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The Nature of Materials

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An understanding of materials is fundamental in the study of manufacturing processes. In Chapter 1, manufacturing was defined as a transformation process. It is the material that is transformed; and it is the behavior of the material when subjected to the particular forces, temperatures, and other physical parameters of the process that determines the success of the operation. Certain materials respond well to certain types of manufacturing processes and poorly or not at all to others. What are the characteristics and properties of materials that determine their capacity to be transformed by the different processes?

Part I of this book consists of four chapters that address this question. The current chapter considers the atomic structure of matter and the bonding between atoms and molecules. It also shows how atoms and molecules in engineering materials organize themselves into two structural forms: crystalline and noncrystalline. It turns out that the basic engineering materials—metals, ceramics, and polymers—can exist in either form, although a preference for a particular form is usually exhibited by a given material. For example, metals almost always exist as crystals in their solid state. Glass (e.g., window glass), a ceramic, assumes a noncrystalline form. Some polymers are mixtures of crystalline and amorphous structures.

Chapters 3 and 4 discuss the mechanical and physical properties that are relevant in manufacturing. Of course, these properties are also important in product design. Chapter 5 is concerned with several part and product

attributes that are specified during product design and must be achieved in manufacturing: dimensions, tolerances, and surface finish. Chapter 5 also describes how these attributes are measured.

2. Atomic Structure and the Elements

The basic structural unit of matter is the atom. Each atom is composed of a positively charged nucleus, surrounded by a sufficient number of negatively charged electrons so that the charges are balanced. The number of electrons identifies the atomic number and the element of the atom. There are slightly more than 100 elements (not counting a few extras that have been artificially synthesized), and these elements are the chemical building blocks of all matter.

Just as there are differences among the elements, there are also similarities. The elements can be grouped into families and relationships established between and within the families by means of the Periodic Table, shown in Figure 2.1. In the horizontal direction there is a certain repetition, or periodicity, in the arrangement of elements. Metallic elements occupy the left and center portions of the chart, and nonmetals are located to the right. Between them, along a diagonal, is a transition zone containing elements called *metalloids* or *semimetals*. In principle, each of the elements can exist as a solid, liquid, or gas, depending on temperature and pressure. At room temperature and atmospheric pressure, they each have a natural phase; e.g., iron (Fe) is a solid, mercury (Hg) is a liquid, and nitrogen (N) is a gas.

Metals																		Transition Zone				Nonmetals					
IA		IIA												IIIA	IVA	VA	VIA	VIIA	VIIIA								
1	1 H													5 B	6 C	7 N	8 O	9 F	10 Ne								
2	3 Li	4 Be											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar									
3	11 Na	12 Mg	IIIB	IVB	VB	VIB	VII B	VIII B			IB	IIB	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr									
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr									
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe									
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn									
7	87 Fr	88 Ra	89 Ac																								
				58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu										
				90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lw										

FIGURE 2.1 Periodic Table of Elements. The atomic number and symbol are listed for the 103 elements.

In the table, the elements are arranged into vertical columns and horizontal rows in such a way that similarities exist among elements in the same columns. For example, in the extreme right column are the **noble gases** (helium, neon, argon, krypton, xenon, and radon), all of which exhibit great chemical stability and low reaction rates. The **halogens** (fluorine, chlorine, bromine, iodine, and astatine) in column VIIA share similar properties (hydrogen is not included among the halogens). The **noble metals** (copper, silver, and gold) in column IB have similar properties. Generally, there are correlations in properties among elements within a given column, whereas differences exist among elements in different columns.

Many of the similarities and differences among the elements can be explained by their respective atomic structures. The simplest model of atomic structure, called the planetary model, shows the electrons of the atom orbiting around the nucleus at certain fixed distances, called shells, as shown in Figure 2.2. The hydrogen atom (atomic number 1) has one electron in the orbit closest to the nucleus. Helium (atomic number 2) has two. Also shown in the figure are the atomic structures for fluorine (atomic number 9), neon (atomic number 10), and sodium (atomic number 11). One might infer from these models that there is a maximum number of electrons that can be contained in a given orbit. This turns out to be correct, and the maximum is defined by

$$\text{Maximum number of electrons in an orbit} = 2n^2$$

where n identifies the orbit, with $n = 1$ closest to the nucleus.

The number of electrons in the outermost shell, relative to the maximum number allowed, determines to a large extent the atom's chemical affinity for other atoms. These outer-shell electrons are called **valence electrons**. For example, because a hydrogen atom has only one electron in its single orbit, it readily combines with another hydrogen atom to form a hydrogen molecule H_2 . For the same reason, hydrogen also reacts readily with various other elements (e.g., to form H_2O). In the helium atom, the two electrons in its only orbit are the maximum allowed ($2n^2 = 2(1)^2 = 2$), and so helium is very stable. Neon is stable for the same reason: Its outermost orbit ($n = 2$) has eight electrons (the maximum allowed), so neon is an inert gas.

In contrast to neon, fluorine has one fewer electron in its outer shell ($n = 2$) than the maximum allowed and is readily attracted to other elements that might share an

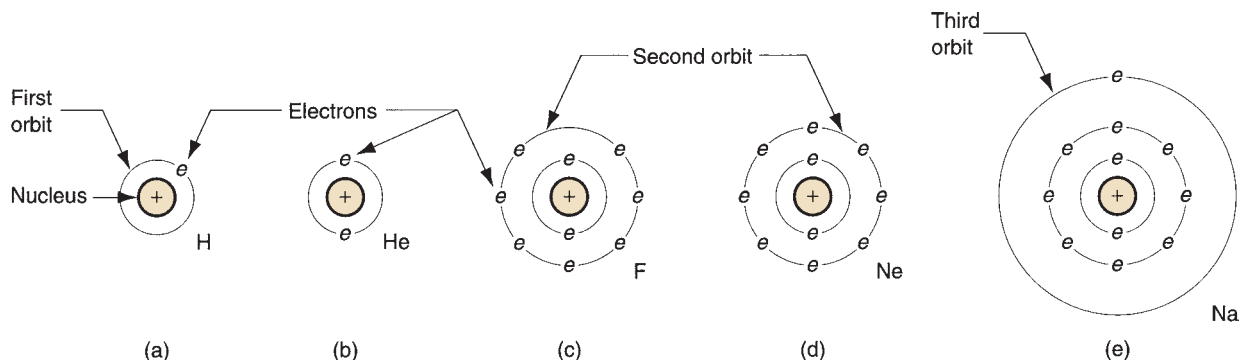
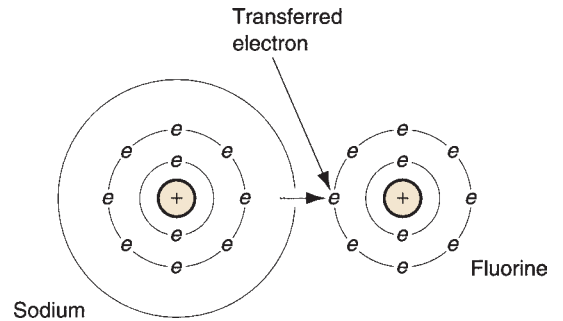


FIGURE 2.2 Simple model of atomic structure for several elements: (a) hydrogen, (b) helium, (c) fluorine, (d) neon, and (e) sodium.

FIGURE 2.3 The sodium fluoride molecule formed by the transfer of the “extra” electron of the sodium atom to complete the outer orbit of the fluorine atom.



electron to make a more stable set. The sodium atom seems divinely made for the situation, with one electron in its outermost orbit. It reacts strongly with fluorine to form the compound sodium fluoride, as pictured in Figure 2.3.

At the low atomic numbers considered here, the prediction of the number of electrons in the outer orbit is straightforward. As the atomic number increases to higher levels, the allocation of electrons to the different orbits becomes somewhat more complicated. There are rules and guidelines, based on quantum mechanics, that can be used to predict the positions of the electrons among the various orbits and explain their characteristics. A discussion of these rules is somewhat beyond the scope of this coverage of manufacturing materials.

2.2 Bonding between Atoms and Molecules

Atoms are held together in molecules by various types of bonds that depend on the valence electrons. By comparison, molecules are attracted to each other by weaker bonds, which generally result from the electron configuration in the individual molecules. Thus, we have two types of bonding: (1) primary bonds, generally associated with the formation of molecules; and (2) secondary bonds, generally associated with attraction between molecules. Primary bonds are much stronger than secondary bonds.

Primary Bonds Primary bonds are characterized by strong atom-to-atom attractions that involve the exchange of valence electrons. Primary bonds include the following forms: (a) ionic, (b) covalent, and (c) metallic, as illustrated in Figure 2.4. Ionic and covalent bonds are called *intramolecular* bonds because they involve attractive forces between atoms within the molecule.

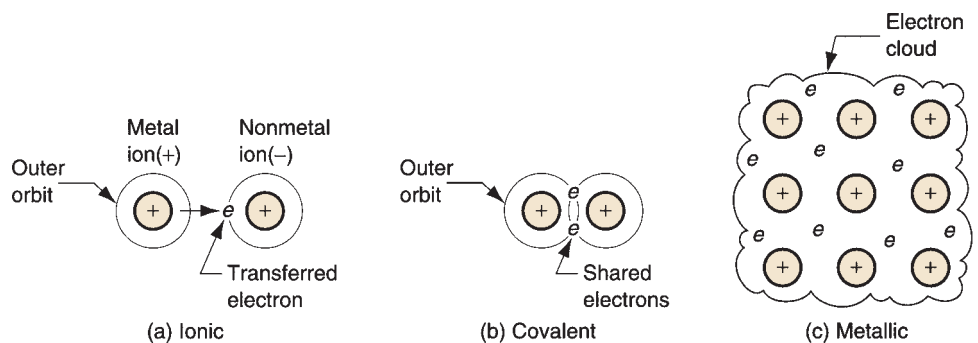


FIGURE 2.4 Three forms of primary bonding: (a) ionic, (b) covalent, and (c) metallic.

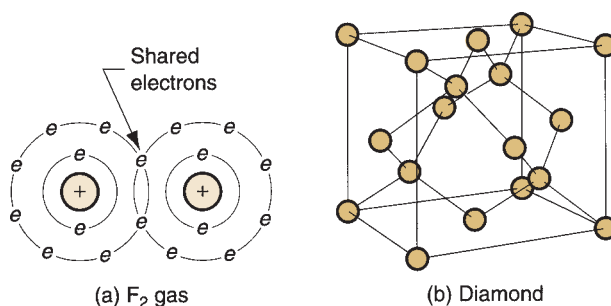
In the **ionic bond**, the atoms of one element give up their outer electron(s), which are in turn attracted to the atoms of some other element to increase their electron count in the outermost shell to eight. In general, eight electrons in the outer shell is the most stable atomic configuration (except for the very light atoms), and nature provides a very strong bond between atoms that achieves this configuration. The previous example of the reaction of sodium and fluorine to form sodium fluoride (Figure 2.3) illustrates this form of atomic bond. Sodium chloride (table salt) is a more common example. Because of the transfer of electrons between the atoms, sodium and fluorine (or sodium and chlorine) **ions** are formed, from which this bonding derives its name. Properties of solid materials with ionic bonding include low electrical conductivity and poor ductility.

The **covalent bond** is one in which electrons are shared (as opposed to transferred) between atoms in their outermost shells to achieve a stable set of eight. Fluorine and diamond are two examples of covalent bonds. In fluorine, one electron from each of two atoms is shared to form F_2 gas, as shown in Figure 2.5(a). In the case of diamond, which is carbon (atomic number 6), each atom has four neighbors with which it shares electrons. This produces a very rigid three-dimensional structure, not adequately represented in Figure 2.5(b), and accounts for the extreme high hardness of this material. Other forms of carbon (e.g., graphite) do not exhibit this rigid atomic structure. Solids with covalent bonding generally possess high hardness and low electrical conductivity.

The metallic bond is, of course, the atomic bonding mechanism in pure metals and metal alloys. Atoms of the metallic elements generally possess too few electrons in their outermost orbits to complete the outer shells for all of the atoms in, say, a given block of metal. Accordingly, instead of sharing on an atom-to-atom basis, **metallic bonding** involves the sharing of outer-shell electrons by all atoms to form a general electron cloud that permeates the entire block. This cloud provides the attractive forces to hold the atoms together and form a strong, rigid structure in most cases. Because of the general sharing of electrons, and their freedom to move within the metal, metallic bonding provides for good electrical conductivity. Other typical properties of materials characterized by metallic bonding include good conduction of heat and good ductility. (Although some of these terms are yet to be defined, the reader's general understanding of material properties is assumed.)

Secondary Bonds Whereas primary bonds involve atom-to-atom attractive forces, secondary bonds involve attraction forces between molecules, or **intermolecular forces**. There is no transfer or sharing of electrons in secondary bonding, and these bonds are

FIGURE 2.5 Two examples of covalent bonding:
(a) fluorine gas F_2 , and
(b) diamond.



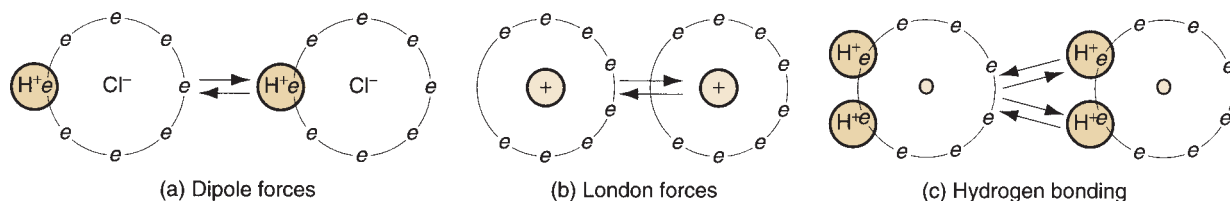


FIGURE 2.6 Three types of secondary bonding: (a) dipole forces, (b) London forces, and (c) hydrogen bonding.

therefore weaker than primary bonds. There are three forms of secondary bonding: (a) dipole forces, (b) London forces, and (c) hydrogen bonding, illustrated in Figure 2.6. Types (a) and (b) are often referred to as *van der Waals* forces, after the scientist who first studied and quantified them.

Dipole forces arise in a molecule comprised of two atoms that have equal and opposite electrical charges. Each molecule therefore forms a dipole, as shown in Figure 2.6(a) for hydrogen chloride. Although the material is electrically neutral in its aggregate form, on a molecular scale the individual dipoles attract each other, given the proper orientation of positive and negative ends of the molecules. These dipole forces provide a net intermolecular bonding within the material.

London forces involve attractive forces between nonpolar molecules; that is, the atoms in the molecule do not form dipoles in the sense of the preceding paragraph. However, owing to the rapid motion of the electrons in orbit around the molecule, temporary dipoles form when more electrons happen to be on one side of the molecule than the other, as suggested by Figure 2.6(b). These instantaneous dipoles provide a force of attraction between molecules in the material.

Finally, **hydrogen bonding** occurs in molecules containing hydrogen atoms that are covalently bonded to another atom (e.g., oxygen in H_2O). Because the electrons needed to complete the shell of the hydrogen atom are aligned on one side of its nucleus, the opposite side has a net positive charge that attracts the electrons of atoms in neighboring molecules. Hydrogen bonding is illustrated in Figure 2.6(c) for water, and is generally a stronger intermolecular bonding mechanism than the other two forms of secondary bonding. It is important in the formation of many polymers.

2.3 Crystalline Structures

Atoms and molecules are used as building blocks for the more macroscopic structure of matter that is considered here and in the following section. When materials solidify from the molten state, they tend to close ranks and pack tightly, in many cases arranging themselves into a very orderly structure, and in other cases, not quite so orderly. Two fundamentally different material structures can be distinguished: (1) crystalline and (2) noncrystalline. Crystalline structures are examined in this section, and noncrystalline in the next.

Many materials form into crystals on solidification from the molten or liquid state. It is characteristic of virtually all metals, as well as many ceramics and polymers. A **crystalline structure** is one in which the atoms are located at regular and recurring positions in three dimensions. The pattern may be replicated millions of times within

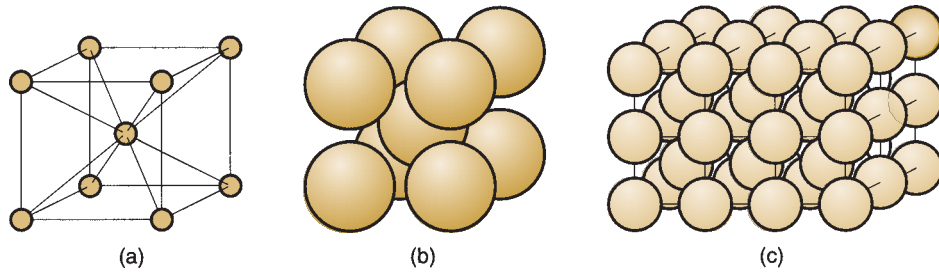


FIGURE 2.7 Body-centered cubic (BCC) crystal structure: (a) unit cell with atoms indicated as point locations in a three-dimensional axis system; (b) unit cell model showing closely packed atoms (sometimes called the hard-ball model); and (c) repeated pattern of the BCC structure.

a given crystal. The structure can be viewed in the form of a **unit cell**, which is the basic geometric grouping of atoms that is repeated. To illustrate, consider the unit cell for the body-centered cubic (BCC) crystal structure shown in Figure 2.7, one of the common structures found in metals. The simplest model of the BCC unit cell is illustrated in Figure 2.7(a). Although this model clearly depicts the locations of the atoms within the cell, it does not indicate the close packing of the atoms that occurs in the real crystal, as in Figure 2.7(b). Figure 2.7(c) shows the repeating nature of the unit cell within the crystal.

2.3.1 TYPES OF CRYSTAL STRUCTURES

In metals, three lattice structures are common: (1) body-centered cubic (BCC), (2) face-centered cubic (FCC), and (3) hexagonal close-packed (HCP), illustrated in Figure 2.8. Crystal structures for the common metals are presented in Table 2.1. It should be noted that some metals undergo a change of structure at different temperatures. Iron, for example, is BCC at room temperature; it changes to FCC above 912°C (1674°F) and back to BCC at temperatures above 1400°C (2550°F). When a metal (or other material) changes structure like this, it is referred to as being **allotropic**.

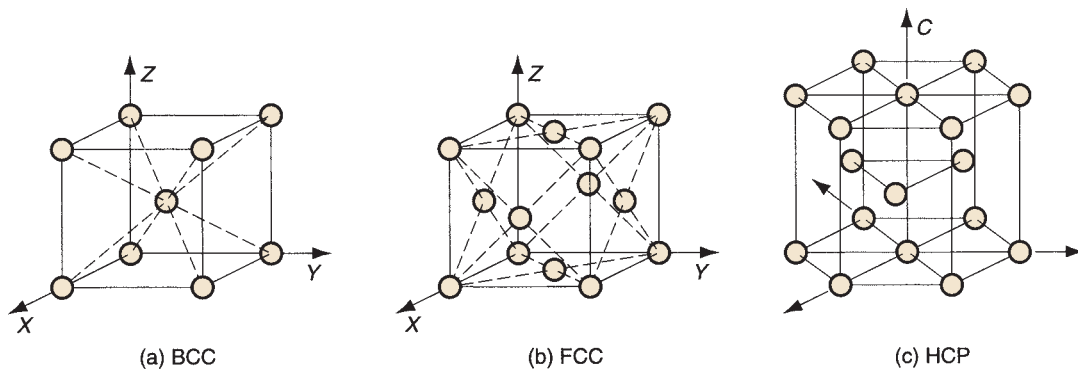


FIGURE 2.8 Three types of crystal structures in metals: (a) body-centered cubic, (b) face-centered cubic, and (c) hexagonal close-packed.

TABLE • 2.1 Crystal structures for the common metals (at room temperature).

Body-Centered Cubic (BCC)	Face-Centered Cubic (FCC)	Hexagonal Close-Packed (HCP)
Chromium (Cr)	Aluminum (Al)	Magnesium (Mg)
Iron (Fe)	Copper (Cu)	Titanium (Ti)
Molybdenum (Mo)	Gold (Au)	Zinc (Zn)
Tantalum (Ta)	Lead (Pb)	
Tungsten (W)	Silver (Ag)	
	Nickel (Ni)	

2.3.2 IMPERFECTIONS IN CRYSTALS

Thus far, crystal structures have been discussed as if they were perfect—the unit cell repeated in the material over and over in all directions. A perfect crystal is sometimes desirable to satisfy aesthetic or engineering purposes. For instance, a perfect diamond (contains no flaws) is more valuable than one containing imperfections. In the production of integrated circuit chips, large single crystals of silicon possess desirable processing characteristics for forming the microscopic details of the circuit pattern.

However, there are various reasons why a crystal's lattice structure may not be perfect. The imperfections often arise naturally because of the inability of the solidifying material to continue the replication of the unit cell indefinitely without interruption. Grain boundaries in metals are an example. In other cases, the imperfections are introduced purposely during the manufacturing process, for example, the addition of an alloying ingredient in a metal to increase its strength.

The various imperfections in crystalline solids are also called defects. Either term, **imperfection** or **defect**, refers to deviations in the regular pattern of the crystalline lattice structure. They can be catalogued as (1) point defects, (2) line defects, and (3) surface defects.

Point defects are imperfections in the crystal structure involving either a single atom or a few atoms. The defects can take various forms including, as shown in Figure 2.9: (a) **vacancy**, the simplest defect, involving a missing atom within the lattice structure; (b) **ion-pair vacancy**, also called a **Schottky defect**, which involves

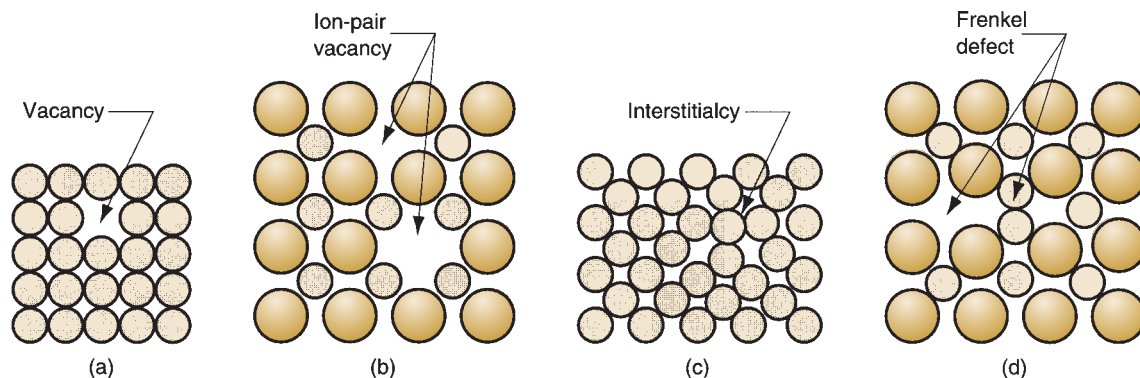


FIGURE 2.9 Point defects: (a) vacancy, (b) ion-pair vacancy, (c) interstitialcy, and (d) displaced ion.

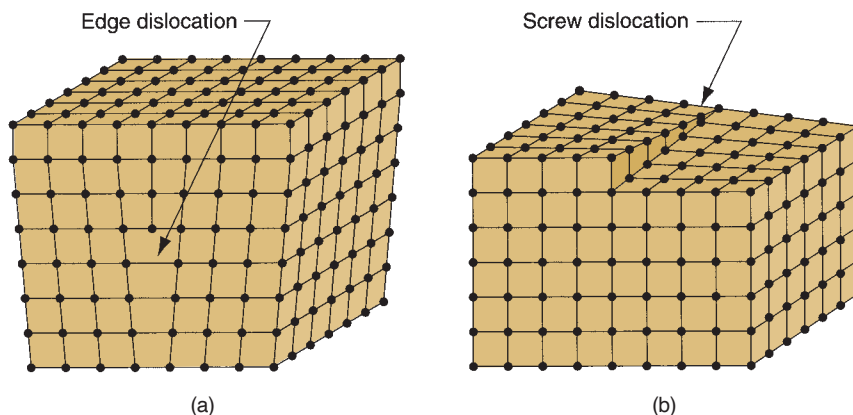


FIGURE 2.10 Line defects: (a) edge dislocation and (b) screw dislocation.

a missing pair of ions of opposite charge in a compound that has an overall charge balance; (c) **interstitialcy**, a lattice distortion produced by the presence of an extra atom in the structure; and (d) **displaced ion**, known as a **Frenkel defect**, which occurs when an ion becomes removed from a regular position in the lattice structure and inserted into an interstitial position not normally occupied by such an ion.

A **line defect** is a connected group of point defects that forms a line in the lattice structure. The most important line defect is the **dislocation**, which can take two forms: (a) edge dislocation and (b) screw dislocation. An **edge dislocation** is the edge of an extra plane of atoms that exists in the lattice, as illustrated in Figure 2.10(a). A **screw dislocation**, Figure 2.10(b), is a spiral within the lattice structure wrapped around an imperfection line, like a screw is wrapped around its axis. Both types of dislocations can arise in the crystal structure during solidification (e.g., casting), or they can be initiated during a deformation process (e.g., metal forming) performed on the solid material. Dislocations are useful in explaining certain aspects of mechanical behavior in metals.

Surface defects are imperfections that extend in two directions to form a boundary. The most obvious example is the external surface of a crystalline object that defines its shape. The surface is an interruption in the lattice structure. Surface boundaries can also lie inside the material. Grain boundaries are the best example of these internal surface interruptions. Metallic grains are discussed in a moment, but first let consider how deformation occurs in a crystal lattice, and how the process is aided by the presence of dislocations.

2.3.3 DEFORMATION IN METALLIC CRYSTALS

When a crystal is subjected to a gradually increasing mechanical stress, its initial response is to deform **elastically**. This can be likened to a tilting of the lattice structure without any changes of position among the atoms in the lattice, in the manner depicted in Figure 2.11(a) and (b). If the force is removed, the lattice structure (and therefore the crystal) returns to its original shape. If the stress reaches a high value relative to the electrostatic forces holding the atoms in their lattice positions, a permanent shape change occurs, called **plastic deformation**. What has happened is that the atoms in the lattice have permanently moved from their previous locations, and a new equilibrium lattice has been formed, as suggested by Figure 2.11(c).

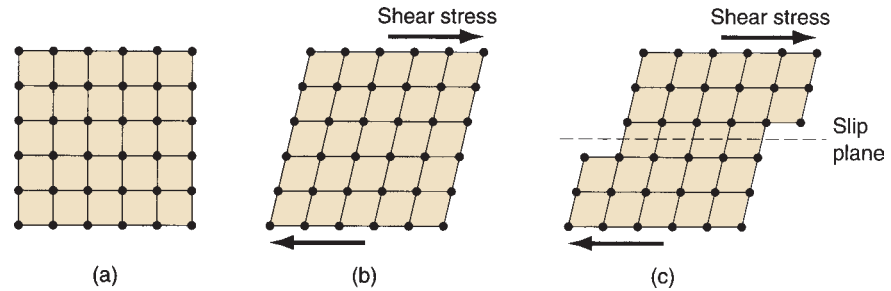


FIGURE 2.11 Deformation of a crystal structure: (a) original lattice; (b) elastic deformation, with no permanent change in positions of atoms; and (c) plastic deformation, in which atoms in the lattice are forced to move to new “homes.”

The lattice deformation shown in (c) of the figure is one possible mechanism, called slip, by which plastic deformation can occur in a crystalline structure. The other is called twinning, discussed later.

Slip involves the relative movement of atoms on opposite sides of a plane in the lattice, called the **slip plane**. The slip plane must be somehow aligned with the lattice structure (as indicated in the sketch), and so there are certain preferred directions along which slip is more likely to occur. The number of these **slip directions** depends on the lattice type. The three common metal crystal structures are somewhat more complicated, especially in three dimensions, than the square lattice depicted in Figure 2.11. It turns out that HCP has the fewest slip directions, BCC the most, and FCC falls in between. HCP metals show poor ductility and are generally difficult to deform at room temperature. Metals with BCC structure would figure to have the highest ductility, if the number of slip directions were the only criterion. However, nature is not so simple. These metals are generally stronger than the others, which complicates the issue, and the BCC metals usually require higher stresses to cause slip. In fact, some of the BCC metals exhibit poor ductility. Low carbon steel is a notable exception; although relatively strong, it is widely used with great commercial success in sheet-metal-forming operations, where it exhibits good ductility. The FCC metals are generally the most ductile of the three crystal structures, combining a good number of slip directions with (usually) relatively low to moderate strength. All three of these metal structures become more ductile at elevated temperatures, and this fact is often exploited in shaping them.

Dislocations play an important role in facilitating slip in metals. When a lattice structure containing an edge dislocation is subjected to a shear stress, the material deforms much more readily than in a perfect structure. This is explained by the fact that the dislocation is put into motion within the crystal lattice in the presence of the stress, as shown in the series of sketches in Figure 2.12. Why is it easier to move a dislocation through the lattice than it is to deform the lattice itself? The answer is that the atoms at the edge dislocation require a smaller displacement within the distorted lattice structure to reach a new equilibrium position. Thus, a lower energy level is needed to realign the atoms into the new positions than if the lattice were missing the dislocation. A lower stress level is therefore required to effect the deformation. Because the new position manifests a similar distorted lattice, movement of atoms at the dislocation continues at the lower stress level.

The slip phenomenon and the influence of dislocations have been explained here on a very microscopic basis. On a larger scale, slip occurs many times over

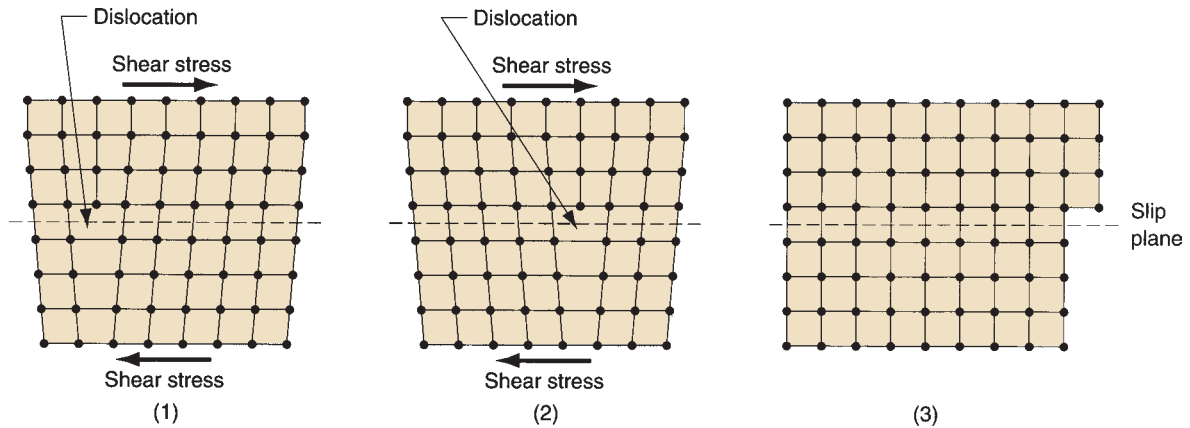


FIGURE 2.12 Effect of dislocations in the lattice structure under stress. In the series of diagrams, the movement of the dislocation allows deformation to occur under a lower stress than in a perfect lattice.

throughout the metal when subjected to a deforming load, thus causing it to exhibit the familiar macroscopic behavior of stretching, compressing, or bending. Dislocations represent a good-news–bad-news situation. Because of dislocations, the metal is more ductile and yields more readily to plastic deformation (forming) during manufacturing. However, from a product design viewpoint, the metal is not nearly as strong as it would be in the absence of dislocations.

Twinning is a second way in which metal crystals plastically deform. **Twinning** can be defined as a mechanism of plastic deformation in which atoms on one side of a plane (called the twinning plane) are shifted to form a mirror image of the other side of the plane. It is illustrated in Figure 2.13. The mechanism is important in HCP metals (e.g., magnesium, zinc) because they do not slip readily. Besides structure, another factor in twinning is the rate of deformation. The slip mechanism requires more time than twinning, which can occur almost instantaneously. Thus, when the deformation rate is very high, metals twin that would otherwise slip. Low carbon steel is an example that illustrates this rate sensitivity; when subjected to high strain rates it twins, whereas at moderate rates it deforms by slip.

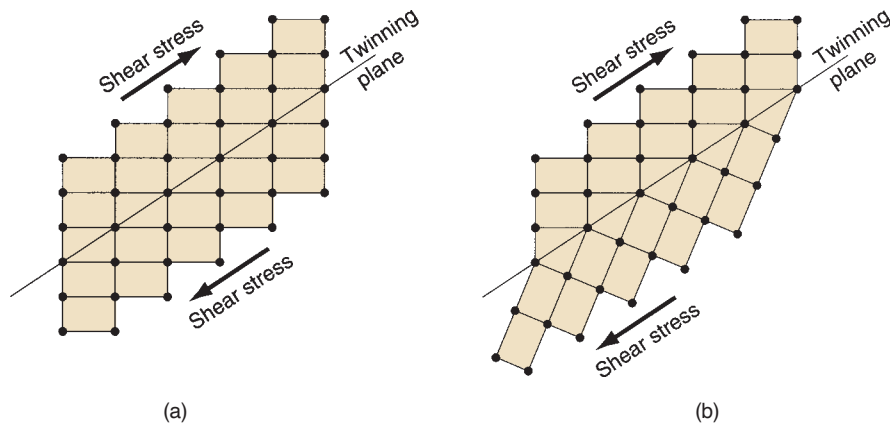


FIGURE 2.13 Twinning involves the formation of an atomic mirror image (i.e., a “twin”) on the opposite side of the twinning plane: (a) before and (b) after twinning.

2.3.4 GRAINS AND GRAIN BOUNDARIES IN METALS

A given block of metal may contain millions of individual crystals, called **grains**. Each grain has its own unique lattice orientation; but collectively, the grains are randomly oriented within the block. Such a structure is referred to as **polycrystalline**. It is easy to understand how such a structure is the natural state of the material. When the block is cooled from the molten state and begins to solidify, nucleation of individual crystals occurs at random positions and orientations throughout the liquid. As these crystals grow they finally interfere with each other, forming at their interface a surface defect—a **grain boundary**. The grain boundary consists of a transition zone, perhaps only a few atoms thick, in which the atoms are not aligned with either grain.

The size of the grains in the metal block is determined by the number of nucleation sites in the molten material and the cooling rate of the mass, among other factors. In a casting process, the nucleation sites are often created by the relatively cold walls of the mold, which motivates a somewhat preferred grain orientation at these walls.

Grain size is inversely related to cooling rate: Faster cooling promotes smaller grain size, whereas slower cooling has the opposite effect. Grain size is important in metals because it affects mechanical properties. Smaller grain size is generally preferable from a design viewpoint because it means higher strength and hardness. It is also desirable in certain manufacturing operations (e.g., metal forming), because it means higher ductility during deformation and a better surface on the finished product.

Another factor influencing mechanical properties is the presence of grain boundaries in the metal. They represent imperfections in the crystalline structure that interrupt the continued movement of dislocations. This helps to explain why smaller grain size—therefore more grains and more grain boundaries—increases the strength of the metal. By interfering with dislocation movement, grain boundaries also contribute to the characteristic property of a metal to become stronger as it is deformed. The property is called **strain hardening**, and it is examined more closely in Chapter 3 on mechanical properties.

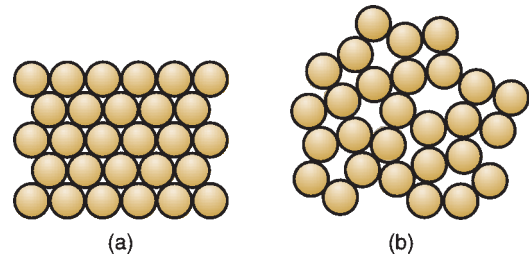
2.4 Noncrystalline (Amorphous) Structures

Many important materials are noncrystalline—liquids and gases, for example. Water and air have noncrystalline structures. A metal loses its crystalline structure when it is melted. Mercury is a liquid metal at room temperature, with its melting point of -38°C (-37°F). Important classes of engineering materials have a noncrystalline form in their solid state; the term **amorphous** is often used to describe these materials. Glass, many plastics, and rubber fall into this category. Many important plastics are mixtures of crystalline and noncrystalline forms. Even metals can be amorphous rather than crystalline, given that the cooling rate during transformation from liquid to solid is fast enough to inhibit the atoms from arranging themselves into their preferred regular patterns. This can happen, for instance, if the molten metal is poured between cold, closely spaced, rotating rolls.

Two closely related features distinguish noncrystalline from crystalline materials: (1) absence of a long-range order in the molecular structure, and (2) differences in melting and thermal expansion characteristics.

The difference in molecular structure can be visualized with reference to Figure 2.14. The closely packed and repeating pattern of the crystal structure is shown on the left; and the less dense and random arrangement of atoms in the noncrystalline

FIGURE 2.14 Illustration of difference in structure between: (a) crystalline and (b) noncrystalline materials. The crystal structure is regular, repeating, and denser, while the noncrystalline structure is more loosely packed and random.



material on the right. The difference is demonstrated by a metal when it melts. The more loosely packed atoms in the molten metal show an increase in volume (reduction in density) compared with the material's solid crystalline state. This effect is characteristic of most materials when melted (ice is a notable exception; liquid water is denser than solid ice). It is a general characteristic of liquids and solid amorphous materials that they are absent of long-range order as on the right in our figure.

The melting phenomenon will now be examined in more detail, and in doing so, the second important difference between crystalline and noncrystalline structures is illustrated. As indicated above, a metal experiences an increase in volume when it melts from the solid to the liquid state. For a pure metal, this volumetric change occurs rather abruptly, at a constant temperature (i.e., the melting temperature T_m), as indicated in Figure 2.15. The change represents a discontinuity from the slopes on either side in the plot. The gradual slopes characterize the metal's **thermal expansion**—the change in volume as a function of temperature, which is usually different in the solid and liquid states. Associated with the sudden volume increase as the metal transforms from solid to liquid at the melting point is the addition of a certain quantity of heat, called the **heat of fusion**, which causes the atoms to lose the dense, regular arrangement of the crystalline structure. The process is reversible; it operates in both directions. If the molten metal is cooled through its melting temperature, the same abrupt change in volume occurs (except that it is a decrease), and the same quantity of heat is given off by the metal.

An amorphous material exhibits quite different behavior than that of a pure metal when it changes from solid to liquid, as shown in Figure 2.15. The process is again reversible, but observe the behavior of the amorphous material during

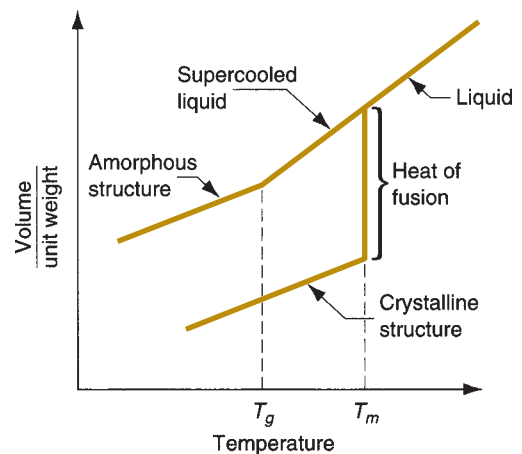


FIGURE 2.15 Characteristic change in volume for a pure metal (a crystalline structure), compared to the same volumetric changes in glass (a noncrystalline structure).

cooling from the liquid state, rather than during melting from the solid, as before. Glass (silica, SiO_2) is used to illustrate. At high temperatures, glass is a true liquid, and the molecules are free to move about as in the usual definition of a liquid. As the glass cools, it gradually transforms into the solid state, going through a transition phase, called a **supercooled liquid**, before finally becoming rigid. It does not show the sudden volumetric change that is characteristic of crystalline materials; instead it passes through its melting temperature T_m without a change in its thermal expansion slope. In this supercooled liquid region, the material becomes increasingly viscous as the temperature continues to decrease. As it cools further, a point is finally reached at which the supercooled liquid converts to a solid. This is called the **glass-transition temperature** T_g . At this point, there is a change in the thermal expansion slope. (It might be more precise to refer to it as the thermal contraction slope; however, the slope is the same for expansion and contraction). The rate of thermal expansion is lower for the solid material than for the supercooled liquid.

The difference in behavior between crystalline and noncrystalline materials can be traced to the response of their respective atomic structures to changes in temperature. When a pure metal solidifies from the molten state, the atoms arrange themselves into a regular and recurring structure. This crystal structure is much more compact than the random and loosely packed liquid from which it formed. Thus, the process of solidification produces the abrupt volumetric contraction observed in Figure 2.15 for the crystalline material. By contrast, amorphous materials do not achieve this repeating and closely packed structure at low temperatures. The atomic structure is the same random arrangement as in the liquid state; thus, there is no abrupt volumetric change as these materials transition from liquid to solid.

2.5 Engineering Materials

This section summarizes how atomic structure, bonding, and crystal structure (or absence thereof) are related to the type of engineering material: metals, ceramics, and polymers.

Metals Metals have crystalline structures in the solid state, almost without exception. The unit cells of these crystal structures are almost always BCC, FCC, or HCP. The atoms of the metals are held together by metallic bonding, which means that their valence electrons can move about with relative freedom (compared with the other types of atomic and molecular bonding). These structures and bonding generally make the metals strong and hard. Many of the metals are quite ductile (capable of being deformed, which is useful in manufacturing), especially the FCC metals. Other general properties of metals related to structure and bonding include high electrical and thermal conductivity, opaqueness (impervious to light rays), and reflectivity (capacity to reflect light rays).

Ceramics Ceramic molecules are characterized by ionic or covalent bonding, or both. The metallic atoms release or share their outermost electrons to the nonmetallic atoms, and a strong attractive force exists within the molecules. The general properties that result from these bonding mechanisms include high hardness and stiffness (even at elevated temperatures) and brittleness (no ductility). The bonding also means that ceramics are electrically insulating (nonconducting), refractory (thermally resistant), and chemically inert.

Ceramics possess either a crystalline or noncrystalline structure. Most ceramics have a crystal structure, whereas glasses based on silica (SiO_2) are amorphous. In certain cases, either structure can exist in the same ceramic material. For example, silica occurs in nature as crystalline quartz. When this mineral is melted and then cooled, it solidifies to form fused silica, which has a noncrystalline structure.

Polymers A polymer molecule consists of many repeating *mers* to form very large molecules held together by covalent bonding. Elements in polymers are usually carbon plus one or more other elements such as hydrogen, nitrogen, oxygen, and chlorine. Secondary bonding (van der Waals) holds the molecules together within the aggregate material (intermolecular bonding). Polymers have either a glassy structure or mixture of glassy and crystalline. There are differences among the three polymer types. In **thermoplastic polymers**, the molecules consist of long chains of mers in a linear structure. These materials can be heated and cooled without substantially altering their linear structure. In **thermosetting polymers**, the molecules transform into a rigid, three-dimensional structure on cooling from a heated plastic condition. If thermosetting polymers are reheated, they degrade chemically rather than soften. **Elastomers** have large molecules with coiled structures. The uncoiling and recoiling of the molecules when subjected to stress cycles motivate the aggregate material to exhibit its characteristic elastic behavior.

The molecular structure and bonding of polymers provide them with the following typical properties: low density, high electrical resistivity (some polymers are used as insulating materials), and low thermal conductivity. Strength and stiffness of polymers vary widely. Some are strong and rigid (although not matching the strength and stiffness of metals or ceramics), whereas others exhibit highly elastic behavior.