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Materials Science and Engineering

This chapter is concerned with Materials Science and Engineering (MSE). As with all the chapters in Part II, there are several sections: overview several specific technical topics illustrative open-ended problems, and open-ended problems. The purpose of the first section is to introduce the reader to the subject of MSE. As one might suppose, a comprehensive treatment is not provided, although numerous references are included. The second section contains three open-ended problems; the authors' solution (there may be other solutions) is also provided. The third (and final) section contains 35 problems; *no* solutions are provided here.

1.1 Overview

This overview section is concerned—as can be noted from its title—with Materials Science and Engineering (MSE). As one might suppose, it was not possible to address all topics directly or indirectly related to MSE. Because of space limitations, only the subject of crystallography of perfect

crystals (CPC) is primarily addressed. However, additional details may be obtained from the references at the end of the chapter.

Note: Those readers already familiar with the details associated with MSE may choose to bypass this Overview.

The title, *Materials Science and Engineering*, implies a double focus—one geared toward a fundamental study of the materials and their properties, and the other towards the production and use of materials for the benefit of society. This chapter is primarily concerned with the former focus.

The terms *Materials* denotes a vast areas of compiled knowledge. There is very little in all of engineering and science that does not involve materials. Obviously, the first task in preparing an abbreviated chapter in the study of materials must be the application of limits on the subject matter to be covered—a focus on specific types of materials. It is generally understood that *Materials* covers only the solid state of matter; liquids are considered only in certain cases where solid-liquid equilibrium is involved. There are many types of solids, however, and further focusing is required.

Most solids can be categorized into one of the three types: metals, plastics, or ceramics. (Ceramics are compounds of metallic and non-metallic elements such as ferrous oxide.) In this chapter, emphasis has been placed on metals because, in the opinion of the authors, this class of materials has the widest impact on all of the four major fields of engineering: chemical, civil, electrical, and mechanical. In the end, the remainder of the chapter was divided into three sections. These are briefly discussed below.

The first topic covered is *Crystallography of Perfect Crystals* (CPC). All matter is ultimately composed of atomic particles. How these particles are put together plays an extremely important role in determining a material's properties and in the various uses of that material. The purpose of this section is to provide the reader some insights into how solids (mainly metals and ionic materials) are *organized* at the atomic level and how this organization is reflected in some of the properties of the solids. Just as the organization of atoms in a solid has a critical role in determining material properties, so too does the occasional *breakdown* of this organization since there is no such thing as a *perfect* crystal. No study of crystallography would therefore be complete without a companion study of crystal imperfections, and this is the role of the CRC (*Crystallography of Real Crystals*) section. These two sections (i.e., CPC and CRC) involve a study of the makeup of the crystalline materials from an atomic standpoint, but what happens on the atomic level must obviously be reflected at the macroscopic

level. The last sections discuss the behavior of materials more in terms of some directly measurable phenomena.

Finally, the reader should note that there are a host of topics that normally fall under the Materials Science and Engineering umbrella. Most of them are listed below:

1. Atomic Structure
2. Crystal Structures
3. Crystal Geometry
4. Crystalline Imperfections
5. Phase Diagrams
6. Mechanical Properties of Metals
7. Polymeric Materials
8. Diffusion in Solids
9. Engineering Alloys
10. Ceramics
11. Composite Materials
12. Corrosion
13. Electrical Properties
14. Optical Properties
15. Magnetic Properties
16. Superconductive Properties

1.2 Crystallography of Perfect Crystals (CPC)

As noted earlier, all matter is ultimately composed of atomic particles. How these particles are put together plays an extremely important role in determining a material's properties and in the various uses of that material. The purpose of the CPC (Crystallography of Perfect Crystals) section is to give the reader some insights into how solids (mainly metals and ionic materials) are organized on the atomic level and how this organization is reflected in some of the properties of the solids.

Solid materials may be either *amorphous* or *crystalline*. The word *amorphous* literally means “without form” and the atoms or molecules of solids in this category have little organization. The word *crystalline* implies that the component atoms, ions or molecules that make up the material are arranged spatially in an *ordered* pattern often referred to as a *crystal lattice*. In the solid state, metallic and ionic materials are almost universally found as crystals in nature; many covalent materials are crystalline as well.

There are many different types of crystal patterns or structures. For ionic and metallic materials, the main factor that determines the pattern

| CN | $(r/R)_{min}$ |
|----|---------------|
| 3 | 0.155 |
| 4 | 0.225 |
| 6 | 0.414 |
| 8 | 0.732 |
| 12 | 1.000 |

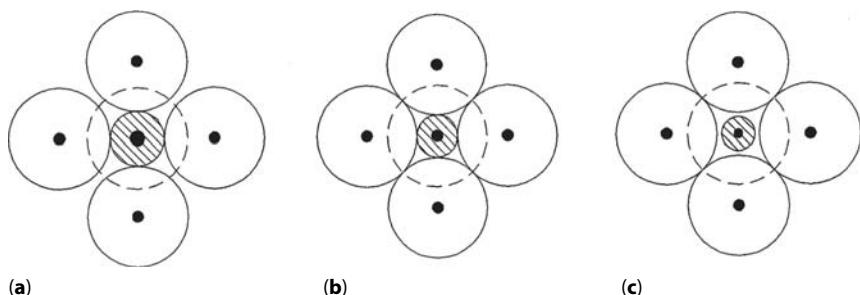


Figure 1.1 Coordination Number

or crystal type is the packing efficiency or the *packing factor*. Both metallic and ionic bonds are electrostatic in nature. As a result, the closer the bonded atoms are, the stronger are the bonding forces and the more stable is the crystal. For purposes of this explanation, assume the atoms of a crystal to be small hard spheres tightly packed together in an ordered pattern. The metallic crystal is composed of spheres all having the same size and an ionic crystal is constructed of spheres of at least two different sizes. The packing factor is defined as the fraction of space occupied by the spheres.

The *coordination number* (CN) of an atom in a crystal is defined as the number of nearest neighbors that atom possesses. All “nearest neighbors” must be equidistant from the atom in question, which shall be referred to as the *central atom*. In the case of ionic crystals, electrical stability requires that the central and neighboring atoms be oppositely charged. In a metal, all atoms of the crystal are positively charged and are held together by an electron cloud which pervades the entire crystal.

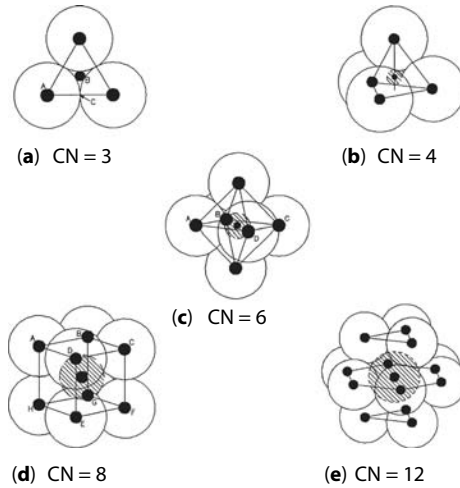


Figure 1.2 Coordination numbers of (a) 3, (b) 4, (c) 6, (d) 8, and (e) 12.

There are five coordination numbers that occur in nature; as noted in Table 1.1, these are 3,4,6,8 and 12. The crystal pattern that a given pair of ions form depends mainly on the relative sizes of the atoms or, equivalently, on the radius ratio (r/R). In this ratio, r represents the radius of the central atom and R the radius of the neighboring atoms. The central atom is always chosen as the smaller of the two ions.

Figure 1-1 shows arrangements for a CN of six. Note that the solid circles represent atoms whose centers are in the plane of the page; the dotted circle represents two atoms whose centers are above and below the plane of the page. In 1(a), the central atom is in contact with all six neighbors simultaneously, a fact which is critical for ionic bonding. As the (r/R) ratio is decreased, the spacing between the neighboring atoms becomes smaller until the situation depicted in 1(b) is achieved. In this diagram, the (r/R) ratio is 0.414, which is the minimum ratio that is capable of supporting a CN of six. For a ratio below this minimum, it is impossible to have the central atom contacting all six neighbors at the same time. In Table 1.1, the minimum radius ratios for the five coordination numbers are presented and in Figure 1.2, the atomic arrangements for the five CNs are depicted. In each of the five diagrams of Figure 1.2, the (r/R) ratio is at the minimum for that coordination number.

The minimum radius ratios in Table 1.1 can be calculated using simple geometric and trigonometric principles. Taking the coordination number of six as an example (see Figure 1-2(c)), the three-dimensional figure obtained by joining the centers of the neighboring atoms is an octahedron.

The two-dimensional figure formed by connecting atom centers A, B, and D is an isosceles right triangle. Since each leg of the triangle is $2R$ and the hypotenuse is $2R+2r$, the application of the Pythagorean theorem yields

$$(2R+2r)^2 = (2R)^2 + (2R)^2 \quad (1.1)$$

or

$$2R+2r = \sqrt{8R} \quad (1.2)$$

which can be rearranged to give

$$\left(\frac{r}{R}\right) = \left(\frac{r}{R}\right)_{min} = 0.414 \quad (1.3)$$

The significance of the information contained in Table 1.1 lies in the fact that it can be used to help explain why ionic and metallic materials form the types of crystals that they do. The radius ratio of sodium chloride, for example, has been determined by x-ray diffraction to be 0.54. Since this ratio is less than 0.732, sodium chloride cannot crystallize in a pattern that requires a CN of 8; the sodium ion is simply too small to fit eight chloride ions around its periphery. This leaves coordination numbers of 6, 4 and 3 as possibilities, with 6 as the most likely prospect, since of the three, it would result in the highest packing factor.

1.2.1 Geometry of Metallic Unit Cells

The term *Bravais lattice* refers to one of 14 different patterns employed in the structure of crystals. Three of these (the only three in which the points are arranged to form a cubic pattern) are shown in Figure 1.3. These three Bravais lattices are called simple cubic (sc), body centered cubic (bcc), and face centered cubic (fcc). Although the points of the Bravais lattices are depicted as spheres in these diagrams, the points do not (at least for now) represent atoms. The *Bravais lattice* is an abstraction consisting only of a six- or eight-sided box with points placed on either inside or on the box surface. Figure 1.4 would show the hexagonal Bravais lattice if the three points that fall completely inside the eight-sided box were absent.

In order to transform the abstraction of the Bravais lattice into a real crystal structure, each point of the lattice is allowed to represent a single

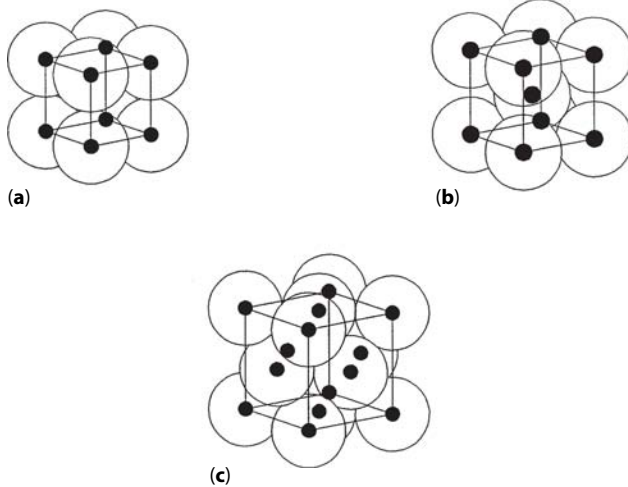


Figure 1.3 Bravais lattices: (a) simple cubic, (b) body-centered cubic, (c) face-centered cubic.

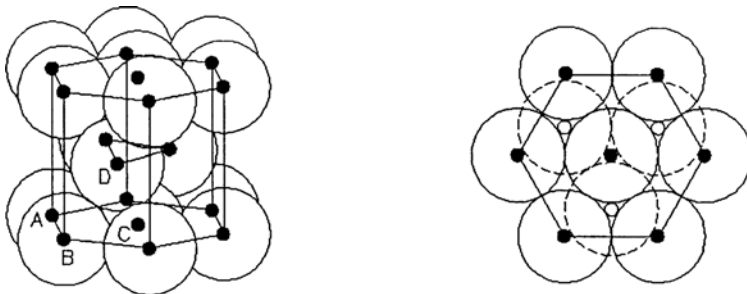


Figure 1.4 The hexagonal close-packed (hcp) unit cell.

atom or a set of atoms (like a pair of ions or a molecule). If each point of the fcc Bravais lattice shown in Figure 1.3(c) is replaced by a methane molecule, for example, the unit cell of the methane crystal (which, since methane is a gas at ambient conditions, is found only at very low temperatures) results. A unit cell can be considered the basic “building block” for the construction of the crystal, and as such must be representative of the entire crystalline material. By repeating the methane unit cell over and over again, the solid methane crystal would result.

1.2.2 Geometry of Ionic Unit Cells

In the previous subsection, it was seen that, for bcc and fcc metallic crystals, the transformation from the Bravais lattice to the unit cell is a matter

of replacing a point by a single spherical atom. For the hcp metallic crystal, each Bravais lattice point is replaced by two spherical atoms. In ionic materials, a *single* ion can never replace a Bravais lattice point; all points of the Bravais lattice must be identical and must have identical neighbors. The sodium chloride structure shown in Figure 1.5, for example, could have been arrived at by replacing a point of the sc Bravais lattice by a sodium ion and an adjacent point by a chloride ion, etc. The sodium chloride structure, however, is *not* simple cubic; it is face-centered cubic. To demonstrate this, if each point of the fcc Bravais lattice pictured in Figure 1.3(c) is replaced by an ion pair, for example, one chloride and a sodium ion placed to its immediate right, the structure shown in Figure 1.5 results.

Although simple cubic *metals* do not exist in nature, simple cubic *salts* (ionic crystals) do. Cesium chloride is an example. The CsCl structure can be demonstrated by replacing each point of the sc lattice shown in Figure 1.3(a) by a cesium ion–chloride ion pair to achieve the structure shown in Figure 1.6. In this case, the chloride ions were placed at each vertex, and only one cesium ion, the one in the center of the cube, is shown. The centers of the other seven cesium ions fall outside of the cube, and are members of adjacent unit cells. In this structure, the spherical ions are in contact along the body diagonal only. Only ions of opposite charge should be touching.

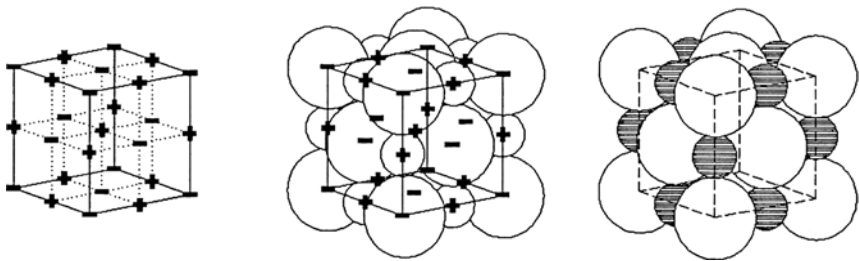


Figure 1.5 A fcc ionic unit cell (NaCl).

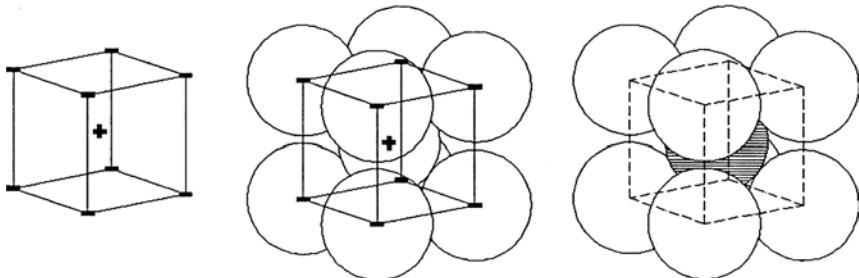


Figure 1.6 A bcc ionic unit cell (CsCl).

1.2.3 Packing Factors

As explained earlier, the *packing factor* is defined as the fraction of space in the crystal occupied by atoms, where once again, it is assumed the atom to be an incompressible sphere. The packing factor is conveniently calculated by first determining the number of atoms in the unit cell of the crystal, calculating the spherical volumes of those atoms and dividing by the total volume of the unit cell. For example, a simple cubic structure would have a packing factor of 0.52. This number is obtained by first finding the volume of *one* sphere of radius, r . (Figure 1.2(a) shows that there is one single atom per unit cell.) This volume is then divided by the unit cell volume which is determined by cubing the edge length, $2r$, as is shown by the following equation.

$$\frac{\left(\frac{4}{3}\right)\pi r^3}{(2r)^3} = 0.52 \quad (1.4)$$

For metals, the calculation of the packing factor depends only on the metal structure and not on the atom size. This is not the case for ionic solids when at least two different atom sizes must be taken into account.

Properties of materials fall into one of two categories: *extensive* and *intensive*. An *extensive* property is one that depends on the size of the material; volume and mass are examples of such properties. An *intensive* property is independent of size and the measurement of that property always yields the same value whether a small or large amount of the material is being used to make the measurement. *Density* is one such property.

The *unit cell* was described earlier as a representative portion of the crystal lattice. If the cell is truly representative, it must possess the same qualities as the crystal that it represents. It is therefore theoretically possible to use a single unit cell as a basis for calculating intensive properties. (Note: the term *basis* is used to indicate that amount of materials on which a calculation is being performed. In many problems, amounts are not specified and as long as the problem involves intensive properties, the choice of a basis is arbitrary and left to the individual performing the calculation.)

1.2.4 Directions and Planes

Many crystal phenomena are directional. For example, when a metal crystal is plastically deformed (i.e., permanently distorted), parts of the crystal

move relative to other parts. This slippage occurs in certain predictable directions and along certain predictable atom planes. Many crystal properties are also directional, e.g., the elastic modulus, ductility and conductivity. It is important, therefore, that directions and planes of a crystal be identifiable.

The right-handed three-dimensional coordinate system that will be used in this discussion is given on the left side of Figure 1.7. In the two cubes shown in Figure 1.7, five directions (indicated by vectors) are also shown. Directions are represented symbolically by $[hkl]$, where h , k , and l are three small whole numbers called *indices* that correspond to the cartesian coordinates x , y , and z . Note that there are no commas between the numbers. The indices for a given direction are determined as follows. The base of the vector is chosen as the origin of the coordinate system. The coordinates of the tip of the arrowhead are then determined. Using direction (a) as an example, the coordinates of the arrowhead are $(0,0,1)$. (Note: the physical coordinates of the arrowhead would have length dimensions and be given in terms of a , the cell constant. In this example, those coordinates are $(0,0,a)$. For purposes of determining the indices, however, the cell constant is considered to be one mathematical unit and the coordinates are given as pure numbers.) The coordinates of the arrowhead tip yield the indices. The directions (a), (b), and (c) are represented by $[001]$, $[111]$ and $[110]$, respectively. The tip of the arrowhead for direction (d) has the coordinates $(1,0,-1)$ and is represented by $[10\bar{1}]$. Note that a negative direction is indicated by a bar over the index. For (e), the arrowhead has the coordinates $(1,0,1/2)$, which, following the rules for finding the indices given so far, would yield $[1\ 0\ 1/2]$. However, the indices should be small whole numbers. Since the direction indicated by vector (e) also passes through the points $(2,0,1)$ and $(4,0,2)$, that direction could also be feasibly represented by $[201]$ and $[402]$. In other words, multiplying the coordinates and indices by a positive number does not alter the direction. The convention used here is to multiply the indices by the smallest positive integer that will convert all three to small whole numbers. Direction (e) should be therefore represented by $[201]$.

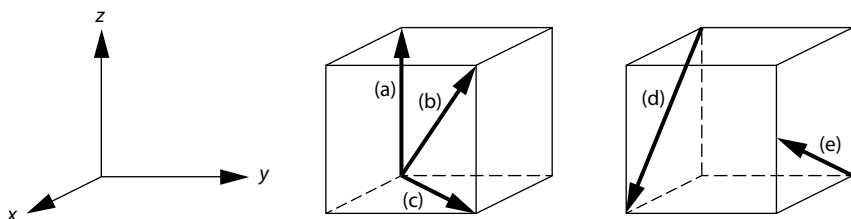


Figure 1.7 Crystal directions.

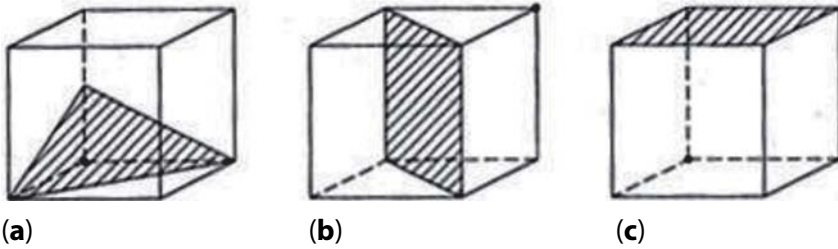


Figure 1.8 Crystal planes.

The atom planes of a crystal are represented by the symbol (hkl) , where once again h , k , and l are small whole numbers. (It is important that the reader distinguish between the symbols used for coordinates and planes. Both employ parentheses, but the coordinates of a point are separated by commas and need not be small whole numbers. No commas appear in the symbol for a plane.) It takes three points to fix the position of a plane in space (see Figure 1.8), unless the points are along the same straight line. The indices of a plane are sometimes referred to as *Miller indices*, and will not be described here. The reader is referred to the literature for additional details.

1.3 Crystallography of Real Crystals (CRC)

Besides structural defects, real crystals also contain impurities (as long as the temperature is above absolute zero). The word *impurity* implies a mixture of at least two substances. In crystals, the mixture; can be one of two types: a single-phase or homogeneous mixture, and a multiphase or heterogeneous mixture. A single-phase mixture is a *true* solution in which the solute is dispersed on an atomic level. This means that the atoms, ions, or molecules of the solute are surrounded mainly by particles of the solvent. A multiphase mixture is not *mixed* on an atomic level and is therefore not the same throughout its volume; it has different parts with different detectable properties. A multiphase metal alloy such as steel at room temperature may appear to be of uniform composition to the naked eye, but through a microscope (and with proper sample preparation), two different phase or parts can be detected. It should be pointed out that in a multiphase mixture, if the phases or parts could be conveniently separated into single phase, these single phases would still be mixtures. A 50-50 w/o (weight percent) alloy of silver and aluminum,

for example, forms two solid phases, which are assigned the symbols, α and β . (Note: A 93 w/o silver- 7 w/o aluminum alloy is called *sterling silver*). Both phases are easily seen through a microscope. The α phase is composed of fcc silver crystals with aluminum atoms occupying about 5-10% of the lattice sites; the β phase is made up of fcc aluminum crystals with silver atoms occupying about 1-3% of the lattice sites. This type of crystal impurity where the impurity atom replaces one of the solvent atoms (the aluminum impurities in the α phase, for example) is called a *substitution* impurity, and the mixture is often referred to as a *substitutional alloy*. There is another type of impurity, the *interstitial* impurity, where the impurity atoms does not occupy a lattice site, but instead is wedged in among the solvent atoms. This type of impurity is the subject of the next subsection.

1.3.1 Interstitial Impurities

The second type of impurity that occurs in crystals is the *interstitial* impurity. When carbon dissolves in iron, it forms such an impurity---the carbon atoms do not replace any iron atoms but wedge into the open spaces among the iron atoms. Iron is a *polymorph*. A *polymorph* is a material that can form more than one crystal structure. At room temperature, and up to 912 °C (1673 °F), the stable crystal structure of iron is bcc (an iron phase given the symbol α). From 912°C to around 1400°C (2550°F), the stable structure is fcc (assigned the symbol γ), and from 1400°C to the melting point at 1540 °C (2800°F), bcc given the symbol, δ .

Carbon has a much higher solubility in fcc iron (about 2.1 w/o at 1150 °C) than in bcc iron (about 0.02 w/o maximum in the α phase and slightly higher in the δ phase). This fact is surprising, at first glance, because the bcc structure is not as well packed as the fcc structure. Metals with a bcc structure have a packing factor of 0.68 and a coordination number of 8; fcc metals have a packing factor 0.72 and a coordination number of 12. This indicates that there is more empty space in the bcc form of iron (which is true), and therefore more carbon atoms should fit into that space (which is false). This apparent discrepancy can be explained by the fact that the greater amount of empty space in the bcc crystal is distributed over openings that are very non-spherical in shape. These non-spherical spaces can comfortably accommodate spherical atoms only if the atoms are extremely small, about one-eighth the size of the carbon atom.

The interstitial holes in fcc iron and bcc iron is pictorially represented in Figure 1.9.

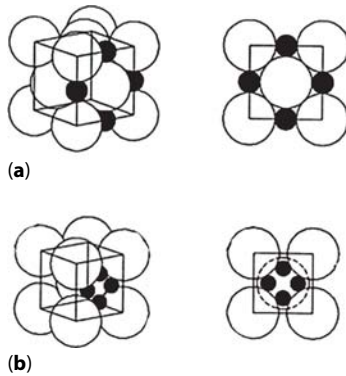


Figure 1.9 Interstitial spherical holes in (a) fcc iron, (b) bcc iron.

1.4 Materials of Construction

The selection of the materials with which to build a chemical or petrochemical process plant is a very important part of process design. It is desirable to select the least expensive material that can be used for any particular piece of equipment in the plant. (Note that “equipment” here refers to piping, valves and fittings as well as to pumps, columns, heat exchangers, etc.) In order to be acceptable, however, a material must have adequate mechanical strength and adequate resistance to chemical attack (corrosion) under plant operating conditions.

Mechanical strength requirements depend on the process conditions (pressure and temperature), the size of the equipment, and the equipment’s own support requirements. In general, the larger the piece of equipment and the higher the pressure, the greater strength is needed. This can be provided either by using thicker materials or by selecting materials with inherently higher strength. For most materials, strength decreases with increasing temperature; so high temperature processes require thicker or different materials.

Corrosion resistance depends on the chemicals being processed and the conditions under which they are handled. Very often, special alloy metals or other exotic materials are required to avoid rapid corrosion of the equipment. Designers usually try to select materials that will have predicted lifetimes of 20 to 50 years or more actual under process conditions. Sometimes this is impossible, and the equipment must be frequently replaced.

Carbon steel and common plastics, such as polyvinyl chloride and polyethylene, are the least expensive materials used in process plants. The selection process starts with them, then considers successively more expensive

materials until one is found that has the required mechanical and corrosion-resistance properties.

1.5 Resistivity

The electrical behavior of certain solids, particularly semiconductors, can be explained (and, to some extent, quantified) using atomic-level phenomena. This was not done to any appreciable degree earlier where the connection between the atomic and macroscopic levels was not as well established, at least in a quantitative sense.

Ohm's law states that, when a potential or voltage difference is placed across a conductor, the resulting current is proportional to the voltage difference. More succinctly stated

$$E = IR \quad (1.5)$$

where E = voltage difference, volt

I = current, amp

R = resistance, ohm

The resistance term R is a proportionality constant that depends on the nature of the conductor, including its size and shape. Although resistance is a strong function of the material that the conductor is made of, it cannot be called a property of that material. For a quantity to be properly called a property, it must be a function only of the material of which it is made.

If the conductor is a wire of length, l, and cross-sectional area, A, it can be shown by experimentation that the wire's resistance depends almost entirely on four variables: the material, the temperature, the cross-sectional area, and the length. For convenience, the temperature may be lumped with the material to reduce the number of independent variables. In other words, copper at 1000 °F is considered a different "material" than copper at 70°F, which it is. This results in the functional relationship

$$R = f(\text{material}, T, A) \quad (1.6)$$

Laboratory experimentation also shows that resistance is directly proportional to wire length and inversely proportional to cross-sectional area. Removing the length and area dependence from R should leave a variable that depends only on the material (at a given temperature), or, in other words, should leave a variable that is, by definition, a property. This is shown in the equation.

$$R = \rho \left(\frac{l}{A} \right) \quad (1.7)$$

Where ρ is the resistivity of the material. The resistivities for many materials at specified temperatures can be found in the literature. Typical units for ρ are ohm·in, etc.

1.6 Semiconductors

Semiconductors fall into one of two categories: *intrinsic* and *extrinsic*. A semiconductor that conducts in the pure state is an *intrinsic semiconductor*. One that has had to have material added to it to get it to conduct is an *extrinsic semiconductor*. Extrinsic semiconductors are commonly used in most electronic applications. The *matrix* or *solvent* material is usually a single crystal of silicon or germanium. Both these elements belong to the carbon family and, like carbon (diamond), form crystals in which there are three-dimensional networks of covalent bonds. In diamond, silicon, and germanium crystals, each atom is covalently bonded to four neighboring atoms arranged in tetrahedral fashion. The angle between any two of the four bonds is the tetrahedral angle of 109.5° .

There are various classes of materials, metals, and alloys. Perry and Green [1] provided the following categorization:

1. Ferrous metals
2. Ferrous alloys
3. Organic non-metallics
4. Thermoplastics

These are also divided into low-temperature metals and high-temperature materials.

A detailed and expanded treatment of materials science and engineering is available in the following three references:

1. W.F. Smith, *Formulations of Materials Science and Engineering*, McGraw-Hill, New York City, NY, 2004. (ref(2))
2. L. VanVlack, *Materials Science for Engineers*, Addison Wesley, Reading, MA, 1970. (ref(3))

3. W. Callister, *Materials Science and Engineering*, 3rd edition, John Wiley & Sons, Hoboken, NJ, 1985. (ref(4))

1.7 Illustrative Open-Ended Problems

This and the last section provide open-ended problems. Solutions *are* provided for the three problems in this Section in order for the reader to obtain a better understanding of these problems which differ from the traditional problems/illustrative examples. The first problem is relatively straightforward while the third (and last problem) is somewhat more difficult and/or more complex. Note that solutions are not provided for the 35 open-ended problems provided in the next Section.

Problem 1: Discuss the periodic table in layman terms.

Solution: At the time of publication, a total of 118 elements were known. These elements vary widely in location, concentration, and abundance on planet Earth. For example, over 75 percent of the Earth's crust consists of oxygen and silicon. Interestingly, approximately 65 percent by mass of the human body is oxygen. As the number and information on elements increased, chemists attempted to find similarities in elemental as well as chemical behavior. These efforts ultimately resulted in the development of the *Periodic Table*. This has gone through significant changes over the years, with the latest "form" arranging elements in order of increasing atomic number and with elements having similar properties placed in vertical columns known as *groups*.

Problem 2: Discuss structural defects in crystals.

(Comment: There are many types of structural defects in crystals, but only a few will be cited. For a more thorough discussion of these defects, the reader is referred to the literature.)

Solution: There is no such thing as a *perfect* crystal. The reason why imperfections exist in crystals is explained below. Just as the organization of atoms in a solid has a critical role in determining material properties, so to does the occasional *breakdown* of this organization have an important effect. No study of crystallography would be complete without a companion study of crystal imperfections.

Unless a system is at the temperature of absolute zero atomic motion must be occurring inside the crystal. *Temperature* is described as a

measure of the *average* kinetic energy of the particles in a system. The use of the word *average* implies that these particle kinetic energies are *distributed*—most particles have energies somewhere around the average, but a few have either very low or excessively high energies. (This distribution of particle energies is called the *Maxwell-Boltzmann distribution*.) Below the melting point, most atoms, ions or molecules of a solid exhibit their kinetic energies by vibrating about fixed positions. In a crystal, the fixed positions are the lattice sites. A relatively small number of particles, however, have kinetic energies that are greater than the bonding energies that hold the other particles close to their assigned sites. These particles are capable of moving away from these sites and causing structural defects in crystals.

Structural defects fall into three categories: point, line and area defects. Two of the more common point defects are the *vacancy* and the *interstitialcy*. A vacancy is defined as a lattice site or position that is unoccupied. If the central atom in a unit cell became one of the *high energy* atoms mentioned earlier, it would move out of the center position, squeeze its way past the vertex atoms (the atoms are not really *hard* spheres and are capable of compression), and end up somewhere else in the lattice. The vertex atoms would tend to collapse in toward the center, but a gaping hole, the *vacancy*, would remain. The center of the cell is now referred to as a vacant site. The movement of the surrounding atoms out of their positions is generally slight and is referred to as *lattice strain*. If the high energy atom discussed above ended up wedged somewhere in the lattice where it does not belong, it becomes an *interstitial defect*. The *interstitial defect* is defined as an atom or ion occupying a non-lattice position. Obviously, the presence of the interstitial defect also produces lattice strain by displacing the neighboring atoms from their positions.

Problem 3: Describe Bragg's Law in technical terms.

Solution: When a pencil-thin beam of monochromatic x-rays (i.e., x-rays of fixed wavelength) is directed at a single crystal, each atom in the crystal, acting individually, scatters a tiny fraction of the radiation in all directions. The amount scattered by one atom is far too small to be measured; the combined scattering by all atoms of the crystal, however, while still only a small fraction of the incident radiation, can be detected fairly easily. The combined scattered, or *diffracted*, radiation does not occur in all directions as does that scattered by the individual atom. When a number of x-ray beams are added together, the combined intensity will be the sum of the individual intensities only if all the individual beams are completely in

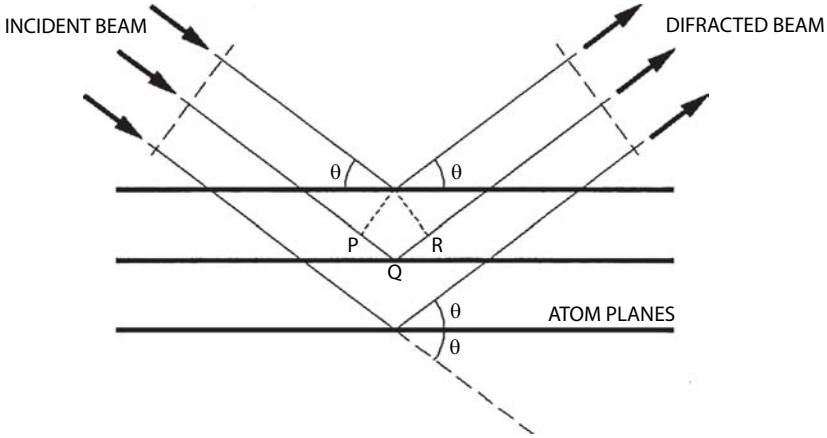


Figure 1.10 Bragg's law of diffraction.

phase. If the individual beams are out of phase with each other, the result will be mutual destructive interference and the total intensity will be from the whole crystal is intense enough to be detected only when all the rays scattered from the individual atoms are completely in phase. This can happen only when a set of atomic planes in the crystal is aligned at a definite angle to the incident x-ray beam.

The above situation is illustrated in Figure 1.10. Note that the angle, θ , must be such that the *difference in path length* traveled between adjacent segments of the x-ray beam (PQR) is exactly one full wavelength (or an integral number of wavelengths). This insures that the diffracted segments are in phase. If this path length difference is any other than an integral number of wavelengths, the result is destructive interference, and in effect, mutual annihilation of the diffracted beam.

The relationship existing among the wavelength, λ , the angle of incidence, θ_{hkl} and the interplanar distance, d_{hkl} is given by *Bragg's Law of Diffraction*:

$$n\lambda = 2d_{hkl} \sin\theta_{hkl} \quad (1.8)$$

where h, k, and l represent the aforementioned Miller indices of the diffracting plane and n is the number (integer) of wavelengths that make up the path length difference (PQR in Figure 1.10). The value of n is referred to as the *order of diffraction* and may usually be assumed to be unity. If this relationship is not satisfied, diffraction cannot occur. This means that

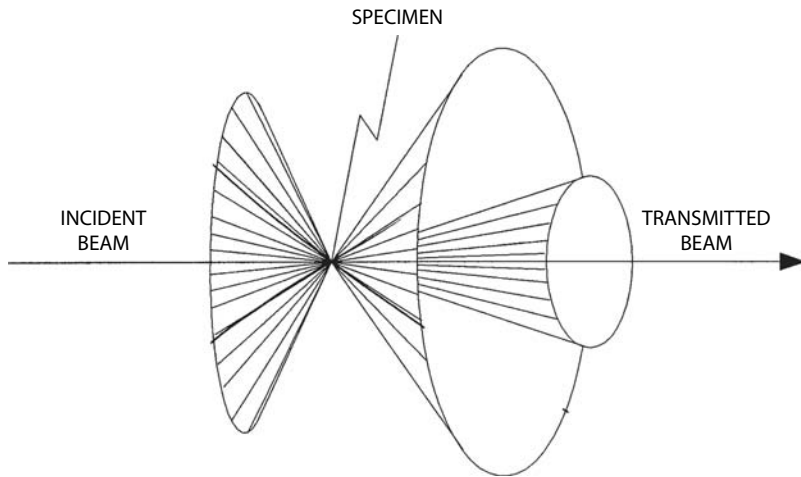


Figure 1.11 X-ray diffraction of finely divided powder.

directing a monochromatic x-ray beam at a single crystal will, in all probability, not result in diffraction unless care is taken to align a set of planes in the crystal at the proper angle of incidence. Taking the (200) planes as an example, the proper angle of incidence would be, according to Bragg's law:

$$\theta_{hkl} = \sin^{-1}(\lambda/2d_{200}) \quad (1.9)$$

If, instead of a single crystal, however, a finely divided powder of the crystalline sample is introduced into the x-ray beam, diffraction is guaranteed. The reason for this is that, in the finely divided powder, all possible crystal orientations are represented and, hence, at least a few of the crystalline grains are bound to have their (hkl) planes aligned at the Bragg angle, θ_{hkl} , to the incident beam. Each beam diffracted from one of the properly aligned crystallites contributes to a cone of radiation which is concentric with the incident beam; the semi-apex angle of this cone is twice the Bragg angle, or $2\theta_{hkl}$. Note that, since the angle formed by the diffracting plane and the incident beam is θ , and the angle formed by the diffracting plane and the diffracted beam is also θ , the angle formed by the transmitted beam and the diffracted beam is 2θ (see Figure 1.11).

The diffraction or Bragg angle, θ , cannot be *directly* measured because there is no instrumentation available for detecting the orientations of atom planes. (These plane orientations can be *calculated*, but not *measured*.) The angle, 2θ , however, can be measured because it is the angle between two

x-ray beams (the transmitted beam and the diffracted beam) and the positions of x-ray beams *can* be detected. In fact, the only measurements that need to be taken in powder x-ray diffraction are those of the angle 2θ . All information such as d-spacings, cell constants, and atomic/ionic radii comes from those measurements.

1.8 Open-Ended Problems

This last Section of the chapter contains open-ended problems as they relate to Materials Science and Engineering. No detailed and/or specific solution is provided; that task is left to the reader, noting that each problem has either a unique solution or a number of solutions or (in some cases) no solution at all. These are characteristics of open-ended problems described earlier.

There are comments associated with some, but not all, of the problems. The comments are included to assist the reader while attempting to solve the problems. However, it is recommended that the solution to each problem should initially be attempted *without* the assistance of the comments.

There are 35 open-ended problems in this Section. As stated above, if difficulty is encountered in solving any particular problem, the reader should next refer to the comment, if any is provided with the problem. The reader should also note that the more difficult problems are generally located at or near the end of the Section.

1. Describe the early history associated with material science and engineering.
2. Discuss the recent advances in materials science and engineering.
3. Select a refereed, published article on materials science and engineering from the literature and provide a review.
4. Provide some normal everyday domestic application involving the general topic of materials science and engineering.
5. Develop an original problem in materials science and engineering that would be suitable as an illustrative example in a book.
6. Prepare a list of the various books that have been written on materials science and engineering. Select the three

- best and justify your answer. Also select the three weakest books and justify your answer.
7. Define and discuss materials science and engineering in layman terms.
 8. Why is the general subject of materials science and engineering important to the chemical engineer?
 9. Attempt to improve on the present state of chemical nomenclature.
 10. Define atomic number and mass number and explain their difference(s). Also discuss the basis/reasoning of representing the atomic mass unit as a Dalton.
 11. Define an isotope in layman terms.
 12. In your own words, provide a description of nuclear chemistry.
 13. Discuss the impact nanotechnology has on the teaching of materials science and engineering.
 14. Explain in technical detail the wave nature of light.
 15. Explain the electronegative spectrum in both technical and layman terms.
 16. Describe the history of the periodic table. (Comment: See Problem 1 in the previous Section.)
 17. Attempt to improve the present format of the periodic table. (Comment: See Problem 1 in the previous Section.)
 18. Discuss the role the Boltzmann constant plays in materials science and engineering.
 19. Describe Bragg's Law in layman terms. (Comment: See problem 3 in the previous Section)
 20. Provide a brief description of ferrous metals and alloys.
 21. List some of the various organic non-metals.
 22. Describe each of the following materials:
 - a. High silicon cast irons
 - b. Stainless steel
 - c. Hastalloy
 23. Describe the various alloys of aluminum.
 24. What is the difference between brass and bronze?
 25. List and describe the various thermoplastics.
 26. Provide examples of low-temperature materials and high-temperature materials.
 27. List some of the various inorganic nonmetallics

28. Provide your own thoughts on the future of ceramic materials.
29. Describe the various corrosion-testing methods.
30. Provide some key properties of the following materials:
 - Wood
 - Natural rubber
 - Carbon and graphite
 - Asphalt
31. Obtain the thermal conductivities of a dozen common insulating materials. (Comment: This will require reviewing the materials literature.)
32. Explain why most pierced ears are allowed to heal with a gold post in the opening.
33. Describe the relationship between the modulus of elasticity of an amorphous polymer and the glass transition temperature. Also provide the explanation in graphical form.
34. You have been hired as a consultant to provide a recommendation to replace gold-plated pieces in computer chips with either copper or steel. Prepare an abstract of a report you would submit in this recommendation.
35. A company's research laboratory determines that the density of platinum is 21.51 g/cc. However, the value listed in the literature is 21.45 g/cc. Assuming that each value is accurate to 4 significant digits, that the discrepancy is due to atom vacancies alone, and that the vacancies have no effect on the crystal volume, determine what fraction of the unit cells with measured density contains vacancies, or, equivalently, the number of vacancies per unit cell. (Comment: One should first note that the number of vacancies per unit cell is equivalent to the fraction of unit cells. To demonstrate this fact, first assume that a unit cell cannot contain more than one vacancy. This is a valid assumption; a minuscule number of cells may, in fact, have more than once vacancy, but because of the extremely small number of vacancies (one out of 369 sites, in this case), one can expect the vacancies to be widely distributed throughout the crystal, and the chances of two vacancies occupying the same cell to be almost non-existent. If 10,000 unit cells contain

11 vacancies (as in this problem), one may conclude that 11 of those cells contain on the average, one vacancy each. This is the same as saying that 11/10,000 or 0.011 of the unit cells contain vacancies.

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