Imperfections in the Atomic and Ionic Arrangements

the arrangement of the atoms or ions in engineered materials contains imperfections or defects. These defects often have a profound effect on the properties of materials. There are three basic types of imperfections: **point defects, line defects (or dislocations), and surface defects**. These imperfections only represent defects in or deviations from the perfect or ideal atomic or ionic arrangements expected in a given crystal structure.

Point Defects

Point defects are localized disruptions in otherwise perfect atomic or ionic arrangements in a crystal structure. These imperfections, shown in Figure 4-1, may be introduced by movement of the atoms or ions when they gain energy by heating, during processing of the material, or by the intentional or unintentional introduction of impurities.

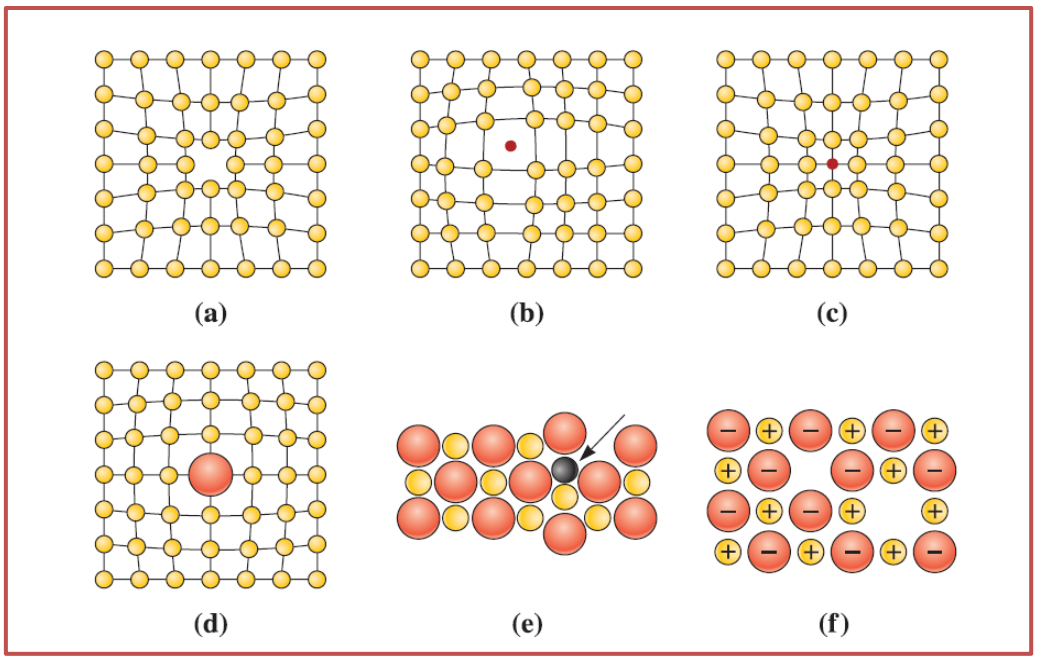

Figure 4-1 Point defects: (a) vacancy, (b) interstitial atom, (c) small substitutional atom, (d) large substitutional atom, (e) Frenkel defect, and (f) Schottky defect. All of these defects disrupt the perfect arrangement of the surrounding atoms.

Impurities are elements or compounds that are present from raw materials or processing. For example, silicon crystals grown in quartz crucibles contain oxygen as an impurity.

Dopants, are elements or compounds that are deliberately added, in known concentrations, at specific locations in the microstructure, with an intended beneficial effect on properties or processing. Phosphorus (P) and boron (B) are examples of dopants that are added to silicon crystals to improve the electrical properties of pure silicon (Si). A point defect typically involves one atom or ion, or a pair of atoms or ions, and thus is different from **extended defects**, such as dislocations or grain boundaries.

Vacancies

A vacancy is produced when an atom or an ion is missing from its normal site in the crystal structure as in Figure 4-1(a). When atoms or ions are missing (i.e., when vacancies are present), the overall randomness or entropy of the material increases, which increases the thermodynamic stability of a crystalline material. All crystalline materials have vacancy defects. Vacancies are introduced into metals and alloys during solidification, at high temperatures, or as a consequence of radiation damage. Vacancies play an important role in determining the rate at which atoms or ions move around or diffuse in a solid material, especially in pure metals.

At room temperature (~298 K), the concentration of vacancies is small, but the concentration of vacancies increases exponentially as the temperature increases, as shown by the following Arrhenius type behavior:

$$n_v = n \exp\left(\frac{-Q_v}{RT}\right) \quad (4\text{-}1)$$

where

n_v is the number of vacancies per cm^3;

n is the number of atoms per cm^3;

Q_v is the energy required to produce one mole of vacancies, in cal/mol or Joules/mol;

R is the gas constant, $1.987 \frac{\text{cal}}{\text{mol} \cdot \text{K}}$ or $8.314 \frac{\text{Joules}}{\text{mol} \cdot \text{K}}$; and

T is the temperature in degrees Kelvin.

Example

Calculate the concentration of vacancies in copper at room temperature (25°C). What temperature will be needed to heat treat copper such that the concentration of vacancies produced will be 1000 times more than the equilibrium concentration of vacancies at room temperature? Assume that 20,000 cal are required to produce a mole of vacancies in copper. Where the lattice parameter of copper 0.36151 nm and number of atom in unit cell is 4

SOLUTION

The lattice parameter of FCC copper is 0.36151 nm. There are four atoms per unit cell; therefore, the number of copper atoms per cm^3 is

$$n = \frac{4 \text{ atoms/cell}}{(3.6151 \times 10^{-8} \text{ cm})^3} = 8.466 \times 10^{22} \text{ copper atoms/cm}^3$$

At room temperature, $T = 25 + 273 = 298$ K:

$$n_v = n \exp\left(\frac{-Q_v}{RT}\right)$$

$$= \left(8.466 \times 10^{22} \frac{\text{atoms}}{\text{cm}^3}\right) \exp\left[\frac{-20{,}000 \frac{\text{cal}}{\text{mol}}}{\left(1.987 \frac{\text{cal}}{\text{mol} \cdot \text{K}}\right)(298 \text{ K})}\right]$$

$$= 1.814 \times 10^8 \text{ vacancies/cm}^3$$

We wish to find a heat treatment temperature that will lead to a concentration of vacancies that is 1000 times higher than this number, or $n_v = 1.814 \times 10^{11}$ vacancies/cm^3.

We could do this by heating the copper to a temperature at which this number of vacancies forms:

$$n_v = 1.814 \times 10^{11} = n \exp\left(\frac{-Q_v}{RT}\right)$$

$$= (8.466 \times 10^{22}) \exp(-20{,}000)/(1.987T)$$

$$\exp\left(\frac{-20{,}000}{1.987T}\right) = \frac{1.814 \times 10^{11}}{8.466 \times 10^{22}} = 0.214 \times 10^{-11}$$

$$\frac{-20{,}000}{1.987T} = \ln(0.214 \times 10^{-11}) = -26.87$$

$$T = \frac{20{,}000}{(1.987)(26.87)} = 375 \text{ K} = 102°\text{C}$$

By heating the copper slightly above 100°C, waiting until equilibrium is reached, and then rapidly cooling the copper back to room temperature, the number of vacancies trapped in the structure may be one thousand times greater than the equilibrium number of vacancies at room temperature. Thus, vacancy concentrations encountered in materials are often dictated by both thermodynamic and kinetic factors.

Example

Calculate the theoretical density of iron, and then determine the number of vacancies needed for a BCC iron crystal to have a density of 7.874 g /cm^3. The lattice parameter of iron is 2.866 * 10^{-8} cm. where two iron atoms are present in each unit cell and atomic weight of iron is 55.847g/mol.

Solution

$\rho = \frac{nA}{V_C N_A}$, where n is atoms/cell, A is atomic weight, V_C is cell volume,

N_A Avogadro's number ($6.022X10^{23}$ atoms/mol.

$$\rho = \frac{(2 \text{ atoms/cell})(55.847 \text{ g/mol})}{(2.866 \times 10^{-8} \text{ cm})^3(6.022 \times 10^{23} \text{ atoms/mol})} = 7.879 \text{ g/cm}^3$$

This calculation assumes that there are no imperfections in the crystal. Let's calculate the number of iron atoms and vacancies that would be present in each unit cell for a density of 7.874 g/cm^3:

$$\rho = \frac{(X \text{ atoms/cell})(55.847 \text{ g/mol})}{(2.866 \times 10^{-8} \text{ cm})^3(6.022 \times 10^{23} \text{ atoms/mol})} = 7.874 \text{ g/cm}^3$$

$$X \text{ atoms/cell} = \frac{(7.874 \text{ g/cm}^3)(2.866 \times 10^{-8} \text{ cm})^3(6.022 \times 10^{23} \text{ atoms/mol})}{(55.847 \text{ g/mol})} = 1.99878$$

There should be 2.00 − 1.99878 = 0.00122 vacancies per unit cell. The number of vacancies per cm^3 is

$$\text{Vacancies/cm}^3 = \frac{0.00122 \text{ vacancies/cell}}{(2.866 \times 10^{-8} \text{ cm})^3} = 5.18 \times 10^{19}$$

Note that other defects such as grain boundaries in a polycrystalline material contribute to a density lower than the theoretical value.

Interstitial Defects

An **interstitial defect** is formed when an extra atom or ion is inserted into the crystal structure at a normally unoccupied position, as in Figure 4-1(b). Interstitial atoms or ions, although much smaller than the atoms or ions located at the lattice points, are still larger than the interstitial sites that they occupy; consequently, the surrounding crystal region is compressed and distorted. Interstitial atoms such as hydrogen are often present as impurities, whereas carbon atoms are intentionally added to iron to produce steel. the interstitial atoms is one important way of increasing the strength of metallic materials. Unlike vacancies, once introduced, the number of interstitial atoms or ions in the structure remains nearly constant, even when the temperature is changed.

Substitutional Defects

A **substitutional defect** is introduced when one atom or ion is replaced by a different type of atom or ion as in Figure 4-1(c) and (d).

The substitutional atoms or ions occupy the normal lattice site. Substitutional atoms or ions may either be larger than the normal atoms or ions in the crystal structure, in which case the surrounding interatomic spacings are reduced, or smaller causing the surrounding atoms to have larger interatomic spacings. In either case, the substitutional defects disturb the surrounding crystal. Again, the substitutional defect can be introduced either as an impurity or as a deliberate alloying addition, and, once introduced, the number of defects is relatively independent of temperature.

Examples of substitutional defects add copper to nickel, copper atoms will occupy crystallographic sites where nickel atoms would normally be present. The substitutional atoms will often increase the strength of the metallic material. Substitutional defects also appear in ceramic materials. For example, if we add MgO to NiO.

Other Point Defects

A **Frenkel defect** is a vacancy-interstitial pair formed when an ion jumps from a normal lattice point to an interstitial site, as in Figure 4-1(e) leaving behind a vacancy. Although, this is usually associated with ionic materials, a Frenkel defect can occur in metals and covalently bonded materials.

A **Schottky defect**, Figure 4-1(f), is unique to ionic materials and is commonly found in many ceramic materials. When vacancies occur in an ionically bonded material, a stoichiometric number of anions and cations must be missing from regular atomic positions if electrical neutrality is to be preserved. For example, one Mg^{+2} vacancy and one O^{-2} vacancy in MgO constitute a Schottky pair. In ZrO2, for one Zr+4 vacancy, there will be two O-2 vacancies. An important substitutional point defect occurs when an ion of one charge replaces an ion of a different charge. This imperfection is observed in materials that have pronounced ionic bonding. Thus, in ionic solids, when point defects are introduced, the following rules have to be observed:

(a) a charge balance must be maintained so that the crystalline material as a whole is electrically neutral;

(b) a mass balance must be maintained; and

(c) the number of crystallographic sites must be conserved.

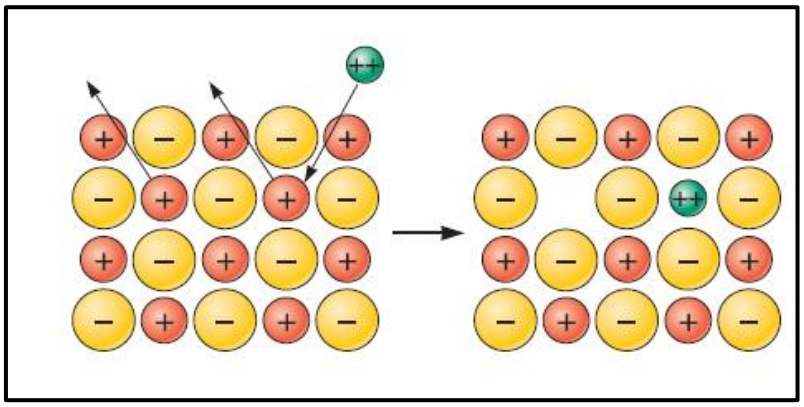

Figure 4-3 when a divalent cation replaces a monovalent cation, a second monovalent cation must also be removed, creating a vacancy.