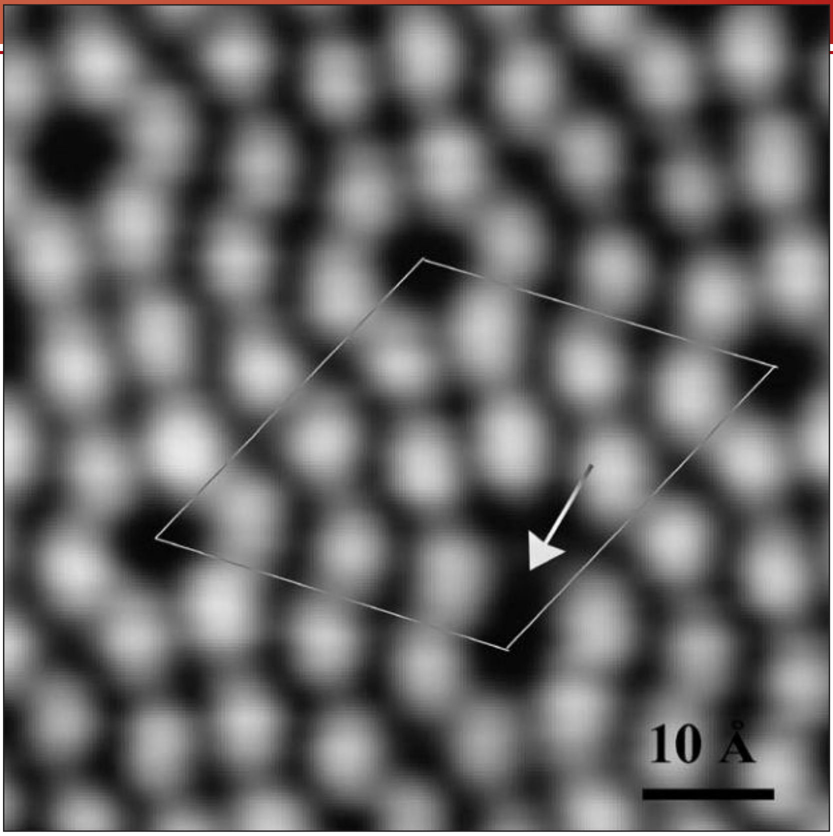
Chapter 5 Imperfections in Solids



A scanning probe micrograph (generated using a scanning-tunneling microscope) that shows a (111)-type surface plane[*] for silicon. The arrow points to the location of a silicon atom that was removed using a tungsten nanotip probe. This site from which an atom is missing is the surface analogue of a vacancy defect—that is, a vacant lattice site within the bulk material. Approximately 20,000,000×. (Micrograph courtesy of D. Huang, Stanford University.)

WHY STUDY *Imperfections in Solids?*

The properties of some materials are profoundly influenced by the presence of imperfections. Consequently, it is important to have knowledge about the types of imperfections that exist and the roles they play in affecting the behavior of materials. For example, the mechanical properties of pure metals experience significant alterations when alloyed (i.e., when impurity atoms are added)—for example, brass (70% copper–30% zinc) is much harder and stronger than pure copper (Section 8.10).

Also, integrated circuit microelectronic devices found in our computers, calculators, and home appliances function because of highly controlled concentrations of specific impurities that are incorporated into small, localized regions of semiconducting materials (Sections 12.11 and 12.15).

---

[*] The plane shown here is termed a "Si(111)-7 × 7 reconstructed surface." The two-dimensional arrangement of atoms in a surface plane is different from the atomic arrangement for the equivalent plane within the interior of the material (i.e., the surface plane has been "reconstructed" by atomic displacements). The "7 × 7" notation pertains to the displacement magnitude. Furthermore, the diamond shape that has been drawn indicates a unit cell for this 7 × 7 structure.

Learning Objectives

After careful study of this chapter you should be able to do the following:

1. Describe both vacancy and self-interstitial crystalline defects.
2. Calculate the equilibrium number of vacancies in a material at some specified temperature, given the relevant constants.
3. Name the two types of solid solutions and provide a brief written definition and/or schematic sketch of each.
4. Name and describe eight different ionic point defects that are found in ceramic materials.
5. Given the masses and atomic weights of two or more elements in a metal alloy, calculate the weight percent and atom percent for each element.
6. For each of edge, screw, and mixed dislocations:
   - (a) describe and make a drawing of the dislocation;
   - (b) note the location of the dislocation line; and
   - (c) indicate the direction along which the dislocation line extends.
7. Describe the atomic structure within the vicinity of (a) a grain boundary, and (b) a twin boundary.

5.1 INTRODUCTION

imperfection

Thus far it has been tacitly assumed that perfect order exists throughout crystalline materials on an atomic scale. However, such an idealized solid does not exist; all contain large numbers of various defects or **imperfections.** As a matter of fact, many of the properties of materials are profoundly sensitive to deviations from crystalline perfection; the influence is not always adverse, and often specific characteristics are deliberately fashioned by the introduction of controlled amounts or numbers of particular defects, as detailed in succeeding chapters.

point defect

By "crystalline defect" is meant a lattice irregularity having one or more of its dimensions on the order of an atomic diameter. Classification of crystalline imperfections is frequently made according to geometry or dimensionality of the defect. Several different imperfections are discussed in this chapter, including **point defects** (those associated with one or two atomic positions), linear (or one-dimensional) defects, as well as interfacial defects, or boundaries, which are two-dimensional. Impurities in solids are also discussed, since impurity atoms may exist as point defects. Finally, techniques for the microscopic examination of defects and the structure of materials are briefly described.

Point Defects

5.2 POINT DEFECTS IN METALS

vacancy

The simplest of the point defects is a **vacancy,** or vacant lattice site, one normally occupied from which an atom is missing (Figure 5.1). All crystalline solids contain vacancies and, in fact, it is not possible to create such a material that is free of these defects. The necessity of the existence of vacancies is explained using principles of thermodynamics; in essence, the presence of vacancies increases the entropy (i.e., the randomness) of the crystal.

The equilibrium number of vacancies N_v for a given quantity of material depends on and increases with temperature according to

Temperature-dependence of the equilibrium number of vacancies

$$N_v = N \exp\left(-\frac{Q_v}{kT}\right) \tag{5.1}$$

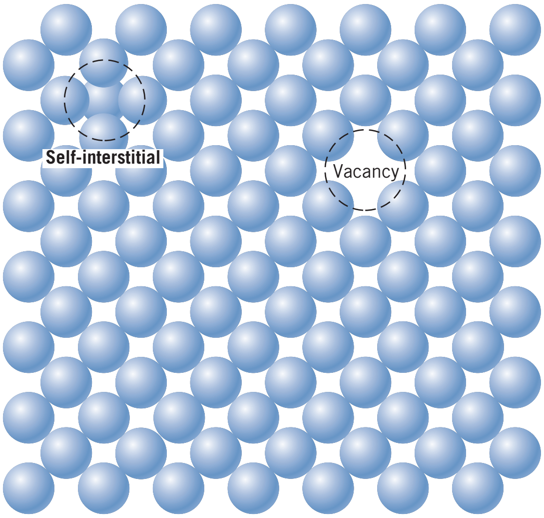


Figure 5.1 Two-dimensional representations of a vacancy and a self-interstitial. (Adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 77. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

Boltzmann's constant

In this expression, N is the total number of atomic sites, Q_v is the energy required for the formation of a vacancy, T is the absolute temperature[1] in kelvins, and k is the gas or **Boltzmann's constant.** The value of k is 1.38×10^{-23} J/atom-K, or 8.62×10^{-5} eV/atom-K, depending on the units of Q_v.[2] Thus, the number of vacancies increases exponentially with temperature; that is, as T in Equation 5.1 increases, so also does the expression $\exp -(Q_v/kT)$. For most metals, the fraction of vacancies N_v/N just below the melting temperature is on the order of 10^{-4}; that is, one lattice site out of 10,000 will be empty. As ensuing discussions indicate, a number of other material parameters have an exponential dependence on temperature similar to that of Equation 5.1.

self-interstitial

A **self-interstitial** is an atom from the crystal that is crowded into an interstitial site, a small void space that under ordinary circumstances is not occupied. This kind of defect is also represented in Figure 5.1. In metals, a self-interstitial introduces relatively large distortions in the surrounding lattice because the atom is substantially larger than the interstitial position in which it is situated. Consequently, the formation of this defect is not highly probable, and it exists in very small concentrations, which are significantly lower than for vacancies.

EXAMPLE PROBLEM 5.1

Number of Vacancies Computation at a Specified Temperature

Calculate the equilibrium number of vacancies per cubic meter for copper at 1000°C. The energy for vacancy formation is 0.9 eV/atom; the atomic weight and density (at 1000°C) for copper are 63.5 g/mol and 8.40 g/cm^3, respectively.

---

[1] Absolute temperature in kelvins (K) is equal to °C + 273.

[2] Boltzmann's constant per mole of atoms becomes the gas constant R; in such a case $R = 8.31$ J/mol-K.

Solution

This problem may be solved by using Equation 5.1; it is first necessary, however, to determine the value of N, the number of atomic sites per cubic meter for copper, from its atomic weight A_{Cu}, its density ρ and Avogadro's number N_A, according to

Number of atoms per unit volume for a metal

$$N = \frac{N_A \rho}{A_{\mathrm{Cu}}} \tag{5.2}$$

$$= \frac{(6.02 \times 10^{23} \text{ atoms/mol})(8.4 \text{ g/cm}^3)(10^6 \text{ cm}^3/\text{m}^3)}{63.5 \text{ g/mol}}$$

$$= 8.0 \times 10^{28} \text{ atoms/m}^3$$

Thus, the number of vacancies at 1000°C (1273 K) is equal to

$$N_v = N \exp\left(-\frac{Q_v}{kT}\right)$$

$$= (8.0 \times 10^{28} \text{ atoms/m}^3)\exp\left[-\frac{(0.9 \text{ eV})}{(8.62 \times 10^{-5} \text{ eV/K})(1273 \text{ K})}\right]$$

$$= 2.2 \times 10^{25} \text{ vacancies/m}^3$$

5.3 POINT DEFECTS IN CERAMICS

Point defects involving host atoms may exist in ceramic compounds. As in metals, both vacancies and interstitials are possible; however, since ceramic materials contain ions of at least two kinds, defects for each ion type may occur. For example, in NaCl, Na interstitials and vacancies and Cl interstitials and vacancies may exist. It is highly improbable that there would be appreciable concentrations of anion (Cl^-) interstitials. The anion is relatively large, and to fit into a small interstitial position, substantial strains on the surrounding ions must be introduced. Anion and cation vacancies and a cation interstitial are represented in Figure 5.2.

defect structure

The expression **defect structure** is often used to designate the types and concentrations of atomic defects in ceramics. Because the atoms exist as charged ions, when defect structures are considered, conditions of electroneutrality must be maintained.

electroneutrality

Electroneutrality is the state that exists when there are equal numbers of positive and negative charges from the ions. As a consequence, defects in ceramics do not occur alone. One such type of defect involves a cation–vacancy and a cation–interstitial pair. This is called a **Frenkel defect** (Figure 5.3). It might be thought of as being formed by a cation leaving its normal position and moving into an interstitial site. There is no change in charge because the cation maintains the same positive charge as an interstitial.

Frenkel defect

Schottky defect

Another type of defect found in AX materials is a cation vacancy–anion vacancy pair known as a **Schottky defect,** also schematically diagrammed in Figure 5.3. This defect might be thought of as being created by removing one cation and one anion from the interior of the crystal and then placing them both at an external surface. Since both cations and anions have the same charge, and since for every anion vacancy there exists a cation vacancy, the charge neutrality of the crystal is maintained.

The ratio of cations to anions is not altered by the formation of either a Frenkel or a Schottky defect. If no other defects are present, the material is said to be

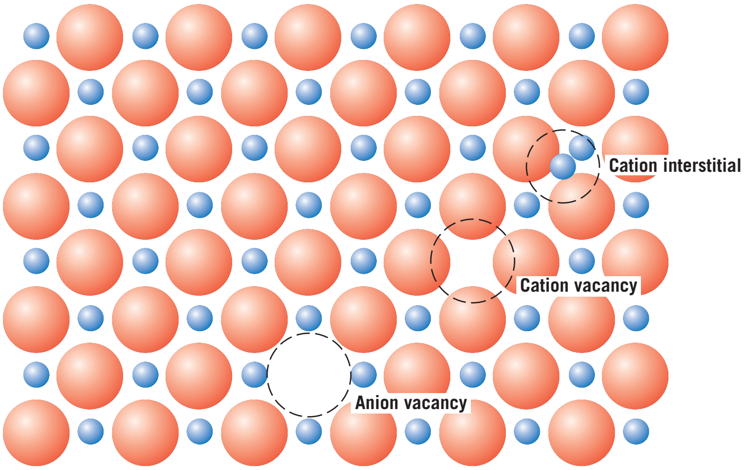


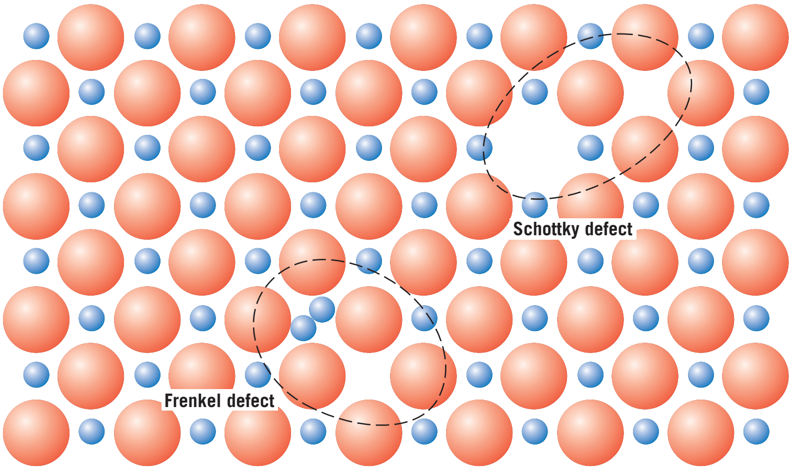
Figure 5.2 Schematic representations of cation and anion vacancies and a cation interstitial. (From W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials,* Vol. I, *Structure,* p. 78. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

stoichiometry

stoichiometric. **Stoichiometry** may be defined as a state for ionic compounds wherein there is the exact ratio of cations to anions predicted by the chemical formula. For example, NaCl is stoichiometric if the ratio of Na^+ ions to Cl^- ions is exactly 1:1. A ceramic compound is *nonstoichiometric* if there is any deviation from this exact ratio.

Nonstoichiometry may occur for some ceramic materials in which two valence (or ionic) states exist for one of the ion types. Iron oxide (wüstite, FeO) is one such material, for the iron can be present in both Fe^{2+} and Fe^{3+} states; the number of each of these ion types depends on temperature and the ambient oxygen pressure. The formation of an Fe^{3+} ion disrupts the electroneutrality of the crystal by introducing an excess +1 charge, which must be offset by some type of defect. This may be accomplished by the formation of one Fe^{2+} vacancy (or the removal of two positive charges) for every two Fe^{3+} ions that are formed (Figure 5.4). The crystal is no longer stoichiometric because there is one more O ion than Fe ion; however, the crystal remains electrically neutral. This phenomenon is fairly common in iron

Figure 5.3 Schematic diagram showing Frenkel and Schottky defects in ionic solids. (From W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials,* Vol. I, *Structure,* p. 78. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)



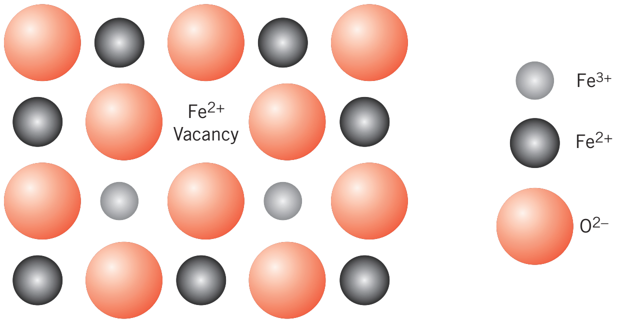


Figure 5.4 Schematic representation of an Fe^{2+} vacancy in FeO that results from the formation of two Fe^{3+} ions.

oxide and, in fact, its chemical formula is often written as $Fe_{1-x}O$ (where x is some small and variable fraction substantially less than unity) to indicate a condition of nonstoichiometry with a deficiency of Fe.

Concept Check 5.1

Can Schottky defects exist in K_2O? If so, briefly describe this type of defect. If they cannot exist, then explain why.

[*The answer may be found at www.wiley.com/college/callister (Student Companion Site).*]

The equilibrium numbers of both Frenkel and Schottky defects increase with and depend on temperature in a manner similar to the number of vacancies in metals (Equation 5.1). For Frenkel defects, the number of cation-vacancy/cation-interstitial defect pairs (N_{fr}) depends on temperature according to the following expression:

$$N_{fr} = N \exp\left(-\frac{Q_{fr}}{2kT}\right) \tag{5.3}$$

Here Q_{fr} is the energy required for the formation of each Frenkel defect, and N is the total number of lattice sites. (Also, as in the previous discussion, k and T represent Boltzmann's constant and the absolute temperature, respectively.) The factor 2 is present in the denominator of the exponential because two defects (a missing cation and an interstitial cation) are associated with each Frenkel defect.

Similarly, for Schottky defects, in an AX-type compound, the equilibrium number (N_s) is a function of temperature as

$$N_s = N \exp\left(-\frac{Q_s}{2kT}\right) \tag{5.4}$$

where Q_s represents the Schottky defect energy of formation.

EXAMPLE PROBLEM 5.2

Computation of the Number of Schottky Defects in KCl

Calculate the number of Schottky defects per cubic meter in potassium chloride at 500°C. The energy required to form each Schottky defect is 2.6 eV, while the density for KCl (at 500°C) is 1.955 g/cm^3.

Solution

To solve this problem it is necessary to use Equation 5.4. However, we must first compute the value of N (the number of lattice sites per cubic meter); this is possible using a modified form of Equation 5.2—i.e.,

$$N = \frac{N_A \rho}{A_K + A_{Cl}} \tag{5.5}$$

where N_A is Avogadro's number (6.02×10^{23} atoms/mol), ρ is the density, and A_K and A_{Cl} are the atomic weights for potassium and chlorine (i.e., 39.10 and 35.45 g/mol), respectively. Therefore,

$$N = \frac{(6.02 \times 10^{23}\ \text{atoms/mol})(1.955\ \text{g/cm}^3)(10^6\ \text{cm}^3/\text{m}^3)}{39.10\ \text{g/mol} + 35.45\ \text{g/mol}}$$
$$= 1.58 \times 10^{28}\ \text{lattice sites/m}^3$$

Now, incorporating this value into Equation 5.4 leads to the following value for N_s:

$$N_s = N \exp\left(-\frac{Q_s}{2kT}\right)$$
$$= (1.58 \times 10^{28}\ \text{lattice sites/m}^3)\exp\left[-\frac{2.6\ \text{eV}}{(2)(8.62 \times 10^{-5}\ \text{eV/K})(500 + 273\ \text{K})}\right]$$
$$= 5.31 \times 10^{19}\ \text{defects/m}^3$$

5.4 IMPURITIES IN SOLIDS

Impurities in Metals

A pure metal consisting of only one type of atom just isn't possible; impurity or foreign atoms will always be present, and some will exist as crystalline point defects. In fact, even with relatively sophisticated techniques, it is difficult to refine metals to a purity in excess of 99.9999%. At this level, on the order of 10^{22} to 10^{23} impurity atoms will be present in one cubic meter of material. Most familiar metals are not highly pure; rather, they are **alloys,** in which impurity atoms have been added intentionally to impart specific characteristics to the material. Ordinarily, alloying is used in metals to improve mechanical strength and corrosion resistance. For example, sterling silver is a 92.5% silver–7.5% copper alloy. In normal ambient environments, pure silver is highly corrosion resistant, but also very soft. Alloying with copper significantly enhances the mechanical strength without depreciating the corrosion resistance appreciably.

alloy

The addition of impurity atoms to a metal will result in the formation of a **solid solution** and/or a new *second phase,* depending on the kinds of impurity, their concentrations, and the temperature of the alloy. The present discussion is concerned with the notion of a solid solution; treatment of the formation of a new phase is deferred to Chapter 10.

solid solution

Several terms relating to impurities and solid solutions deserve mention. With regard to alloys, **solute** and **solvent** are terms that are commonly employed. "Solvent" represents the element or compound that is present in the greatest amount; on occasion, solvent atoms are also called *host atoms*. "Solute" is used to denote an element or compound present in a minor concentration.

solute, solvent

Solid Solutions

A solid solution forms when, as the solute atoms are added to the host material, the crystal structure is maintained and no new structures are formed. Perhaps it is useful to draw an analogy with a liquid solution. If two liquids soluble in each other (such as water and alcohol) are combined, a liquid solution is produced as the molecules intermix, and its composition is homogeneous throughout. A solid solution is also compositionally homogeneous; the impurity atoms are randomly and uniformly dispersed within the solid.

substitutional solid solution

interstitial solid solution

Impurity point defects are found in solid solutions, of which there are two types: **substitutional** and **interstitial.** For the substitutional type, solute or impurity atoms replace or substitute for the host atoms (Figure 5.5). There are several features of the solute and solvent atoms that determine the degree to which the former dissolves in the latter, as follows:

1. *Atomic size factor*. Appreciable quantities of a solute may be accommodated in this type of solid solution only when the difference in atomic radii between the two atom types is less than about ±15%. Otherwise the solute atoms will create substantial lattice distortions and a new phase will form.
2. *Crystal structure*. For appreciable solid solubility the crystal structures for metals of both atom types must be the same.
3. *Electronegativity*. The more electropositive one element and the more electronegative the other, the greater is the likelihood that they will form an intermetallic compound instead of a substitutional solid solution.
4. *Valences*. Other factors being equal, a metal will have a stronger tendency to dissolve another metal of higher valency than one of a lower valency.

An example of a substitutional solid solution is found for copper and nickel. These two elements are completely soluble in one another at all proportions. With regard to the aforementioned rules that govern degree of solubility, the atomic radii for copper and nickel are 0.128 and 0.125 nm, respectively, both have the FCC crystal structure, and their electronegativities are 1.9 and 1.8 (Figure 2.7); finally, the most common valences are +1 for copper (although it sometimes can be +2) and +2 for nickel.

For interstitial solid solutions, impurity atoms fill the voids or interstices among the host atoms (see Figure 5.5). For metallic materials that have relatively high atomic packing factors, these interstitial positions are relatively small. Consequently, the

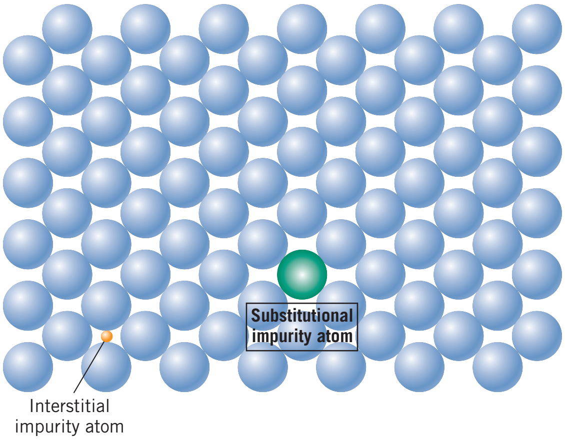


Figure 5.5 Two-dimensional schematic representations of substitutional and interstitial impurity atoms. (Adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials,* Vol. I, *Structure,* p. 77. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

atomic diameter of an interstitial impurity must be substantially smaller than that of the host atoms. Normally, the maximum allowable concentration of interstitial impurity atoms is low (less than 10%). Even very small impurity atoms are ordinarily larger than the interstitial sites, and as a consequence they introduce some lattice strains on the adjacent host atoms. Problem W5.6 (found on the book's Web site) calls for determination of the radii of impurity atoms (in terms of R, the host atom radius) that will just fit into interstitial positions without introducing any lattice strains for both FCC and BCC crystal structures.

Carbon forms an interstitial solid solution when added to iron; the maximum concentration of carbon is about 2%. The atomic radius of the carbon atom is much less than that of iron: 0.071 nm versus 0.124 nm.

Impurities in Ceramics

Impurity atoms can form solid solutions in ceramic materials much as they do in metals. Solid solutions of both substitutional and interstitial types are possible. For an interstitial, the ionic radius of the impurity must be relatively small in comparison to the anion. Since there are both anions and cations, a substitutional impurity will substitute for the host ion to which it is most similar in an electrical sense: if the impurity atom normally forms a cation in a ceramic material, it most probably will substitute for a host cation. For example, in sodium chloride, impurity Ca^{2+} and O^{2-} ions would most likely substitute for Na^+ and Cl^- ions, respectively. Schematic representations for cation and anion substitutional as well as interstitial impurities are shown in Figure 5.6. To achieve any appreciable solid solubility of substituting impurity atoms, the ionic size and charge must be very nearly the same as those of one of the host ions. For an impurity ion having a charge different from the host ion for which it substitutes, the crystal must compensate for this difference in charge so that electroneutrality is maintained with the solid. One way this is accomplished is by the formation of lattice defects—vacancies or interstitials of both ion types, as discussed above.

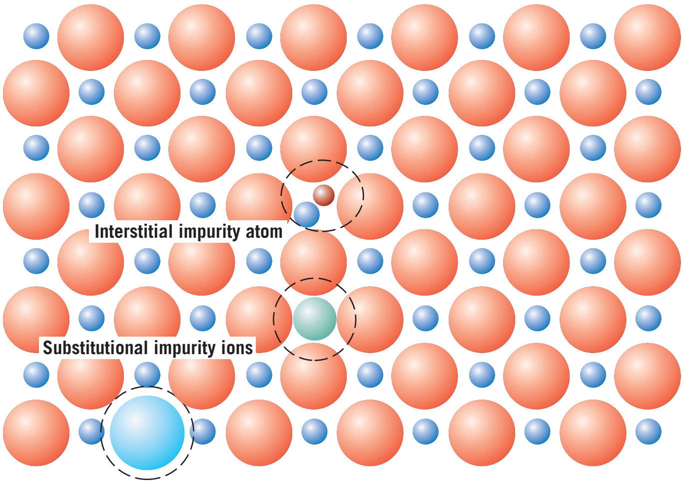


Figure 5.6 Schematic representations of interstitial, anion-substitutional, and cation-substitutional impurity atoms in an ionic compound. (Adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 78. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

EXAMPLE PROBLEM 5.3

Determination of Possible Point Defect Types in NaCl Due to the Presence of Ca^{2+} Ions

If electroneutrality is to be preserved, what point defects are possible in NaCl when a Ca^{2+} substitutes for an Na^+ ion? How many of these defects exist for every Ca^{2+} ion?

Solution

Replacement of an Na^+ by a Ca^{2+} ion introduces one extra positive charge. Electroneutrality is maintained when either a single positive charge is eliminated or another single negative charge is added. Removal of a positive charge is accomplished by the formation of one Na^+ vacancy. Alternatively, a Cl^- interstitial will supply an additional negative charge, negating the effect of each Ca^{2+} ion. However, as mentioned above, the formation of this defect is highly unlikely.

Concept Check 5.2

What point defects are possible for MgO as an impurity in Al_2O_3? How many Mg^{2+} ions must be added to form each of these defects?

[*The answer may be found at www.wiley.com/college/callister (Student Companion Site).*]

5.5 POINT DEFECTS IN POLYMERS

The point defect concept is different in polymers (than in metals and ceramics) as a consequence of the chain-like macromolecules and the nature of the crystalline state for polymers. Point defects similar to those found in metals have been observed in crystalline regions of polymeric materials; these include vacancies and interstitial atoms and ions. Chain ends are considered to be defects because they are chemically dissimilar to normal chain units. Vacancies are also associated with the chain ends (Figure 5.7). However, additional defects can result from branches in the polymer chain or chain segments that emerge from the crystal. A chain section can leave a polymer crystal and reenter it at another point creating a loop, or can enter a second crystal to act as a tie molecule (see Figure 4.13). Impurity atoms/ions or groups of atoms/ions may be incorporated in the molecular structure as interstitials; they may also be associated with main chains or as short side branches.

5.6 SPECIFICATION OF COMPOSITION

composition

weight percent

It is often necessary to express the **composition** (or *concentration*)[3] of an alloy in terms of its constituent elements. The two most common ways to specify composition are weight (or mass) percent and atom percent. The basis for **weight percent** (wt%) is the weight of a particular element relative to the total alloy weight. For an alloy that

---

[3] The terms *composition* and *concentration* are assumed to have the same meaning in this book (i.e., the relative content of a specific element or constituent in an alloy) and are used interchangeably.

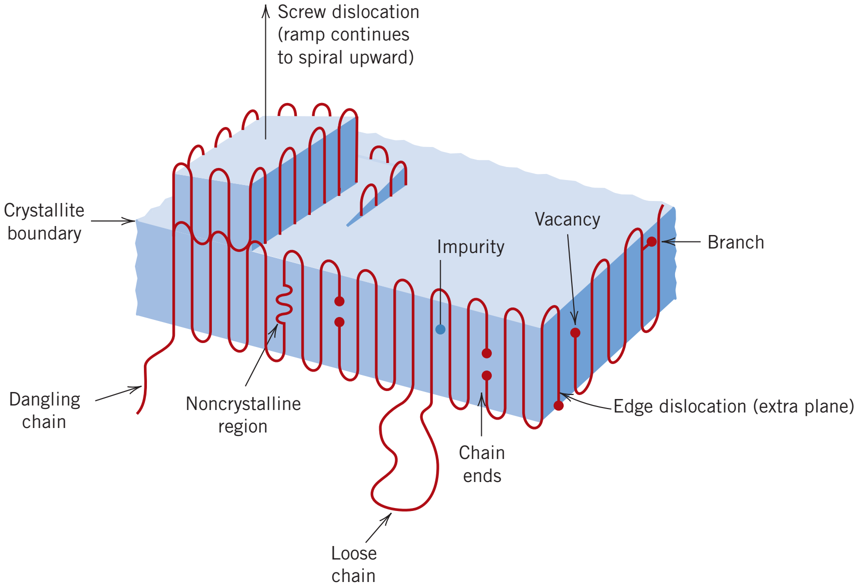


Figure 5.7 Schematic representation of defects in polymer crystallites.

contains two hypothetical atoms denoted by 1 and 2, the concentration of 1 in wt%, C_1, is defined as

Computation of weight percent (for a two-element alloy)

$$C_1 = \frac{m_1}{m_1 + m_2} \times 100 \tag{5.6}$$

where m_1 and m_2 represent the weight (or mass) of elements 1 and 2, respectively. The concentration of 2 would be computed in an analogous manner.

atom percent

The basis for **atom percent** (at%) calculations is the number of moles of an element in relation to the total moles of the elements in the alloy. The number of moles in some specified mass of a hypothetical element 1, n_{m1}, may be computed as follows:

$$n_{m1} = \frac{m_1'}{A_1} \tag{5.7}$$

Here, m_1' and A_1 denote the mass (in grams) and atomic weight, respectively, for element 1.

Concentration in terms of atom percent of element 1 in an alloy containing 1 and 2 atoms, C_1' is defined by[4]

Computation of atom percent (for a two-element alloy)

$$C_1' = \frac{n_{m1}}{n_{m1} + n_{m2}} \times 100 \tag{5.8}$$

In like manner, the atom percent of 2 may be determined.

---

[4] In order to avoid confusion in notations and symbols used in this section, we should point out that the prime (as in C_1' and m_1') is used to designate both composition, in atom percent, and mass of material in units of grams.

Atom percent computations also can be carried out on the basis of the number of atoms instead of moles, since one mole of all substances contains the same number of atoms.

Composition Conversions

Sometimes it is necessary to convert from one composition scheme to another—for example, from weight percent to atom percent. We will now present equations for making these conversions in terms of the two hypothetical elements 1 and 2. Using the convention of the previous section (i.e., weight percents denoted by C_1 and C_2, atom percents by C'_1 and C'_2, and atomic weights as A_1 and A_2), these conversion expressions are as follows:

Conversion of weight percent to atom percent (for a two-element alloy)

$$C'_1 = \frac{C_1A_2}{C_1A_2 + C_2A_1} \times 100 \tag{5.9a}$$

$$C'_2 = \frac{C_2A_1}{C_1A_2 + C_2A_1} \times 100 \tag{5.9b}$$

Conversion of atom percent to weight percent (for a two-element alloy)

$$C_1 = \frac{C'_1A_1}{C'_1A_1 + C'_2A_2} \times 100 \tag{5.10a}$$

$$C_2 = \frac{C'_2A_2}{C'_1A_1 + C'_2A_2} \times 100 \tag{5.10b}$$

Since we are considering only two elements, computations involving the preceding equations are simplified when it is realized that

$$C_1 + C_2 = 100 \tag{5.11a}$$

$$C'_1 + C'_2 = 100 \tag{5.11b}$$

In addition, it sometimes becomes necessary to convert concentration from weight percent to mass of one component per unit volume of material (i.e., from units of wt% to kg/m^3); this latter composition scheme is often used in diffusion computations (Section 6.3). Concentrations in terms of this basis will be denoted using a double prime (i.e., C''_1 and C''_2), and the relevant equations are as follows:

Conversion of weight percent to mass per unit volume (for a two-element alloy)

$$C''_1 = \left(\frac{C_1}{\dfrac{C_1}{\rho_1} + \dfrac{C_2}{\rho_2}}\right) \times 10^3 \tag{5.12a}$$

$$C''_2 = \left(\frac{C_2}{\dfrac{C_1}{\rho_1} + \dfrac{C_2}{\rho_2}}\right) \times 10^3 \tag{5.12b}$$

For density ρ in units of g/cm^3, these expressions yield C''_1 and C''_2 in kg/m^3.

Furthermore, on occasion we desire to determine the density and atomic weight of a binary alloy given the composition in terms of either weight percent or atom percent. If we represent alloy density and atomic weight by ρ_{ave} and A_{ave}, respectively, then

Computation of density (for a two-element metal alloy)

$$\rho_{\text{ave}} = \frac{100}{\dfrac{C_1}{\rho_1} + \dfrac{C_2}{\rho_2}} \tag{5.13a}$$

$$\rho_{\text{ave}} = \frac{C_1'A_1 + C_2'A_2}{\dfrac{C_1'A_1}{\rho_1} + \dfrac{C_2'A_2}{\rho_2}} \tag{5.13b}$$

Computation of atomic weight (for a two-element metal alloy)

$$A_{\text{ave}} = \frac{100}{\dfrac{C_1}{A_1} + \dfrac{C_2}{A_2}} \tag{5.14a}$$

$$A_{\text{ave}} = \frac{C_1'A_1 + C_2'A_2}{100} \tag{5.14b}$$

It should be noted that Equations 5.12 and 5.14 are not always exact. In their derivations, it is assumed that total alloy volume is exactly equal to the sum of the volumes of the individual elements. This normally is not the case for most alloys; however, it is a reasonably valid assumption and does not lead to significant errors for dilute solutions and over composition ranges where solid solutions exist.

EXAMPLE PROBLEM 5.4

Derivation of Composition-Conversion Equation

Derive Equation 5.9a.

Solution

To simplify this derivation, we will assume that masses are expressed in units of grams and denoted with a prime (e.g., m_1'). Furthermore, the total alloy mass (in grams) M' is

$$M' = m_1' + m_2' \tag{5.15}$$

Using the definition of C_1' (Equation 5.8) and incorporating the expression for n_{m1}, Equation 5.7, and the analogous expression for n_{m2} yields

$$\begin{aligned} C_1' &= \frac{n_{m1}}{n_{m1} + n_{m2}} \times 100 \\ &= \frac{\dfrac{m_1'}{A_1}}{\dfrac{m_1'}{A_1} + \dfrac{m_2'}{A_2}} \times 100 \end{aligned} \tag{5.16}$$

Rearrangement of the mass-in-grams equivalent of Equation 5.6 leads to

$$m_1' = \frac{C_1 M'}{100} \tag{5.17}$$

Substitution of this expression and its m_2' equivalent into Equation 5.16 gives

$$C_1' = \frac{\dfrac{C_1 M'}{100A_1}}{\dfrac{C_1 M'}{100A_1} + \dfrac{C_2 M'}{100A_2}} \times 100 \tag{5.18}$$

Upon simplification we have

$$C_1' = \frac{C_1 A_2}{C_1 A_2 + C_2 A_1} \times 100$$

which is identical to Equation 5.9a.

EXAMPLE PROBLEM 5.5

Composition Conversion—From Weight Percent to Atom Percent

Determine the composition, in atom percent, of an alloy that consists of 97 wt% aluminum and 3 wt% copper.

Solution

If we denote the respective weight percent compositions as $C_{\mathrm{Al}} = 97$ and $C_{\mathrm{Cu}} = 3$, substitution into Equations 5.9a and 5.9b yields

$$\begin{aligned} C_{\mathrm{Al}}' &= \frac{C_{\mathrm{Al}} A_{\mathrm{Cu}}}{C_{\mathrm{Al}} A_{\mathrm{Cu}} + C_{\mathrm{Cu}} A_{\mathrm{Al}}} \times 100 \\ &= \frac{(97)(63.55\ \mathrm{g/mol})}{(97)(63.55\ \mathrm{g/mol}) + (3)(26.98\ \mathrm{g/mol})} \times 100 \\ &= 98.7\ \mathrm{at\%} \end{aligned}$$

and

$$\begin{aligned} C_{\mathrm{Cu}}' &= \frac{C_{\mathrm{Cu}} A_{\mathrm{Al}}}{C_{\mathrm{Cu}} A_{\mathrm{Al}} + C_{\mathrm{Al}} A_{\mathrm{Cu}}} \times 100 \\ &= \frac{(3)(26.98\ \mathrm{g/mol})}{(3)(26.98\ \mathrm{g/mol}) + (97)(63.55\ \mathrm{g/mol})} \times 100 \\ &= 1.30\ \mathrm{at\%} \end{aligned}$$

Miscellaneous Imperfections

5.7 DISLOCATIONS—LINEAR DEFECTS

VMSE

► Edge

edge dislocation

A *dislocation* is a linear or one-dimensional defect around which some of the atoms are misaligned. One type of dislocation is represented in Figure 5.8: an extra portion of a plane of atoms, or half-plane, the edge of which terminates within the crystal. This is termed an **edge dislocation;** it is a linear defect that centers around the line that is defined along the end of the extra half-plane of atoms. This is sometimes termed

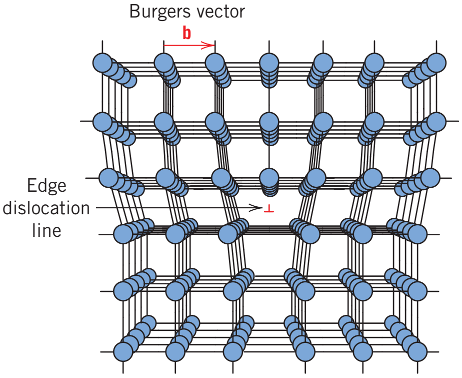


Figure 5.8 The atom positions around an edge dislocation; extra half-plane of atoms shown in perspective. (Adapted from A. G. Guy, *Essentials of Materials Science,* McGraw-Hill Book Company, New York, 1976, p. 153.)

dislocation line

the **dislocation line,** which, for the edge dislocation in Figure 5.8, is perpendicular to the plane of the page. Within the region around the dislocation line there is some localized lattice distortion. The atoms above the dislocation line in Figure 5.8 are squeezed together, and those below are pulled apart; this is reflected in the slight curvature for the vertical planes of atoms as they bend around this extra half-plane. The magnitude of this distortion decreases with distance away from the dislocation line; at positions far removed, the crystal lattice is virtually perfect. Sometimes the edge dislocation in Figure 5.8 is represented by the symbol ⊥, which also indicates the position of the dislocation line. An edge dislocation may also be formed by an extra half-plane of atoms that is included in the bottom portion of the crystal; its designation is a ⊤.

screw dislocation

VMSE

► Screw

Another type of dislocation, called a **screw dislocation,** exists that may be thought of as being formed by a shear stress that is applied to produce the distortion shown in Figure 5.9*a*: the upper front region of the crystal is shifted one atomic distance to the right relative to the bottom portion. The atomic distortion associated with a screw dislocation is also linear and along a dislocation line, line *AB* in Figure 5.9*b*. The screw dislocation derives its name from the spiral or helical path or ramp that is traced around the dislocation line by the atomic planes of atoms. Sometimes the symbol ↻ is used to designate a screw dislocation.

VMSE

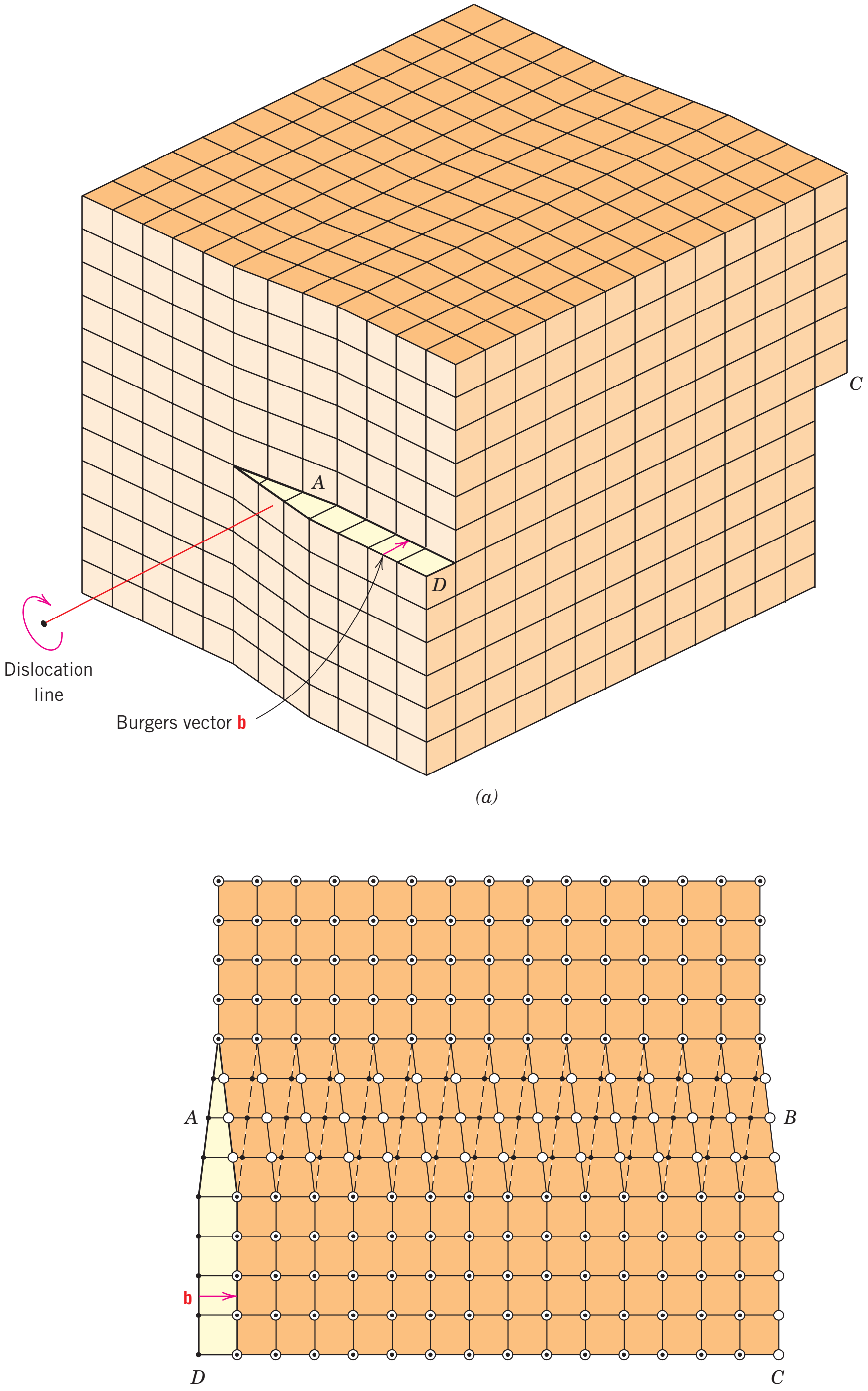
► Mixed

mixed dislocation

Most dislocations found in crystalline materials are probably neither pure edge nor pure screw, but exhibit components of both types; these are termed **mixed dislocations.** All three dislocation types are represented schematically in Figure 5.10; the lattice distortion that is produced away from the two faces is mixed, having varying degrees of screw and edge character.

Burgers vector

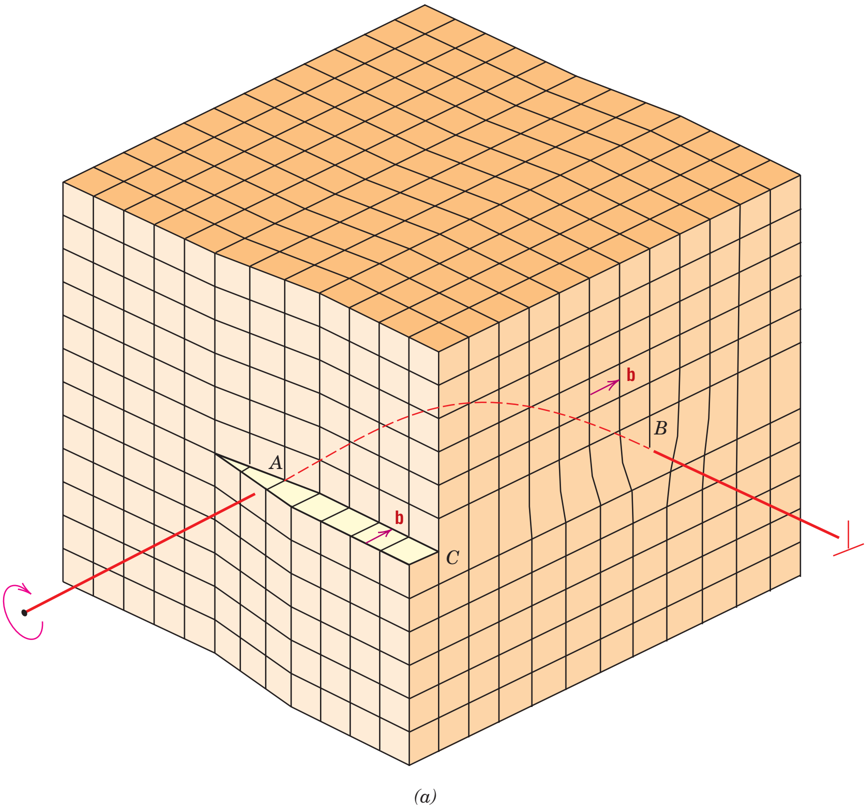
The magnitude and direction of the lattice distortion associated with a dislocation is expressed in terms of a **Burgers vector,** denoted by a **b**. Burgers vectors are indicated in Figures 5.8 and 5.9 for edge and screw dislocations, respectively. Furthermore, the nature of a dislocation (i.e., edge, screw, or mixed) is defined by the relative orientations of dislocation line and Burgers vector. For an edge, they are perpendicular (Figure 5.8), whereas for a screw, they are parallel (Figure 5.9); they are neither perpendicular nor parallel for a mixed dislocation. Also, even though a dislocation changes direction and nature within a crystal (e.g., from edge to mixed to screw), the Burgers vector will be the same at all points along its line. For example, all positions of the curved dislocation in Figure 5.10 will have the Burgers vector shown. For metallic materials, the Burgers vector for a dislocation will point in a close-packed crystallographic direction and will be of magnitude equal to the interatomic spacing.



(*a*)

(*b*)

Figure 5.9 (*a*) A screw dislocation within a crystal. (*b*) The screw dislocation in (*a*) as viewed from above. The dislocation line extends along line *AB*. Atom positions above the slip plane are designated by open circles, those below by solid circles. [Figure (*b*) from W. T. Read, Jr., *Dislocations in Crystals,* McGraw-Hill Book Company, New York, 1953.]



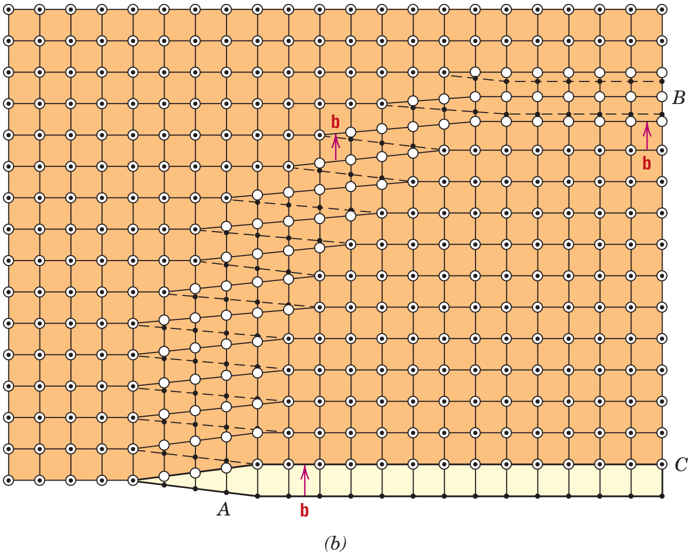


Figure 5.10 (*a*) Schematic representation of a dislocation that has edge, screw, and mixed character. (*b*) Top view, where open circles denote atom positions above the slip plane. Solid circles are atom positions below. At point *A*, the dislocation is pure screw, while at point *B*, it is pure edge. For regions in between where there is curvature in the dislocation line, the character is mixed edge and screw. [Figure (*b*) from W. T. Read, Jr., *Dislocations in Crystals,* McGraw-Hill Book Company, New York, 1953.]

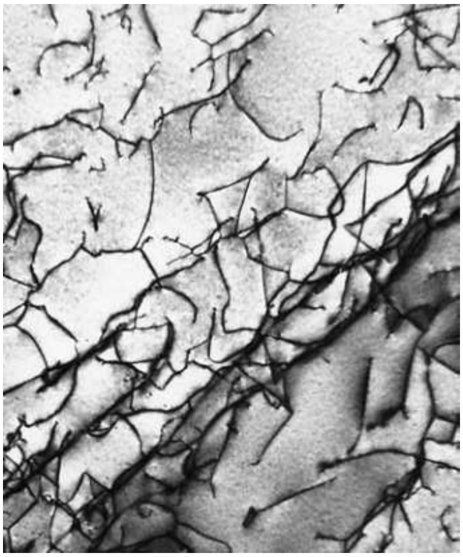


Figure 5.11 A transmission electron micrograph of a titanium alloy in which the dark lines are dislocations. 51,450×. (Courtesy of M. R. Plichta, Michigan Technological University.)

As we note in Section 8.3, the permanent deformation of most crystalline materials is by the motion of dislocations. In addition, the Burgers vector is an element of the theory that has been developed to explain this type of deformation.

Dislocations can be observed in crystalline materials using electron-microscopic techniques. In Figure 5.11, a high-magnification transmission electron micrograph, the dark lines are the dislocations.

Virtually all crystalline materials contain some dislocations that were introduced during solidification, during plastic deformation, and as a consequence of thermal stresses that result from rapid cooling. Dislocations are involved in the plastic deformation of crystalline materials, both metals and ceramics, as discussed in Chapter 8. They have also been observed in polymeric materials; a screw dislocation is represented schematically in Figure 5.7.

5.8 INTERFACIAL DEFECTS

Interfacial defects are boundaries that have two dimensions and normally separate regions of the materials with different crystal structures and/or crystallographic orientations. These imperfections include external surfaces, grain boundaries, twin boundaries, stacking faults, and phase boundaries.

External Surfaces

One of the most obvious boundaries is the external surface, along which the crystal structure terminates. Surface atoms are not bonded to the maximum number of nearest neighbors, and are therefore in a higher energy state than the atoms at interior positions. The bonds of these surface atoms that are not satisfied give rise to a surface energy, expressed in units of energy per unit area (J/m^2 or erg/cm^2). To reduce this energy, materials tend to minimize, if at all possible, the total surface area. For example, liquids assume a shape having a minimum area—the droplets become spherical. Of course, this is not possible with solids, which are mechanically rigid.

Grain Boundaries

Another interfacial defect, the grain boundary, was introduced in Section 3.18 as the boundary separating two small grains or crystals having different crystallographic orientations in polycrystalline materials. A grain boundary is represented schematically from an atomic perspective in Figure 5.12. Within the boundary region, which is probably just several atom distances wide, there is some atomic mismatch in a transition from the crystalline orientation of one grain to that of an adjacent one.

Various degrees of crystallographic misalignment between adjacent grains are possible (Figure 5.12). When this orientation mismatch is slight, on the order of a few degrees, then the term *small-* (or *low-*) *angle grain boundary* is used. These boundaries can be described in terms of dislocation arrays. One simple small-angle grain boundary is formed when edge dislocations are aligned in the manner of Figure 5.13. This type is called a *tilt boundary*; the angle of misorientation, θ, is also indicated in the figure. When the angle of misorientation is parallel to the boundary, a *twist boundary* results, which can be described by an array of screw dislocations.

The atoms are bonded less regularly along a grain boundary (e.g., bond angles are longer), and consequently, there is an interfacial or grain boundary energy similar to the surface energy described above. The magnitude of this energy is a function of the degree of misorientation, being larger for high-angle boundaries. Grain boundaries are more chemically reactive than the grains themselves as a consequence of this boundary energy. Furthermore, impurity atoms often preferentially segregate along these boundaries because of their higher energy state. The total interfacial energy is lower in large- or coarse-grained materials than in fine-grained ones, since there is less total boundary area in the former. Grains grow at elevated temperatures to reduce the total boundary energy, a phenomenon explained in Section 8.14.

In spite of this disordered arrangement of atoms and lack of regular bonding along grain boundaries, a polycrystalline material is still very strong; cohesive forces within and across the boundary are present. Furthermore, the density of a polycrystalline specimen is virtually identical to that of a single crystal of the same material.

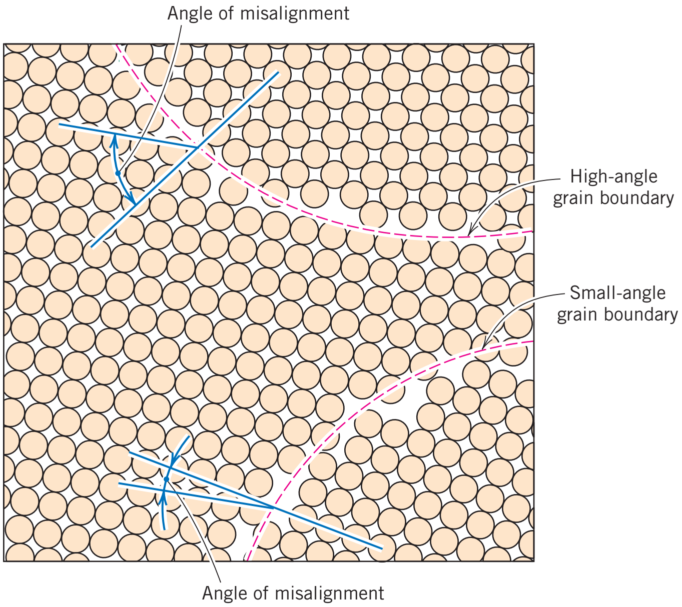


Figure 5.12 Schematic diagram showing small- and high-angle grain boundaries and the adjacent atom positions.

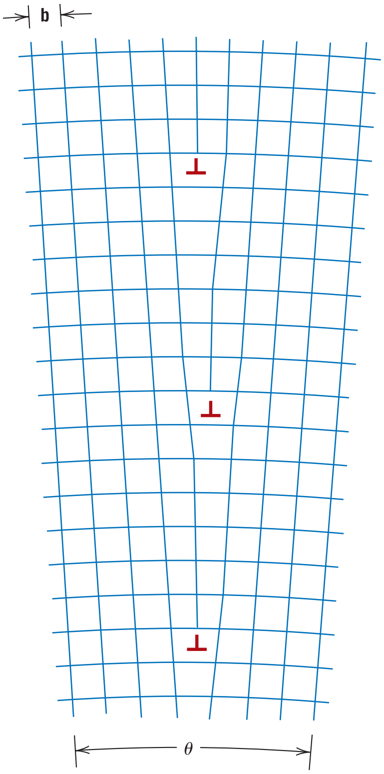


Figure 5.13 Demonstration of how a tilt boundary having an angle of misorientation θ results from an alignment of edge dislocations.

Phase Boundaries

Phase boundaries exist in multiphase materials (Section 10.3), wherein a different phase exists on each side of the boundary; furthermore, each of the constituent phases has its own distinctive physical and/or chemical characteristics. As we shall see in subsequent chapters, phase boundaries play an important role in determining the mechanical characteristics of some multiphase metal alloys.

Twin Boundaries

A *twin boundary* is a special type of grain boundary across which there is a specific mirror lattice symmetry; that is, atoms on one side of the boundary are located in mirror-image positions of the atoms on the other side (Figure 5.14). The region

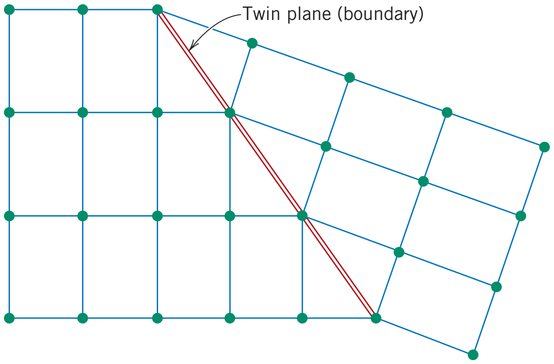


Figure 5.14 Schematic diagram showing a twin plane or boundary and the adjacent atom positions (colored circles).

of material between these boundaries is appropriately termed a *twin*. Twins result from atomic displacements that are produced from applied mechanical shear forces (mechanical twins), and also during annealing heat treatments following deformation (annealing twins). Twinning occurs on a definite crystallographic plane and in a specific direction, both of which depend on the crystal structure. Annealing twins are typically found in metals that have the FCC crystal structure, while mechanical twins are observed in BCC and HCP metals. The role of mechanical twins in the deformation process is discussed in Section 8.8. Annealing twins may be observed in the photomicrograph of the polycrystalline brass specimen shown in Figure 5.18*c*. The twins correspond to those regions having relatively straight and parallel sides and a different visual contrast from the untwinned regions of the grains within which they reside. An explanation of the variety of textural contrasts in this photomicrograph is provided in Section 5.12.

Miscellaneous Interfacial Defects

Other possible interfacial defects include stacking faults and ferromagnetic domain walls. Stacking faults are found in FCC metals when there is an interruption in the *ABCABCABC* . . . stacking sequence of close-packed planes (Section 3.16). For ferromagnetic and ferrimagnetic materials, the boundary that separates regions having different directions of magnetization is termed a domain wall, which is discussed in Section 18.7.

With regard to polymeric materials, the surfaces of chain-folded layers (Figure 4.13) are considered to be interfacial defects, as are boundaries between two adjacent crystalline regions.

Associated with each of the defects discussed in this section is an interfacial energy, the magnitude of which depends on boundary type, and which will vary from material to material. Normally, the interfacial energy will be greatest for external surfaces and least for domain walls.

Concept Check 5.3

The surface energy of a single crystal depends on crystallographic orientation. Does this surface energy increase or decrease with an increase in planar density. Why?

[*The answer may be found at www.wiley.com/college/callister (Student Companion Site).*]

5.9 BULK OR VOLUME DEFECTS

Other defects that are much larger than those heretofore discussed exist in all solid materials. These include pores, cracks, foreign inclusions, and other phases. They are normally introduced during processing and fabrication steps. Some of these defects and their effects on the properties of materials are discussed in subsequent chapters.

5.10 ATOMIC VIBRATIONS

atomic vibration

Every atom in a solid material is vibrating very rapidly about its lattice position within the crystal. In a sense, these **atomic vibrations** may be thought of as imperfections or defects. At any instant of time not all atoms vibrate at the same frequency and amplitude, nor with the same energy. At a given temperature there will exist a distribution of energies for the constituent atoms about an average energy. Over time the

MATERIALS OF IMPORTANCE

Catalysts (and Surface Defects)

A *catalyst* is a substance that speeds up the rate of a chemical reaction without participating in the reaction itself (i.e., it is not consumed). One type of catalyst exists as a solid; reactant molecules in a gas or liquid phase are adsorbed[5] onto the catalytic surface, at which point some type of interaction occurs that promotes an increase in their chemical reactivity rate.

Adsorption sites on a catalyst are normally surface defects associated with planes of atoms; an interatomic/intermolecular bond is formed between a defect site and an adsorbed molecular species. Several types of surface defects, represented schematically in Figure 5.15, include ledges, kinks, terraces, vacancies, and individual adatoms (i.e., atoms adsorbed on the surface).

One important use of catalysts is in catalytic converters on automobiles, which reduce the emission of exhaust gas pollutants such as carbon monoxide (CO), nitrogen oxides (NO_x, where x is variable), and unburned hydrocarbons. Air is introduced into the exhaust emissions from the automobile engine; this mixture of gases then passes over the catalyst, which adsorbs on its surface molecules of CO, NO_x, and O_2. The NO_x dissociates into N and O atoms, whereas the O_2 dissociates into its atomic species. Pairs of nitrogen atoms combine to form N_2 molecules, and carbon monoxide is oxidized to form carbon dioxide (CO_2). Furthermore, any unburned hydrocarbons are also oxidized to CO_2 and H_2O.

One of the materials used as a catalyst in this application is $(Ce_{0.5}Zr_{0.5})O_2$. Figure 5.16 is a high-resolution transmission electron micrograph showing several single crystals of this material. Individual atoms are resolved in this micrograph as well as some of the defects presented in Figure 5.15. These surface defects act as adsorption sites for the atomic and molecular species noted in the previous paragraph. Consequently, dissociation, combination, and oxidation reactions involving these species are facilitated, such that the content of pollutant species (CO, NO_x, and unburned hydrocarbons) in the exhaust gas stream is reduced significantly.

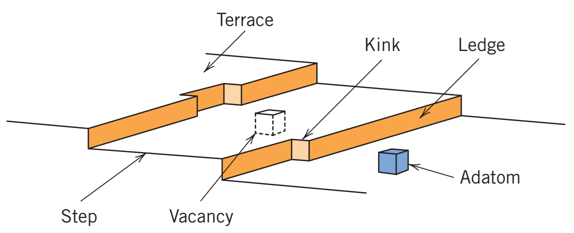


Figure 5.15 Schematic representations of surface defects that are potential adsorption sites for catalysis. Individual atom sites are represented as cubes. (From BOUDART, MICHEL, *KINETICS OF HETEROGENEOUS CATALYTIC REACTIONS*. © 1984 Princeton University Press. Reprinted by permission of Princeton University Press.)

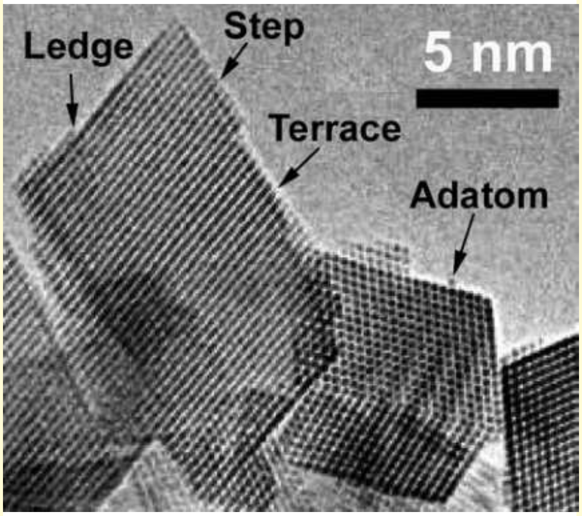


Figure 5.16 High-resolution transmission electron micrograph that shows single crystals of $(Ce_{0.5}Zr_{0.5})O_2$; this material is used in catalytic converters for automobiles. Surface defects represented schematically in Figure 5.15 are noted on the crystals. [From W. J. Stark, L. Mädler, M. Maciejewski, S. E. Pratsinis, A. Baiker, "Flame-Synthesis of Nanocrystalline Ceria/Zirconia: Effect of Carrier Liquid," *Chem. Comm.*, 588–589 (2003). Reproduced by permission of The Royal Society of Chemistry.]

---

[5] ***Adsorption*** is the adhesion of molecules of a gas or liquid to a solid surface. It should not be confused with ***absorption***, which is the assimilation of molecules into a solid or liquid.

Figure 5.17 High-purity polycrystalline lead ingot in which the individual grains may be discerned. 0.7×. (Reproduced with permission from *Metals Handbook,* Vol. 9, 9th edition, *Metallography and Microstructures,* American Society for Metals, Metals Park, OH, 1985.)

vibrational energy of any specific atom will also vary in a random manner. With rising temperature, this average energy increases, and, in fact, the temperature of a solid is really just a measure of the average vibrational activity of atoms and molecules. At room temperature, a typical vibrational frequency is on the order of 10^{13} vibrations per second, whereas the amplitude is a few thousandths of a nanometer.

Many properties and processes in solids are manifestations of this vibrational atomic motion. For example, melting occurs when the vibrations are vigorous enough to rupture large numbers of atomic bonds. A more detailed discussion of atomic vibrations and their influence on the properties of materials is presented in Chapter 17.

Microscopic Examination

5.11 GENERAL

On occasion it is necessary or desirable to examine the structural elements and defects that influence the properties of materials. Some structural elements are of *macroscopic* dimensions; that is, they are large enough to be observed with the unaided eye. For example, the shape and average size or diameter of the grains for a polycrystalline specimen are important structural characteristics. Macroscopic grains are often evident on aluminum streetlight posts and also on highway guard rails. Relatively large grains having different textures are clearly visible on the surface of the sectioned lead ingot shown in Figure 5.17. However, in most materials the constituent grains are of *microscopic* dimensions, having diameters that may be on the order of microns,[6] and their details must be investigated using some type of microscope. Grain size and shape are only two features of what is termed the **microstructure;** these and other microstructural characteristics are discussed in subsequent chapters.

microstructure

Optical, electron, and scanning-probe microscopes are commonly used in **microscopy.** These instruments aid in investigations of the microstructural features of all material types. Some of these techniques employ photographic equipment in

microscopy

---

[6] A micron (μm), sometimes called a micrometer, is 10^{-6} m.

photomicrograph

conjunction with the microscope; the photograph on which the image is recorded is called a **photomicrograph.** In addition, many microstructural images are computer generated and/or enhanced.

Microscopic examination is an extremely useful tool in the study and characterization of materials. Several important applications of microstructural examinations are as follows: to ensure that the associations between the properties and structure (and defects) are properly understood, to predict the properties of materials once these relationships have been established, to design alloys with new property combinations, to determine whether or not a material has been correctly heat treated, and to ascertain the mode of mechanical fracture. Several techniques that are commonly used in such investigations are discussed next.

5.12 MICROSCOPIC TECHNIQUES

Optical Microscopy

With optical microscopy, the light microscope is used to study the microstructure; optical and illumination systems are its basic elements. For materials that are opaque to visible light (all metals and many ceramics and polymers), only the surface is subject to observation, and the light microscope must be used in a reflecting mode. Contrasts in the image produced result from differences in reflectivity of the various regions of the microstructure. Investigations of this type are often termed *metallographic,* since metals were first examined using this technique.

Normally, careful and meticulous surface preparations are necessary to reveal the important details of the microstructure. The specimen surface must first be ground and polished to a smooth and mirrorlike finish. This is accomplished by using successively finer abrasive papers and powders. The microstructure is revealed by a surface treatment using an appropriate chemical reagent in a procedure termed *etching*. The chemical reactivity of the grains of some single-phase materials depends on crystallographic orientation. Consequently, in a polycrystalline specimen, etching characteristics vary from grain to grain. Figure 5.18*b* shows how normally incident light is reflected by three etched surface grains, each having a different orientation. Figure 5.18*a* depicts the surface structure as it might appear when viewed with the microscope; the luster or texture of each grain depends on its reflectance properties. A photomicrograph of a polycrystalline specimen exhibiting these characteristics is shown in Figure 5.18*c*.

Also, small grooves form along grain boundaries as a consequence of etching. Since atoms along grain boundary regions are more chemically active, they dissolve at a greater rate than those within the grains. These grooves become discernible when viewed under a microscope because they reflect light at an angle different from that of the grains themselves; this effect is displayed in Figure 5.19*a*. Figure 5.19*b* is a photomicrograph of a polycrystalline specimen in which the grain boundary grooves are clearly visible as dark lines.

When the microstructure of a two-phase alloy is to be examined, an etchant is often chosen that produces a different texture for each phase so that the different phases may be distinguished from each other.

Electron Microscopy

The upper limit to the magnification possible with an optical microscope is approximately 2000 times. Consequently, some structural elements are too fine or small to

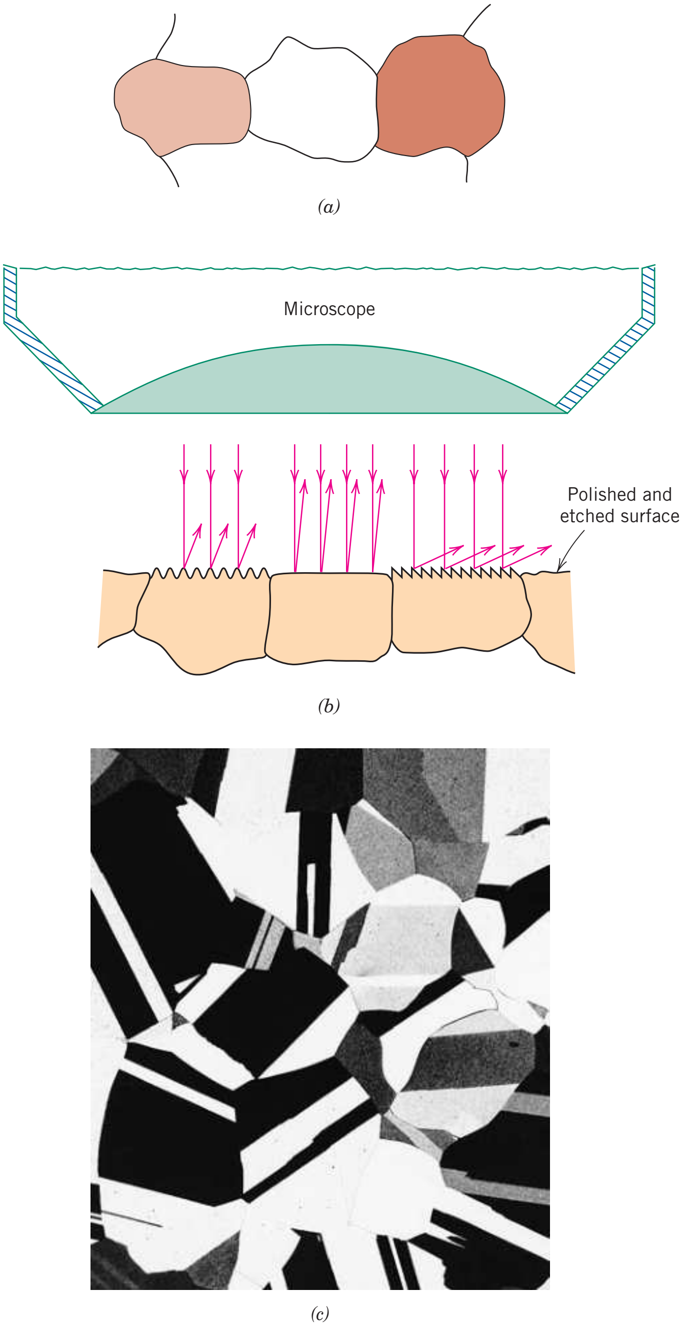
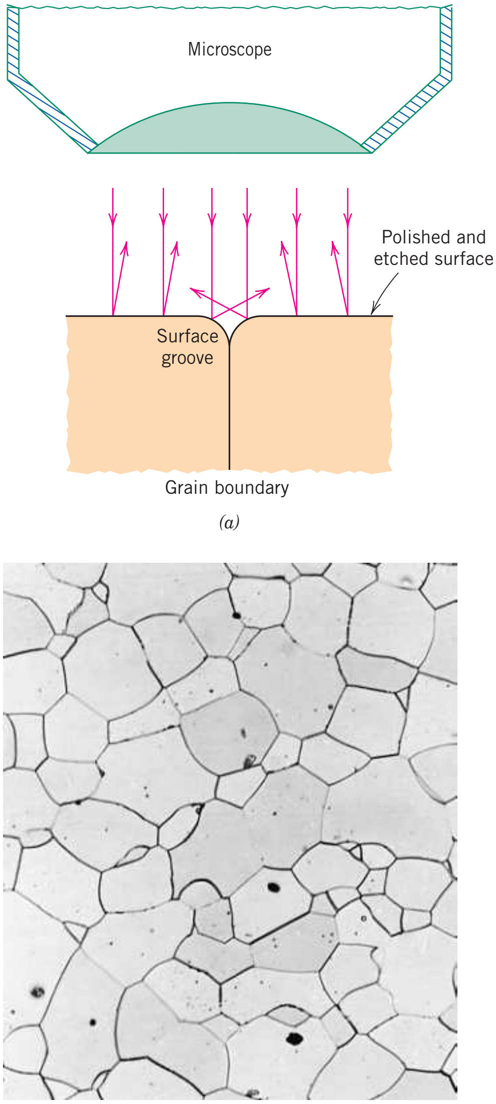


Figure 5.18 (*a*) Polished and etched grains as they might appear when viewed with an optical microscope. (*b*) Section taken through these grains showing how the etching characteristics and resulting surface texture vary from grain to grain because of differences in crystallographic orientation. (*c*) Photomicrograph of a polycrystalline brass specimen. 60×. (Photomicrograph courtesy of J. E. Burke, General Electric Co.)

permit observation using optical microscopy. Under such circumstances the electron microscope, which is capable of much higher magnifications, may be employed.

An image of the structure under investigation is formed using beams of electrons instead of light radiation. According to quantum mechanics, a high-velocity electron will become wave-like, having a wavelength that is inversely proportional to its velocity. When accelerated across large voltages, electrons can be made to have wavelengths on the order of 0.003 nm (3 pm). The high magnifications and resolving powers of these microscopes are consequences of the short wavelengths of electron



(a)

(b)

Figure 5.19 (*a*) Section of a grain boundary and its surface groove produced by etching; the light reflection characteristics in the vicinity of the groove are also shown. (*b*) Photomicrograph of the surface of a polished and etched polycrystalline specimen of an iron-chromium alloy in which the grain boundaries appear dark. 100×. [Photomicrograph courtesy of L. C. Smith and C. Brady, the National Bureau of Standards, Washington, DC (now the National Institute of Standards and Technology, Gaithersburg, MD).]

beams. The electron beam is focused and the image formed with magnetic lenses; otherwise the geometry of the microscope components is essentially the same as with optical systems. Both transmission and reflection beam modes of operation are possible for electron microscopes.

Transmission Electron Microscopy

transmission electron microscope (TEM)

The image seen with a **transmission electron microscope (TEM)** is formed by an electron beam that passes through the specimen. Details of internal microstructural features are accessible to observation; contrasts in the image are produced by differences in beam scattering or diffraction produced between various elements of the microstructure or defect. Since solid materials are highly absorptive to electron beams, a specimen to be examined must be prepared in the form of a very thin foil; this ensures transmission through the specimen of an appreciable fraction of the incident beam. The transmitted beam is projected onto a fluorescent screen or a photographic film so that the image may be viewed. Magnifications approaching 1,000,000 times are possible with transmission electron microscopy, which is frequently utilized in the study of dislocations.

Scanning Electron Microscopy

scanning electron microscope (SEM)

A more recent and extremely useful investigative tool is the **scanning electron microscope (SEM).** The surface of a specimen to be examined is scanned with an electron beam, and the reflected (or back-scattered) beam of electrons is collected, then displayed at the same scanning rate on a cathode ray tube (similar to a CRT television screen). The image on the screen, which may be photographed, represents the surface features of the specimen. The surface may or may not be polished and etched, but it must be electrically conductive; a very thin metallic surface coating must be applied to nonconductive materials. Magnifications ranging from 10 to in excess of 50,000 times are possible, as are also very great depths of field. Accessory equipment permits qualitative and semiquantitative analysis of the elemental composition of very localized surface areas.

Scanning Probe Microscopy

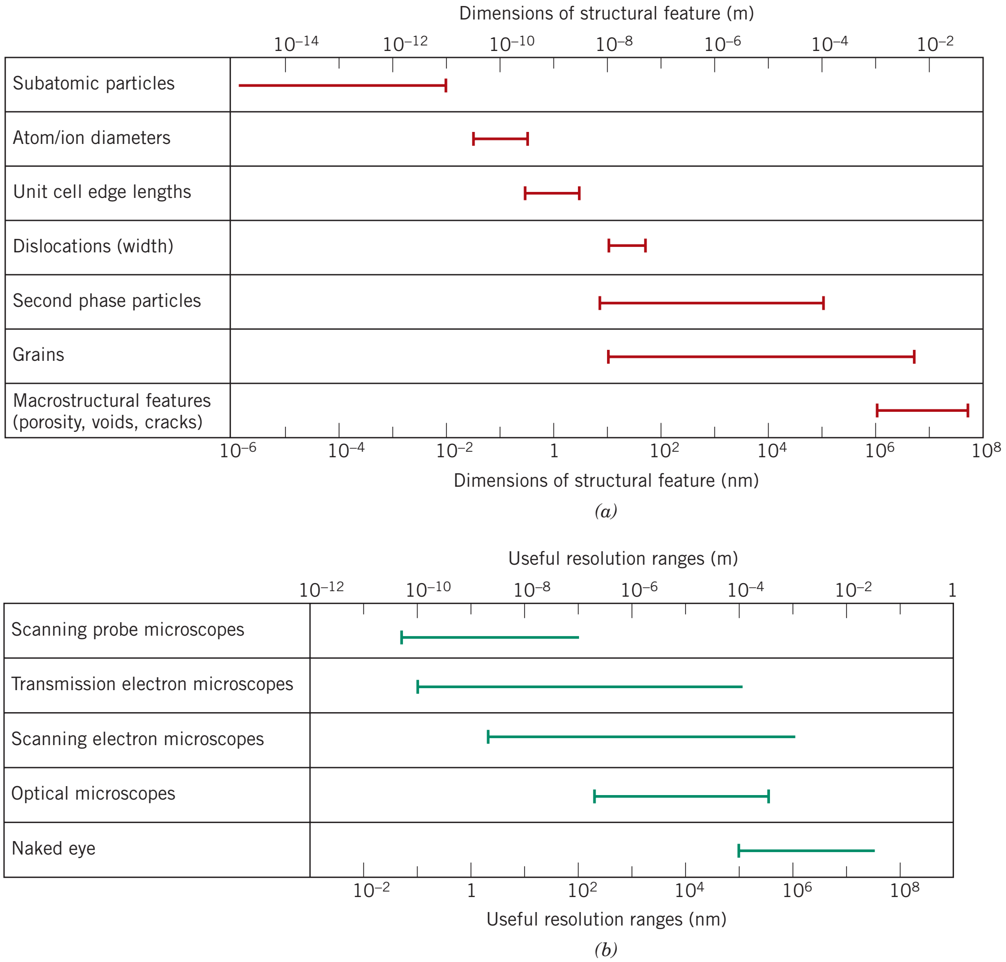
scanning probe microscope (SPM)

In the past decade and a half, the field of microscopy has experienced a revolution with the development of a new family of scanning probe microscopes. This **scanning probe microscope (SPM),** of which there are several varieties, differs from the optical and electron microscopes in that neither light nor electrons is used to form an image. Rather, the microscope generates a topographical map, on an atomic scale, that is a representation of surface features and characteristics of the specimen being examined. Some of the features that differentiate the SPM from other microscopic techniques are as follows:

- Examination on the nanometer scale is possible inasmuch as magnifications as high as 10^9 times are possible; much better resolutions are attainable than with other microscopic techniques.
- Three-dimensional magnified images are generated that provide topographical information about features of interest.
- Some SPMs may be operated in a variety of environments (e.g., vacuum, air, liquid); thus, a particular specimen may be examined in its most suitable environment.

Scanning probe microscopes employ a tiny probe with a very sharp tip that is brought into very close proximity (i.e., to within on the order of a nanometer) of the specimen surface. This probe is then raster-scanned across the plane of the surface. During scanning, the probe experiences deflections perpendicular to this plane, in response to electronic or other interactions between the probe and specimen surface. The in-surface-plane and out-of-plane motions of the probe are controlled by piezoelectric (Section 12.25) ceramic components that have nanometer resolutions. Furthermore, these probe movements are monitored electronically and transferred to and stored in a computer, which then generates the three-dimensional surface image.

Specific scanning probe microscopic techniques differ from one another with regard to the type of interaction that is monitored. A scanning probe micrograph in which may be observed the atomic structure and a missing atom on the surface of silicon is shown in the chapter-opening photograph for this chapter.



(a)

(b)

Figure 5.20 (*a*) Bar-chart showing size ranges for several structural features found in materials. (*b*) Bar-chart showing the useful resolution ranges for four microscopic techniques discussed in this chapter, in addition to the naked eye. (Courtesy of Prof. Sidnei Paciornik, DCMM PUC-Rio, Rio de Janeiro, Brazil, and Prof. Carlos Pérez Bergmann, Federal University of Rio Grande do Sul, Porto Alegre, Brazil.)

These new SPMs, which allow examination of the surface of materials at the atomic and molecular level, have provided a wealth of information about a host of materials, from integrated circuit chips to biological molecules. Indeed, the advent of the SPMs has helped to usher in the era of nanomaterials—materials whose properties are designed by engineering atomic and molecular structures.

Figure 5.20*a* is a bar-chart showing dimensional size ranges for several types of structures found in materials (note that the horizontal axes are scaled logarithmically). Likewise, the useful dimensional resolution ranges for the several microscopic techniques discussed in this chapter (plus the naked eye) are presented in the bar-chart of Figure 5.20*b*. For three of these techniques (viz. SPM, TEM, and SEM), an upper resolution value is not imposed by the characteristics of the microscope, and, therefore, is somewhat arbitrary and not well defined. Furthermore, by comparing Figures 5.20*a* and 5.20*b*, it is possible to decide which microscopic technique(s) is (are) best suited for examination of each of the structure types.

5.13 GRAIN SIZE DETERMINATION

grain size

The **grain size** is often determined when the properties of a polycrystalline material are under consideration. In this regard, there exist a number of techniques by which size is specified in terms of average grain volume, diameter, or area. Grain size may be estimated by using an intercept method, described as follows. Straight lines all the same length are drawn through several photomicrographs that show the grain structure. The grains intersected by each line segment are counted; the line length is then divided by an average of the number of grains intersected, taken over all the line segments. The average grain diameter is found by dividing this result by the linear magnification of the photomicrographs.

Probably the most common method utilized, however, is that devised by the American Society for Testing and Materials (ASTM).[7] The ASTM has prepared several standard comparison charts, all having different average grain sizes. To each is assigned a number ranging from 1 to 10, which is termed the *grain size number*. A specimen must be properly prepared to reveal the grain structure, which is photographed at a magnification of 100×. Grain size is expressed as the grain size number of the chart that most nearly matches the grains in the micrograph. Thus, a relatively simple and convenient visual determination of grain size number is possible. Grain size number is used extensively in the specification of steels.

The rationale behind the assignment of the grain size number to these various charts is as follows. Let n represent the grain size number and N the average number of grains per square inch at a magnification of 100×. These two parameters are related to each other through the expression

Relationship between ASTM grain size number and number of grains per square inch (at 100×)

$$N = 2^{n-1}. \tag{5.19}$$

Concept Check 5.4

Does the grain size number (n of Equation 5.19) increase or decrease with decreasing grain size? Why?

[*The answer may be found at www.wiley.com/college/callister (Student Companion Site).*]

EXAMPLE PROBLEM 5.6

Computations of ASTM Grain Size Number and Number of Grains Per Unit Area

(a) Determine the ASTM grain size number of a metal specimen if 45 grains per square inch are measured at a magnification of 100×.

(b) For this same specimen, how many grains per square inch will there be at a magnification of 85×?

---

[7] ASTM Standard E 112, "Standard Methods for Estimating the Average Grain Size for Metals."

Solution

(a) In order to determine the ASTM grain size number (n) it is necessary to employ Equation 5.19. Taking logarithms of both sides of this expression leads to

$$\log N = (n - 1)\log 2$$

And solving for n yields

$$n = \frac{\log N}{\log 2} + 1$$

From the problem statement, $N = 45$, and, therefore

$$n = \frac{\log 45}{\log 2} + 1 = 6.5$$

(b) At magnifications other than 100×, use of the following modified form of Equation 5.19 is necessary:

$$N_M\left(\frac{M}{100}\right)^2 = 2^{n-1} \tag{5.20}$$

In this expression N_M = the number of grains per square inch at magnification M. In addition, the inclusion of the $(M/100)^2$ term makes use of the fact that, while magnification is a length parameter, area is expressed in terms of units of length squared. As a consequence, the number of grains per unit area increases with the square of the increase in magnification.

Solving Equation 5.20 for N_M, realizing that $M = 85$ and $n = 6.5$, leads to

$$\begin{aligned} N_M &= 2^{n-1}\left(\frac{100}{M}\right)^2 \\ &= 2^{(6.5-1)}\left(\frac{100}{85}\right)^2 = 62.6 \text{ grains/in.}^2 \end{aligned}$$

SUMMARY

Point Defects in Metals

All solid materials contain large numbers of imperfections or deviations from crystalline perfection. The several types of imperfection are categorized on the basis of their geometry and size. Point defects are those associated with one or two atomic positions; in metals these include vacancies (or vacant lattice sites), self-interstitials (host atoms that occupy interstitial sites), and impurity atoms.

Point Defects in Ceramics

With regard to atomic point defects in ceramics, interstitials and vacancies for each anion and cation type are possible. These imperfections often occur in pairs as Frenkel and Schottky defects to ensure that crystal electroneutrality is maintained.

Defects in Polymers

Although the point defect state concept in polymers is different from in metals and ceramics, vacancies, interstitial atoms, and impurity atoms/ions and groups of atoms/ions as interstitials have been found to exist in crystalline regions. Other defects include chains ends, dangling and loose chains, as well as dislocations.

Impurities in Solids

A solid solution may form when impurity atoms are added to a solid, in which case the original crystal structure is retained and no new phases are formed. For substitutional solid solutions, impurity atoms substitute for host atoms, and appreciable solubility is possible only when atomic diameters and electronegativities for both atom types are similar, when both elements have the same crystal structure, and when the impurity atoms have a valence that is the same as or less than the host material. Interstitial solid solutions form for relatively small impurity atoms that occupy interstitial sites among the host atoms.

For ceramic materials, the addition of impurity atoms may result in the formation of substitutional or interstitial solid solutions. Any charge imbalance created by the impurity ions may be compensated by the generation of host ion vacancies or interstitials.

Specification of Composition

Composition of an alloy may be specified in weight percent or atom percent. The basis for weight percent computations is the weight (or mass) of each alloy constituent relative to the total alloy weight. Atom percents are calculated in terms of the number of moles for each constituent relative to the total moles of all the elements in the alloy. Equations were provided for the conversion of one composition scheme to another.

Dislocations—Linear Defects

Dislocations are one-dimensional crystalline defects of which there are two pure types: edge and screw. An edge may be thought of in terms of the lattice distortion along the end of an extra half-plane of atoms; a screw, as a helical planar ramp. For mixed dislocations, components of both pure edge and screw are found. The magnitude and direction of lattice distortion associated with a dislocation are specified by its Burgers vector. The relative orientations of Burgers vector and dislocation line are (1) perpendicular for edge, (2) parallel for screw, and (3) neither perpendicular nor parallel for mixed.

Interfacial Defects
Bulk or Volume Defects
Atomic Vibrations

Other imperfections include interfacial defects [external surfaces, grain boundaries (both small- and high-angle), twin boundaries, etc.], volume defects (cracks, pores, etc.), and atomic vibrations. Each type of imperfection has some influence on the properties of a material.

Microscopic Techniques

Many of the important defects and structural elements of materials are of microscopic dimensions, and observation is possible only with the aid of a microscope. Both optical and electron microscopes are employed, usually in conjunction with photographic equipment. Transmissive and reflective modes are possible for each microscope type;

preference is dictated by the nature of the specimen as well as the structural element or defect to be examined.

More recent scanning probe microscopic techniques have been developed that generate topographical maps representing the surface features and characteristics of the specimen. Examinations on the atomic and molecular levels are possible using these techniques.

Grain Size Determination

Grain size of polycrystalline materials is frequently determined using photomicrographic techniques. Two methods are commonly employed: intercept and standard comparison charts.

IMPORTANT TERMS AND CONCEPTS

Alloy
Atom percent
Atomic vibration
Boltzmann's constant
Burgers vector
Composition
Defect structure
Dislocation line
Edge dislocation
Electroneutrality
Frenkel defect
Grain size
Imperfection
Interstitial solid solution
Microscopy
Microstructure
Mixed dislocation
Photomicrograph
Point defect
Scanning electron microscope (SEM)
Scanning probe microscope (SPM)
Schottky defect
Screw dislocation
Self-interstitial
Solid solution
Solute
Solvent
Stoichiometry
Substitutional solid solution
Transmission electron microscope (TEM)
Vacancy
Weight percent

REFERENCES

ASM Handbook, Vol. 9, *Metallography and Microstructures*, ASM International, Materials Park, OH, 2004.

Brandon, D. and W. D. Kaplan, *Microstructural Characterization of Materials*, Wiley, New York, 1999.

Chiang, Y. M., D. P. Birnie, III, and W. D. Kingery, *Physical Ceramics: Principles for Ceramic Science and Engineering*, Wiley, New York, 1997.

Clarke, A. R. and C. N. Eberhardt, *Microscopy Techniques for Materials Science*, CRC Press, Boca Raton, FL, 2002.

Kingery, W. D., H. K. Bowen, and D. R. Uhlmann, *Introduction to Ceramics*, 2nd edition, Wiley, New York, 1976. Chapters 4 and 5.

Van Bueren, H. G., *Imperfections in Crystals*, North-Holland, Amsterdam (Wiley-Interscience, New York), 1960.

Vander Voort, G. F., *Metallography, Principles and Practice*, ASM International, Materials Park, OH, 1984.

QUESTIONS AND PROBLEMS

Additional problems and questions for this chapter may be found on both Student and Instructor Companion Sites at *www.wiley.com/college/callister*.

Point Defects in Metals

5.1 Calculate the fraction of atom sites that are vacant for copper at its melting temperature of 1084°C (1357 K). Assume an energy for vacancy formation of 0.90 eV/atom.

5.2 Calculate the energy for vacancy formation in silver, given that the equilibrium number of vacancies at 800°C (1073 K) is 3.6×10^{23} m^{-3}. The atomic weight and density (at 800°C) for silver are, respectively, 107.9 g/mol and 9.5 g/cm^3.

Point Defects in Ceramics

5.3 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.

5.4 Using the data given below 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, and

(c) the identity of the oxide (i.e., what is the metal M?)

$T(°C)$	$\rho\ (g/cm^3)$	$N_s\ (m^{-3})$
750	3.50	5.7×10^9
1000	3.45	?
1500	3.40	5.8×10^{17}

Impurities in Solids

5.5 Below, atomic radius, crystal structure, electronegativity, and the most common valence are tabulated, for several elements; for those that are nonmetals, only atomic radii are indicated.

Element	*Atomic Radius (nm)*	*Crystal Structure*	*Electro-negativity*	*Valence*
Ni	0.1246	FCC	1.8	+2
C	0.071			
H	0.046			
O	0.060			
Ag	0.1445	FCC	1.9	+1
Al	0.1431	FCC	1.5	+3
Co	0.1253	HCP	1.8	+2
Cr	0.1249	BCC	1.6	+3
Fe	0.1241	BCC	1.8	+2
Pt	0.1387	FCC	2.2	+2
Zn	0.1332	HCP	1.6	+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

5.6 (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?

Specification of Composition

5.7 What is the composition, in atom percent, of an alloy that consists of 92.5 wt% Ag and 7.5 wt% Cu?

5.8 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.

5.9 What is the composition, in atom percent, of an alloy that contains 44.5 lb_m of silver, 83.7 lb_m of gold, and 5.3 lb_m of Cu?

5.10 Convert the atom percent composition in Problem 5.9 to weight percent.

5.11 Determine the approximate density of a Ti-6Al-4V titanium alloy that has a composition of 90 wt% Ti, 6 wt% Al, and 4 wt% V.

5.12 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, whereas 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.

5.13 Molybdenum forms a substitutional solid solution with tungsten. 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. [*Hint:* you may want to consult Problem W5.16 (Equation 5.21), which is found on the book's Web site.]

5.14 Sometimes it is desirable to be able 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:

$$C_1 = \frac{100}{1 + \dfrac{N_A \rho_2}{N_1 A_1} - \dfrac{\rho_2}{\rho_1}} \qquad (5.22)$$

where

N_A = Avogadro's number
ρ_1 and ρ_2 = densities of the two elements
A_1 and A_2 = the atomic weights of the two elements

Derive Equation 5.22 using Equation 5.2 and expressions contained in Section 5.6.

5.15 Germanium forms a substitutional solid solution with silicon. 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.

5.16 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.

Interfacial Defects

5.17 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 W3.45, found on the book's Web site.)

5.18 **(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?

5.19 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* . . .

Now, copy the stacking sequences and indicate the position(s) of planar defect(s) with a vertical dashed line.

Grain Size Determination

5.20 **(a)** Employing the intercept technique, determine the average grain size for the steel specimen whose microstructure is shown in Figure 10.29(*a*); use at least seven straight-line segments.

(b) Estimate the ASTM grain size number for this material.

5.21 For an ASTM grain size of 6, approximately how many grains would there be per square inch at

(a) a magnification of 100, and

(b) without any magnification?

5.22 Determine the ASTM grain size number if 25 grains per square inch are measured at a magnification of 75.

DESIGN PROBLEMS

Specification of Composition

5.D1 Aluminum–lithium 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.

5.D2 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.