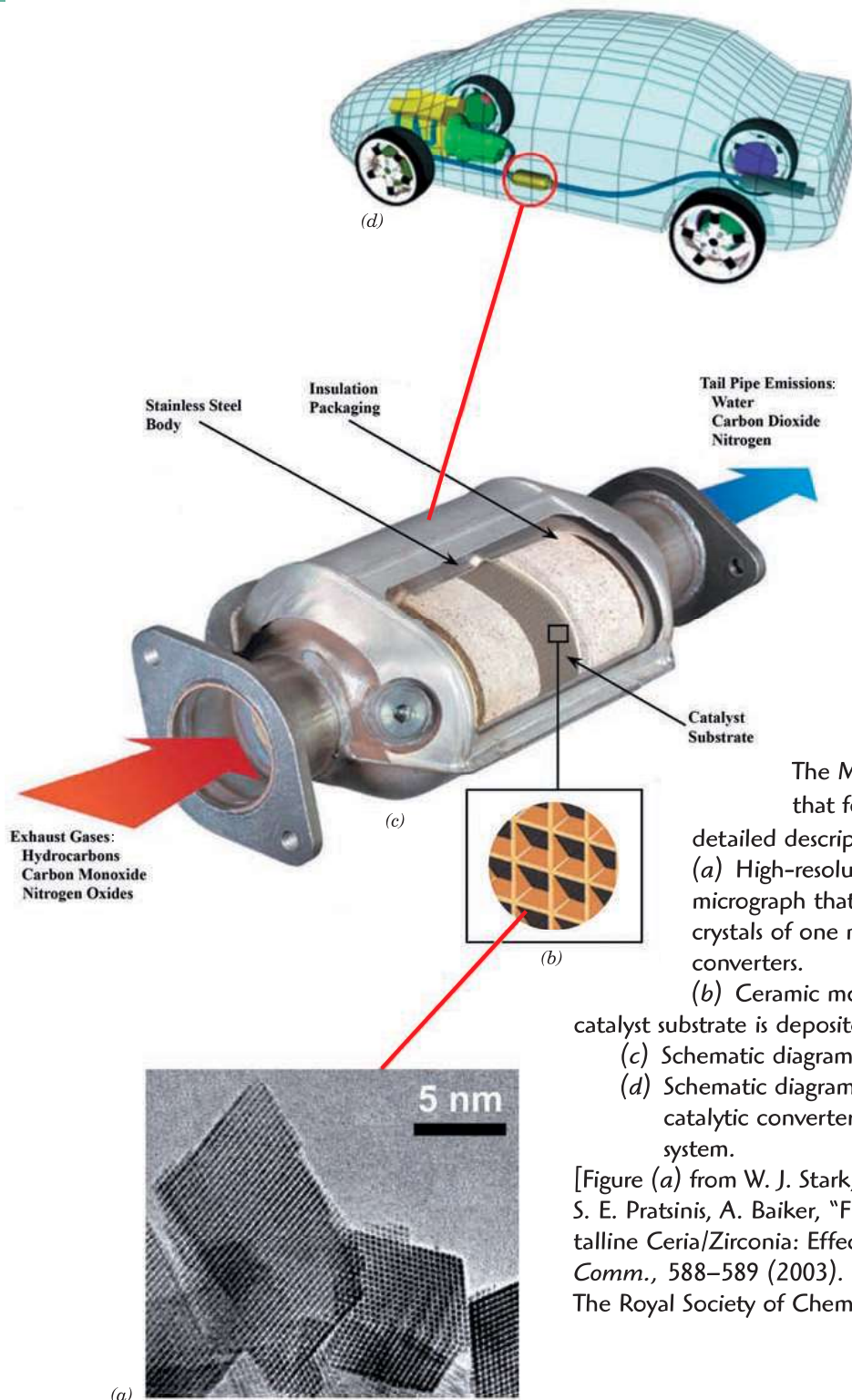


Chapter 4 Imperfections in Solids



Atomic defects are responsible for reductions of gas pollutant emissions from today's automobile engines. A catalytic converter is the pollutant-reducing device that is located in the automobile's exhaust system. Molecules of pollutant gases become attached to surface defects of crystalline metallic materials found in the catalytic converter. While attached to these sites, the molecules experience chemical reactions that convert them into other non- or less-polluting substances.

The Materials of Importance box that follows Section 4.6 contains a detailed description of this process.

(a) High-resolution transmission electron micrograph that shows surface defects on single crystals of one material that is used in catalytic converters.

(b) Ceramic monolith on which the metallic catalyst substrate is deposited.

(c) Schematic diagram of a catalytic converter.

(d) Schematic diagram showing the location of the catalytic converter in an automobile's exhaust system.

[Figure (a) 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.]

WHY STUDY *Imperfections in Solids*?

The properties of some materials are profoundly influenced by the presence of imperfections. Consequently, it is important to have a 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 7.9).

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 18.11 and 18.15).

In the processing/structure/properties/performance scheme, reasons for studying imperfections in solids are as follows:

- For the processing of silicon as a semiconducting material, it is important to specify impurity concentration in appropriate units.
- Development of the desirable mechanical properties for steel alloys relies on the presence of specific impurities, some of which form solid solutions. Thus, an understanding of the concept of a solid solution is important.
- The mechanisms of hardening and strengthening for steel alloys involve a crystalline defect called a dislocation. In this chapter we discuss the dislocation concept and the different types.

Learning Objectives

After studying 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. 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.
5. 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.
6. Describe the atomic structure within the vicinity of (a) a grain boundary and (b) a twin boundary.

4.1 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.

Crystalline defect refers to 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.

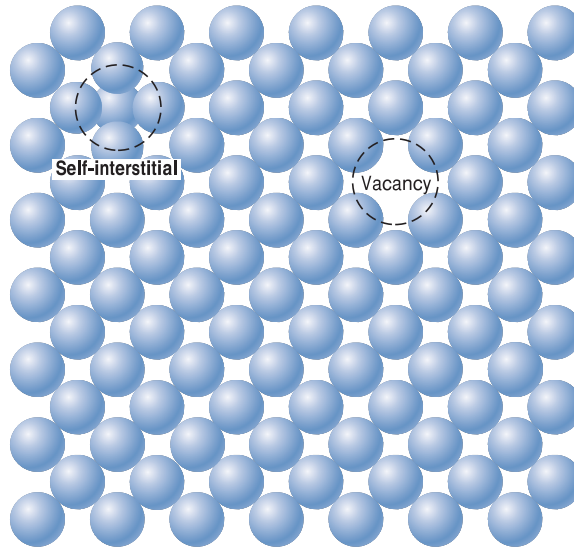


Figure 4.1 Two-dimensional representations of a vacancy and a self-interstitial. (Adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 77. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

point 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, and interfacial defects, or boundaries, which are two-dimensional. Impurities in solids are also discussed, because 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

4.2 VACANCIES AND SELF-INTERSTITIALS

vacancy

The simplest of the point defects is a **vacancy**, or vacant lattice site, one normally occupied from which an atom is missing (Figure 4.1). 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

$$N_v = N \exp\left(-\frac{Q_v}{kT}\right) \quad (4.1)$$

Temperature dependence of the equilibrium number of vacancies

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 temperature¹ 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

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.

increases exponentially with temperature; that is, as T in Equation 4.1 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 4.1.

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 4.1. 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 4.1

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 8.4 g/cm^3 , respectively.

Solution

This problem may be solved by using Equation 4.1; 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

$$\begin{aligned} N &= \frac{N_A \rho}{A_{\text{Cu}}} & (4.2) \\ &= \frac{(6.022 \times 10^{23} \text{ atoms/mol})(8.4 \text{ g/cm}^3)(10^6 \text{ cm}^3/\text{m}^3)}{63.5 \text{ g/mol}} \\ &= 8.0 \times 10^{28} \text{ atoms/m}^3 \end{aligned}$$

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

$$\begin{aligned} N_v &= N \exp\left(-\frac{Q_v}{kT}\right) \\ &= (8.0 \times 10^{28} \text{ atoms/m}^3) \exp\left[-\frac{(0.9 \text{ eV})}{(8.62 \times 10^{-5} \text{ eV/K})(1273 \text{ K})}\right] \\ &= 2.2 \times 10^{25} \text{ vacancies/m}^3 \end{aligned}$$

Number of atoms per unit volume for a metal

4.3 IMPURITIES IN SOLIDS

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

alloy

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.

solid solution

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 9.

solute, solvent

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.

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

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 4.2). Several features of the solute and solvent atoms determine the degree to which the former dissolves in the latter, as follows:

interstitial solid solution

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 $\pm 15\%$. Otherwise the solute atoms will create substantial lattice distortions and a new phase will form.

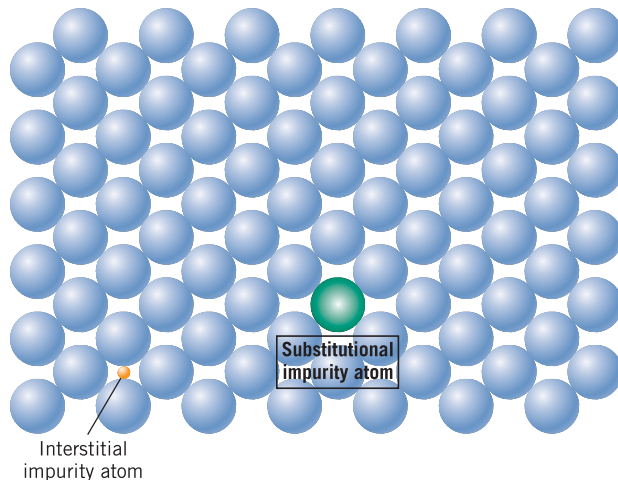


Figure 4.2 Two-dimensional schematic representations of substitutional and interstitial impurity atoms. (Adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 77. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

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 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 more of a 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 4.2). For metallic materials that have relatively high atomic packing factors, these interstitial positions are relatively small. Consequently, the 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 4.5 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 for iron: 0.071 nm versus 0.124 nm. Solid solutions are also possible for ceramic materials, as discussed in Section 12.5.

4.4 SPECIFICATION OF COMPOSITION

composition

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 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)

$$C_1 = \frac{m_1}{m_1 + m_2} \times 100 \quad (4.3)$$

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

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

moles in some specified mass of a hypothetical element 1, n_{m1} , may be computed as follows:

$$n_{m1} = \frac{m'_1}{A_1} \quad (4.4)$$

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 element 1 and element 2 atoms, C'_1 is defined by⁴

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

$$C'_1 = \frac{n_{m1}}{n_{m1} + n_{m2}} \times 100 \quad (4.5)$$

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

Atom percent computations also can be carried out on the basis of the number of atoms instead of moles, because 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)

$$C'_1 = \frac{C_1 A_2}{C_1 A_2 + C_2 A_1} \times 100 \quad (4.6a)$$

$$C'_2 = \frac{C_2 A_1}{C_1 A_2 + C_2 A_1} \times 100 \quad (4.6b)$$

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

$$C_1 = \frac{C'_1 A_1}{C'_1 A_1 + C'_2 A_2} \times 100 \quad (4.7a)$$

$$C_2 = \frac{C'_2 A_2}{C'_1 A_1 + C'_2 A_2} \times 100 \quad (4.7b)$$

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

$$C_1 + C_2 = 100 \quad (4.8a)$$

$$C'_1 + C'_2 = 100 \quad (4.8b)$$

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

⁴In order to avoid confusion in notations and symbols that are being 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.

computations (Section 5.3). 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)

$$C_1'' = \left(\frac{C_1}{\frac{C_1}{\rho_1} + \frac{C_2}{\rho_2}} \right) \times 10^3 \quad (4.9a)$$

$$C_2'' = \left(\frac{C_2}{\frac{C_1}{\rho_1} + \frac{C_2}{\rho_2}} \right) \times 10^3 \quad (4.9b)$$

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)

$$\rho_{\text{ave}} = \frac{100}{\frac{C_1}{\rho_1} + \frac{C_2}{\rho_2}} \quad (4.10a)$$

$$\rho_{\text{ave}} = \frac{C_1' A_1 + C_2' A_2}{\frac{C_1' A_1}{\rho_1} + \frac{C_2' A_2}{\rho_2}} \quad (4.10b)$$

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

$$A_{\text{ave}} = \frac{100}{\frac{C_1}{A_1} + \frac{C_2}{A_2}} \quad (4.11a)$$

$$A_{\text{ave}} = \frac{C_1' A_1 + C_2' A_2}{100} \quad (4.11b)$$

It should be noted that Equations 4.9 and 4.11 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 4.2

Derivation of Composition-Conversion Equation

Derive Equation 4.6a.

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

$$M' = m'_1 + m'_2 \quad (4.12)$$

Using the definition of C'_1 (Equation 4.5) and incorporating the expression for n_{m1} , Equation 4.4, and the analogous expression for n_{m2} yields

$$\begin{aligned} C'_1 &= \frac{n_{m1}}{n_{m1} + n_{m2}} \times 100 \\ &= \frac{\frac{m'_1}{A_1}}{\frac{m'_1}{A_1} + \frac{m'_2}{A_2}} \times 100 \end{aligned} \quad (4.13)$$

Rearrangement of the mass-in-grams equivalent of Equation 4.3 leads to

$$m'_1 = \frac{C_1 M'}{100} \quad (4.14)$$

Substitution of this expression and its m'_2 equivalent into Equation 4.13 gives

$$C'_1 = \frac{\frac{C_1 M'}{100 A_1}}{\frac{C_1 M'}{100 A_1} + \frac{C_2 M'}{100 A_2}} \times 100 \quad (4.15)$$

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 4.6a.

EXAMPLE PROBLEM 4.3

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 $C_{Al} = 97$ and $C_{Cu} = 3$, substitution into Equations 4.6a and 4.6b yields

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

and

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

Miscellaneous Imperfections

4.5 DISLOCATIONS—LINEAR DEFECTS

edge dislocation

dislocation line

VMSE



Edge

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 4.3: 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 on the line that is defined along the end of the extra half-plane of atoms. This is sometimes termed the **dislocation line**, which, for the edge dislocation in Figure 4.3, 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 4.3 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 4.3 is represented by the symbol \perp , 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 \top .

screw dislocation

VMSE



Screw

Another type of dislocation, called a **screw dislocation**, may be thought of as being formed by a shear stress that is applied to produce the distortion shown in Figure 4.4a: 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 4.4b. 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 \curvearrowright is used to designate a screw dislocation.

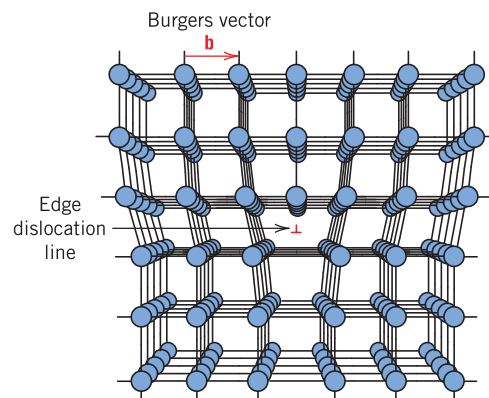
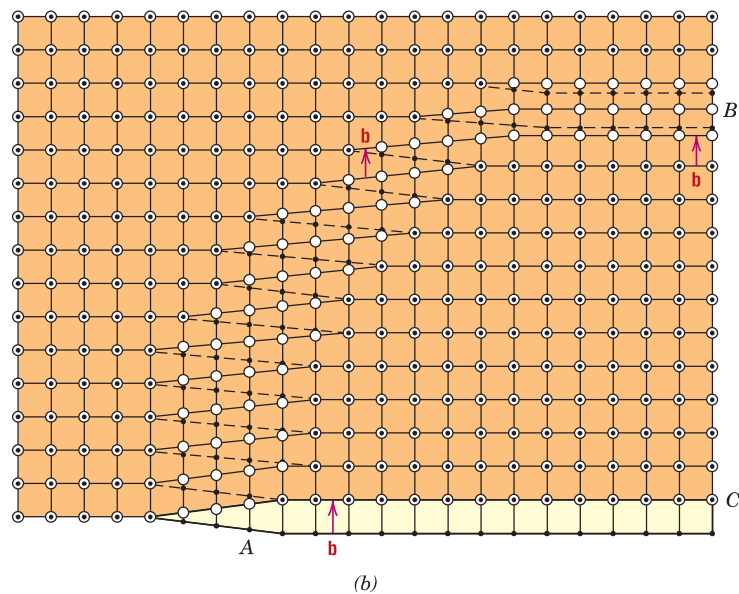
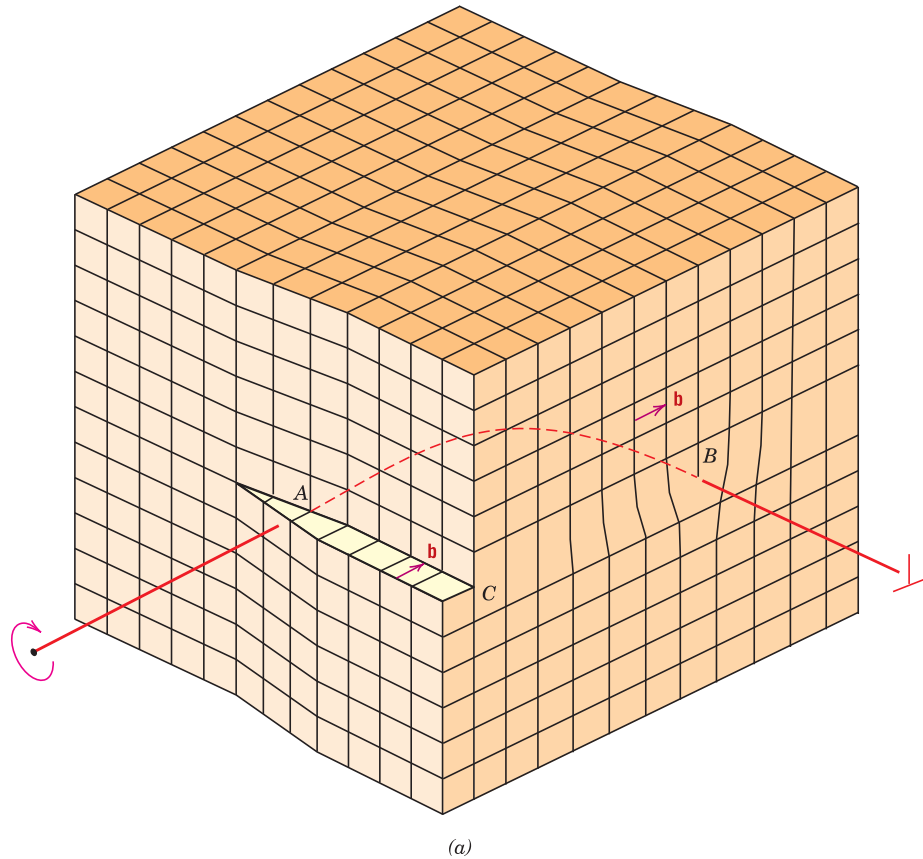


Figure 4.3 The atom positions around an edge dislocation; extra half-plane of atoms shown in perspective. (Adapted from A. G. Guy, *Essentials of Materials Science*, McGraw-Hill Book Company, New York, 1976, p. 153.)

Figure 4.5 (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, and solid circles, 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.]



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 4.3 and 4.4 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

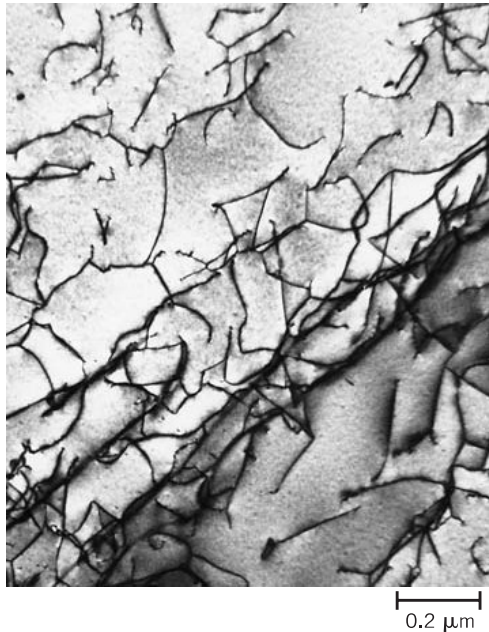


Figure 4.6 A transmission electron micrograph of a titanium alloy in which the dark lines are dislocations. 51,450 \times . (Courtesy of M. R. Plichta, Michigan Technological University.)

(Figure 4.3), whereas for a screw, they are parallel (Figure 4.4); 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 4.5 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.

As we note in Section 7.2, 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 4.6, 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 Chapters 7 and 12. They have also been observed in polymeric materials and are discussed in Section 14.13.

4.6 INTERFACIAL DEFECTS

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

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

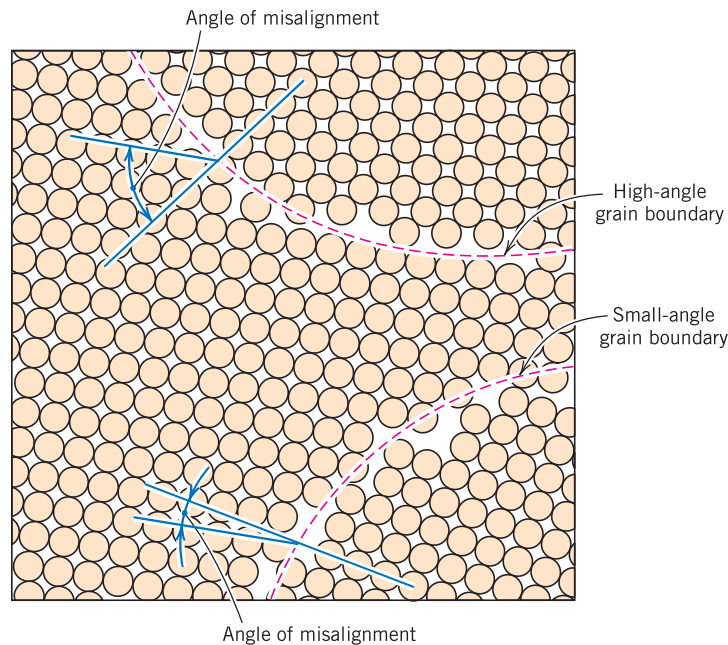


Figure 4.7 Schematic diagram showing small- and high-angle grain boundaries and the adjacent atom positions.

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 3.14 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 4.7. 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 4.7). 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 4.8. 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 just described. 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, because 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 7.13.

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