rewrite Equation 19.4a as follows:

$$V_f - V_0 = V_0 \alpha_v \Delta T$$

From this expression we want to solve for the final volume V_f at 700°C; therefore we may rewrite the above equation as follows:

$$V_f = V_0 \alpha_v \Delta T + V_0 = V_0(1 + \alpha_v \Delta T)$$

Also, $\alpha_v = 3\alpha_l$, as noted in the problem statement, which, when substituted into the above equation leads to the following:

$$V_f = V_0(1 + 3\alpha_l \Delta T) \tag{19.4b}$$

The value of α_l for iron given in Table 19.1 is 11.8×10^{-6} (°C)$^{-1}$. Therefore, the volume of this specimen of Fe at 700°C (V_f), using Equation 19.4b is the following:

$$V_f = V_0(1 + 3\alpha_l \Delta T)$$

$$= (1\ \text{cm}^3)\left\{1 + (3)\left[11.8 \times 10^{-6}\ (^\circ\text{C})^{-1}\right](700^\circ\text{C} - 20^\circ\text{C})\right\}$$

$$= 1.02471\ \text{cm}^3$$

(*Note:* In this computation we have taken room temperature to be 20°C.) Thus, the 700°C density is just the 7.870 g mass divided by this new volume—i.e.,

$$\rho = \frac{7.870\ \text{g}}{1.02471\ \text{cm}^3} = 7.680\ \text{g/cm}^3$$

19.11 *When a metal is heated its density decreases. There are two sources that give rise to this decrease of ρ: (1) the thermal expansion of the solid and (2) the formation of vacancies (Section 4.2). Consider a specimen of gold at room temperature (20°C) that has a density of 19.320 g/cm*^{3}.

(a) Determine its density upon heating to 800°C when only thermal expansion is considered.

(b) Repeat the calculation when the introduction of vacancies is taken into account. Assume that the energy of vacancy formation is 0.98 eV/atom and that the volume coefficient of thermal expansion, α_v *is equal to* $3\alpha_l$.

Solution

(a) In this portion of the problem we are asked to determine the density of gold at 800°C when only thermal expansion is considered. Let us use as the basis for this determination 1 cm^3 of gold at 20°C that has a mass of 19.320 g. If it is assumed that the mass of gold (19.320 g) remains constant upon heating, then the density at 800°C is just this mass divided by the 800°C volume; this volume will be greater than 1 cm^3, as a result of thermal expansion. Let us compute the volume of this specimen of gold when it is heated to 800°C. A volume expansion expression is given in Equation 19.4—viz.,

$$\frac{\Delta V}{V_0} = \alpha_v \Delta T$$

or, rearranging leads to

$$\Delta V = V_0 \alpha_v \Delta T \tag{19.4a}$$

But since

$$\Delta V = V_f - V_0$$

in which V_f and V_0 represent the final and initial volumes, respectively, we can rewrite Equation 19.4a as follows:

$$V_f - V_0 = V_0 \alpha_v \Delta T$$

From this expression we want to solve for the final volume V_f at 800°C; therefore we may rewrite the above equation as follows:

$$V_f = V_0 \alpha_v \Delta T + V_0 = V_0 (1 + \alpha_v \Delta T)$$

Also, $\alpha_v = 3\alpha_l$, as noted in the problem statement, which, when substituted into the above equation leads to the following:

$$V_f = V_0 (1 + 3\alpha_l \Delta T) \tag{19.4b}$$

The value of α_l for gold given in Table 19.1 is 14.2 × 10^{-6} $(°\text{C})^{-1}$. Therefore, the volume of this specimen of Au at 800°C (V_f), using Equation 19.4b, is determined as follows:

$$V_f = V_0(1 + 3\alpha_l \Delta T)$$

$$= (1\ \text{cm}^3)\left\{1 + (3)\left[14.2 \times 10^{-6}\ (°\text{C})^{-1}\right](800°\text{C} - 20°\text{C})\right\}$$

$$= 1.03323\ \text{cm}^3$$

(*Note:* In this computation we have taken room temperature to be 20°C.) Thus, the 800°C density is just the 19.320 g mass divided by this new volume—i.e.,

$$\rho = \frac{19.320\ \text{g}}{1.03323\ \text{cm}^3} = 18.699\ \text{g/cm}^3$$

(b) Now we are asked to compute the density at 800°C taking into consideration the creation of vacancies which will further lower the density. To begin, this determination requires that we calculate the number of vacancies using Equation 4.1. But it first becomes necessary to compute the number of Au atoms per cubic centimeter (N_{Au}) at 800°C using Equation 4.2. Thus,

$$N_{\text{Au}} = \frac{N_{\text{A}}\ \rho_{\text{Au}}}{A_{\text{Au}}}$$

And since the atomic weight of gold (A_{Au}) is 196.97 g/mol (as taken from the insider cover of the book), then

$$N_{\text{Au}} = \frac{(6.022 \times 10^{23}\ \text{atoms/mol})(18.699\ \text{g/cm}^3)}{196.97\ \text{g/mol}}$$

$$= 5.717 \times 10^{22}\ \text{atoms/cm}^3$$

Now, from Equation 4.1, the total number of vacancies per centimeter cubed, N_v, is computed as follows:

$$N_v = N_{\text{Au}} \exp\left(-\frac{Q_v}{kT}\right)$$

$$= (5.717 \times 10^{22}\ \text{atoms/cm}^3) \exp\left[-\frac{0.98\ \text{eV/atom}}{(8.62 \times 10^{-5}\ \text{eV/K})(800 + 273\ \text{K})}\right]$$

$$= 1.431 \times 10^{18}\ \text{vacancies/cm}^3$$

We now want to determine the number of vacancies per unit cell, which is possible if the unit cell volume is multiplied by N_v. The unit cell volume (V_C) may be calculated using Equation 3.8 taking $n = 4$ inasmuch as Au has the FCC crystal structure. Thus, from a rearranged form of Equation 3.8 we compute the value of V_C as follows:

$$V_C = \frac{nA_{\text{Au}}}{\rho_{\text{Au}} N_{\text{A}}}$$

$$= \frac{(4 \text{ atoms/unit cell})(196.97 \text{ g/mol})}{\left(18.699 \text{ g/cm}^3\right)\left(6.022 \times 10^{23} \text{ atoms/mol}\right)}$$

$$= 6.997 \times 10^{-23} \text{ cm}^3\text{/unit cell}$$

Now, the number of vacancies per unit cell, n_v, is equal to

$$n_v = N_v V_C$$

$$= \left(1.431 \times 10^{18} \text{ vacancies/cm}^3\right)\left(6.997 \times 10^{-23} \text{ cm}^3\text{/unit cell}\right)$$

$$= 0.0001001 \text{ vacancies/unit cell}$$

What this means is that instead of there being 4.0000 atoms per unit cell, there are only 4.0000 – 0.0001001 = 3.9998999 atoms per unit cell. And, finally, the density may be computed using Equation 3.8 taking $n = 3.9998999$; thus

$$\rho_{\text{Au}} = \frac{nA_{\text{Au}}}{V_C N_{\text{A}}}$$

$$= \frac{(3.9998999 \text{ atoms/unit cell})(196.97 \text{ g/mol})}{\left(6.997 \times 10^{-23} \text{ cm}^3\text{/unit cell}\right)\left(6.022 \times 10^{23} \text{ atoms/mol}\right)}$$

$$= 18.698 \text{ g/cm}^3$$

Thus, the influence of the vacancies is almost insignificant—their presence reduces the density by only 0.001 g/cm^3 (from 18.699 g/cm^3 to 18.698 g/cm^3).

19.12 *The difference between the specific heats at constant pressure and constant volume is described by the expression*

$$c_p - c_v = \frac{\alpha_v^2 v_0 T}{\beta} \qquad (19.10)$$

where α_v *is the volume coefficient of thermal expansion,* v_0 *is the specific volume (i.e., volume per unit mass, or the reciprocal of density),* β *is the compressibility, and T is the absolute temperature. Compute the values of* c_v *at room temperature (293 K) for aluminum and iron using the data in Table 19.1, assuming that* $\alpha_v = 3\alpha_l$ *and given that the values of* β *for Al and Fe are* 1.77×10^{-11} *and* 2.65×10^{-12} $(\mathrm{Pa})^{-1}$*, respectively.*

Solution

This problem asks that we calculate the values of c_v for aluminum and iron at room temperature using Equation 19.10, the data in Table 19.1, given that $\alpha_v = 3\alpha_l$, and also values of the compressibility. Rearrangement of Equation 19.10 such that c_v is the dependent variable leads to the following:

$$c_v = c_p - \frac{\alpha_v^2 v_0 T}{\beta}$$

And, from Table 19.1 and the problem statement we have the following values for parameters in this equation for both Al and Fe:

$c_p(\mathrm{Al}) = 900$ J/kg-K
$c_p(\mathrm{Fe}) = 448$ J/kg-K
$\alpha_v(\mathrm{Al}) = (3)[23.6 \times 10^{-6}\ (°\mathrm{C})^{-1}] = 7.08 \times 10^{-5}\ (°\mathrm{C})^{-1}$
$\alpha_v(\mathrm{Fe}) = (3)[(11.8 \times 10^{-6}\ (°\mathrm{C})^{-1}] = 3.54 \times 10^{-5}\ (°\mathrm{C})^{-1}$
$\beta(\mathrm{Al}) = 1.77 \times 10^{-11}\ (\mathrm{Pa})^{-1}$
$\beta(\mathrm{Fe}) = 2.65 \times 10^{-12}\ (\mathrm{Pa})^{-1}$

The specific volume is just the reciprocal of the density; thus, for units of $\mathrm{m^3/kg}$

$$v_0(\mathrm{Al}) = \frac{1}{\rho} = \left(\frac{1}{2.71\ \mathrm{g/cm^3}}\right)\left(\frac{1000\,\mathrm{g}}{\mathrm{kg}}\right)\left(\frac{1\ \mathrm{m}}{100\ \mathrm{cm}}\right)^3 = 3.69 \times 10^{-4}\ \mathrm{m^3/kg}$$

$$v_0(\mathrm{Fe}) = \left(\frac{1}{7.87\ \mathrm{g/cm^3}}\right)\left(\frac{1000\,\mathrm{g}}{\mathrm{kg}}\right)\left(\frac{1\ \mathrm{m}}{100\ \mathrm{cm}}\right)^3 = 1.27 \times 10^{-4}\ \mathrm{m^3/kg}$$

Therefore, we compute the value of c_v for aluminum as follows:

$$c_v(\text{Al}) = c_p(\text{Al}) - \frac{\alpha_v^2(\text{Al})\, v_0(\text{Al})T}{\beta(\text{Al})}$$

$$= 900 \text{ J/kg-K} - \frac{\left[7.08 \times 10^{-5}\ (^\circ\text{C})^{-1}\right]^2 \left(3.69 \times 10^{-4}\ \text{m}^3/\text{kg}\right)(293\ \text{K})}{1.77 \times 10^{-11}\ (\text{N/m}^2)^{-1}}$$

$$= 869 \text{ J/kg-K}$$

Likewise for iron:

$$c_v(\text{Fe}) = 448 \text{ J/kg-K} - \frac{\left[3.54 \times 10^{-5}\ (^\circ\text{C})^{-1}\right]^2 \left(1.27 \times 10^{-4}\ \text{m}^3/\text{kg}\right)(293\ \text{K})}{2.65 \times 10^{-12}\ (\text{N/m}^2)^{-1}}$$

$$= 430 \text{ J/kg-K}$$

19.13 *To what temperature must a cylindrical rod of tungsten 15.025 mm in diameter and a plate of 1025 steel having a circular hole 15.000 mm in diameter have to be heated for the rod to just fit into the hole? Assume that the initial temperature is 25°C.*

Solution

This problem asks for us to determine the temperature to which a cylindrical rod of tungsten 15.025 mm in diameter must be heated in order for it of just fit into a 15.000 mm diameter circular hole in a plate of 1025 steel (which, of course, is also heated), assuming that the initial temperature is 25°C. This requires the use of Equation 19.3a, which is applied to the diameters of both the rod and hole. That is

$$\frac{d_f - d_0}{d_0} = \alpha_l (T_f - T_0)$$

Solving this expression for the final diameter d_f yields the following

$$d_f = d_0 \left[1 + \alpha_l (T_f - T_0)\right]$$

Now all we need do is to establish expressions for d_f(steel) and d_f (W), set them equal to one another, and solve for T_f. According to Table 19.1, α_l(steel) = 12.0 × 10^{-6} (°C)$^{-1}$ and α_l (W) = 4.5 × 10^{-6} (°C)$^{-1}$. Thus

$$d_f(\text{steel}) = d_f(\text{W})$$

$$(15.000 \text{ mm})\left[1 + \left\{12.0 \times 10^{-6} (^\circ\text{C})^{-1}\right\} (T_f - 25^\circ\text{C})\right]$$

$$= (15.025 \text{ mm})\left[1 + \left\{4.5 \times 10^{-6} (^\circ\text{C})^{-1}\right\} (T_f - 25^\circ C)\right]$$

Now solving for T_f gives T_f = 247.4°C

Thermal Conductivity

19.14 *(a) Calculate the heat flux through a sheet of brass 7.5 mm (0.30 in.) thick if the temperatures at the two faces are 150°C and 50°C (302°F and 122°F); assume steady-state heat flow.*

(b) What is the heat loss per hour if the area of the sheet is 0.5 m^2 (5.4 ft^2)?

(c) What will be the heat loss per hour if soda–lime glass is used instead of brass?

(d) Calculate the heat loss per hour if brass is used and the thickness is increased to 15 mm (0.59 in.).

Solution

(a) The steady-state heat flux through the plate may be computed using Equation 19.5; the thermal conductivity for brass, found in Table 19.1, is 120 W/m-K. Therefore,

$$q = -k\frac{\Delta T}{\Delta x}$$

$$= -(120\ \text{W/m-K})\left[\frac{(50 + 273\ \text{K}) - (150 + 273\ \text{K})}{7.5 \times 10^{-3}\,\text{m}}\right]$$

$$= 1.60 \times 10^{6}\ \text{W/m}^2$$

(b) Let *dQ*/*dt* represent the total heat loss such that

$$\frac{dQ}{dt} = qAt$$

where *A* and *t* are the cross-sectional area and time, respectively. Thus,

$$\frac{dQ}{dt} = (1.60 \times 10^{6}\ \text{J/s-m}^2)(0.5\ \text{m}^2)(60\ \text{s/min})(60\ \text{min/h})$$

$$= 2.88 \times 10^{9}\ \text{J/h} \quad (2.73 \times 10^{6}\ \text{Btu/h})$$

(c) If soda-lime glass is used (*k* = 1.7 W/m-K, Table 19.1),

$$\frac{dQ}{dt} = -kAt\frac{\Delta T}{\Delta x}$$

$$= -(1.7\ \text{J/s-m-K})(0.5\ \text{m}^2)(3600\ \text{s/h})\left(\frac{-100\ \text{K}}{7.5 \times 10^{-3}\ \text{m}}\right)$$

$$= 4.08 \times 10^{7}\ \text{J/h} \quad (3.9 \times 10^{4}\ \text{Btu/h})$$

(d) If the thickness of the brass is increased to 15 mm, then

$$\frac{dQ}{dt} = -kAt\frac{\Delta T}{\Delta x}$$

$$= -(120\ \text{W/m-K})(0.5\ \text{m}^2)(3600\ \text{s/h})\left(\frac{-100\ \text{K}}{15 \times 10^{-3}\ \text{m}}\right)$$

$$= 1.44 \times 10^{9}\ \text{J/h} \quad (1.36 \times 10^{6}\ \text{Btu/h})$$

19.15 *(a) Would you expect Equation 19.7 to be valid for ceramic and polymeric materials? Why or why not?*

(b) Estimate the value for the Wiedemann–Franz constant L [in Ω•W/(K)^2] at room temperature (293 K) for the following nonmetals: zirconia (3 mol% Y_2O_3), diamond (synthetic), gallium arsenide (intrinsic), poly(ethylene terephthalate) (PET), and silicone. Consult Tables B.7 and B.9 in Appendix B.

Solution

(a) Equation 19.7 is not valid for ceramic and polymeric materials since, in the development of this expression, it is assumed that free electrons are responsible for both electrical and thermal conduction. Such is the case for most metals. For ceramics and polymers, free electrons are the primary contributors to the electrical conductivity. However, free electrons do not contribute significantly to the thermal conductivity. For ceramics, thermal conduction is primarily by means of phonons; for polymers, the energy transfer is by chain vibrations, translations, and rotations.

(b) Estimated room-temperature values of L, in Ω-W/(K)^2, for the several materials are determined below, using Equation 19.7. Electrical conductivity values were determined by taking reciprocals of the electrical resistivities given in Table B.9, Appendix B; thermal conductivities are taken from Table B.7 in the same appendix. (*Note:* when a range of values is given in these tables, an average value is used in the computation.)

For zirconia (3 mol% Y_2O_3)

$$L = \frac{k}{\sigma T} = \frac{2.65 \text{ W/m-K}}{\left[\frac{1}{10^{10}\ (\Omega\text{-m})}\right](293 \text{ K})} = 9.0 \times 10^{7}\ \Omega\text{-W/K}^2$$

For synthetic diamond

$$L = \frac{3150 \text{ W/m-K}}{\left[\frac{1}{1.5 \times 10^{-2}\ (\Omega\text{-m})}\right](293 \text{ K})} = 0.161\ \Omega\text{-W/K}^2$$

For intrinsic gallium arsenide

$$L = \frac{45.5 \text{ W/m-K}}{\left[\frac{1}{10^{6}\ (\Omega\text{-m})}\right](293 \text{ K})} = 1.55 \times 10^{5}\ \Omega\text{-W/K}^2$$

For poly(ethylene terephthalate) (PET)

$$L = \frac{0.15\ \text{W/m-K}}{\left[\dfrac{1}{10^{12}\ (\Omega\text{-m})}\right](293\ \text{K})} = 5.12 \times 10^{8}\ \ \Omega\text{-W/K}^{2}$$

For silicone

$$L = \frac{0.23\ \text{W/m-K}}{\left[\dfrac{1}{10^{13}\ (\Omega\text{-m})}\right](293\ \text{K})} = 7.85 \times 10^{9}\ \Omega\text{-W/K}^{2}$$

19.16 *Briefly explain why the thermal conductivities are higher for crystalline than for noncrystalline ceramics.*

Answer

Thermal conductivities are higher for crystalline than for noncrystalline ceramics because, for noncrystalline, phonon scattering, and thus the resistance to heat transport, is much more effective due to the highly disordered and irregular atomic structure.

19.17 *Briefly explain why metals are typically better thermal conductors than ceramic materials.*

Answer

Metals are typically better thermal conductors than are ceramic materials because, for metals, most of the heat is transported by free electrons (of which there are relatively large numbers). In ceramic materials, the primary mode of thermal conduction is via phonons, and phonons are more easily scattered than are free electrons.

19.18 (*a) Briefly explain why porosity decreases the thermal conductivity of ceramic and polymeric materials, rendering them more thermally insulative.*

(b) Briefly explain how the degree of crystallinity affects the thermal conductivity of polymeric materials and why.

Answer

(a) Porosity decreases the thermal conductivity of ceramic and polymeric materials because the thermal conductivity of a gas phase that occupies pore space is extremely small relative to that of the solid material. Furthermore, contributions from gaseous convection are generally insignificant.

(b) Increasing the degree of crystallinity of a semicrystalline polymer enhances its thermal conductivity; the vibrations, rotations, etc. of the molecular chains are more effective modes of thermal transport when a crystalline structure prevails.

19.19 *For some ceramic materials, why does the thermal conductivity first decrease and then increase with rising temperature?*

Answer

For some ceramic materials, the thermal conductivity first decreases with rising temperature because the scattering of lattice vibrations increases with temperature. At higher temperatures, the thermal conductivity will increase for some ceramics that are porous because radiant heat transfer across pores may become important, which process increases with rising temperature.

19.20 *For each of the following pairs of materials, decide which has the larger thermal conductivity. Justify your choices.*

(a) Pure silver; sterling silver (92.5 wt% Ag–7.5 wt% Cu)

(b) Fused silica; polycrystalline silica

(c) Linear and syndiotactic poly(vinyl chloride) (DP = 1000); linear and syndiotactic polystyrene (DP = 1000)

(d) Atactic polypropylene ($\bar{M}_w$ = 10^6 g/mol); isotactic polypropylene ($\bar{M}_w$ = 10^5 g/mol)

Solution

This question asks for us to decide, for each of several pairs of materials, which has the larger thermal conductivity and why.

(a) Pure silver will have a larger conductivity than sterling silver because the impurity atoms in the latter will lead to a greater degree of free electron scattering.

(b) Polycrystalline silica will have a larger conductivity than fused silica because fused silica is noncrystalline and lattice vibrations are more effectively scattered in noncrystalline materials.

(c) The poly(vinyl chloride) will have the larger conductivity than the polystyrene because the former will have the higher degree of crystallinity. Both polymers are syndiotactic and have the same degree of polymerization. However, with regard to side-group bulkiness, the PVC is more likely to crystallize. Since heat transfer is by molecular chain vibrations, and the coordination of these vibrations increases with percent crystallinity, the higher the crystallinity, the greater the thermal conductivity.

(d) The isotactic polypropylene will have a larger thermal conductivity than the atactic polypropylene because isotactic polymers have higher degrees of crystallinity. The influence of crystallinity on conductivity is explained in part (c).

19.21 *We might think of a porous material as being a composite in which one of the phases is a pore phase. Estimate upper and lower limits for the room-temperature thermal conductivity of an aluminum oxide material having a volume fraction of 0.25 of pores that are filled with still air.*

Solution

This problem asks that we treat a porous material as a composite wherein one of the phases is a pore phase, and that we estimate upper and lower limits for the room-temperature thermal conductivity of an aluminum oxide material having a 0.25 volume fraction of pores. The upper limit of k (k_{upper}) may be determined using Equation 16.1 with thermal conductivity substituted for the elastic modulus, E. From Table 19.1, the value of k for Al_2O_3 is 39 W/m-K, while for still air in the pore phase, k = 0.02 W/m-K (Section 19.4). Thus, using the modified form of Equation 16.1, the upper limit of the thermal conductivity is determined as follows:

$$k_{\text{upper}} = V_p k_{\text{air}} + V_{\text{Al}_2\text{O}_3} k_{\text{Al}_2\text{O}_3}$$

$$= (0.25)(0.02\ \text{W/m-K}) + (0.75)(39\ \text{W/m-K})$$

$$= 29.3\ \text{W/m-K}$$

For the lower limit we employ a modification of Equation 16.2 as follows:

$$k_{\text{lower}} = \frac{k_{\text{air}} k_{\text{Al}_2\text{O}_3}}{V_p k_{\text{Al}_2\text{O}_3} + V_{\text{Al}_2\text{O}_3} k_{\text{air}}}$$

$$= \frac{(0.02\ \text{W/m-K})(39\ \text{W/m-K})}{(0.25)(39\ \text{W/m-K}) + (0.75)(0.02\ \text{W/m-K})} = 0.080\ \text{W/m-K}$$

19.22 *Nonsteady-state heat flow may be described by the following partial differential equation:*

$$\frac{\partial T}{\partial t} = D_T \frac{\partial^2 T}{\partial x^2}$$

where D_T is the thermal diffusivity; this expression is the thermal equivalent of Fick's second law of diffusion (Equation 5.4b). The thermal diffusivity is defined according to

$$D_T = \frac{k}{\rho c_p}$$

In this expression, k, ρ, and c_p represent the thermal conductivity, the mass density, and the specific heat at constant pressure, respectively.

(a) What are the SI units for D_T?

(b) Determine values of D_T for copper, brass, magnesia, fused silica, polystyrene, and polypropylene using the data in Table 19.1. Density values are included in Table B.1, Appendix B.

Solution

(a) The units for D_T are determined as follows:

$$D_T = \frac{k(\text{J/s-m-K})}{\rho(\text{kg/m}^3)c_p(\text{J/kg-K})} = \text{m}^2/\text{s}$$

(b) The values of D_T for the several materials are determined below. (*Note:* values for k and c_p are taken from Table 19.1; density values are from Table B.1, Appendix B, and converted to units of kilograms per meter cubed using the following relationship: 1 g/cm^3 = 1000 kg/m^3

For copper

$$D_T = \frac{k}{\rho c_p} = \frac{398 \text{ W/m-K}}{(8.89 \times 10^3 \text{kg/m}^3)(386 \text{ J/kg-K})} = 1.16 \times 10^{-4} \text{ m}^2/\text{s}$$

For brass

$$D_T = \frac{120 \text{ W/m-K}}{(8.53 \times 10^3 \text{ kg/m}^3)(375 \text{ J/kg-K})} = 3.75 \times 10^{-5} \text{ m}^2/\text{s}$$

For magnesia

$$D_T = \frac{37.7\ \text{W/m-K}}{(3.58 \times 10^3\ \text{kg/m}^3)(940\ \text{J/kg-K})} = 1.12 \times 10^{-5}\ \text{m}^2/\text{s}$$

For fused silica

$$D_T = \frac{1.4\ \text{W/m-K}}{(2.33 \times 10^3\ \text{kg/m}^3)(740\ \text{J/kg-K})} = 8.12 \times 10^{-7}\ \text{m}^2/\text{s}$$

For polystyrene

$$D_T = \frac{0.13\ \text{W/m-K}}{(1.05 \times 10^3\ \text{kg/m}^3)(1170\ \text{J/kg-K})} = 1.06 \times 10^{-7}\ \text{m}^2/\text{s}$$

For polypropylene

$$D_T = \frac{0.12\ \text{W/m-K}}{(0.91 \times 10^3\ \text{kg/m}^3)(1925\ \text{J/kg-K})} = 6.85 \times 10^{-8}\ \text{m}^2/\text{s}$$

Thermal Stresses

19.23 *Beginning with Equation 19.3, show that Equation 19.8 is valid.*

Solution

We want to show that Equation 19.8 is valid beginning with Equation 19.3. From Equation 19.3b,

$$\frac{\Delta l}{l_0} = \alpha_l \Delta T$$

it may be noted that the term on the left-hand side is the same expression as that for the definition of engineering strain (Equation 6.2); that is

$$\varepsilon = \frac{\Delta l}{l_0}$$

Furthermore, elastic stress and strain are related through Hooke's law, Equation 6.5 as follows:

$$\sigma = E\varepsilon$$

Making appropriate substitutions and algebraic manipulations gives the following:

$$\frac{\Delta l}{l_0} = \varepsilon = \frac{\sigma}{E} = \alpha_l \Delta T$$

And, solving for σ results in the following expression

$$\sigma = E\alpha_l \Delta T$$

which is Equation 19.8.

19.24 *(a) Briefly explain why thermal stresses may be introduced into a structure by rapid heating or cooling.*

(b) For cooling, what is the nature of the surface stresses?

(c) For heating, what is the nature of the surface stresses?

Answer

(a) Thermal stresses may be introduced into a structure by rapid heating or cooling because temperature gradients are established across the cross section due to more rapid temperature changes at the surface than within the interior; thus, the surface will expand or contract at a different rate than the interior and since this surface expansion or contraction will be restrained by the interior, stresses will be introduced.

(b) For cooling, the surface stresses will be tensile in nature since the interior contracts to a lesser degree than the cooler surface.

(c) For heating, the surface stresses will be compressive in nature since the interior expands to a lesser degree than the hotter surface.

19.25 *(a) If a rod of brass 0.35 m (13.8 in.) long is heated from 15°C to 85°C (60°F to 185°F) while its ends are maintained rigid, determine the type and magnitude of stress that develops. Assume that at 15°C the rod is stress-free.*

(b) What will be the stress magnitude if a rod 1 m (39.4 in.) long is used?

(c) If the rod in part (a) is cooled from 15°C to –15°C (60°F to 5°F), what type and magnitude of stress results?

Solution

(a) We are asked to compute the magnitude of the stress within a brass rod that is heated while its ends are maintained rigid. To solve this part of the problem we employ Equation 19.8, using a value of 97 GPa for the modulus of elasticity of brass (Table 6.1), and a value of 20.0×10^{-6} (°C)$^{-1}$ for α_l (Table 19.1). Therefore, we calculate the magnitude of the stress as follows:

$$\sigma = E\alpha_l(T_0 - T_f)$$

$$= (97 \times 10^3 \text{ MPa})\left[20.0 \times 10^{-6}(°\text{C})^{-1}\right](15°\text{C} - 85°\text{C})$$

$$= -136 \text{ MPa} \quad (-19{,}600 \text{ psi})$$

The stress will be compressive since its sign is negative.

(b) The stress will be the same [–136 MPa (–19,600 psi)], since stress is independent of bar length.

(c) Upon cooling the indicated amount, the stress becomes

$$\sigma = E\alpha_l(T_0 - T_f)$$

$$= (97 \times 10^3 \text{ MPa})\left[20.0 \times 10^{-6}(°\text{C})^{-1}\right]\left[(15°\text{C} - (-15°\text{C})\right]$$

$$= +58 \text{ MPa} \quad (+8620 \text{ psi})$$

This stress will be tensile since its sign is positive.

19.26 *A steel wire is stretched with a stress of 70 MPa (10,000 psi) at 20°C (68°F). If the length is held constant, to what temperature must the wire be heated to reduce the stress to 17 MPa (2500 psi)?*

Solution

We want to heat the steel wire in order to reduce the stress level from 70 MPa to 17 MPa; in doing so, we reduce the stress in the wire by 70 MPa – 17 MPa = 53 MPa, which stress will be a compressive one (i.e., $\sigma = -53$ MPa). Solving for T_f from Equation 19.8 [and using values for E = 207 GPa (Table 6.1) and $\alpha_l = 12.0 \times 10^{-6}\ (°\mathrm{C})^{-1}$ (Table 19.1), respectively] yields the following:

$$T_f = T_0 - \frac{\sigma}{E\alpha_l}$$

$$= 20°\mathrm{C} - \frac{-53\ \mathrm{MPa}}{(207 \times 10^3\ \mathrm{MPa})\left[12.0 \times 10^{-6}\ (°\mathrm{C})^{-1}\right]}$$

$$= 20°\mathrm{C} + 21.3°\mathrm{C} = 41.3°\mathrm{C}\ \ (105°\mathrm{F})$$

19.27 *If a cylindrical rod of brass 150.00 mm long and 10.000 mm in diameter is heated from 20°C to 160°C while its ends are maintained rigid, determine its change in diameter. Hint: You may want to consult Table 6.1.*

Solution

This problem asks for us to determine the change in diameter of a cylindrical brass rod 150.00 mm long and 10.000 mm in diameter when it is heated from 20°C to 160°C while its ends are maintained rigid. There will be two contributions to the diameter increase of the rod; the first is due to thermal expansion (which will be denoted as Δd_1), while the second is from Poisson's lateral expansion as a result of elastic deformation from stresses that are established from the inability of the rod to elongate as it is heated (denoted as Δd_2). The magnitude of Δd_1 may be computed using a modified form of Equation 19.3 as follows:

$$\Delta d_1 = d_0 \alpha_l (T_f - T_0)$$

From Table 19.1 the value of α_l for brass is 20.0 × 10^{-6} $(°\text{C})^{-1}$. Thus,

$$\Delta d_1 = (10.000 \text{ mm})\left[20.0 \times 10^{-6} (°\text{C})^{-1}\right](160°\text{C} - 20°\text{C})$$

$$= 0.0280 \text{ mm}$$

Now, Δd_2 is related to the transverse strain (ε_x) according to a modified form of Equation 6.2 as follows:

$$\frac{\Delta d_2}{d_0} = \varepsilon_x$$

Also, transverse strain and longitudinal strain (ε_z) are related according to Equation 6.8—that is,

$$\varepsilon_x = -\nu \varepsilon_z$$

where ν is Poisson’s ratio. Substitution of this expression for ε_x into the first equation above leads to

$$\frac{\Delta d_2}{d_0} = -\nu \varepsilon_z$$

Furthermore, the longitudinal strain is related to the modulus of elasticity through Equation 6.5—i.e.,

$$\varepsilon_z = \frac{\sigma}{E}$$

And, therefore, making these substitutions leads to the following expression:

$$\frac{\Delta d_2}{d_0} = -\nu\frac{\sigma}{E}$$

Now, from Equation 19.8 stress is equal to

$$\sigma = E\alpha_l(T_0 - T_f)$$

which, when substituted into the preceding equation leads to

$$\frac{\Delta d_2}{d_0} = -\frac{\nu E\alpha_l(T_0 - T_f)}{E}$$

$$= -\nu\alpha_l(T_0 - T_f)$$

Solving for Δd_2 and realizing that, for brass, $\nu = 0.34$ (Table 6.1) yields

$$\Delta d_2 = -d_0\nu\alpha_l(T_0 - T_f)$$

$$= -(10.000\text{ mm})(0.34)\left[20.0 \times 10^{-6}\ (^\circ\text{C})^{-1}\right](20^\circ\text{C} - 160^\circ\text{C})$$

$$= 0.0095\text{ mm}$$

Finally, the total Δd is just $\Delta d_1 + \Delta d_2$ = 0.0280 mm + 0.0095 mm = 0.0375 mm.

19.28 *The two ends of a cylindrical rod of nickel 120.00 mm long and 12.000 mm in diameter are maintained rigid. If the rod is initially at 70°C, to what temperature must it be cooled in order to have a 0.023-mm reduction in diameter?*

Solution

This problem asks for us to determine to what temperature a cylindrical rod of nickel 120.00 mm long and 12.000 mm in diameter must be cooled from 70°C in order to have a 0.023-mm reduction in diameter if the rod ends are maintained rigid. There will be two contributions to the diameter decrease of the rod; the first is due to thermal contraction (which will be denoted as Δd_1), while the second is from Poisson's lateral contraction as a result of elastic deformation from stresses that are established from the inability of the rod to contract as it is cooled (denoted as Δd_2). The magnitude of Δd_1 may be computed using a modified form of Equation 19.3b as follows:

$$\Delta d_1 = d_0 \alpha_l (T_f - T_0)$$

Now, Δd_2 is related to the transverse strain (ε_x) according to a modified form of Equation 6.2 as

$$\frac{\Delta d_2}{d_0} = \varepsilon_x$$

Also, transverse strain and longitudinal strain (ε_z) are related according to Equation 6.8—that is

$$\varepsilon_x = -\nu\varepsilon_z$$

where ν is Poisson’s ratio. Substitution of this expression for ε_x into the first equation above leads to

$$\frac{\Delta d_2}{d_0} = -\nu\varepsilon_z$$

Furthermore, the longitudinal strain is related to the modulus of elasticity through Equation 6.5—i.e.,

$$\varepsilon_z = \frac{\sigma}{E}$$

And, therefore, we may write the following:

$$\frac{\Delta d_2}{d_0} = -\nu\frac{\sigma}{E}$$

Now, from Equation 19.8 stress is equal to

$$\sigma = E\alpha_l(T_0 - T_f)$$

which, when substituted into the preceding equation, leads to

$$\frac{\Delta d_2}{d_0} = -\frac{\nu E\alpha_l(T_0 - T_f)}{E}$$

$$= -\nu\alpha_l(T_0 - T_f)$$

And, solving for Δd_2 from this expression

$$\Delta d_2 = -d_0\nu\alpha_l(T_0 - T_f)$$

Now, the total Δd is just $\Delta d = \Delta d_1 + \Delta d_2$, as follows:

$$\Delta d = d_0\alpha_l(T_f - T_0) + d_0\nu\alpha_l(T_f - T_0)$$

$$= d_0\alpha_l(T_f - T_0)(1 + \nu)$$

The values of ν and α_l for nickel are 0.31 and $13.3 \times 10^{-6}\ (°\text{C})^{-1}$, respectively (Tables 6.1 and 19.1). Incorporating, into the above equation, these values, as well as those for Δd, d_0, and T_0 cited in the problem statement gives

$$-(0.023\text{ mm}) = (12.000\text{ mm})\left[13.3 \times 10^{-6}\ (°\text{C})^{-1}\right](T_f - 70°\text{C})(1 + 0.31)$$

And, finally, solving the above expression for T_f yields $T_f = -40°\text{C}$.

19.29 *What measures may be taken to reduce the likelihood of thermal shock of a ceramic piece?*

Answer

According to Equation 19.9, the thermal shock resistance of a ceramic piece may be enhanced by increasing the fracture strength and thermal conductivity, and by decreasing the elastic modulus and linear coefficient of thermal expansion. Of these parameters, σ_f and α_l are most amenable to alteration, usually by changing the composition and/or the microstructure.

DESIGN PROBLEMS

Thermal Expansion

19.D1 *Railroad tracks made of 1025 steel are to be laid during the time of year when the temperature averages 4°C (40°F). If a joint space of 5.4 mm (0.210 in.) is allowed between standard rails of length 11.9 m (39 ft), what is the highest possible temperature that can be tolerated without the introduction of thermal stresses?*

Solution

For these railroad tracks, each end is allowed to expand one-half of the joint space distance, or the track may expand a total of this distance (Δl = 5.4 mm). Equation 19.3a is used to solve for T_f, where the value α_l for the 1025 steel [12.0×10^{-6} $(°\text{C})^{-1}$] is found in Table 19.1. Thus, solving for T_f from Equation 19.3a leads to the following:

$$T_f = \frac{\Delta l}{\alpha_l l_0} + T_0$$

$$= \frac{5.4 \times 10^{-3}\ \text{m}}{\left[12.0 \times 10^{-6}\ (°\text{C})^{-1}\right](11.9\ \text{m})} + 4°\text{C}$$

$$= 37.8°\text{C} + 4°\text{C} = 41.8°\text{C} \qquad (106.8°\text{F})$$

Thermal Stresses

19.D2 *The ends of a cylindrical rod 6.4 mm (0.25 in.) in diameter and 250 mm (10 in.) long are mounted between rigid supports. The rod is stress free at room temperature [20°C (68°F)]; upon cooling to –60°C (– 76°F), a maximum thermally induced tensile stress of 138 MPa (20,000 psi) is possible. Of which of the following metals or alloys may the rod be fabricated: aluminum, copper, brass, 1025 steel, and tungsten? Why?*

Solution

This is a materials selection problem wherein we must decide for which of the five metals listed, the stress in the rod will not exceed 138 MPa (20,000 psi), when it is heated while its ends are mounted between rigid supports. Upon examination of Equation 19.8, it may be noted that all we need do is to compute the $E\alpha_l\Delta T$ product for each of the candidate materials, and then note for which of them the stress is less than the stipulated maximum. The value of ΔT is equal to the following:

$$\Delta T = T_0 - T_f = 20^\circ\text{C} - (-60^\circ\text{C})$$

$$= 80^\circ\text{C}$$

Values of α_l, E, and the $E\alpha_l\Delta T$ product are listed below for each of the alloys. (Modulus of elasticity values were taken from Table 6.1, while the α_l values came from Table 19.1.)

Alloy	α_l (°C)$^{-1}$	E (MPa)	$E\alpha_l\Delta T$ (MPa)
Aluminum	23.6×10^{-6}	69×10^3	130
Copper	17.0×10^{-6}	110×10^3	150
Brass	20.0×10^{-6}	97×10^3	155
1025 Steel	12.0×10^{-6}	207×10^3	200
Tungsten	4.5×10^{-6}	407×10^3	145

Thus, aluminum is the only suitable candidate—that is for which $E\alpha_l\Delta T < 138$ MPa.

19.D3 *(a) What are the units for the thermal shock resistance parameter (TSR)?*

(b) Rank the following ceramic materials according to their thermal shock resistance: soda–lime glass, fused silica, and silicon [<100> direction and {100} orientation, as-cut surface]. Appropriate data may be found in Tables B.2, B.4, B.6, and B.7 of Appendix B.

Solution

(a) This portion of the problem asks that we cite the units for the thermal shock resistance parameter (*TSR*). Let us include units for all of the parameters in Equation 19.9, as follows:

$$TSR = \frac{\sigma_f (\text{N/m}^2)\, k (\text{W/m-K})}{E(\text{N/m}^2)\, \alpha_l (°\text{C})^{-1}} = \text{W/m}$$

(Note: in reducing units in the above expression, we have assumed that units of temperature in K and °C are equivalent)

(b) Now we are asked to rank soda-lime glass, fused silica, and silicon as to their thermal shock resistance. Thus, all we need do is calculate, for each, the value of *TSR* using Equation 19.9. Values of *E*, σ_f, α_l, and *k* are found, respectively, in Tables B.2, B.4, B.6, and B.7, Appendix B. (Note: whenever a range for a property value in these tables is cited, the average of the extremes is used.)

The magnitude of the *TSR* for soda-lime glass is computed as follows:

$$TSR = \frac{\sigma_f\, k}{E\, \alpha_l}$$

$$= \frac{(69 \text{ MPa})(1.7 \text{ W/m-K})}{(69 \times 10^3 \text{ MPa})\left[9.0 \times 10^{-6} (°\text{C})^{-1}\right]} = 189 \text{ W/m}$$

For fused silica

$$TSR = \frac{(104 \text{ MPa})(1.4 \text{ W/m-K})}{(73 \times 10^3 \text{ MPa})\left[0.4 \times 10^{-6} (°\text{C})^{-1}\right]} = 4986 \text{ W/m}$$

And, for silicon

$$TSR = \frac{(130 \text{ MPa})(141 \text{ W/m-K})}{(129 \times 10^3 \text{ MPa})\left[2.5 \times 10^{-6} (°\text{C})^{-1}\right]} = 56{,}800 \text{ W/m}$$

Thus, these materials may be ranked according to their thermal shock resistance from the greatest to the least as follows: silicon, fused silica, and soda-lime glass.

19.D4 *Equation 19.9, for the thermal shock resistance of a material, is valid for relatively low rates of heat transfer. When the rate is high, then, upon cooling of a body, the maximum temperature change allowable without thermal shock,* ΔT_f*, is given by approximately*

$$\Delta T_f \cong \frac{\sigma_f}{E\alpha_l}$$

where σ_f *is the fracture strength. Using the data in Tables B.2, B.4, and B.6 (Appendix B), determine* ΔT_f *for soda–lime glass, borosilicate (Pyrex) glass, aluminum oxide (96% pure), and gallium arsenide [<100> direction and {100} orientation, as-cut surface].*

Solution

We want to compute the maximum temperature change allowable without thermal shock for these several ceramic materials, which temperature change is a function of the fracture strength, elastic modulus, and linear coefficient of thermal expansion. These data and the ΔT_f's are tabulated below. (Values for E, σ_f, and α_l are taken from Tables B.2, B.4, B.6 in Appendix B.)

Material	σ_f (MPa)	E (MPa)	α_l (°C)$^{-1}$	ΔT_f (°C)
Soda-lime glass	69	69×10^3	9.0×10^{-6}	111
Borosilicate glass	69	70×10^3	3.3×10^{-6}	300
Aluminum oxide (96%)	358	303×10^3	7.4×10^{-6}	160
Gallium arsenide	57	85×10^3	5.9×10^{-6}	114

FUNDAMENTALS OF ENGINEERING QUESTIONS AND PROBLEMS

19.1FE *To what temperature would 23.0 kg of some material at 100°C be raised if 255 kJ of heat is supplied? Assume a* c_p *value of 423 J/kg-K for this material.*

(A) 26.2°C
(B) 73.8°C
(C) 126°C
(D) 152°C

Solution

The change in temperature (ΔT) when ΔQ of heat is supplied to a mass of material *m* is equal to a revised form of Equation 19.1 as follows:

$$\frac{\Delta Q}{c_p m} = \Delta T = T_f - T_0$$

where T_0 and T_f are the initial and final temperatures, respectively. Solving this equation for the final temperature yields the following:

$$T_f = T_0 + \frac{\Delta Q}{c_p m}$$

Using values provided in the problem statement—that is

$T_0 = 100°\text{C}$
$\Delta Q = 255 \text{ kJ} = 255{,}000 \text{ J}$
$c_p = 423 \text{ J/kg-K}$
$m = 23.0 \text{ kg}$

We compute the final temperature as follows:

$$T_f = 100°\text{C} + \frac{255{,}000 \text{ J}}{(423 \text{ J/kg-K})(23.0 \text{ kg})} = 126°\text{C}$$

which is answer C.

19.2FE *A rod of some material 0.50 m long elongates 0.40 mm on heating from 50°C to 151°C. What is the value of the linear coefficient of thermal expansion for this material?*

(A) $5.30 \times 10^{-6}\ (°\mathrm{C})^{-1}$

(B) $7.92 \times 10^{-6}\ (°\mathrm{C})^{-1}$

(C) $1.60 \times 10^{-5}\ (°\mathrm{C})^{-1}$

(D) $1.24 \times 10^{-6}\ (°\mathrm{C})^{-1}$

Solution

The relationship among change in length (Δl), coefficient of thermal expansion (α_l), and change in temperature (ΔT) is given by Equation 19.3b—that is

$$\frac{\Delta l}{l_0} = \alpha_l \Delta T = \alpha_l (T_f - T_0)$$

where T_f and T_0 are the final and initial temperatures, respectively. Thus, the linear coefficient of thermal expansion may be determined using a rearranged form of the above equation as follows:

$$\alpha_l = \frac{\Delta l}{l_0 (T_f - T_0)}$$

Incorporation of values of Δl, l_0, T_f, and T_0 provided in the problem statements leads to the following value of α_l

$$\alpha_l = \frac{(0.40 \times 10^{-3}\ \mathrm{m})}{(0.50\ \mathrm{m})(151°\mathrm{C} - 50°\mathrm{C})} = 7.92 \times 10^{-6}\ (°\mathrm{C})^{-1}$$

which is answer B.

19.3FE *Which of the following sets of properties leads to a high degree of thermal shock resistance?*

(A) High fracture strength
High thermal conductivity
High modulus of elasticity
High coefficient of thermal expansion

(B) Low fracture strength
Low thermal conductivity
Low modulus of elasticity
Low coefficient of thermal expansion

(C) High fracture strength
High thermal conductivity
Low modulus of elasticity
Low coefficient of thermal expansion

(D) Low fracture strength
Low thermal conductivity
High modulus of elasticity
High coefficient of thermal expansion

Answer

The correct answer is C.

Thermal shock resistance is defined by Equation 19.9; therefore, a material that has a high *TSR* will have a high fracture strength, a high thermal conductivity, a low modulus of elasticity, and a low coefficient of thermal expansion.

CHAPTER 20

MAGNETIC PROPERTIES

PROBLEM SOLUTIONS

Basic Concepts

20.1 *A coil of wire 0.25 m long and having 400 turns carries a current of 15 A.*

(a) What is the magnitude of the magnetic field strength H?

(b) Compute the flux density B if the coil is in a vacuum.

(c) Compute the flux density inside a bar of chromium that is positioned within the coil. The susceptibility for chromium is given in Table 20.2.

(d) Compute the magnitude of the magnetization M.

Solution

(a) We calculate the magnetic field strength generated by this coil using Equation 20.1 as follows:

$$H = \frac{NI}{l}$$

$$= \frac{(400 \text{ turns})(15 \text{ A})}{0.25 \text{ m}} = 24{,}000 \text{ A-turns/m}$$

(b) In a vacuum, the flux density is determined using Equation 20.3. Thus,

$$B_0 = \mu_0 H$$

$$= (1.257 \times 10^{-6} \text{ H/m})(24{,}000 \text{ A-turns/m}) = 3.0168 \times 10^{-2} \text{ tesla}$$

(c) When a bar of chromium is positioned within the coil, we must combine Equations 20.5 and 20.6 in order to compute the flux density given the magnetic susceptibility. Inasmuch as $\chi_m = 3.13 \times 10^{-4}$ (Table 20.2), then

$$B = \mu_0 H + \mu_0 M$$

$$= \mu_0 H + \mu_0 \chi_m H$$

$$= \mu_0 H (1 + \chi_m)$$

$$= (1.257 \times 10^{-6}\ \text{H/m})(24{,}000\ \text{A-turns/m})(1 + 3.13 \times 10^{-4})$$

$$= 3.0177 \times 10^{-2}\ \text{tesla}$$

which is essentially the same result as part (b). This is to say that the influence of the chromium bar within the coil makes an imperceptible difference in the magnitude of the *B* field.

(d) The magnetization is computed from Equation 20.6 as follows:

$$M = \chi_m H = (3.13 \times 10^{-4})(24{,}000\ \text{A-turns/m}) = 7.51\ \text{A/m}$$

20.2 *Demonstrate that the relative permeability and the magnetic susceptibility are related according to Equation 20.7.*

Solution

This problem asks us to show that χ_m and μ_r are related according to $\chi_m = \mu_r - 1$. We begin with Equation 20.5 and substitute for *M* using Equation 20.6. Thus,

$$B = \mu_0 H + \mu_0 M$$

$$= \mu_0 H + \mu_0 \chi_m H$$

However, *B* is also defined in Equation 20.2 as

$$B = \mu H$$

When the above two expressions for *B* are set equal to one another then

$$\mu H = \mu_0 H + \mu_0 \chi_m H$$

which leads to the following:

$$\mu = \mu_0 (1 + \chi_m)$$

If we divide both sides of this expression by μ_0, then

$$\frac{\mu}{\mu_0} = 1 + \chi_m$$

Now from Equation 20.4

$$\frac{\mu}{\mu_0} = \mu_r$$

Substitution of this equation into the previous one leads to the following:

$$\mu_r = 1 + \chi_m$$

And, upon rearrangement, we have

$$\chi_m = \mu_r - 1$$

the desired result.

20.3 *It is possible to express the magnetic susceptibility* χ_m *in several different units. For the discussion of this chapter,* χ_m *was used to designate the volume susceptibility in SI units—that is, the quantity that gives the magnetization per unit volume* (m^3) *of material when multiplied by H. The mass susceptibility* $\chi_m(kg)$ *yields the magnetic moment (or magnetization) per kilogram of material when multiplied by H; similarly, the atomic susceptibility* $\chi_m(a)$ *gives the magnetization per kilogram-mole. The last two quantities are related to* χ_m *through the following relationships:*

$\chi_m = \chi_m(kg) \times$ *mass density (in* kg/m^3*)*

$\chi_m(a) = \chi_m(kg) \times$ *atomic weight (in kg)*

When using the cgs–emu system, comparable parameters exist, which may be designated by χ'_m, $\chi'_m(g)$, *and* $\chi'_m(a)$*; the* χ_m *and* χ'_m *are related in accordance with Table 20.1. From Table 20.2,* χ_m *for copper is* -0.96×10^{-5}*; convert this value into the other five susceptibilities.*

Solution

For this problem, we want to convert the volume susceptibility of copper (i.e., -0.96×10^{-5}) into other systems of units.

From the expression for the mass susceptibility given in the problem statement we may write

$$\chi_m(\mathrm{kg}) = \frac{\chi_m}{\rho(\mathrm{kg/m^3})}$$

The density of copper is 8.94 g/cm^3, we convert into units of kg/m^3 as follows:

$$\rho = (8.94\ \mathrm{g/cm^3})\left(\frac{1\ \mathrm{kg}}{1000\ \mathrm{g}}\right)\left(\frac{100\ \mathrm{cm}}{\mathrm{m}}\right)^3$$

$$= 8.94 \times 10^3\ \mathrm{kg/m^3}$$

We now compute the mass density susceptibility as follows:

$$\chi_m(\mathrm{kg}) = \frac{\chi_m}{\rho(\mathrm{kg/m^3})}$$

$$= \frac{-0.96 \times 10^{-5}}{8.94 \times 10^3\ \mathrm{kg/m^3}} = -1.07 \times 10^{-9}$$

The atomic susceptibility is defined above as follows:

$$\chi_m(\mathrm{a}) = \chi_m(\mathrm{kg}) \times \left[\text{atomic weight (in kg)}\right]$$

The atomic weight of copper (in g/mol) is 63.55 g/mol, which converts into kg/mol as follows:

$$\text{atomic weight (in kg)} = (63.55\ \text{g/mol})\left(\frac{1\ \text{kg}}{1000\ \text{g}}\right) = 6.355 \times 10^{-2}\ \text{kg/mol}$$

Therefore we compute the atomic susceptibility

$$\chi_m(\text{a}) = \chi_m(\text{kg}) \times [\text{atomic weight (in kg)}]$$

$$= (-1.07 \times 10^{-9})(6.355 \times 10^{-2}\ \text{kg/mol}) = -6.80 \times 10^{-11}$$

From Table 20.1 the cgs-emu volume susceptibility is equal to the following:

$$\chi'_m = \frac{\chi_m}{4\pi}$$

Here χ_m is the SI volume susceptibility, which was provided in the problem statement. Therefore,

$$\chi'_m = \frac{\chi_m}{4\pi}$$

$$= \frac{-0.96 \times 10^{-5}}{4\pi} = -7.64 \times 10^{-7}$$

The next susceptibility we want to determine is $\chi'_m(\text{g})$, which in, cgs-emu units, is equal to

$$\chi'_m(\text{g}) = \frac{\chi'_m}{\text{mass density (in g/cm}^3)}$$

Therefore,

$$\chi'_m(\text{g}) = \frac{-7.64 \times 10^{-7}}{8.94\ \text{g/cm}^3}$$

$$= -8.55 \times 10^{-8}$$

And finally, the cgs-emu atomic susceptibility $\chi'_m(\text{a})$ is defined as follows:

$$\chi'_m(\text{a}) = \chi'_m(\text{g}) \times [\text{atomic weight (in g)}]$$

which for copper has a value of

$$\chi'_m(\text{a}) = (-8.55 \times 10^{-8})(63.55\ \text{g/mol}) = -5.43 \times 10^{-6}$$

20.4 *(a) Explain the two sources of magnetic moments for electrons.*

(b) Do all electrons have a net magnetic moment? Why or why not?

(c) Do all atoms have a net magnetic moment? Why or why not?

Answer

(a) The two sources of magnetic moments for electrons are the electron's orbital motion around the nucleus, and also, its spin.

(b) Each electron will have a net magnetic moment from spin, and possibly, orbital contributions, which do not cancel for an isolated atom.

(c) All atoms do not have a net magnetic moment. If an atom has completely filled electron shells or subshells, there will be a cancellation of both orbital and spin magnetic moments.

Diamagnetism and Paramagnetism

Ferromagnetism

20.5 *The magnetic flux density within a bar of some material is 0.630 tesla at an H field of 5 × 10^5 A/m. Compute the following for this material: (a) the magnetic permeability and (b) the magnetic susceptibility. (c) What type(s) of magnetism would you suggest is (are) being displayed by this material? Why?*

Solution

(a) The magnetic permeability of this material may be determined according to a rearranged form of Equation 20.2 as follows:

$$\mu = \frac{B}{H}$$

$$= \frac{0.630 \text{ tesla}}{5 \times 10^5 \text{ A/m}} = 1.260 \times 10^{-6} \text{ H/m}$$

(b) The magnetic susceptibility is calculated using a combined form of Equations 20.4 and 20.7 as follows:

$$\chi_m = \mu_r - 1 = \frac{\mu}{\mu_0} - 1$$

$$= \frac{1.260 \times 10^{-6} \text{ H/m}}{1.257 \times 10^{-6} \text{ H/m}} - 1 = 2.387 \times 10^{-3}$$

(c) This material would display both diamagnetic and paramagnetic behavior. All materials are diamagnetic, and since χ_m is positive and on the order of 10^{-3}, there would also be a paramagnetic contribution.

20.6 *The magnetization within a bar of some metal alloy is 1.2 × 10^6 A/m at an H field of 200 A/m. Compute the following: (a) the magnetic susceptibility, (b) the permeability, and (c) the magnetic flux density within this material. (d) What type(s) of magnetism would you suggest is (are) being displayed by this material? Why?*

Solution

(a) This portion of the problem calls for us to compute the magnetic susceptibility within a bar of some metal alloy when $M = 1.2 \times 10^6$ A/m and $H = 200$ A/m. This requires that we solve for χ_m from Equation 20.6 as follows:

$$\chi_m = \frac{M}{H} = \frac{1.2 \times 10^6 \text{ A/m}}{200 \text{ A/m}} = 6000$$

(b) In order to calculate the permeability we must employ a combined form of Equations 20.4 and 20.7 as follows:

$$\mu = \mu_r \mu_0$$

$$= (\chi_m + 1)\mu_0$$

$$= (6000 + 1)(1.257 \times 10^{-6} \text{ H/m}) = 7.54 \times 10^{-3} \text{ H/m}$$

(c) The magnetic flux density may be determined using Equation 20.2 as

$$B = \mu H = (7.54 \times 10^{-3} \text{ H/m})(200 \text{ A/m}) = 1.51 \text{ tesla}$$

(d) This metal alloy would exhibit ferromagnetic behavior on the basis of the magnitude of its χ_m (6000), which is considerably larger than the χ_m values for diamagnetic and paramagnetic materials listed in Table 20.2.

20.7 *Compute (a) the saturation magnetization and (b) the saturation flux density for iron, which has a net magnetic moment per atom of 2.2 Bohr magnetons and a density of 7.87 g/cm*^{3}.

Solution

(a) The saturation magnetization for Fe may be determined in the same manner as was done for Ni in Example Problem 20.1. Thus, using a modified form of Equation 20.9

$$M_s = 2.2\,\mu_B N \tag{20.9a}$$

in which μ_B is the Bohr magneton and N is the number of Fe atoms per cubic meter. Also, there are 2.2 Bohr magnetons per Fe atom. Now, N (the number of iron atoms per cubic meter) is related to the density and atomic weight of Fe, and Avogadro's number according to Equation 20.10 as

$$N = \frac{\rho_{\text{Fe}} N_A}{A_{\text{Fe}}}$$

$$= \frac{(7.87\text{ g/cm}^3)(100\text{ cm/m})^3(6.022 \times 10^{23}\text{ atoms/mol})}{55.85\text{ g/mol}}$$

$$= 8.49 \times 10^{28}\text{ atoms/m}^3$$

Therefore, we determine the saturation magnetization using Equation 20.9a shown above:

$$M_s = 2.2\,\mu_B N$$

$$= (2.2\text{ BM/atom})(9.27 \times 10^{-24}\text{ A-m}^2/\text{BM})(8.49 \times 10^{28}\text{ atoms/m}^3)$$

$$= 1.73 \times 10^6\text{ A/m}$$

(b) The saturation flux density is determined according to Equation 20.8 as follows:

$$B_s = \mu_0 M_s$$

$$= (1.257 \times 10^{-6}\text{ H/m})(1.73 \times 10^6\text{ A/m}) = 2.17\text{ tesla}$$

20.8 *Confirm that there are 1.72 Bohr magnetons associated with each cobalt atom, given that the saturation magnetization is 1.45 × 10^6 A/m, that cobalt has an HCP crystal structure with an atomic radius of 0.1253 nm and a c/a ratio of 1.623.*

Solution

We want to confirm that there are 1.72 Bohr magnetons associated with each cobalt atom. Therefore, let n'_B be the number of Bohr magnetons per atom, which we will calculate. This is possible using a modified and rearranged form of Equation 20.9—that is

$$n'_B = \frac{M_s}{\mu_B N} \tag{20.9b}$$

Now, N is just the number of atoms per cubic meter, which is the number of atoms per unit cell (six for HCP, Section 3.4) divided by the unit cell volume--that is,

$$N = \frac{6}{V_C}$$

which, when substituted into Equation 20.9b gives the following expression:

$$n'_B = \frac{M_s V_C}{6\mu_B} \tag{20.9c}$$

The unit cell volume for HCP metals is given in Equation 3.7a as follows:

$$V_C = \frac{3a^2 c\sqrt{3}}{2}$$

And since c = 1.623a (as given in the problem statement), we rewrite the above equation as follows:

$$V_C = \frac{3a^2(1.632a)\sqrt{3}}{2}$$

Furthermore, for HCP the unit cell parameter a and the atomic radius are related as follows:

$$a = 2R$$

such that we may rewrite the preceding equation as

$$V_C = \frac{(3)(1.632)(2R)^3\sqrt{3}}{2}$$

$$= 19.58 R^3 \sqrt{3}$$

The atomic radius, *R*, was given in the problem statement as 0.1253 nm or 0.1253 × 10^{-9} m. We now compute the unit cell volume for cobalt as follows:

$$V_C = (19.58)\left(0.1253 \times 10^{-9} \text{ m}\right)^3 (\sqrt{3})$$

$$= 6.67 \times 10^{-29} \text{ m}^3$$

We now compute the number of Bohr magnetons per cobalt atom using Equation 20.9c, given above as

$$n'_\text{B} = \frac{M_s V_C}{6 \mu_\text{B}}$$

$$= \frac{(1.45 \times 10^6 \text{ A/m})(6.67 \times 10^{-29} \text{ m}^3/\text{unit cell})}{(6 \text{ atoms/unit cell})(9.27 \times 10^{-24} \text{A-m}^2/\text{Bohr magneton})}$$

$$= 1.74 \text{ Bohr magnetons/atom}$$

This value is very close to the 1.72 Bohr magnetons/atom cited in the problem statement.

20.9 *Assume there exists some hypothetical metal that exhibits ferromagnetic behavior and that has (1) a simple cubic crystal structure (Figure 3.3), (2) an atomic radius of 0.125 nm, and (3) a saturation flux density of 0.85 tesla. Determine the number of Bohr magnetons per atom for this material.*

Solution

We are to determine the number of Bohr magnetons per atom for a hypothetical metal that has a simple cubic crystal structure, an atomic radius of 0.125 nm, and a saturation flux density of 0.85 tesla. It becomes necessary to employ Equation 20.8 and a modified form of Equation 20.9 as follows:

$$n_B = \frac{M_s}{\mu_{\mathrm{B}} N}$$

$$= \frac{\dfrac{B_s}{\mu_0}}{\mu_{\mathrm{B}} N} = \frac{B_s}{\mu_0 \mu_{\mathrm{B}} N}$$

Here n_{B} is the number of Bohr magnetons per atom, and N is just the number of atoms per cubic meter, which is the number of atoms per unit cell [one for simple cubic (Figure 3.3)] divided by the unit cell volume—that is,

$$N = \frac{\text{1 atom/unit cell}}{V_C}$$

which, when substituted into the above equation gives

$$n_{\mathrm{B}} = \frac{B_s V_C}{\mu_0 \mu_{\mathrm{B}}}$$

For the simple cubic crystal structure (Figure 3.3), $a = 2R$, where R is the atomic radius, and $V_C = a^3 = (2R)^3$. Substituting this relationship into the above equation yields

$$n_{\mathrm{B}} = \frac{B_s (2R)^3}{\mu_0 \, \mu_{\mathrm{B}}}$$

Values for the following parameters are provided in the problem statement:

B_s = 0.85 tesla

R = 0.125 nm = 0.125×10^{-9} m

Therefore, we compute the number of Bohr magnetons per atom as follows using the previous equation

$$n_{\mathrm{B}} = \frac{B_s\,(2R)^3}{\mu_0\,\mu_{\mathrm{B}}}$$

$$= \frac{(0.85\ \text{tesla})(8)\left(0.125 \times 10^{-9}\,\text{m}\right)^3}{\left(1.257 \times 10^{-6}\ \text{H/m}\right)\left(9.27 \times 10^{-24}\ \text{A-m}^2/\text{BM}\right)} = 1.14\ \text{Bohr magnetons/atom}$$

20.10 *A net magnetic moment is associated with each atom in paramagnetic and ferromagnetic materials. Explain why ferromagnetic materials can be permanently magnetized whereas paramagnetic ones cannot.*

Answer

Ferromagnetic materials may be permanently magnetized (whereas paramagnetic ones may not) because of the ability of net spin magnetic moments of adjacent atoms to align with one another. This mutual magnetic moment alignment in the same direction exists within small volume regions—domains. When a magnetic field is applied, favorably oriented domains grow at the expense of unfavorably oriented ones, by the motion of domain walls. When the magnetic field is removed, there remains a net magnetization by virtue of the resistance to movement of domain walls; even after total removal of the magnetic field, the magnetization of some net domain volume will be aligned near the direction that the external field was oriented.

For paramagnetic materials, there is no magnetic dipole coupling, and, consequently, domains do not form. When a magnetic field is removed, the atomic dipoles assume random orientations, and no magnetic moment remains.

Antiferromagnetism and Ferrimagnetism

20.11 *Consult a reference in which Hund's rule is outlined, and on its basis explain the net magnetic moments for each of the cations listed in Table 20.4.*

Answer

Hund's rule states that the spins of the electrons of a shell will add together in such a way as to yield the maximum magnetic moment. This means that as electrons fill a shell the spins of the electrons that fill the first half of the shell are all oriented in the same direction; furthermore, the spins of the electrons that fill the last half of this same shell will all be aligned and oriented in the opposite direction. For example, consider the iron ions in Table 20.4; from Table 2.2, the electron configuration for the outermost shell for the Fe atom is $3d^6 4s^2$. For the Fe^{3+} ion the outermost shell configuration is $3d^5$, which means that five of the ten possible $3d$ states are filled with electrons. According to Hund's rule the spins of all of these electrons are aligned, there will be no cancellation, and therefore, there are five Bohr magnetons associated with each Fe^{3+} ion, as noted in the table. For Fe^{2+} the configuration of the outermost shell is $3d^6$, which means that the spins of five electrons are aligned in one direction, and the spin of a single electron is aligned in the opposite direction, which cancels the magnetic moment of one of the other five; thus, this yields a net moment of four Bohr magnetons.

For Mn^{2+} the electron configuration is $3d^5$, the same as Fe^{3+}, and, therefore it will have the same number of Bohr magnetons (i.e., five).

For Co^{2+} the electron configuration is $3d^7$, which means that the spins of five electrons are in one direction, and two are in the opposite direction, which gives rise to a net moment of three Bohr magnetons.

For Ni^{2+} the electron configuration is $3d^8$ which means that the spins of five electrons are in one direction, and three are in the opposite direction, which gives rise to a net moment of two Bohr magnetons.

For Cu^{2+} the electron configuration is $3d^9$ which means that the spins of five electrons are in one direction, and four are in the opposite direction, which gives rise to a net moment of one Bohr magneton.

20.12 *Estimate (a) the saturation magnetization and (b) the saturation flux density of cobalt ferrite* $[(CoFe_2O_4)_8]$*, which has a unit cell edge length of 0.838 nm.*

Solution

(a) The saturation magnetization of cobalt ferrite is computed in the same manner as Example Problem 20.2; from Equation 20.13

$$M_s = \frac{n_B \mu_B}{a^3}$$

Now, n_B is just the number of Bohr magnetons per unit cell. The net magnetic moment arises from the Co^{2+} ions, of which there are eight per unit cell, each of which has a net magnetic moment of three Bohr magnetons (Table 20.4). Thus, n_B is twenty-four. Therefore, from the above equation

$$M_s = \frac{(24 \text{ BM/unit cell})(9.27 \times 10^{-24} \text{ A-m}^2/\text{BM})}{(0.838 \times 10^{-9} \text{ m})^3/\text{unit cell}}$$

$$= 3.78 \times 10^5 \text{ A/m}$$

(b) This portion of the problem calls for us to compute the saturation flux density, B_s. This is possible using Equation 20.8 as follows:

$$B_s = \mu_0 M_s$$

$$= (1.257 \times 10^{-6} \text{ H/m})(3.78 \times 10^5 \text{ A/m}) = 0.475 \text{ tesla}$$

20.13 *The chemical formula for copper ferrite may be written as* $(CuFe_2O_4)_8$ *because there are eight formula units per unit cell. If this material has a saturation magnetization of* 1.35×10^5 *A/m and a density of 5.40 g/cm*^{3}*, estimate the number of Bohr magnetons associated with each* Cu^{2+} *ion.*

Solution

We want to compute the number of Bohr magnetons per Cu^{2+} ion in $(CuFe_2O_4)_8$. Let n_B represent the number of Bohr magnetons per Cu^{2+} ion; then, using Equation 20.9, we write

$$M_s = n_B \mu_B N$$

in which N is the number of Cu^{2+} ions per cubic meter of material. But, from Equation 20.10

$$N = \frac{\rho N_A}{A}$$

Here A is the molecular weight of $CuFe_2O_4$ (239.25 g/mol). Thus, combining the previous two equations leads to the following:

$$M_s = \frac{n_B \mu_B \rho N_A}{A}$$

or, upon rearrangement (and expressing the density in units of grams per meter cubed), the number of Bohr magnetons per Cu^{2+} ion (n_B) is computed as follows:

$$n_B = \frac{M_s A}{\mu_B \rho N_A}$$

$$= \frac{(1.35 \times 10^5 \text{ A/m})(239.25 \text{ g/mol})}{(9.27 \times 10^{-24} \text{ A-m}^2/\text{BM})(5.40 \times 10^6 \text{ g/m}^3)(6.022 \times 10^{23} \text{ ions/mol})}$$

$$= 1.07 \text{ Bohr magnetons/Cu}^{2+} \text{ ion}$$

20.14 *The formula for samarium iron garnet ($Sm_3Fe_5O_{12}$) may be written in the form* $\mathrm{Sm}_3^c\mathrm{Fe}_2^a\mathrm{Fe}_3^d\mathrm{O}_{12}$, *where the superscripts a, c, and d represent different sites on which the Sm^{3+} and Fe^{3+} ions are located. The spin magnetic moments for the Sm^{3+} and Fe^{3+} ions positioned in a and c sites are oriented parallel to one another and antiparallel to the Fe^{3+} ions in d sites. Compute the number of Bohr magnetons associated with each Sm^{3+} ion, given the following information: (1) each unit cell consists of eight formula ($Sm_3Fe_5O_{12}$) units; (2) the unit cell is cubic with an edge length of 1.2529 nm; (3) the saturation magnetization for this material is 1.35 × 10^5 A/m; and (4) there are 5 Bohr magnetons associated with each Fe^{3+} ion.*

Solution

In this problem we are to determine the number of Bohr magnetons associated with each Sm^{3+} ion given that each unit cell consists of eight formula units, the unit cell is cubic with an edge length of 1.2529 nm, the saturation magnetization for the material is 1.35 × 10^5 A/m, and that there are 5 Bohr magnetons for each Fe^{3+} ion.

The first thing to do is to calculate the number of Bohr magnetons per unit cell, which we will denote n_B. Solving for n_B in Equation 20.13, we get

$$n_B = \frac{M_s a^3}{\mu_B}$$

$$= \frac{(1.35 \times 10^5 \text{ A/m})(1.2529 \times 10^{-9} \text{ m})^3}{9.27 \times 10^{-24} \text{ A-m}^2/\text{BM}}$$

$$= 28.64 \text{ Bohr magnetons/unit cell}$$

Now, there are 8 formula units per unit cell or $\frac{28.64}{8} = 3.58$ Bohr magnetons per formula unit. Furthermore, for each formula unit there are two Fe^{3+} ions on *a* sites and three Fe^{3+} on *d* sites which magnetic moments are aligned antiparallel. Since there are 5 Bohr magnetons associated with each Fe^{3+} ion, the net magnetic moment contribution per formula unit from the Fe^{3+} ions is 5 Bohr magnetons. This contribution is antiparallel to the contribution from the Sm^{3+} ions, and since there are three Sm^{3+} ions per formula unit, then

$$\text{No. of Bohr magnetons/Sm}^{3+} = \frac{3.58 \text{ BM} + 5 \text{ BM}}{3} = 2.86 \text{ BM}$$

The Influence of Temperature on Magnetic Behavior

20.15 *Briefly explain why the magnitude of the saturation magnetization decreases with increasing temperature for ferromagnetic materials, and why ferromagnetic behavior ceases above the Curie temperature.*

Answer

For ferromagnetic materials, the saturation magnetization decreases with increasing temperature because the atomic thermal vibrational motions counteract the coupling forces between the adjacent atomic dipole moments, causing some magnetic dipole misalignment. Ferromagnetic behavior ceases above the Curie temperature because the atomic thermal vibrations are sufficiently violent so as to completely destroy the mutual spin coupling forces.

Domains and Hysteresis

20.16 *Briefly describe the phenomenon of magnetic hysteresis and why it occurs for ferro- and ferrimagnetic materials.*

The phenomenon of magnetic hysteresis and an explanation as to why it occurs for ferromagnetic and ferrimagnetic materials is given in Section 20.7.

20.17 *A coil of wire 0.5 m long and having 20 turns carries a current of 1.0 A.*

(a) Compute the flux density if the coil is within a vacuum.

(b) A bar of an iron–silicon alloy, the B-H behavior for which is shown in Figure 20.29, is positioned within the coil. What is the flux density within this bar?

(c) Suppose that a bar of molybdenum is now situated within the coil. What current must be used to produce the same B field in the Mo as was produced in the iron–silicon alloy (part b) using 1.0 A?

Solution

(a) This portion of the problem asks that we compute the flux density in a coil of wire 0.5 m long, having 20 turns, and carrying a current of 1.0 A, that is situated in a vacuum. Combining Equations 20.1 and 20.3, and solving for B yields

$$B_0 = \mu_0 H = \frac{\mu_0 NI}{l}$$

$$= \frac{(1.257 \times 10^{-6} \text{ H/m})(20 \text{ turns})(1.0 \text{ A})}{0.5 \text{ m}} = 5.03 \times 10^{-5} \text{ tesla}$$

(b) Now we are to compute the flux density with a bar of the iron-silicon alloy, the B-H behavior for which is shown in Figure 20.29. It is necessary to determine the value of H using Equation 20.1 as follows:

$$H = \frac{NI}{l} = \frac{(20 \text{ turns})(1.0 \text{ A})}{0.5 \text{ m}} = 40 \text{ A-turns/m}$$

Using the curve in Figure 20.29, B = 1.30 tesla at H = 40 A-turns/m.

(c) Finally, we are to assume that a bar of Mo is situated within the coil, and to calculate the current that is necessary to produce the same B field as when the iron-silicon alloy in part (b) was used. Molybdenum is a paramagnetic material having a χ_m of 1.19×10^{-4} (Table 20.2). Combining Equations 20.2, 20.4, and 20.7 and solving for H leads to the following expression:

$$H = \frac{B}{\mu}$$

$$= \frac{B}{\mu_0 \mu_r}$$

$$= \frac{B}{\mu_0 (1 + \chi_m)}$$

When Mo is positioned within the coil, then, from the above equation

$$H = \frac{1.30 \text{ tesla}}{(1.257 \times 10^{-6} \text{ H/m})(1 + 1.19 \times 10^{-4})} = 1.034 \times 10^{6} \text{ A-turns/m}$$

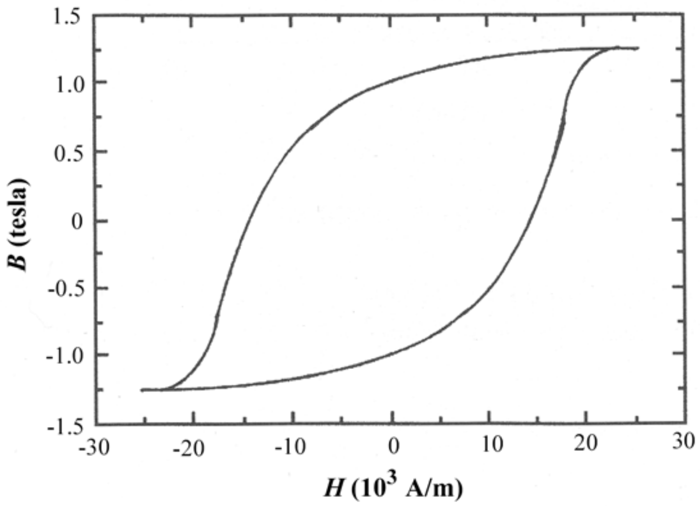
Now, the current may be determined using a rearranged form of Equation 20.1 as follows:

$$I = \frac{Hl}{N} = \frac{(1.034 \times 10^{6} \text{ A-turns/m})(0.5 \text{ m})}{20 \text{ turns}} = 25{,}850 \text{ A}$$

20.18 *A ferromagnetic material has a remanence of 1.0 tesla and a coercivity of 15,000 A/m. Saturation is achieved at a magnetic field strength of 25,000 A/m, at which the flux density is 1.25 teslas. Using these data, sketch the entire hysteresis curve in the range H = –25,000 to +25,000 A/m. Be sure to scale and label both coordinate axes.*

<u>Solution</u>

The *B* versus *H* curve for this material is shown below.



20.19 *The following data are for a plain carbon steel alloy:*

H (A/m)	***B* (teslas)**	***H (A/m)***	***B* (teslas)**
0	*0*	*80*	*0.90*
15	*0.007*	*100*	*1.14*
30	*0.033*	*150*	*1.34*
50	*0.10*	*200*	*1.41*
60	*0.30*	*300*	*1.48*
70	*0.63*		

(a) Construct a graph of B versus H.

(b) What are the values of the initial permeability and initial relative permeability?

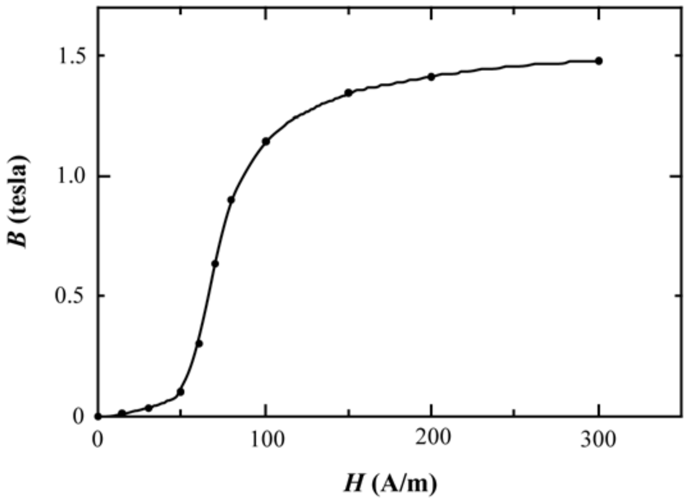
(c) What is the value of the maximum permeability?

(d) At about what H field does this maximum permeability occur?

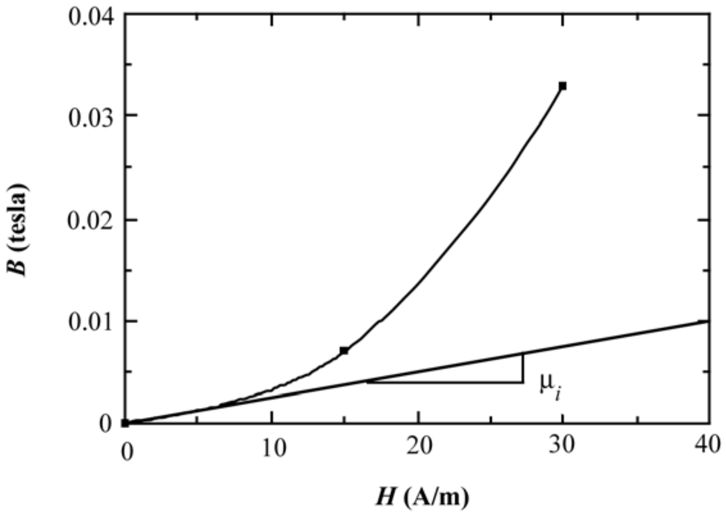
(e) To what magnetic susceptibility does this maximum permeability correspond?

Solution

(a) The *B*-*H* data for the plain carbon steel provided in the problem statement are plotted below.



(b) The first three data points are plotted as follows:



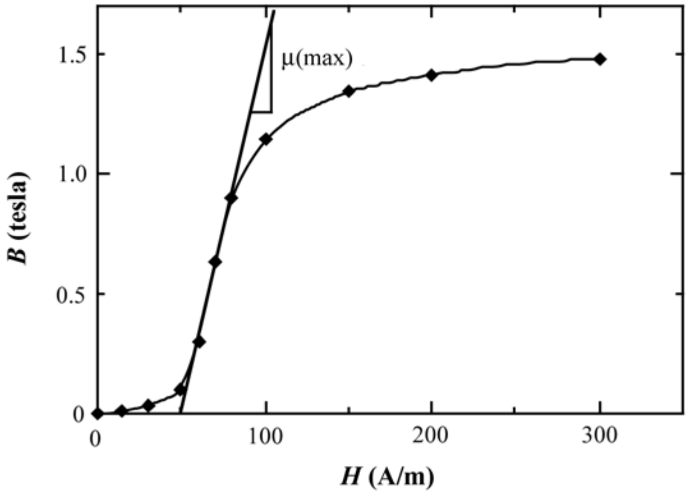
The slope of the initial portion of the curve is μ_i (as shown), is

$$\mu_i = \frac{\Delta B}{\Delta H} = \frac{(0.01 - 0)\ \text{tesla}}{(40 - 0)\ \text{A/m}} = 2.5 \times 10^{-4}\ \text{H/m}$$

Also, the initial relative permeability, μ_{ri}, (Equation 20.4) is just

$$\mu_{ri} = \frac{\mu_i}{\mu_0} = \frac{2.5 \times 10^{-4}\ \text{H/m}}{1.257 \times 10^{-6}\ \text{H/m}} = 200$$

(c) The maximum permeability is the tangent to the *B*-*H* curve having the greatest slope; it is drawn on the plot below, and designated as μ(max).



The value of μ(max) is determined using a modified form of Equation 20.2 as follows:

$$\mu(\max) = \frac{\Delta B}{\Delta H} = \frac{(1.5 - 0)\text{ tesla}}{(100 - 50)\text{ A-m}} = 3.0 \times 10^{-2}\text{ H/m}$$

(d) The H field at which μ(max) occurs is approximately 70 A/m [as taken from the plot shown in part (c)].

(e) We are asked for the maximum susceptibility, χ(max). Combining modified forms of Equations 20.7 and 20.4 yields the following:

$$\chi(\max) = \mu_r(\max) - 1$$

$$= \frac{\mu(\max)}{\mu_0} - 1$$

$$= \frac{3.0 \times 10^{-2}\text{ H/m}}{1.257 \times 10^{-6}\text{ H/m}} - 1 = 23{,}865$$

20.20 *An iron bar magnet having a coercivity of 7000 A/m is to be demagnetized. If the bar is inserted within a cylindrical wire coil 0.25 m long and having 150 turns, what electric current is required to generate the necessary magnetic field?*

Solution

In order to demagnetize a magnet having a coercivity of 7000 A/m, an *H* field of 7000 A/m must be applied in a direction opposite to that of magnetization. According to Equation 20.1

$$I = \frac{Hl}{N}$$

$$= \frac{(7000 \text{ A/m})(0.25 \text{ m})}{150 \text{ turns}} = 11.7 \text{ A}$$

20.21 *A bar of an iron–silicon alloy having the B–H behavior shown in Figure 20.29 is inserted within a coil of wire 0.40 m long and having 50 turns through which passes a current of 0.1 A.*

(a) What is the B field within this bar?

(b) At this magnetic field,

(i) What is the permeability?

(ii) What is the relative permeability?

(iii) What is the susceptibility?

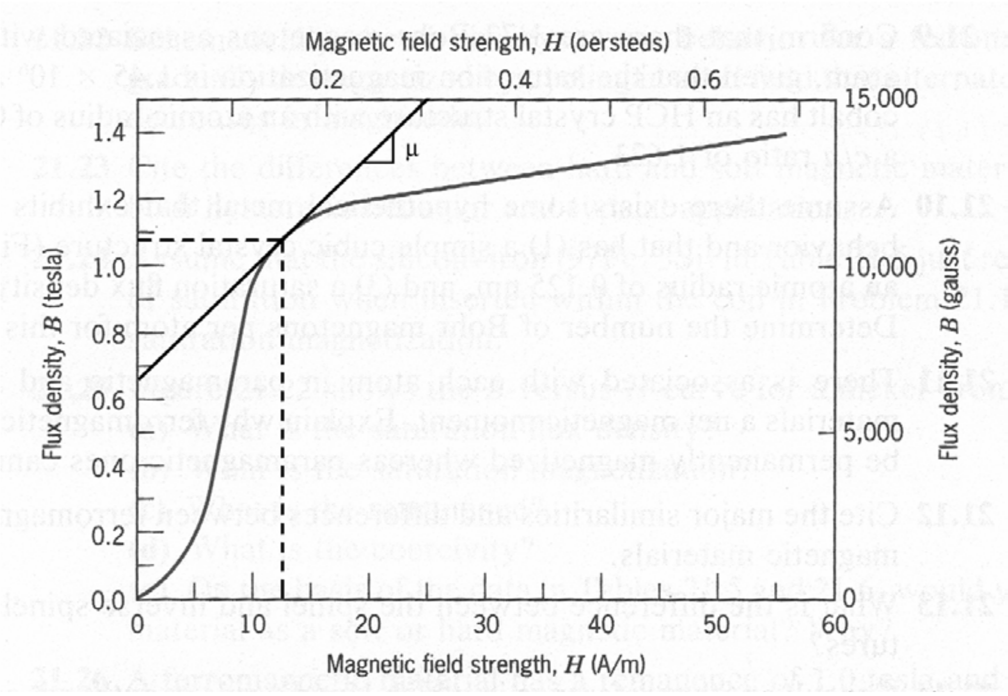
(iv) What is the magnetization?

Solution

(a) We want to determine the magnitude of the *B* field within an iron-silicon alloy, the *B*-*H* behavior for which is shown in Figure 20.29, when l = 0.40 m, N = 50 turns, and I = 0.1 A. Applying Equation 20.1 we calculate the value of *H* as follows:

$$H = \frac{NI}{l} = \frac{\text{(50 turns)(0.1 A)}}{\text{0.40 m}} = \text{12.5 A/m}$$

Below is shown the *B*-versus-*H* plot for this material. The *B* value from the curve corresponding to *H* = 12.5 A/m is about 1.07 tesla.



(b)

(i) The permeability at this field is just $\Delta B/\Delta H$ of the tangent of the B-H curve at H = 12.5 A/m. The slope of this line as drawn in the above figure is

$$\mu = \frac{\Delta B}{\Delta H} = \frac{(1.50 - 0.66)\text{ tesla}}{(25 - 0)\text{ A/m}} = 3.36 \times 10^{-2}\text{ H/m}$$

(ii) From Equation 20.4, the relative permeability is computed a follows:

$$\mu_r = \frac{\mu}{\mu_0} = \frac{3.36 \times 10^{-2}\text{ H/m}}{1.257 \times 10^{-6}\text{ H/m}} = 26{,}730$$

(iii) Using Equation 20.7, the susceptibility is

$$\chi_m = \mu_r - 1$$

$$= 26{,}730 - 1 = 26{,}729$$

(iv) The magnetization is determined from Equation 20.6 as follows:

$$M = \chi_m H = (26{,}729)(12.5\text{ A/m}) = 3.34 \times 10^5\text{ A/m}$$

Magnetic Anisotropy

20.22 *Estimate saturation values of H for single-crystal nickel in the [100], [110], and [111] directions.*

Solution

This problem asks for us to estimate saturation values of *H* for single crystal nickel in the [100], [110], and [111] directions. All we need do is read values of *H* at points A, B, and C on the curves shown in Figure 20.17. Saturation in the [111] direction (point A) is approximately 3000 A/m. Corresponding values in [110] and [111] directions are approximately 15,000 and 17,500 A/m, respectively.

20.23 *The energy (per unit volume) required to magnetize a ferromagnetic material to saturation (E_s) is defined by the following equation:*

$$E_s = \int_0^{M_s} \mu_0 H dM$$

that is, E_s is equal to the product of μ_0 and the area under an M versus H curve, to the point of saturation referenced to the ordinate (or M) axis—for example, in Figure 20.17 the area between the vertical axis and the magnetization curve to M_s. Estimate E_s values (in J/m^3) for single-crystal iron in [100], [110], and [111] directions.

Solution

In this problem we are asked to estimate the energy required to magnetize single crystals of iron in [100], [110], and [111] directions. These energies correspond to the products of μ_0 and the areas between the vertical axis of Figure 20.17 and the three curves for single crystal iron taken to the saturation magnetization. For the [100] direction this area is about 6.8×10^8 A^2/m^2. When this value is multiplied by the value of μ_0 (1.257×10^{-6} H/m), we get a value of about 850 J/m^3. The corresponding approximate areas for [110] and [111] directions are 9×10^9 A^2/m^2 and 1.2×10^{10} A^2/m^2, respectively; when multiplied by μ_0 the respective energies for [110] and [111] directions are 1.1×10^4 and 1.5×10^4 J/m^3.

Soft Magnetic Materials

Hard Magnetic Materials

20.24 *Cite the differences between hard and soft magnetic materials in terms of both hysteresis behavior and typical applications.*

Answer

Relative to hysteresis behavior, a hard magnetic material has a high remanence, a high coercivity, a high saturation flux density, high hysteresis energy losses, and a low initial permeability; a soft magnetic material, on the other hand, has a high initial permeability, a low coercivity, and low hysteresis energy losses.

With regard to applications:

Soft magnetic materials are used in devices that experience alternating and when energy losses must be low—such as transformer cores, generators, motors (electromagnet), and switching circuits.

Hard magnetic materials are used in applications that require permanent magnets—such as motors (permanent magnet motors), audio and video recorders, hearing aids, and computer peripherals.

20.25 *Assume the silicon–iron (97 Fe, 3 Si) in Table 20.5 just reaches the point of saturation when inserted within the coil in Problem 20.1. Compute the saturation magnetization.*

Solution

We want to determine the saturation magnetization of the silicon-iron (97 Fe-3 Si) in Table 20.5, if it just reaches saturation when inserted within the coil described in Problem 20.1—i.e., for l = 0.25 m, N = 400 turns, and A = 15 A. It is first necessary to compute the H field within this coil using Equation 20.1 as follows:

$$H_s = \frac{NI}{l}$$

$$= \frac{(400 \text{ turns})(15 \text{ A})}{0.25 \text{ m}} = 24{,}000 \text{ A-turns/m}$$

Now, the saturation magnetization may be determined from a rearranged form of Equation 20.5—that is,

$$M_s = \frac{B_s - \mu_0 H_s}{\mu_0}$$

The value of B_s in Table 20.5 is 2.01 tesla; thus, we compute the saturation magnetization as follows:

$$M_s = \frac{(2.01 \text{ tesla}) - \left(1.257 \times 10^{-6} \text{ H/m}\right)\left(24{,}000 \text{ A/m}\right)}{1.257 \times 10^{-6} \text{ H/m}}$$

$$= 1.58 \times 10^6 \text{ A/m}$$

20.26 *Figure 20.30 shows the B-versus-H curve for a nickel–iron alloy.*

(a) What is the saturation flux density?

(b) What is the saturation magnetization?

(c) What is the remanence?

(d) What is the coercivity?

(e) On the basis of data in Tables 20.5 and 20.6, would you classify this material as a soft or hard magnetic material? Why?

Solution

(a) The saturation flux density for the nickel-iron, the *B-H* behavior for which is shown in Figure 20.30, is 1.5 tesla, the maximum *B* value found on the curve.

(b) The saturation magnetization is computed from a rearranged form of Equation 20.8, as follows:

$$M_s = \frac{B_s}{\mu_0}$$

$$= \frac{1.5 \text{ tesla}}{1.257 \times 10^{-6} \text{ H/m}} = 1.19 \times 10^6 \text{ A/m}$$

(c) The remanence, B_r, is read from this plot as from the hysteresis loop shown in Figure 20.14; its value is about 1.47 tesla.

(d) The coercivity, H_c, is read from this plot as from Figure 20.14; the value is about 17 A/m.

(e) On the basis of Tables 20.5 and 20.6, this is most likely a soft magnetic material. The saturation flux density (1.5 tesla) lies within the range of values cited for soft materials, and the remanence (1.47 tesla) is close to the values given in Table 20.6 for hard magnetic materials. However, the H_c (17 A/m) is significantly lower than for hard magnetic materials. Also, if we estimate the area within the hysteresis curve, we get a value of approximately 100 J/m^3, which is in line with the hysteresis loss per cycle for soft magnetic materials.

Magnetic Storage

20.27 *Briefly explain the manner in which information is stored magnetically*.

The manner in which information is stored magnetically is discussed in Section 20.11.

Superconductivity

20.28 *For a superconducting material at a temperature T below the critical temperature T_C, the critical field $H_C(T)$ depends on temperature according to the relationship*

$$H_C(T) = H_C(0)\left(1 - \frac{T^2}{T_C^2}\right) \qquad (20.14)$$

where $H_C(0)$ is the critical field at 0 K.

(a) Using the data in Table 20.7, calculate the critical magnetic fields for lead at 2.5 and 5.0 K.

(b) To what temperature must lead be cooled in a magnetic field of 15,000 A/m for it to be superconductive?

Solution

(a) Given Equation 20.14 and the data in Table 20.7, we are asked to calculate the critical magnetic fields for lead at 2.5 and 5.0 K. From the table, for Pb, T_C = 7.19 K and $B_C(0)$ = 0.0803 tesla. Thus, from a rearranged form of Equation 20.2 we write the following:

$$H_C(0) = \frac{B_C(0)}{\mu_0}$$

$$= \frac{0.0803 \text{ tesla}}{1.257 \times 10^{-6} \text{ H/m}} = 6.39 \times 10^4 \text{ A/m}$$

Now, solving for $H_C(2.5)$ and $H_C(5.0)$ using Equation 20.14 yields

$$H_C(T) = H_C(0)\left[1 - \frac{T^2}{T_C^2}\right]$$

$$H_C(2.5) = \left(6.39 \times 10^4 \text{ A/m}\right)\left[1 - \frac{(2.5 \text{ K})^2}{(7.19 \text{ K})^2}\right] = 5.62 \times 10^4 \text{ A/m}$$

$$H_C(5.0) = \left(6.39 \times 10^4 \text{ A/m}\right)\left[1 - \frac{(5.0 \text{ K})^2}{(7.19 \text{ K})^2}\right] = 3.30 \times 10^4 \text{ A/m}$$

(b) Now we are to determine the temperature to which lead must be cooled in a magnetic field of 15,000 A/m in order for it to be superconductive. All we need do is to solve for *T* from Equation 20.14—i.e.,

$$T = T_C \sqrt{1 - \frac{H_C(T)}{H_C(0)}}$$

And, since the value of $H_C(0)$ was computed in part (a), then

$$T = (7.19\ \text{K})\sqrt{1 - \frac{15{,}000\ \text{A/m}}{63{,}900\ \text{A/m}}} = 6.29\ \text{K}$$

20.29 *Using Equation 20.14, determine which of the superconducting elements in Table 20.7 are superconducting at 2 K and a magnetic field of 40,000 A/m.*

Solution

We are asked to determine which of the superconducting elements in Table 20.7 are superconducting at 2 K and in a magnetic field of 40,000 A/m. First of all, in order to be superconductive at 2 K within any magnetic field, the critical temperature must be greater than 2 K. Thus, aluminum, titanium, and tungsten may be eliminated upon inspection. Now, for each of lead, mercury, and tin it is necessary, using Equation 20.14, to compute the value of $H_C(2)$—also substituting for $H_C(0)$ from Equation 20.3; if $H_C(2)$ is greater than 40,000 A/m then the element will be superconductive. Hence, for Pb

$$H_C(2) = H_C(0)\left[1 - \frac{T^2}{T_C^2}\right]$$

$$= \frac{B_C(0)}{\mu_0}\left[1 - \frac{T^2}{T_C^2}\right]$$

$$= \frac{0.0803 \text{ tesla}}{1.257 \times 10^{-6} \text{ H/m}}\left[1 - \frac{(2.0 \text{ K})^2}{(7.19 \text{ K})^2}\right] = 5.89 \times 10^4 \text{ A/m}$$

Since this value is greater than 40,000 A/m, Pb *will be superconductive*.

Similarly for Hg

$$H_C(2) = \frac{0.0411 \text{ tesla}}{1.257 \times 10^{-6} \text{ H/m}}\left[1 - \frac{(2.0 \text{ K})^2}{(4.15 \text{ K})^2}\right] = 2.51 \times 10^4 \text{ A/m}$$

Inasmuch as this value is less than 40,000 A/m, Hg *will not be superconductive*.

As for Sn

$$H_C(2) = \frac{0.0305 \text{ tesla}}{1.257 \times 10^{-6} \text{ H/m}}\left[1 - \frac{(2.0 \text{ K})^2}{(3.72 \text{ K})^2}\right] = 1.73 \times 10^3 \text{ A/m}$$

Therefore, Sn is *not superconductive*.

20.30 *Cite the differences between type I and type II superconductors.*

Answer

For type I superconductors, with increasing magnetic field the material is completely diamagnetic and superconductive below H_C, while at H_C conduction becomes normal and complete magnetic flux penetration takes place. On the other hand, for type II superconductors upon increasing the magnitude of the magnetic field, the transition from the superconducting to normal conducting states is gradual between lower-critical and upper-critical fields; so also is magnetic flux penetration gradual. Furthermore, type II superconductors generally have higher critical temperatures and critical magnetic fields.

20.31 *Briefly describe the Meissner effect.*

Answer

The Meissner effect is a phenomenon found in superconductors wherein, in the superconducting state, the material is diamagnetic and completely excludes any external magnetic field from its interior. In the normal conducting state complete magnetic flux penetration of the material occurs.

20.32 *Cite the primary limitation of the new superconducting materials that have relatively high critical temperatures.*

Answer

The primary limitation of the new superconducting materials that have relatively high critical temperatures is that, being ceramics, they are inherently brittle and difficult to form into useful shapes.

DESIGN PROBLEMS

Ferromagnetism

20.D1 *A cobalt–iron alloy is desired that has a saturation magnetization of 1.47 × 10^6 A/m. Specify its composition in weight percent iron. Cobalt has an HCP crystal structure with c/a ratio of 1.623. Assume that the unit cell volume for this alloy is the same as for pure Co.*

Solution

For this problem we are asked to determine the composition of a Co-Fe alloy that will yield a saturation magnetization of 1.47 × 10^6 A/m. To begin, let us compute the number of Bohr magnetons per unit cell n_B for this alloy from an expression that results from combining Equations 20.11 and 20.12. That is

$$n_\mathrm{B} = \frac{M_s V_C}{\mu_B} \qquad \text{(S20.D1a)}$$

in which M_s is the saturation magnetization, V_C is the unit cell volume, and μ_B is the magnitude of the Bohr magneton. For HCP, an expression for unit cell volume in terms of the a and c lattice parameters is given in Equation 3.7a as follows:

$$V_C = \frac{3a^2 c}{2}\sqrt{3}$$

Furthermore, for HCP, the unit cell edge length, a, and the atomic radius, R are related as $a = 2R$; also, as stipulated in the problem statement, $c = 1.623a$. Making these substitutions into the above equation leads to the following:

$$V_C = \frac{(3)(1.623)(2R)^3}{2}\sqrt{3}$$

From the inside of the front cover of the book, the value of R for Co is given as 0.125 nm (1.25 × 10^{-10} m). Therefore,

$$V_C = \frac{(3)(1.623)\left[(2)(1.25 \times 10^{-10}\ \mathrm{m})\right]^3(\sqrt{3})}{2}$$

$$= 6.59 \times 10^{-29}\ \mathrm{m}^3$$

And, now solving for n_B from Equation S20.D1a above yields the following:

$$n_\mathrm{B} = \frac{M_s V_C}{\mu_B}$$

$$= \frac{(1.47 \times 10^6 \text{ A/m})(6.59 \times 10^{-29} \text{ m}^3\text{/unit cell})}{\dfrac{9.27 \times 10^{-24} \text{ A-m}^2}{\text{Bohr magneton}}}$$

$$= \frac{10.45 \text{ Bohr magneton}}{\text{unit cell}}$$

Inasmuch as there are 1.72 and 2.22 Bohr magnetons for each of Co and Fe (Section 20.4), and, for HCP, there are 6 equivalent atoms per unit cell (Section 3.4), if we represent the fraction of Fe atoms by *x*, then we may write the following:

$$n_B = 10.45 \text{ Bohr magnetons/unit cell}$$

$$= \left(\frac{2.22 \text{ Bohr magnetons}}{\text{Fe atom}}\right)\left(\frac{6x \text{ Fe atoms}}{\text{unit cell}}\right) + \left(\frac{1.72 \text{ Bohr magnetons}}{\text{Co atom}}\right)\left[\frac{(6)(1 - x) \text{ Co atoms}}{\text{unit cell}}\right]$$

And solving for *x*, the fraction of Fe atoms, *x* = 0.0433, of 4.33 at% Fe.

In order to convert this composition to weight percent, we employ Equation 4.7 as follows:

$$C_{\text{Fe}} = \frac{C'_{\text{Fe}} A_{\text{Fe}}}{C'_{\text{Fe}} A_{\text{Fe}} + C'_{\text{Co}} A_{\text{Co}}} \times 100$$

In the above discussion it was determined that $C'_{\text{Fe}} = 4.33 \text{ at\%}$. It also follows that

$$C'_{\text{Co}} = 100 \text{ at\%} - C'_{\text{Fe}}$$

$$= 100 \text{ at\%} - 4.33 \text{ at\%} = 95.67 \text{ at\%}$$

Therefore the composition of iron, in weight percent (C_{Fe}) needed is computed as follows:

$$C_{\text{Fe}} = \frac{C'_{\text{Fe}} A_{\text{Fe}}}{C'_{\text{Fe}} A_{\text{Fe}} + C'_{\text{Co}} A_{\text{Co}}} \times 100$$

$$= \frac{(4.33 \text{ at\%})(55.85 \text{ g/mol})}{(4.33 \text{ at\%})(55.85 \text{ g/mol}) + (95.67 \text{ at\%})(58.93 \text{ g/mol})} \times 100$$

$$= 4.11 \text{ wt\%}$$

Ferrimagnetism

20.D2 *Design a cubic mixed-ferrite magnetic material that has a saturation magnetization of 4.25 × 10^5 A/m.*

Solution

This problem asks that we design a cubic mixed-ferrite magnetic material that has a saturation magnetization of 4.25 × 10^5 A/m. From Example Problem 20.2 the saturation magnetization for Fe_3O_4 is 5.0 × 10^5 A/m. In order to decrease the magnitude of M_s it is necessary to replace some fraction of the Fe^{2+} with another divalent metal ion that has a smaller magnetic moment. From Table 20.4 it may be noted that Co^{2+}, Ni^{2+}, and Cu^{2+}, with 3, 2, and 1 Bohr magnetons per ion, respectively, have fewer than the 4 Bohr magnetons/Fe^{2+} ion. Let us first consider Ni^{2+} (with 2 Bohr magnetons per ion) and employ Equation 20.13 to compute the number of Bohr magnetons per unit cell (n_B), assuming that the Ni^{2+} addition does not change the unit cell edge length (0.839 nm, Example Problem 20.2). Thus, solving for n_B in Equation 20.13 results in the following:

$$n_B = \frac{M_s a^3}{\mu_B}$$

$$= \frac{(4.25 \times 10^5 \text{ A/m})(0.839 \times 10^{-9} \text{ m})^3/\text{unit cell}}{9.27 \times 10^{-24} \text{ A-m}^2/\text{Bohr magneton}}$$

= 27.08 Bohr magnetons/unit cell

If we let x represent the fraction of Ni^{2+} that have substituted for Fe^{2+}, then the remaining unsubstituted Fe^{2+} fraction is equal to 1 – x. Furthermore, inasmuch as there are 8 divalent ions per unit cell, and

4 Bohr magnetons/Fe^{2+} ion
2 Bohr magnetons/Ni^{2+} ion

we may write the following expression:

$$n_B = 8\left[2x + 4(1 - x)\right] = 27.08$$

which leads to x = 0.308. Thus, if 30.8 at% of the Fe^{2+} in Fe_3O_4 are replaced with Ni^{2+}, the saturation magnetization will be decreased to 4.25 × 10^5 A/m.

Upon going through this same procedure for Co and Cu, we find that x_{Co} = 0.615 (or 61.5 at%) and x_{Cu} = 0.205 (20.5 at%) will yield the 4.25 × 10^5 A/m saturation magnetization.

FUNDAMENTALS OF ENGINEERING QUESTIONS AND PROBLEMS

20.1FE *The magnetization within a bar of some metal alloy is* 4.6×10^5 *A/m at an H field of 52 A/m. What is this alloy's magnetic susceptibility?*

(A) 1.13×10^{-4}

(B) 8.85×10^3

(C) 1.11×10^{-2} *H/m*

(D) 5.78×10^{-1} *tesla*

Solution

From Equation 20.6 the magnetization may be computed as follows:

$$M = \chi_m H$$

Or, upon rearrangement of this expression, the magnetic susceptibility, χ_m, is equal to

$$\chi_m = \frac{M}{H}$$

Whereas for this problem

$M = 4.6 \times 10^5$ A/m

$H = 52$ A/m

which lead to the following value for the susceptibility:

$$\chi_m = \frac{4.6 \times 10^5 \text{ A/m}}{52 \text{ A/m}} = 8.85 \times 10^3$$

which is answer B.

20.2FE *Which of the following pairs of materials displays ferromagnetic behavior?*

(A) Aluminum oxide and copper

(B) Aluminum and titanium

(C) MnO and Fe_3O_4

(D) Iron (α-ferrite) and nickel

Answer

The correct answer is D**.** Of the given pairs of materials only *iron* (*α-ferrite*) and *nickel* are ferromagnetic.

CHAPTER 21

OPTICAL PROPERTIES

PROBLEM SOLUTIONS

Electromagnetic Radiation

21.1 *Visible light having a wavelength of 5 × 10^{-7} m appears green. Compute the frequency and energy of a photon of this light.*

Solution

In order to compute the frequency ν of a photon of green light, we use a rearranged form of Equation 21.2 as follows:

$$\nu = \frac{c}{\lambda}$$

$$= \frac{3 \times 10^8 \text{ m/s}}{5 \times 10^{-7} \text{ m}}$$

$$= 6 \times 10^{14} \text{ s}^{-1}$$

Now, for the energy computation, we employ Equation 21.3 as follows:

$$E = \frac{hc}{\lambda}$$

$$= \frac{(6.63 \times 10^{-34} \text{ J-s})(3 \times 10^8 \text{ m/s})}{5 \times 10^{-7} \text{ m}}$$

$$= 3.98 \times 10^{-19} \text{ J} \quad (2.48 \text{ eV})$$

Light Interactions with Solids

21.2 *Distinguish among materials that are opaque, translucent, and transparent in terms of their appearance and light transmittance.*

Answer

Opaque materials are impervious to light transmission; it is not possible to see through them.

Light is transmitted diffusely through translucent materials (there is some internal light scattering). Objects are not clearly distinguishable when viewed through a translucent material.

Virtually all of the incident light is transmitted through transparent materials, and one can see clearly through them.

Atomic and Electronic Interactions

21.3 *(a) Briefly describe the phenomenon of electronic polarization by electromagnetic radiation.*

(b) What are two consequences of electronic polarization in transparent materials?

Answer

(a) The phenomenon of electronic polarization by electromagnetic radiation is described in Section 21.4.

(b) Two consequences of electronic polarization in transparent materials are *absorption* and *refraction*.

Optical Properties of Metals

21.4 *Briefly explain why metals are opaque to electromagnetic radiation having photon energies within the visible region of the spectrum.*

Answer

The electron band structures of metals are such that empty and available electron states are adjacent to filled states. Electron excitations from filled to empty states are possible with the absorption of electromagnetic radiation having frequencies within the visible spectrum, according to Equation 21.6. The light energy is totally absorbed or reflected, and, since none is transmitted, the material is opaque.

Refraction

21.5 *In ionic materials, how does the size of the component ions affect the extent of electronic polarization?*

Answer

In ionic materials the larger the size of the component ions the greater the degree of electronic polarization.

21.6 *Can a material have a positive index of refraction less than unity? Why or why not?*

Answer

In order for a material to have an index of refraction less than unity, the velocity of light in the material (*v*) would necessarily have to be greater than the velocity of light in a vacuum (Equation 21.7). This is not possible.

21.7 *Compute the velocity of light in diamond, which has a dielectric constant* ε_r *of 5.5 (at frequencies within the visible range) and a magnetic susceptibility of* -2.17×10^{-5}.

Solution

We want to compute the velocity of light in diamond given that $\varepsilon_r = 5.5$ and $\chi_m = -2.17 \times 10^{-5}$. The velocity is determined using Equation 21.8; but first, we must calculate the values of ε and μ for diamond. According to Equation 18.27

$$\varepsilon = \varepsilon_r \varepsilon_0 = (5.5)(8.85 \times 10^{-12}\ \text{F/m}) = 4.87 \times 10^{-11}\ \text{F/m}$$

Now, combining Equations 20.4 and 20.7 leads to the following:

$$\mu = \mu_0 \mu_r = \mu_0 (\chi_m + 1)$$

$$= (1.257 \times 10^{-6}\ \text{H/m})[1 + (-2.17 \times 10^{-5})] = 1.257 \times 10^{-6}\ \text{H/m}$$

And, finally, from Equation 21.8 the velocity of light is computed as follows:

$$v = \frac{1}{\sqrt{\varepsilon \mu}}$$

$$= \frac{1}{\sqrt{(4.87 \times 10^{-11}\ \text{F/m})(1.257 \times 10^{-6}\ \text{H/m})}}$$

$$= 1.28 \times 10^{8}\ \text{m/s}$$

21.8 *The indices of refraction of fused silica and polystyrene within the visible spectrum are 1.458 and 1.60, respectively. For each of these materials determine the fraction of the relative dielectric constant at 60 Hz that is due to electronic polarization, using the data of Table 18.5. Neglect any orientation polarization effects.*

Solution

The frequencies of visible radiation are on the order of 10^{15} Hz (Figure 21.2). At these frequencies only electronic polarization is operable (Figure 18.34). Thus, ε_r from Equation 21.10 is the electronic contribution to ε_r; let us designate it as ε_r'. In other words

$$\varepsilon_r' = n^2$$

For fused silica, ε_r' is equal to

$$\varepsilon_r'(\text{silica}) = (1.458)^2 = 2.13$$

And, for polystyrene (PS)

$$\varepsilon_r'(\text{PS}) = (1.60)^2 = 2.56$$

The fraction of the electronic contribution is just the ratio of ε_r' and ε_r, where ε_r values are taken from Table 18.5 (4.0 and 2.6 for fused silica and polystyrene, respectively, at a frequency of 60 Hz). Thus, for fused silica

$$\frac{\varepsilon_r'(\text{silica})}{\varepsilon_r(60\text{ Hz})} = \frac{2.13}{4.0} = 0.53$$

and for polystyrene we have

$$\frac{\varepsilon_r'(\text{PS})}{\varepsilon_r(60\text{ Hz})} = \frac{2.56}{2.60} = 0.98$$

21.9 *Using the data in Table 21.1, estimate the dielectric constants for silica glass (fused silica), soda–lime glass, polytetrafluoroethylene, polyethylene, and polystyrene, and compare these values with those cited in the following table. Briefly explain any discrepancies.*

Material	***Dielectric Constant (1 MHz)***
Silica glass	*3.8*
Soda-lime glass	*6.9*
Polytetrafluoroethylene	*2.1*
Polyethylene	*2.3*
Polystyrene	*2.6*

Solution

This problem asks for us, using data in Table 21.1, to estimate the dielectric constants for silica glass, soda-lime glass, PTFE, polyethylene, and polystyrene, and then to compare these values with those cited in table provided, and briefly explain any discrepancies. From Equation 21.10

$$\varepsilon_r = n^2$$

Thus, for fused silica, since n = 1.458, and therefore

$$\varepsilon_r = (1.458)^2 = 2.13$$

Similarly, for soda-lime glass

$$\varepsilon_r = (1.51)^2 = 2.28$$

And, for PTFE

$$\varepsilon_r = (1.35)^2 = 1.82$$

For polyethylene

$$\varepsilon_r = (1.51)^2 = 2.28$$

For polystyrene

$$\varepsilon_r = (1.60)^2 = 2.56$$

When we compare the values of ε_r for polymers determined in this problem, with those in those provided in the problem statement, at frequencies of 1 MHz, there is reasonable agreement (i.e., 1.82 versus 2.1 for PTFE, 2.28 versus 2.3 for polyethylene, and 2.56 versus 2.6 for polystyrene). However, for fused silica and soda-lime glass there are some significant discrepancies (i.e., 2.13 versus 3.8 for the fused silica, and 2.28 versus 6.9 for the soda-lime glass). The reason for these discrepancies is that for these two materials an ionic component to the dielectric constant is present at 1 MHz, but is absent at frequencies within the visible electromagnetic spectrum, which frequencies are on the order 10^9 MHz (10^{15} Hz). These effects may be noted in Figure 18.34.

21.10 *Briefly describe the phenomenon of dispersion in a transparent medium.*

Answer

Dispersion in a transparent medium is the phenomenon wherein the index of refraction varies slightly with the wavelength of the electromagnetic radiation, as noted in the left-margin photograph found of page 845.

Reflection

21.11 *It is desired that the reflectivity of light at normal incidence to the surface of a transparent medium be less than 5.0%. Which of the following materials in Table 21.1 are likely candidates: soda–lime glass, Pyrex glass, periclase, spinel, polystyrene, and polypropylene? Justify your selections.*

Solution

For this problem we want to compute the maximum value of n_s in Equation 21.13 that will give $R = 0.050$. Then we are to consult Table 21.1 in order to ascertain which of the materials listed have indices of refraction less than this maximum value. From Equation 21.13, using $R = 0.050$ we have the following:

$$0.050 = \frac{(n_s - 1)^2}{(n_s + 1)^2}$$

$$= \frac{n_s^2 - 2\,n_s + 1}{n_s^2 + 2\,n_s + 1}$$

Upon rearrangement, this expression may be written

$$0.95\,n_s^2 \;-\; 2.10\,n_s + 0.95 = 0$$

The value of n_s is determined by using the quadratic equation solution as follows:

$$n_s = \frac{-(-2.10) \pm \sqrt{(-2.10)^2 - (4)(0.95)(0.95)}}{(2)(0.95)}$$

$$= \frac{2.10 \pm 0.894}{1.90}$$

The two solutions are: $n_s(+) = 1.576$ and $n_s(-) = 0.634$. The $n_s(+)$ solution is the one that is physically reasonable. Thus, of the materials listed, soda-lime glass, Pyrex glass, and polypropylene have indices of refraction less than 1.576, and would be suitable for this application.

21.12 *Briefly explain how reflection losses of transparent materials are minimized by thin surface coatings.*

Answer

The thickness and dielectric constant of a thin surface coating are selected such that there is destructive interference (see Figure 3.21*b*) between the light beam that is reflected from the lens-coating interface and the light beam that is reflected from the coating-air interface; thus, the net intensity of the total reflected beam is very low.

21.13 *The index of refraction of quartz is anisotropic. Suppose that visible light is passing from one grain to another of different crystallographic orientation and at normal incidence to the grain boundary. Calculate the reflectivity at the boundary if the indices of refraction for the two grains are 1.544 and 1.553 in the direction of light propagation.*

Solution

This problem calls for a calculation of the reflectivity between two quartz grains having different orientations and indices of refraction (1.544 and 1.553) in the direction of light propagation, when the light is at normal incidence to the grain boundary. We must employ Equation 21.12 since the beam is normal to the grain boundary. Thus,

$$R = \frac{(n_2 - n_1)^2}{(n_2 + n_1)^2}$$

$$= \frac{(1.553 - 1.544)^2}{(1.553 + 1.544)^2}$$

$$= 8.45 \times 10^{-6}$$

Absorption

21.14 *Zinc selenide has a band gap of 2.58 eV. Over what range of wavelengths of visible light is it transparent?*

Solution

This problem asks us to determine the range of visible light wavelengths over which ZnSe (E_g = 2.58 eV) is transparent. Only photons having energies of 2.58 eV or greater are absorbed by valence-band-to-conduction-band electron transitions. Thus, photons having energies less than 2.58 eV are not absorbed; the minimum photon energy for visible light is 1.8 eV (Equation 21.16b), which corresponds to a wavelength of 0.7 μm. From Equation 21.3, the wavelength of a photon having an energy of 2.58 eV (i.e., the band-gap energy) is just

$$\lambda = \frac{hc}{E}$$

$$= \frac{(4.13 \times 10^{-15} \text{ eV-s})(3 \times 10^{8} \text{ m/s})}{2.58 \text{ eV}}$$

$$= 4.80 \times 10^{-7} \text{ m} = 0.48 \ \mu\text{m}$$

Thus, pure ZnSe is transparent to visible light having wavelengths between 0.48 and 0.7 μm.

21.15 *Briefly explain why the magnitude of the absorption coefficient (β in Equation 21.18) depends on the radiation wavelength.*

Answer

The magnitude of the absorption coefficient (β in Equation 21.18) depends on the radiation wavelength for intrinsic insulators and semiconducting materials. This is because, for photons having energies less than the band-gap energy (or in terms of wavelength, when $\lambda > \frac{hc}{E_g}$), photon absorption due to valence-band-to-conduction-band electron transitions are not possible, and, therefore, the value of β will be relatively small. On the other hand, when photons having energies equal to or greater than the band gap energy (i.e., when $\lambda \le \frac{hc}{E_g}$) these electron transitions by the absorption of photons will occur with the result that the magnitude of β will be relatively large.

In addition, there may be impurity levels that lie within the band gap (Section 21.7) from or to which electron excitations may occur with the absorption of light radiation at specific wavelengths.

21.16 *The fraction of nonreflected radiation that is transmitted through a 5-mm thickness of a transparent material is 0.95. If the thickness is increased to 12 mm, what fraction of light will be transmitted?*

Solution

In this problem we are asked to calculate the fraction of nonreflected light transmitted through a 12-mm thickness of transparent material, given that the fraction transmitted through a 5-mm thickness is 0.95. From Equation 21.18, the fraction of nonreflected light transmitted is just $\frac{I'_T}{I'_0}$. Thus, we may rewrite Equation 21.18 as follows:

$$\frac{I'_T}{I'_0} = e^{-\beta x} \tag{21.18a}$$

Using this expression and the first set of data in the problem statement, we must first determine the value of β. This is possible by algebraic manipulation of Equation 21.18a. Taking natural logarithms of both sides of Equation 21.18a leads to the following expression:

$$\ln\left(\frac{I'_T}{I'_0}\right) = -\beta x$$

Now solving for β in this expression gives the following:

$$\beta = -\frac{1}{x}\ln\left(\frac{I'_T}{I'_0}\right)$$

The value of β is determined by using the following data given in the problem statement:

x = 5 mm

$\frac{I'_T}{I'_0} = 0.95$

as follows:

$$\beta = -\frac{1}{x}\ln\left(\frac{I'_T}{I'_0}\right)$$

$$= -\left(\frac{1}{5\text{ mm}}\right)\ln(0.95)$$

$$= 1.026 \times 10^{-2}\text{ mm}^{-1}$$

We now compute $\frac{I'_T}{I'_0}$ when x = 12 mm using Equation 21.18a as follows:

$$\frac{I'_T}{I'_0} = \exp\,(-\beta x)$$

$$= \exp\left[-(1.026 \times 10^{-2}\ \text{mm}^{-1})(12\ \text{mm})\right]$$

$$= 0.884$$

Transmission

21.17 *Derive Equation 21.19, starting from other expressions given in this chapter.*

Solution

The problem asks that we derive Equation 21.19—that is

$$I_T = I_0(1 - R)^2 \, e^{-\beta l}$$

If we examine Figure 21.7, at the front (or left) interface, some of the incident beam having intensity I_0 is reflected. Since $I_R = I_0R$ at this surface, then

$$I'_T = I_0 - I_0R = I_0(1 - R)$$

in which I'_T is the intensity of the nonreflected beam at the front surface that is transmitted.

Now there will be absorption of this transmitted beam as it passes through the solid and transparent medium, according to Equation 21.18. Just inside the back (or right) interface, the beam has passed through a thickness l of this material ($x = l$) and, therefore, the intensity of the transmitted beam at this point (I''_T) is just

$$I''_T = I'_T e^{-\beta l}$$

$$= I_0(1 - R)e^{-\beta l}$$

Finally, a second reflection will occur at the back interface as the beam passes out of the medium (on the right-hand side of the solid piece of Figure 21.7). The intensity of the reflected beam at this interface (I''_R) is described by the following expression:

$$I''_R = I''_T R$$

and substitution into this expression the equation for I''_T from above, leads to

$$I''_R = I''_T R$$

$$= I_0R(1 - R)e^{-\beta l}$$

And the intensity of the final transmitted beam (I_T) becomes

$$I_T = I''_T - I''_R$$

$$= I_0(1 - R)e^{-\beta l} - I_0R(1 - R)e^{-\beta l}$$

$$= I_0(1 - R)^2 e^{-\beta l}$$

which is Equation 21.19, the desired expression.

21.18 *The transmissivity T of a transparent material 15 mm thick to normally incident light is 0.80. If the index of refraction of this material is 1.5, compute the thickness of material that will yield a transmissivity of 0.70. All reflection losses should be considered.*

Solution

We are asked to compute the thickness of material to yield a transmissivity of 0.70 given that T is 0.80 when l = 15 mm, n = 1.5, and for normally incident radiation. The first requirement is that we calculate the value of β for this material using Equations 21.13 and 21.19. The value of R is determined using Equation 21.13 as follows:

$$R = \frac{(n_s - 1)^2}{(n_s + 1)^2}$$

$$= \frac{(1.5 - 1)^2}{(1.5 + 1)^2} = 4.0 \times 10^{-2}$$

Now, it is necessary to compute the value of β using Equation 21.19. Dividing both sides of Equation 21.19 by $I_0(1 - R)^2$ leads to the following:

$$\frac{I_T}{I_0(1 - R)^2} = e^{-\beta l}$$

Now, taking the natural logarithms of both sides of this expression gives

$$\ln\left[\frac{I_T}{I_0(1 - R)^2}\right] = -\beta l$$

and solving for β we get

$$\beta = -\frac{1}{l}\ln\left[\frac{I_T}{I_0(1 - R)^2}\right]$$

Since the transmissivity T is equal to I_T/I_0, the above equation takes the form

$$\beta = -\frac{1}{l}\ln\left[\frac{T}{(1 - R)^2}\right] \qquad \text{(S21.18)}$$

Using values for l and T provided in the problem statement, as well as the value of R determined above—i.e.,

$l = 15$ mm

$T = 0.80$

$R = 4.0 \times 10^{-2}$

we solve for β as follows:

$$\beta = -\frac{1}{l} \ln \left[\frac{T}{(1-R)^2} \right]$$

$$= -\left(\frac{1}{15 \text{ mm}}\right) \ln \left[\frac{0.80}{(1 - 4.0 \times 10^{-2})^2} \right] = 9.43 \times 10^{-3} \text{ mm}^{-1}$$

Now, solving for l when $T = 0.70$ using the rearranged form of Equation S21.18 given above leads to

$$l = -\frac{1}{\beta} \ln \left[\frac{T}{(1-R)^2} \right]$$

$$= -\frac{1}{9.43 \times 10^{-3} \text{ mm}^{-1}} \ln \left[\frac{0.70}{(1 - 4.0 \times 10^{-2})^2} \right]$$

$$= 29.2 \text{ mm}$$

Color

21.19 *Briefly explain what determines the characteristic color of (a) a metal and (b) a transparent nonmetal.*

Answer

(a) The characteristic color of a metal is determined by the distribution of wavelengths of nonabsorbed light radiation that is reflected.

(b) The characteristic color of a transparent nonmetal is determined by the distribution of wavelengths of the nonabsorbed light radiation that is transmitted through the material.

21.20 *Briefly explain why some transparent materials appear colored whereas others are colorless.*

Answer

For a transparent material that appears colorless, any absorption within its interior is the same for all visible wavelengths. On the other hand, if there is any selective absorption of visible light (usually by electron excitations), the material will appear colored, its color being dependent on the frequency distribution of the transmitted light beam.

Opacity and Translucency in Insulators

21.21 *Briefly describe the three absorption mechanisms in nonmetallic materials.*

Answer

The three absorption mechanisms in nonmetallic materials involve electronic polarization, electron transitions, and scattering. Electronic polarization is described in Section 21.4; absorption by electron transitions is discussed in Sections 21.4 and 21.7; and scattering is discussed in Section 21.10.

21.22 *Briefly explain why amorphous polymers are transparent, whereas predominantly crystalline polymers appear opaque or, at best, translucent.*

Answer

Amorphous polymers are normally transparent because there is no scattering of a light beam within the material. However, for semicrystalline polymers, visible light will be scattered at boundaries between amorphous and crystalline regions since they have different indices of refraction. This leads to translucency or, for extensive scattering, opacity, except for semicrystalline polymers having very small crystallites.

Luminescence

Photoconductivity

Lasers

21.23 *(a) In your own words, briefly describe the phenomenon of luminescence.*
(b) What is the distinction between fluorescence and phosphorescence?

<u>Answer</u>

(a) The phenomenon of luminescence is described in Section 21.11.

(b) The feature that distinguishes fluorescence from phosphorescence is the magnitude of the time interval between photon absorption and reemission events. Fluorescence is for delay times less than a second; phosphorescence occurs for longer times.

21.24 *In your own words, briefly describe the phenomenon of photoconductivity.*

The phenomenon of photoconductivity is explained in Section 21.12.

21.25 *Briefly explain the operation of a photographic lightmeter.*

Answer

A photographic light meter is used to measure the intensity of incident light radiation. Each photon of incident light induces a valence-band-to-conduction band electron transition in which both electrons and holes are produced, as depicted in Figure 21.5*a*. The magnitude of the photo-induced current resulting from these transitions is registered, which is proportional to the numbers of electrons and holes, and thus, the number of incident photons, or, equivalently, the intensity of the incident light radiation.

21.26 *In your own words, describe how a ruby laser operates.*

Section 21.13 contains a description of the operation of a ruby laser.

21.27 *Compute the difference in energy between metastable and ground electron states for the ruby laser.*

Solution

This problem asks for the difference in energy between metastable and ground electron states for a ruby laser. The wavelength of the radiation emitted by an electron transition from the metastable to ground state is cited as 0.6943 μm. The difference in energy between these states, Δ*E*, may be determined from a combined form of Equations 21.6 and 21.2, as follows:

$$\Delta E = h\nu = \frac{hc}{\lambda}$$

$$= \frac{(4.13 \times 10^{-15} \text{ eV-s})(3 \times 10^{8} \text{ m/s})}{6.943 \times 10^{-7} \text{ m}}$$

$$= 1.78 \text{ eV}$$

Optical Fibers in Communications

21.28 *At the end of Section 21.14 it was noted that the intensity of light absorbed while passing through a 16-km length of optical fiber glass is equivalent to the light intensity absorbed through a 25-mm thickness of ordinary window glass. Calculate the absorption coefficient β of the optical fiber glass if the value of β for the window glass is* 10^{-4} *mm*$^{-1}$.

<u>Solution</u>

This problem asks for us to determine the value of the absorption coefficient for optical fiber glass given that β for window glass is 10^{-4} mm^{-1}; also, the intensity of nonabsorbed light transmitted through a 25-mm thickness of window glass is equivalent to the nonabsorbed light transmitted through a 16-km length of the optical fiber material. Using Equation 21.18, it is first necessary to compute the fraction of light transmitted through the window glass—that is, $\frac{I'_T}{I'_0}$, or

$$\frac{I'_T}{I'_0} = e^{-\beta x} \tag{21.18a}$$

$$= e^{-(10^{-4}\ \text{mm}^{-1})(25\ \text{mm})} = 0.9975$$

In order to solve for the value of β for the optical fiber glass, it is necessary to make β the dependent variable of Equation 21.18. It is first necessary to take natural logarithms of both sides of Equation 21.18a above (which is a rearranged form of Equation 21.18) as follows:

$$\ln\left(\frac{I'_T}{I'_0}\right) = -\beta x$$

Now, solving for β from this expression leads to

$$\beta = -\frac{1}{x}\ln\left(\frac{I'_T}{I'_0}\right)$$

Into this equation we substitute the value of $\frac{I'_T}{I'_0}$ determined above for window glass (0.9975), and take the value of x, 16 km, which we convert to millimeters (i.e, 16 km = 16 × 10^3 m = 16 × 10^6 mm). Thus, the value of β for the optical fiber glass is equal to

$$\beta = -\frac{1}{x}\ln\left(\frac{I'_T}{I'_0}\right)$$

$$= -\frac{1}{16 \times 10^{6}\,\mathrm{mm}} \ln(0.9975) = 1.56 \times 10^{-10}\,\mathrm{mm}^{-1}$$

DESIGN PROBLEM

Atomic and Electronic Interactions

21.D1 *Gallium arsenide (GaAs) and gallium phosphide (GaP) are compound semiconductors that have room-temperature band gap energies of 1.42 and 2.26 eV, respectively, and form solid solutions in all proportions. The band gap of the alloy increases approximately linearly with GaP additions (in mol%). Alloys of these two materials are used for light-emitting diodes (LEDs), in which light is generated by conduction band-to-valence band electron transitions. Determine the composition of a GaAs–GaP alloy that will emit red light having a wavelength of 0.68 μm.*

Solution

We are asked to determine the composition of a GaAs-GaP alloy that will emit red light having a wavelength of 0.68 μm. It first becomes necessary to compute the band-gap energy corresponding to this wavelength of light using Equation 21.3 as follows:

$$E_g = \frac{hc}{\lambda}$$

$$= \frac{(4.13 \times 10^{-15}\ \text{eV-s})(3 \times 10^{8}\ \text{m/s})}{0.68 \times 10^{-6}\ \text{m}} = 1.82\ \text{eV}$$

Realizing that at 0 mol% GaP, E_g = 1.42 eV, while at 100 mol% GaP, E_g = 2.26 eV, it is possible to set up the following composition-band gap energy relationship:

$$\frac{100\ \text{mol\%} - C_{\text{GaP}}}{100\ \text{mol\%} - 0\ \text{mol\%}} = \frac{2.26\ \text{eV} - 1.82\ \text{eV}}{2.26\ \text{eV} - 1.42\ \text{eV}}$$

Solving for C_{GaP}, the composition of GaP, leads to

$$C_{\text{GaP}} = 47.6\ \text{mol\%}.$$

FUNDAMENTALS OF ENGINEERING QUESTIONS AND PROBLEMS

21.1FE *What is the energy (in eV) of a photon of light having a wavelength of* 3.9×10^{-7} *m?*

(A) 1.61 eV *(C) 31.8 eV*

(B) 3.18 eV *(D) 9.44 eV*

Solution

The energy of a photon may be calculated using either the wavelength or the frequency using Equation 21.3 as follows:

$$E = h\nu = \frac{hc}{\lambda}$$

where *h*, Planck's constant, has a value of 4.13×10^{-15} eV-s. Using the value of the photon wavelength given in the problem statement, we calculate the photon energy as

$$E = \frac{hc}{\lambda}$$

$$= \frac{(4.13 \times 10^{-15}\ \text{eV-s})(3 \times 10^{8}\ \text{m/s})}{3.9 \times 10^{-7}\ \text{m}}$$

$$= 3.18\ \text{eV}$$

which is answer B.

21.2FE *A completely amorphous and nonporous polymer will be:*

(A) transparent	*(C) opaque*
(B) translucent	*(D) ferromagnetic*

Answer

The correct answer is A—that is, a completely amorphous and nonporous polymer will be *transparent*.