

1 Introduction

Properties

One material is chosen over another for a particular application because its properties are better suited for the intended use. Among the important properties are strength, corrosion resistance, electrical conductivity, weight, material cost, processing costs, and appearance. Usually several properties are important.

In many applications, stiffness is important. Materials deform when a stress is applied to them. If the stress is low, the deformation will be elastic. In this case the deformation will disappear and the material will regain its original shape when the stress is removed. Good examples are elastic bands and paper clips. With greater stress, a material may deform plastically. In this case the deformation does not disappear when the stress is removed, so the shape change is permanent. This happens when the stress exceeds the yield strength of the material. With a still higher stress, the material may reach its tensile strength and fail. Ductility and toughness are also important. The ductility of a material is the amount of deformation a material may undergo before breaking. Toughness is a measure of how much energy a material absorbs per area before fracture.

Electrical properties are of paramount importance in some applications. Electrical conductors should have high conductivities and insulators very low conductivities. Integrated circuits for computers require semiconductors. The dielectric constant may be important in applications involving high frequencies. Piezoelectric behavior is required for sonar transmitters and receivers.

The corrosion resistance of metals in aqueous solutions is important in many applications. At high temperatures, resistance to direct oxidation is necessary. With polymeric materials, resistance to solvents and irradiation controls many applications.

All materials respond to magnetic fields to some extent. The magnetic properties of the few materials that have strong responses are discussed in Chapter 22.

Where weight is important, density must be considered. Surface appearance is often a crucial consideration. In almost all applications, material cost is of vital

importance. Although prices of materials are usually quoted in price per weight (\$/lb), weight per volume is usually more important. In addition, the cost of processing different materials is paramount.

Bonding

The bonds that hold materials together are classified as metallic, ionic, covalent, or van der Waals. In metals, individual atoms lose their valence electrons to form an “electron gas.” This negatively charged electron gas holds the positively charged atoms together.

There is a transfer of valence electrons in ionic solids. Anions (metallic ions) lose valence electrons and become positively charged. Cations (non-metal ions) accept the extra electrons and become negatively charged. The electrostatic attraction bonds anions to cations.

Covalent bonding is the result of sharing electrons so the outer shells can be complete. For example, if a carbon atom with four valence electrons shares one electron with four neighboring carbon atoms, each carbon atom will have eight outer electrons. Bonding is usually partially ionic and partially covalent in character.

Van der Waals bonding is much weaker than metallic, ionic, and covalent bonding. It arises from the weak dipoles of molecules. Asymmetric molecules are likely to have dipoles, and bonding results from the attraction between the dipoles. Even symmetric molecules and atoms have statistical dipoles, which result in even weaker bonding. Hydrogen atoms in covalent molecules create strong dipoles. The term *hydrogen bonding* refers to van der Waals bonds resulting from these dipoles. Figure 1.1 schematically illustrates this.

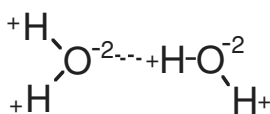


Figure 1.1. Hydrogen bond between adjacent water molecules resulting from the dipole of the hydrogen atom.

Table 1.1 gives the approximate ranges of the strengths of the different types of bonds. Bond strengths of organic compounds are given in Appendix 4.

Table 1.1. *Bond strengths*

Bond Type	Energy (kJ/mol)
Van der Waals	0.0–10
Hydrogen	10–40
Ionic	50–1000
Covalent	200–1000
Metallic	50–1000

Data from R. A. Flinn and P. T. Trojan, *Engineering Materials and Their Applications*, 4th ed. Houghton Mifflin, 1990.

Types of Materials

Types of Materials

Most solid materials can be classified into three groups: metals, ceramics, and polymers.

In metals, the valence electrons are free to move about and are not bound to individual atoms. This explains their good electrical and thermal conductivities. It also explains the high reflectivity of metals. Photons are absorbed by promoting valence electrons to higher energy states and then re-emitting photons as the electrons drop to lower energy states. Metals are usually stiff and have high strengths but have enough ductility to be formed into useful shapes. Metals and alloys are crystalline. Aluminum and copper are typical metals. Brass (copper alloyed with zinc) and stainless steel (iron alloyed with chromium) are alloys.

The periodic table is useful in understanding some of the properties of metals. Densities correlate well with position in the periodic table, as shown in Figure 1.2. Figure 1.3 shows the melting points of various elements superimposed on the periodic table.

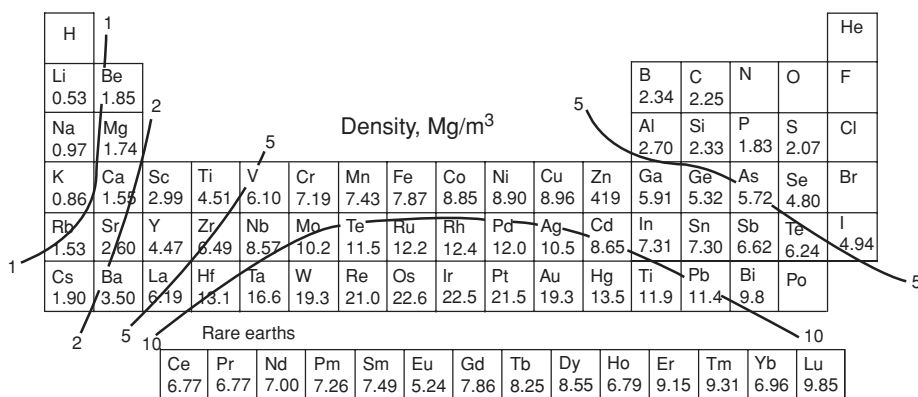


Figure 1.2. The heaviest elements are in the middle of the bottom of the periodic table. From W. F. Hosford, *Physical Metallurgy*, CRC, 2005.

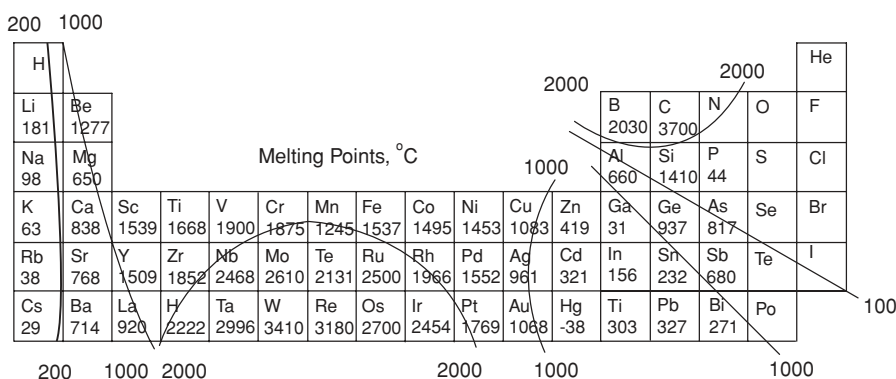


Figure 1.3. The metals with the lowest melting points are on the left of the periodic table, and those with the highest melting points, except boron and carbon, are in the middle at the bottom. From W. F. Hosford, *ibid.*

Ceramics are compounds of metals and non-metals. Oxides are particularly important. Because bonding is either ionic or covalent, or more likely partially ionic and partially covalent, electrons are not free to move, so most ceramics are electrical insulators. Ceramics with strong bonds are hard and have very high melting points. Extremes are alumina, which is mostly covalent bonded, and sodium chloride, in which the bonding is mostly ionic. Ceramics may be either crystalline or amorphous. Most are stiff, hard, and brittle. Clay products and glasses are considered ceramics.

Polymers (commonly called plastics) consist of very large molecules that contain many repeating parts (*mers*). Weak van der Waals bonding between covalently bonded long chain molecules of thermoplastics explains their low stiffness and low melting points. Examples include polyethylene and polystyrene. In some polymers, all of the bonds are covalent and the molecules form three-dimensional networks. Examples include polyurethanes and bakelite. These polymers cannot be melted without decomposition. Silicones are polymers with silicon-oxygen backbones instead of carbon-carbon backbones.

Some materials, such as the various forms of carbon (graphite, diamond, and fullerenes), do not fit neatly into this classification. Graphite consists of sheets in which the bonding is metallic with only weak van der Waals bonding holding the sheets together. Diamond is similar to ceramics in that it is covalently bonded solid, but it consists of only one element. Bonding in semiconductors is similar to that in metals except that electrons are not free to move unless excited into a higher energy state.

Composites are mixtures of two or more different materials. Examples include glass fibers bonded by epoxy and graphite reinforcing polyester. Concrete is a composite of sand, gravel, and a cement paste. Foams and honeycombs may be regarded as composites of a solid with a gas.

Biological materials include wood, flesh, and bone. Flesh is an example of a soft biological material, and bone a hard biological material. Appendix 1 treats the structure and properties of wood.

Crystalline Materials

Materials can be classified as either crystalline or amorphous. In crystals, the atoms, ions, or molecules are arranged in three-dimensional patterns, described by unit cells, that repeat in space, thousands or millions of times in each dimension. Metals are almost always crystalline. There are several different crystal structures that are common in metals. In face-centered cubic (fcc) crystals, the atoms are on the corners of a cube and in the centers of the faces. Figure 1.4 shows the basic unit cell of an fcc crystal. Among the metals that have this structure are copper, silver, gold, aluminum, lead, nickel, and iron at elevated temperatures. Appendix 2 describes the system used to identify different planes and directions in a crystal, and Appendix 3 describes how X-ray diffraction can be used to determine crystal structures.

Example Problem 1–1

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Example Problem 1–1

How many atoms are there in an fcc unit cell?

Solution: Counting each corner atom as $1/8$ because it is shared by 8 cells and each face atom as $1/2$ because it is shared by 2 cells, there are $(8 \text{ corners})(1/8) + (6 \text{ faces})(1/2) = 4$ atoms per units cell.

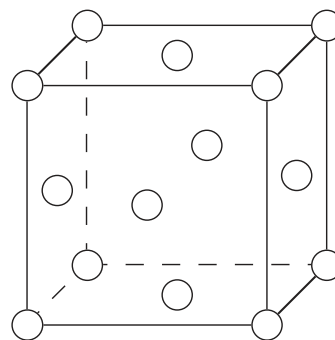


Figure 1.4. Face-centered cubic unit cell.

Another common metal structure is body-centered cubic (bcc). Atoms are on the corners and the center of a cubic cell (Figure 1.5). Iron at room temperature, chromium, vanadium, tungsten, and molybdenum are among the metals that have the bcc structure.

The third common crystal structure of metals is hexagonal close-packed (Figure 1.6). Magnesium, zinc beryllium, and zirconium and titanium (at room temperature) have this structure, which is composed of planes with atoms arranged in hexagonal patterns. The atoms in each hexagonal plane sit in the valleys of the plane below.

Many ceramics are crystalline. Bonding is usually partially ionic and partially covalent. They have crystal structures in which anions and cations are in contact. One of the simple structures is that of sodium chloride (Figure 1.7). Ceramic compounds that have this structure include MgO, FeO, and MnS. Figure 1.8 shows the unit cell of fluorite, CaF_2 .

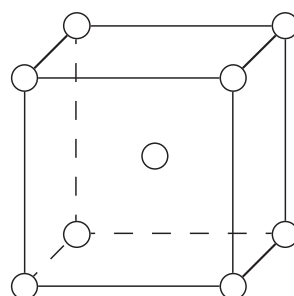


Figure 1.5. Body-centered cubic unit cell.

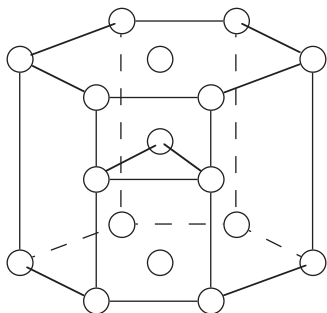


Figure 1.6. Close-packed hexagonal cell.

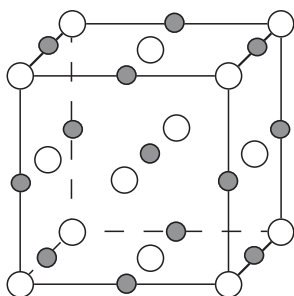


Figure 1.7. Unit cell of sodium chloride.

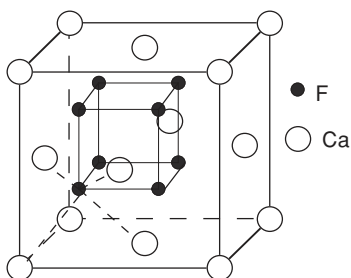


Figure 1.8. The unit cell of fluorite.

Amorphous Materials

Noncrystalline structures are said to be *amorphous*. Glasses are amorphous. Some polymers are partially crystalline and partially amorphous. Generally, stretching a polymer increases the degree of crystallinity by aligning its molecules. Polymers with three-dimensional networks are completely amorphous.

Amorphous materials have short-range order but not long-range order. Their structures are similar to liquids. Glasses have the structures of frozen liquids, but they are not liquids. Examples of amorphous materials include silicate glass (as in windows and bottles), most polymers, and even metallic alloys of complex compositions that have been cooled extremely rapidly from the melt.

Problems

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Note of Interest

Johannes Diderik van der Waals was born on November 23, 1837, in Leyden, Netherlands. His first job was as a secondary school teacher. His lack of knowledge of the classic languages initially prevented him from enrolling at a university, until legislation removed this requirement for students in the sciences. His 1873 doctoral thesis “on the continuity of the gas and liquid state” demonstrated that the gas and liquid states merged. This work brought him to the attention of the scientific world. He continued with classic papers on binary surfaces and capillarity.

Problems

1. How many atoms are there in a body-centered cubic unit cell?
2. How many Na^+ ions are there in a unit cell of NaCl ?
3. Knowing the bonding and structure of graphite, speculate as to why graphite is a good solid lubricant.
4. How many Ca^{2+} ions surround each F^- ion in the fluorite structure?
5. How many F^- ions surround each Ca^{2+} ion in the fluorite structure?

2 Phases

What Is a Phase?

A *phase* is a state of aggregation of matter that has a distinctive structure. Phases may be solid, liquid, or gaseous. A phase may be a pure material or a solution of several components. A solid phase is either amorphous or has a characteristic crystal structure and definite composition range. A physical system may contain more than one solid phase with different crystal structures, or different ranges of possible compositions – one or more mutually insoluble liquid phases (for example oil and water) and a gas phase. All gasses are mutually soluble, and therefore only one gaseous phase is possible.

Single-phase materials include brass (a solid solution of zinc in copper with zinc atoms occupying lattice sites), sodium chloride crystals, glass, and polyethylene. Most plain carbon steels are two-phase materials, consisting of an iron-rich solid solution and iron carbide. A glass of ice water consists of two phases: liquid water and ice. In a glass of tonic water there may be three phases: liquid, ice, and gas bubbles.

The composition of a single phase may vary from place to place, but composition change is always gradual and without abrupt changes. In multiple-phase systems, however, there are discontinuities of composition and structure at phase boundaries. The compositions on each side of the boundary are usually in equilibrium. For example, the oxygen concentration changes abruptly between copper with some oxygen dissolved in it and copper oxide.

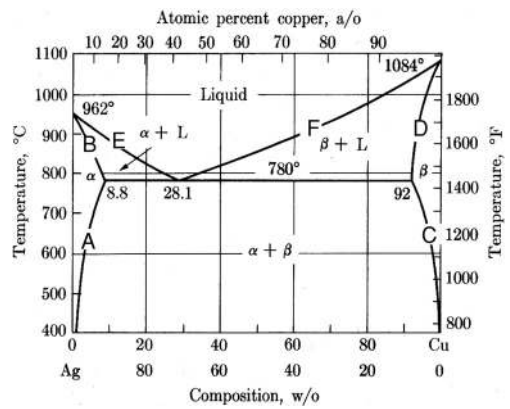
Phase Diagrams

Phase diagrams describe the equilibrium between phases. Figure 2.1 shows the copper-silver phase diagram. Molten silver and copper form a single liquid in all proportions. When cooled, two different solid solutions form. There are two ways to consider this diagram. It may be thought of as a map, showing what phase or combination of phases exists at any temperature and composition. For example, in an alloy of 80% copper, a liquid and a copper-rich phase (β) exist at 850 °C. At 600 °C there

Lever Law

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Figure 2.1. Copper-silver phase diagram.



are two solid phases – silver-rich α and copper-rich phase β . Above 1000 °C there is only one phase – a liquid.

A phase diagram may also be thought of as a plot of solubility limits. The lines A and B at the left of the diagram represent the solubility of copper in the silver lattice. The lines C and D at the right of the diagram represent the solubility of silver in the copper lattice. The lines E and F represent the solubility of silver and copper in the liquid.

At 600 °C, the solubility of copper in α -silver is about 3%, and the solubility of silver in β -copper is about 2.5%. All alloys in the two-phase α - β region will contain α saturated with silver and β saturated with copper. The compositions of two phases that are in equilibrium can be read by looking at the ends of a horizontal tie line connecting the two phases.

At 780 °C, three phases – liquid, α , and β – coexist, and their compositions are fixed. As liquid containing 28.1% Cu is cooled through 780 °C, the reaction, liquid $\rightarrow \alpha + \beta$, occurs. This is called a *eutectic* reaction, and 780 °C is called the eutectic temperature.

Lever Law

A simple mass balance can be used to find the relative amounts of each phase in a two-phase region. For example, in one gram of an alloy of 80% copper at 600 °C, there is 0.8 gram of copper, divided between the two phases. If we designate the fraction of the microstructure that is α by f_α , the amount of copper in the α -phase is $0.03f_\alpha$. Likewise, there will be $0.975(1-f_\alpha)$ grams of copper in $(1-f_\alpha)$ grams of β -phase. A mass balance gives

$$0.8 = 0.03 f_\alpha + 0.975(1 - f_\alpha) \quad \text{or}$$

$$f_\alpha = (0.8 - 0.03)/(0.975 - 0.03) = 81.5\%.$$

This procedure can be generalized as the lever law

$$f_\alpha = (c_{av} - c_\alpha)/(c_\beta - c_\alpha). \quad 2.1$$

Example Problem 2-1:

Consider an alloy containing 90% silver and 10% copper at 779°C. What are the compositions of each phase, and what fraction of the alloy would be in the form of the silver-rich α -phase?

Solution: From Figure 2.1, the composition of the α -phase is 8.8% copper and the composition of the β -phase is 92% copper. Using the lever law, $f_\alpha = (92-10)/(92-8.8) = 96.7\%$.

Figures 2.2 through 2.4 are phase diagrams for several alloy systems. Copper and nickel are miscible in all proportions in both the liquid and solid states (Figure 2.2). Lead and tin form a simple eutectic (Figure 2.3). At the eutectic temperature (183°C) $L \rightarrow \alpha + \beta$ on cooling. Figure 2.4 shows the copper-rich end of the copper-zinc phase diagram. In this system there is a *peritectic* reaction, $L + \alpha \rightarrow \beta$, on cooling through the peritectic temperature, 903°C.

Probably the phase diagram with the greatest industrial importance is the iron-iron carbide phase diagram (Figure 2.5). The reaction $\gamma \rightarrow \alpha + \text{Fe}_3\text{C}$ at 727°C is called a *eutectoid* reaction.

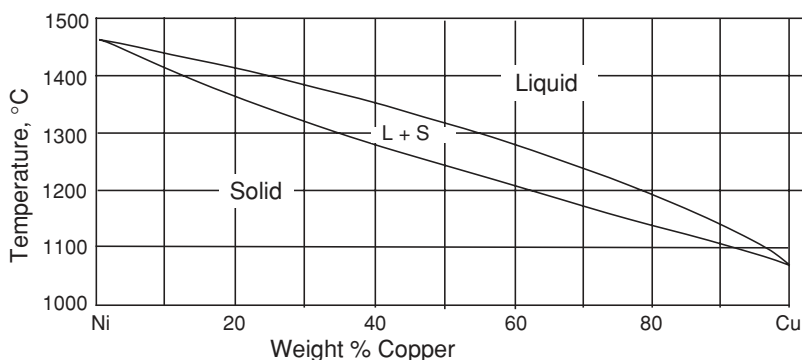


Figure 2.2. The copper-nickel phase diagram. From D. S. Clark and W. R. Varney, *Physical Metallurgy for Engineers*, Van Nostrand Reinhold, 1962.

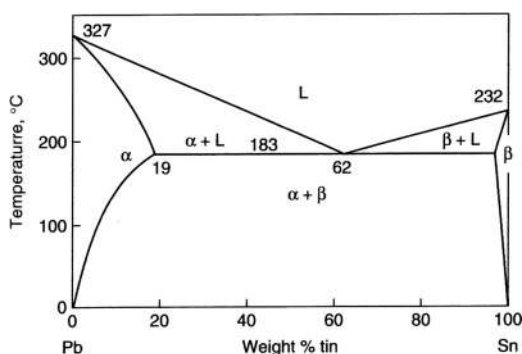


Figure 2.3. The lead-tin phase diagram. From W. F. Hosford, *Physical Metallurgy*, CRC, 2005.