Al-Mustaqbal University / College of Engineering & Technology
Department (Chemical Engineering)
Class (Second)
Subject (Material Engineering)
Lecturer (Zainab Hassan)
1st/2nd term – Lecture No. & Lecture Name (Imperfections in Solids)

INTRODUCTION

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. Crystalline defect refers to a lattice irregularity having one or more of its dimensions on the order of an atomic diameter. Classification of crystalline imper fections 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, 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.

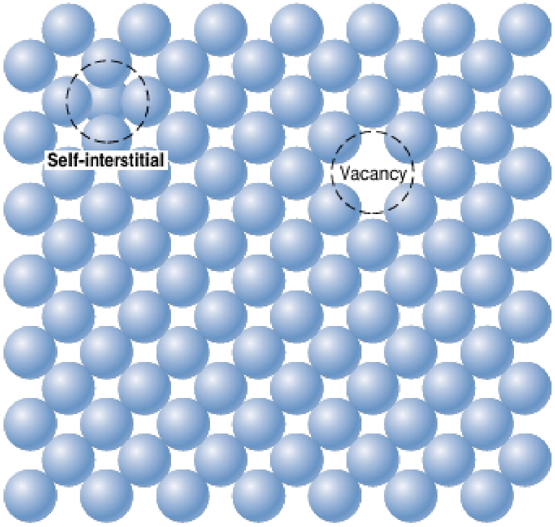

Figure 4.1 Two-dimensional representations of a vacancy and a self-interstitial. (Adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials,* Vol. I, *Structure,* p. 77. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley &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

Point Defects

VACANCIES AND SELF-INTERSTITIALS

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

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

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 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.

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[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.

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

$$N = \frac{N_A \rho}{A_{\mathrm{Cu}}} \tag{4.2}$$

$$= \frac{(6.022 \times 10^{23}\ \text{atoms/mol})(8.4\ \text{g/cm}^3)(10^6\ \text{cm}^3/\text{m}^3)}{63.5\ \text{g/mol}}$$

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

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

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

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

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

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 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.

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.

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.

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:

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.

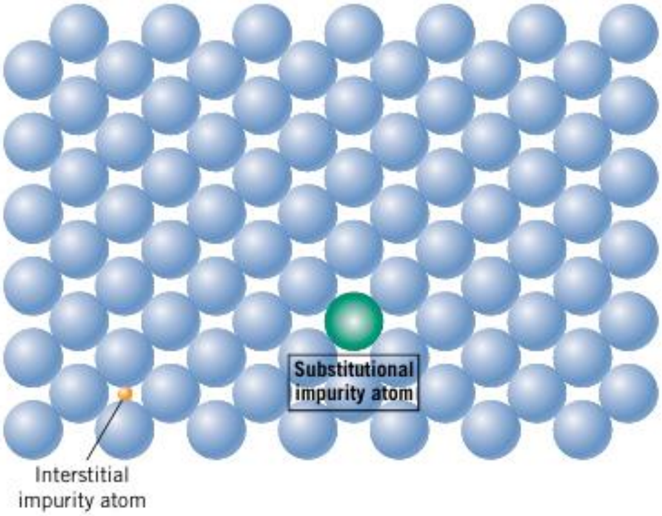

Figure 4.2 Two-dimensional schematic representations of substitutional and interstitial impurity atoms. (Adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials,* Vol. I, *Structure,* p. 77. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission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

SPECIFICATION OF 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

$$C_1 = \frac{m_1}{m_1 + m_2} \times 100 \tag{4.3}$$

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.

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:

$$n_{m1} = \frac{m_1'}{A_1} \tag{4.4}$$

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 by[4]

$$C_1' = \frac{n_{m1}}{n_{m1} + n_{m2}} \times 100 \tag{4.5}$$

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.

Miscellaneous Imperfections

DISLOCATIONS—LINEAR DEFECTS

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 ⊥, 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 ⊤.

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 4.4*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 4.4*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.

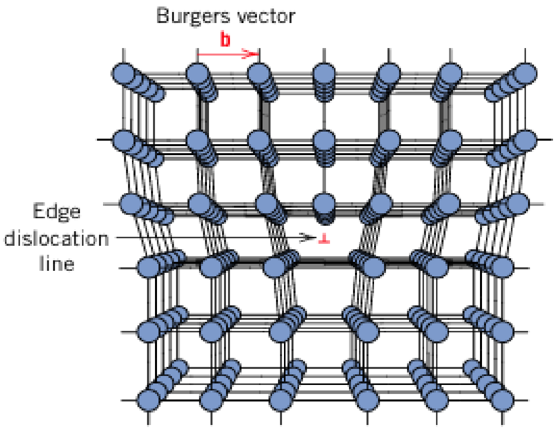

Figure 4.3 The atom positions around an edge dislocation; extra half-plane of atoms shown in perspective. (Adapted from A. G. Guy, *Essentials of Materials Science,* McGraw-Hill Book Company, New York, 1976, p. 153.)

INTERFACIAL DEFECTS

Interfacial defects are imperfections that occur at the boundary (interface) between two different phases or regions within a material for example, between two grains in a polycrystalline solid, between a fiber and the matrix in a composite, or between two layers in a thin film.

1. **Grain Boundaries:**
   These occur where crystals (grains) of different orientations meet. The atomic arrangement at the interface is mismatched, leading to localized strain or disordered regions.
2. **Phase Boundaries:**
   Found between two different phases (e.g., between α and β phases in alloys). The atomic structure changes across the interface.
3. **Twin Boundaries:**
   A special type of grain boundary where the crystal structure on one side is a mirror image of the other. These can strengthen materials by blocking dislocation movement.
4. **Interphase Boundaries in Composites:**
   In polymer composites or fiber-reinforced materials, interfacial defects occur when the adhesion between the matrix and the reinforcement (fiber, filler, etc.) is poor — leading to voids, cracks, or delamination.
5. **Surface Defects:**
   The outermost interface between a solid and its environment. Any contamination, oxidation, or irregular atomic arrangement here can be considered an interfacial defect.

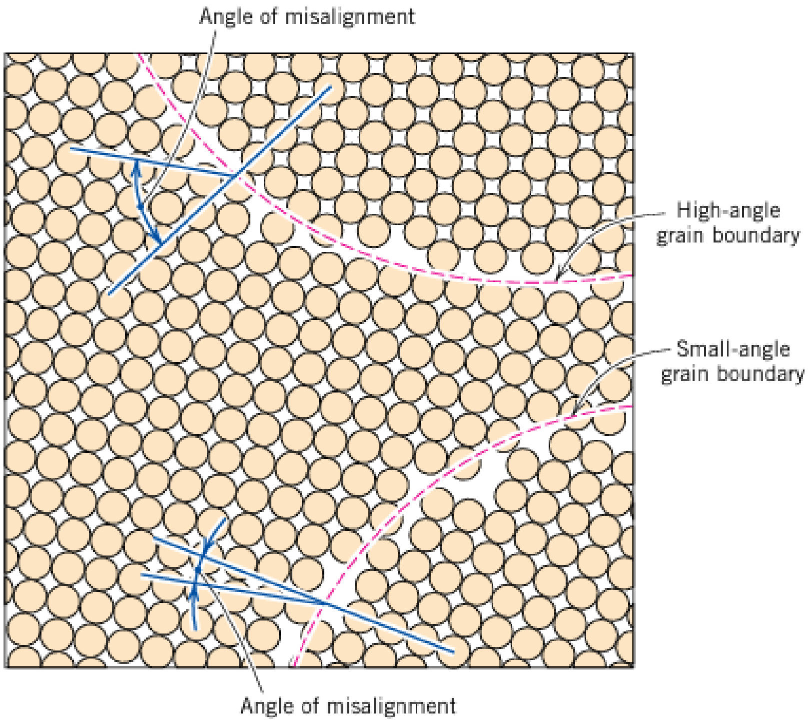

Figure 4.7 Schematic diagram showing small- and high-angle grain boundaries and the adjacent atom positions.

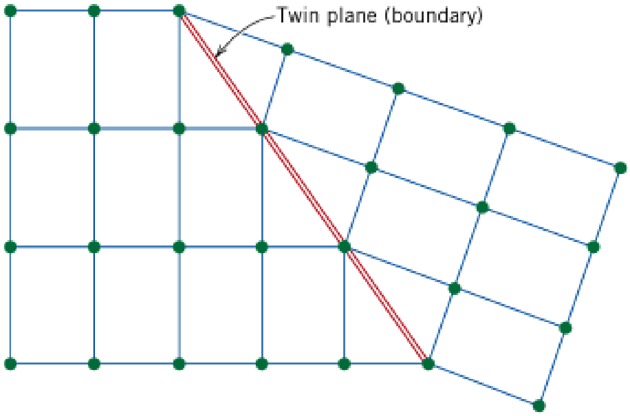

Figure 4.9 Schematic diagram showing a twin plane or boundary and the adjacent atom positions (colored circles).

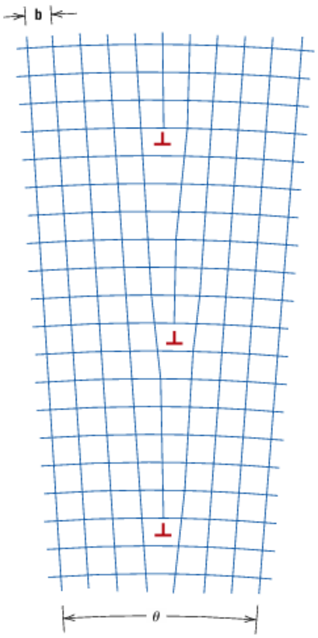

Figure 4.8 Demonstration of how a tilt boundary having an angle of misorientation θ results from an alignment of edge dislocations.

BULK OR VOLUME DEFECTS

These include pores, cracks, foreign inclusions, and other phases. They are normally introduced during processing and fabrication steps.

ATOMIC VIBRATIONS

Atoms in a solid vibrate constantly around their fixed lattice positions. These vibrations vary in frequency, amplitude, and energy, creating small imperfections in the crystal. As temperature increases, the average vibrational energy rises in fact, temperature measures atomic vibration intensity. At room temperature, atoms vibrate about 10^{13} times per second with amplitudes of a few thousandths of a nanometer. These vibrations affect many properties of solids for example, melting occurs when vibrations become strong enough to break atomic bonds.