6.2 For the preceding problem, use the inverse lever rule to determine the proportions of liquid and solid phases present in the alloy.

6.3 In the iron-iron carbide phase diagram of Figure 6.4, identify the phase or phases present at the following temperatures and nominal compositions: (a) 650°C (1200°F) and 2% Fe_3C, (b) 760°C (1400°F) and 2% Fe_3C, and (c) 1095°C (2000°F) and 1% Fe_3C.

Ceramics

7

Metals are usually thought to be the most important class of engineering materials. However, it is of interest to note that ceramic materials are actually more abundant and widely used. Included in this category are clay products (e.g., bricks and pottery), glass, cement, and more modern ceramic materials such as tungsten carbide and cubic boron nitride. This is the class of materials discussed in this chapter. Several elements related to ceramics are also covered because they are sometimes used in similar applications. These elements are carbon, silicon, and boron.

The importance of ceramics as engineering materi- als derives from their abundance in nature and their mechanical and physical properties, which are quite different from those of metals. A *ceramic* material is an inorganic compound consisting of a metal (or semi-metal) and one or more nonmetals. The word *ceramic* traces from the Greek *keramos* meaning potter's clay or wares made from fired clay. Important examples of ceramic materials are *silica*, or silicon dioxide (SiO_2), the main ingredient in most glass products; *alumina*, or aluminum oxide (Al_2O_3), used in applications rang- ing from abrasives to artificial bones; and more com- plex compounds such as hydrous aluminum silicate ($Al_2Si_2O_5(OH)_4$), known as *kaolinite*, the principal in- gredient in most clay products. The elements in these compounds are the most common in Earth's crust; see Table 7.1. The group includes many additional com- pounds, some of which occur naturally while others are manufactured.

The general properties that make ceramics useful in engineered products are high hardness, good electrical and thermal insulating characteristics, chemical stabil- ity, and high melting temperatures. Some ceramics are translucent—window glass being the clearest example. They are also brittle and possess virtually no ductility, which can cause problems in both processing and per- formance of ceramic products.

TABLE • 7.1 Most common elements in the earth's crust, with approximate percentages.

Oxygen	Silicon	Aluminum	Iron	Calcium	Sodium	Potassium	Magnesium
50%	26%	7.6%	4.7%	3.5%	2.7%	2.6%	2.0%

Compiled from [6].

The commercial and technological importance of ceramics is best demonstrated by the variety of products and applications that are based on this class of material. The list includes:

➢ *Clay construction products*, such as bricks, clay pipe, and building tile

➢ *Refractory ceramics*, which are capable of high temperature applications such as furnace walls, crucibles, and molds

➢ *Cement used in concrete*, used for construction and roads (concrete is a composite material, but its components are ceramics)

➢ *Whiteware products*, including pottery, stoneware, fine china, porcelain, and other tableware, based on mixtures of clay and other minerals

➢ *Glass* used in bottles, glasses, lenses, window panes, and light bulbs

➢ *Glass fibers* for thermal insulating wool, reinforced plastics (fiberglass), and fiber optics communications lines

➢ *Abrasives*, such as aluminum oxide and silicon carbide

➢ *Cutting tool materials*, including tungsten carbide, aluminum oxide, and cubic boron nitride

➢ *Ceramic insulators*, which are used in applications such as electrical transmission components, spark plugs, and microelectronic chip substrates

➢ *Magnetic ceramics*, for example, in computer memories

➢ *Nuclear fuels* based on uranium oxide (UO_2)

➢ *Bioceramics*, which include materials used in artificial teeth and bones

For purposes of organization, ceramic materials are classified into three basic types: (1) *traditional ceramics*—silicates used for clay products such as pottery and bricks, common abrasives, and cement; (2) *new ceramics*—more recently developed ceramics based on nonsilicates such as oxides and carbides, and generally possessing mechanical or physical properties that are superior or unique compared to tradi- tional ceramics; and (3) *glasses*—based primarily on silica and distinguished from the other ceramics by their noncrystalline structure. In addition to the three basic types, there are *glass ceramics*—glasses that have been transformed into a largely crystalline structure by heat treatment.

7. Structure and Properties of Ceramics

Ceramic compounds are characterized by covalent and ionic bonding. These bonds are stronger than metallic bonding in metals, which accounts for the high hardness and stiffness but low ductility of ceramic materials. Just as the presence of free electrons in the metallic bond explains why metals are good conductors of heat and

electricity, the presence of tightly held electrons in ceramic molecules explains why these materials are poor conductors. The strong bonding also provides these materials with high melting temperatures, although some ceramics decompose, rather than melt, at elevated temperatures.

Most ceramics take a crystalline structure. The structures are generally more complex than those of most metals. There are several reasons for this. First, ceramic molecules usually consist of atoms that are significantly different in size. Second, the ion charges are often different, as in many of the common ceramics such as SiO_2 and Al_2O_3. Both of these factors tend to force a more complicated physical arrangement of the atoms in the molecule and in the resulting crystal structure. In addition, many ceramic materials consist of more than two elements, such as $(Al_2Si_2O_5(OH)_4)$, also leading to further complexity in the molecular structure. Crystalline ceramics can be single crystals or polycrystalline substances. In the more common second form, mechanical and physical properties are affected by grain size; higher strength and toughness are achieved in the finer-grained materials.

Some ceramic materials tend to assume an amorphous structure or **glassy** phase, rather than a crystalline form. The most familiar example is, of course, glass. Chemi- cally, most glasses consist of fused silica. Variations in properties and colors are ob- tained by adding other glassy ceramic materials such as oxides of aluminum, boron, calcium, and magnesium. In addition to these pure glasses, many ceramics that have a crystal structure use the glassy phase as a binder for their crystalline phase.

7.1.1 MECHANICAL PROPERTIES

Basic mechanical properties of ceramics are presented in Chapter 3. Ceramic materials are rigid and brittle, exhibiting a stress-strain behavior best characterized as perfectly elastic (see Figure 3.6). As seen in Table 7.2, hardness and elastic modulus

TABLE • 7.2 Selected mechanical and physical properties of ceramic materials.

Material	Hardness (Vickers)	Elastic modulus, E		Specific Gravity	Melting Temperature	
		GPa	(lb/in²)		°C	°F
Traditional ceramics						
Brick-fireclay	N.A.	95	14×10^6	2.3	N.A.	N.A.
Cement, Portland	N.A.	50	7×10^6	2.4	N.A.	N.A.
Silicon carbide (SiC)	2600 HV	460	68×10^6	3.2	2700[a]	4892[a]
New Ceramics						
Alumina (Al_2O_3)	2200 HV	345	50×10^6	3.8	2054	3729
Cubic boron nitride (cBN)	6000 HV	N.A.	N.A.	2.3	3000[a]	5430[a]
Titanium carbide (TiC)	3200 HV	300	45×10^6	4.9	3250	5880
Tungsten carbide (WC)	2600 HV	700	100×10^6	15.6	2870	5198
Glass						
Silica glass (SiO_2)	500 HV	69	10×10^6	2.2	7[b]	7[b]

Compiled from [3], [4], [5], [6], [9], [10], and other sources. Key: N.A. = Not available or not applicable.
[a]The ceramic material chemically dissociates or, in the case of diamond and graphite, sublimes (vaporizes), rather than melts.
[b]Glass, being noncrystalline, does not melt at a specific melting point. Instead, it gradually exhibits fluid properties with increasing temperature. It becomes liquid at around 1400°C (2500°F).

for many of the new ceramics are greater than those of metals (see Tables 3.1, 3.6, and 3.7). Stiffness and hardness of traditional ceramics and glasses are significantly less than for new ceramics.

Theoretically, the strength of ceramics should be higher than that of metals be- cause of their atomic bonding. The covalent and ionic bonding types are stronger than metallic bonding. However, metallic bonding has the advantage that it allows for slip, the basic mechanism by which metals deform plastically when subjected to high stresses. Bonding in ceramics is more rigid and does not permit slip under stress. The inability to slip makes it much more difficult for ceramics to absorb stresses. Yet ceramics contain the same imperfections in their crystal structure as metals—vacancies, interstitialcies, displaced atoms, and microscopic cracks. These internal flaws tend to concentrate the stresses, especially when a tensile, bending, or impact loading is involved. As a result of these factors, ceramics fail by brittle fracture under ap- plied stress much more readily than metals. Their tensile strength and toughness are relatively low. Also, their performance is much less predictable due to the random nature of the imperfections and the influence of processing variations, especially in products made of traditional ceramics.

The frailties that limit the tensile strength of ceramic materials are not nearly so operative when compressive stresses are applied. Ceramics are substantially strong- er in compression than in tension. For engineering and structural applications, de- signers have learned to use ceramic components so that they are loaded in compres- sion rather than tension or bending.

Various methods have been developed to strengthen ceramics, nearly all of which have as their fundamental approach the minimization of surface and internal flaws and their effects. These methods include [7]: (1) making the starting materials more uniform; (2) decreasing grain size in polycrystalline ceramic products; (3) minimiz- ing porosity; (4) introducing compressive surface stresses; for example, through ap- plication of glazes with low thermal expansions, so that the body of the product contracts after firing more than the glaze, thus putting the glaze in compression; (5) using fiber reinforcement; and (6) heat treatments, such as quenching alumina from temperatures in the slightly plastic region to strengthen it.

7.1.2 *PHYSICAL PROPERTIES*

Several of the physical properties of ceramics are presented in Table 7.2. Most ceramic materials are lighter than metals and heavier than polymers (see Table 4.1). Melting temperatures are higher than for most metals, some ceramics preferring to decompose rather than melt.

Electrical and thermal conductivities of most ceramics are lower than for metals; but the range of values is greater, permitting some ceramics to be used as insulators while others are electrical conductors. Thermal expansion coefficients are somewhat less than for the metals, but the effects are more damaging in ceramics because of their brittleness. Ceramic materials with relatively high thermal expansions and low thermal conductivities are especially susceptible to failures of this type, which result from significant temperature gradients and associated volumetric changes in differ- ent regions of the same part. The terms ***thermal shock*** and ***thermal cracking*** are used in connection with such failures. Certain glasses (for example, those containing high proportions of SiO_2) and glass ceramics are noted for their low thermal expansion and are particularly resistant to these thermal failures (***Pyrex*** is a familiar example).

7.2 Traditional Ceramics

These materials are based on mineral silicates, silica, and mineral oxides. The pri- mary products are fired clay (pottery, tableware, brick, and tile), cement, and natural abrasives such as alumina. These products, and the processes used to make them, date back thousands of years (Historical Note 7.1). Glass is also a silicate ceramic material and is often included within the traditional ceramics group [5], [6] Glass is covered in a later section because it is distinguished from the above crystalline materials by its amorphous or vitreous structure (the term *vitreous* means glassy, or possessing the characteristics of glass).

Historical Note 7.1   *Ancient pottery ceramics*

Making pottery has been an art since the earliest civilizations. Archeologists examine ancient pottery and similar artifacts to study the cultures of the ancient world. Ceramic pottery does not corrode or disintegrate with age nearly as rapidly as artifacts made of wood, metal, or cloth.

Somehow, early tribes discovered that clay is transformed into a hard solid when placed near an open fire. Burnt clay articles have been found in the Middle East that date back nearly 10,000 years. Earthenware pots and similar products became an established commercial trade in Egypt by around 4000 B.C.E.

The greatest advances in pottery making were made in China, where fine white stoneware was first crafted as early as 1400 B.C.E. By the ninth century, the Chinese were making articles of porcelain, which was fired at higher temperatures than earthenware or stoneware to partially vitrify the more complex mixture of raw materials and produce translucency in the final product. Dinnerware made of Chinese porcelain was highly valued in Europe; it was called "china." It contributed significantly to trade between China and Europe and influenced the development of European culture.

7.2.1 RAW MATERIALS

Mineral silicates, such as clays of various compositions, and silica, such as quartz, are among the most abundant substances in nature and constitute the principal raw materials for traditional ceramics. These solid crystalline compounds have been formed and mixed in the Earth's crust over billions of years by complex geological processes.

The clays are the raw materials used most widely in ceramics. They consist of fine particles of hydrous aluminum silicate that become a plastic substance that is formable and moldable when mixed with water. The most common clays are based on the mineral *kaolinite* ($Al_2Si_2O_5(OH)_4$). Other clay minerals vary in composition, both in terms of proportions of the basic ingredients and through additions of other elements such as magnesium, sodium, and potassium.

Besides its plasticity when mixed with water, a second characteristic of clay that makes it so useful is that it fuses into a dense, strong material when heated to a sufficiently elevated temperature. The heat treatment is known as *firing*. Suitable firing temperatures depend on clay composition. Thus, clay can be shaped while wet and soft, and then fired to obtain the final hard ceramic product.

Silica (SiO_2) is another major raw material for the traditional ceramics. It is the principal component in glass, and an important ingredient in other ceramic products including whiteware, refractories, and abrasives. Silica is available naturally in various forms, the most important of which is *quartz*. The main source of quartz is *sandstone*. The abundance of sandstone and its relative ease of processing means

that silica is low in cost; it is also hard and chemically stable. These features account for its widespread use in ceramic products. It is generally mixed in various proportions with clay and other minerals to achieve the appropriate characteristics in the final product. Feldspar is one of the other minerals often used. *Feldspar* refers to any of several crystalline minerals that consist of aluminum silicate combined with either potassium, sodium, calcium, or barium. The potassium blend, for example, has the chemical composition $KAlSi_3O_8$. Mixtures of clay, silica, and feldspar are used to make stoneware, china, and other tableware.

Still another important raw material for traditional ceramics is *alumina*. Most alumina is processed from the mineral *bauxite*, which is an impure mixture of hydrous aluminum oxide and aluminum hydroxide plus similar compounds of iron or manganese. Bauxite is also the principal ore in the production of aluminum metal. A purer but less common form of Al_2O_3 is the mineral *corundum*, which contains alumina in massive amounts. Slightly impure forms of corundum crystals are the colored gemstones sapphire and ruby. Alumina ceramic is used as an abrasive in grinding wheels and as a refractory brick in furnaces.

Silicon carbide, also used as an abrasive, does not occur as a mineral. Instead, it is produced by heating mixtures of sand (source of silicon) and coke (carbon) to a temperature of around 2200°C (3900°F), so that the resulting chemical reaction forms SiC and carbon monoxide.

7.2.2   TRADITIONAL CERAMIC PRODUCTS

The minerals discussed above are the ingredients for a variety of ceramic products. The coverage is organized by major categories of traditional ceramic products. A summary of these products, and the raw materials and ceramics out of which they are made, is presented in Table 7.3. The coverage is limited to materials commonly used in manufactured products, thus omitting certain commercially important ceramics such as cement.

Pottery and Tableware   This category is one of the oldest, dating back thousands of years; yet it is still one of the most important. It includes tableware products that we all use: earthenware, stoneware, and china. The raw materials for these products are clay usually combined with other minerals such as silica and feldspar. The wetted mixture is shaped and then fired to produce the finished piece.

Earthenware is the least refined of the group; it includes pottery and similar articles made in ancient times. Earthenware is relatively porous and is often glazed. *Glazing* involves application of a surface coating, usually a mixture of oxides such

TABLE • 7.3 Summary of traditional ceramic products.

Product	Principal Chemistry	Minerals and Raw Materials
Pottery, tableware	$Al_2Si_2O_5(OH)_4$, SiO_2, $KAlSi_3O_8$	Clay + silica + feldspar
Porcelain	$Al_2Si_2O_5(OH)_4$, SiO_2, $KAlSi_3O_8$	Clay + silica + feldspar
Brick, tile	$Al_2 Si_2O_5(OH)_4$, SiO_2 plus fine stones	Clay + silica + other
Refractory	Al_2O_3, SiO_2 Others: MgO, CaO	Alumina and silica
Abrasive: silicon carbide	SiC	Silica + coke
Abrasive: aluminum oxide	Al_2O_3	Bauxite or alumina

as silica and alumina, to make the product less pervious to moisture and more attractive to the eye. **Stoneware** has lower porosity than earthenware, resulting from closer control of ingredients and higher firing temperatures. **China** is fired at even higher temperatures, which produces the translucence in the finished pieces that characterize their fine quality. The reason for this is that much of the ceramic material has been converted to the glassy (vitrified) phase, which is relatively transparent compared to the polycrystalline form. Modern **porcelain** is nearly the same as china and is produced by firing the components, mainly clay, silica, and feldspar, at still higher temperatures to achieve a very hard, dense, glassy material. Porcelain is used in a variety of products ranging from electrical insulation to bathtub coatings.

Brick and Tile   Building brick, clay pipe, unglazed roof tile, and drain tile are made from various low-cost clays containing silica and gritty matter widely available in natural deposits. These products are shaped by pressing (molding) and firing at rela- tively low temperatures.

Refractories Refractory ceramics, often in the form of bricks, are critical in many industrial processes that require furnaces and crucibles to heat and/or melt materials. The useful properties of refractory materials are high temperature resistance, thermal insulation, and resistance to chemical reaction with the materials (usually molten metals) being heated. As mentioned, alumina is often used as a refractory ceramic, together with silica. Other refractory materials include magnesium oxide (MgO) and calcium oxide (CaO). The refractory lining often contains two layers, the outside layer being more porous because this increases the insulation properties.

Abrasives   Traditional ceramics used for abrasive products, such as grinding wheels and sandpaper, are **alumina** and **silicon carbide**. Although SiC is the harder mate- rial (hardness of SiC is 2600 HV vs. 2200 HV for alumina), the majority of grinding wheels are based on Al_2O_3 because it gives better results when grinding steel, the most widely used metal. The abrasive particles (grains of ceramic) are distributed throughout the wheel using a bonding material such as shellac, polymer resin, or rubber. The use of abrasives in industry involves material removal, and the technology of grinding wheels and other abrasive methods to remove material is presented in Chapter 24.

7.3   New Ceramics

The term new ceramics refers to ceramic materials that have been developed synthetically over the last several decades and to improvements in processing techniques that have provided greater control over the structures and properties of ceramic materials. In general, new ceramics are based on compounds other than variations of aluminum silicate (which form the bulk of the traditional ceramic materials). New ceramics are usually simpler chemically than traditional ceramics; for example, oxides, carbides, nitrides, and borides. The dividing line between traditional and new ceramics is sometimes fuzzy, because aluminum oxide and silicon carbide are included among the traditional ceramics. The distinction in these cases is based more on methods of processing than chemical composition.

The new ceramics are organized into chemical compound categories: oxides, carbides, and nitrides, discussed in the following sections. More complete coverage of new ceramics is presented in references [3], [5], and [8].

7.3.1 OXIDE CERAMICS

The most important oxide new ceramic is ***alumina***. Although also discussed in the context of traditional ceramics, alumina is today produced synthetically from bauxite, using an electric furnace method. Through control of particle size and impurities, refinements in processing methods, and blending with small amounts of other ceramic ingredients, strength and toughness of alumina have been improved substantially compared to its natural counterpart. Alumina also has good hot hardness, low thermal conductivity, and good corrosion resistance. This is a combination of properties that promote a wide variety of applications, including [13]: abrasives (grinding wheel grit), bioceramics (artificial bones and teeth), electrical insulators, electronic components, alloying ingredients in glass, refractory brick, cutting tool inserts (Section 22.3.1), spark plug barrels, and engineering components. Figure 7.1 shows a collection of new ceramic parts, most of which are made of alumina.

7.3.2 CARBIDES

The carbide ceramics include silicon carbide (SiC), tungsten carbide (WC), titanium carbide (TiC), tantalum carbide (TaC), and chromium carbide (Cr_3C_2). Silicon carbide was discussed previously. A part made of SiC is also shown in Figure 7.1. Although it is a man-made ceramic, the methods for its production were developed a century ago, and therefore it is generally included in the traditional ceramics group. In addition to its use as an abrasive, other SiC applications include resistance heating elements and additives in steelmaking.

FIGURE 7.1
A collection of ceramic components. The white parts are alumina and the black parts are silicon carbide and silicon nitride. (Photo courtesy of Insaco Inc.)

WC, TiC, and TaC are valued for their hardness and wear resistance in cutting tools and other applications requiring these properties. ***Tungsten carbide*** was the first to be developed (Historical Note 7.2) and is the most important and widely used material in the group. WC is typically produced by carburizing tungsten powders that have been reduced from tungsten ores such as ***wolframite*** ($FeMnWO_4$) and scheelite ($CaWO_4$). ***Titanium carbide*** is produced by carburizing the minerals ***rutile*** (TiO_2) or ***ilmenite*** ($FeTiO_3$). And ***tantalum carbide*** is made by carburizing either pure tantalum powders or tantalum pentoxide (Ta_2O_5) [11]. ***Chromium carbide*** is more suited to applications where chemical stability and oxidation resistance are important. Cr_3C_2 is prepared by carburizing chromium oxide (Cr_2O_3) as the starting compound. Carbon black is the usual source of carbon in all of these reactions.

Historical Note 7.2   *Tungsten carbide*

The compound WC does not occur in nature. It was first fabricated in the late 1890s by the Frenchman Henri Moissan. However, the technological and commercial importance of the development was not recognized for two decades.

Tungsten became an important metal for incandescent lamp filaments in the early 1900s. Wire drawing was required to produce the filaments. The traditional tool steel draw dies of the period were unsatisfactory for drawing tungsten wire due to excessive wear. There was a need for a much harder material. The compound WC was known to possess such hardness. In 1914 in Germany, H. Voigtlander and H. Lohmann developed a fabrication process for hard carbide draw dies by sintering parts pressed from powders of tungsten carbide and/or molybdenum carbide. Lohmann is credited with the first commercial production of sintered carbides.

The breakthrough leading to the modern technology of cemented carbides is linked to the work of K. Schroter in Germany in the early and mid–1920s. He used WC powders mixed with about 10% of a metal from the iron group, finally settling on cobalt as the best binder, and sintering the mixture at a temperature close to the melting point of the metal. The hard material was first marketed in Germany as "Widia" in 1926. The Schroter patents were assigned to the General Electric Company under the trade name "Carboloy"— first produced in the United States around 1928.

Widia and Carboloy were used as cutting tool materials, with cobalt content in the range 4% to 13%. They were effective in the machining of cast iron and many nonferrous metals, but not in the cutting of steel. When steel was machined, the tools would wear rapidly by cratering. In the early 1930s, carbide cutting tool grades with WC and TiC were developed for steel cutting. In 1931, the German firm Krupp started production of Widia X, which had a composition 84% WC, 10% TiC, and 6% Co. And Carboloy Grade 831 was introduced in the United States in 1932; it contained 69% WC, 21% TiC, and 10% Co.

Except for SiC, each carbide discussed here must be combined with a metallic binder such as cobalt or nickel in order to fabricate a useful solid product. In effect, the carbide powders bonded in a metal framework creates what is known as a ***cemented carbide***—a composite material, specifically a ***cermet*** (reduced from ***cer***amic and ***met***al). Cemented carbides and other cermets are discussed in Section 9.2. The carbides have little engineering value except as constituents in a composite system.

7.3.3 *NITRIDES*

The important nitride ceramics are silicon nitride (Si_3N_4), boron nitride (BN), and titanium nitride (TiN). As a group, the nitride ceramics are hard and brittle, and they melt at high temperatures (but not generally as high as the carbides). They are usually electrically insulating, except for TiN.

Silicon nitride shows promise in high temperature structural applications. Si_3N_4 oxidizes at about 1200°C (2200°F) and chemically decomposes at around 1900°C

(3400°F). It has low thermal expansion, good resistance to thermal shock and creep, and resists corrosion by molten nonferrous metals. These properties have provided applications for this ceramic in gas turbines, rocket engines, and melting crucibles.

Boron nitride exists in several structures, similar to carbon. The important forms of BN are (1) hexagonal, similar to graphite; and (2) cubic, same as diamond; in fact, its hardness is comparable to that of diamond. This latter structure goes by the names **cubic boron nitride** and **borazon**, symbolized cBN, and is produced by heating hexagonal BN under very high pressures. Owing to its extreme hardness, the principal applications of cBN are in cutting tools (Section 22.2.5) and abrasive wheels (Section 24.1.1). Interestingly, it does not compete with diamond cutting tools and grinding wheels. Diamond is suited to nonsteel machining and grinding, while cBN is appropriate for steel.

Titanium nitride has properties similar to those of other nitrides in this group, ex- cept for its electrical conductivity; it is a conductor. TiN has high hardness, good wear resistance, and a low coefficient of friction with the ferrous metals. This combination of properties makes TiN an ideal material as a surface coating on cutting tools. The coating is only around 0.006 mm (0.0003 in) thick, so the amounts of material used in this application are low. The gold color of titanium nitride makes it suitable for decorative coatings. Finally, its non-toxic properties allow its use in medical applica- tions as a coating material for implants.

A new ceramic material related to the nitride group, and also to the oxides, is the oxynitride ceramic called **sialon**. It consists of the elements silicon, aluminum, oxygen, and nitrogen; and its name derives from these ingredients: Si-Al-O-N. Its chemical composition is variable, a typical composition being $Si_4Al_2O_2N_6$. Properties of sialon are similar to those of silicon nitride, but it has better resistance to oxidation at high temperatures than Si_3N_4. Its principal application is for cutting tools, but its properties may make it suitable for other high temperature applications in the future.

7.4 Glass

The term glass is somewhat confusing because it describes a state of matter as well as a type of ceramic. As a state of matter, the term refers to an amorphous, or non-crystalline, structure of a solid material. The glassy state occurs in a material when insufficient time is allowed during cooling from the molten condition for the crystal-line structure to form. It turns out that all three categories of engineering materials (metals, ceramics, and polymers) can assume the glassy state, although the circum-stances for metals to do so are quite rare.

As a type of ceramic, **glass** is an inorganic, nonmetallic compound (or mixture of compounds) that cools to a rigid condition without crystallizing; it is a ceramic that is in the glassy state as a solid material. This is the material discussed in this section—a material that dates back 4500 years (Historical Note 7.3).

Historical Note 7.3   *History of glass*

The oldest glass specimens, dating from around 2500 B.C.E., are glass beads and other simple shapes found in Mesopotamia and ancient Egypt. These were made by painstakingly sculpturing glass solids, rather than by molding or shaping molten glass. It was a thousand years before the ancient cultures exploited the fluid

properties of hot glass, by pouring it in successive layers over a sand core until sufficient thickness and rigidity had been attained in the product, a cup-shaped vessel. This pouring technique was used until around 200 B.C.E., when a simple tool was developed that revolutionized glassworking—the blowpipe.

Glassblowing was probably first accomplished in Babylon and later by the Romans. It was performed using an iron tube several feet long, with a mouthpiece on one end and a fixture for holding the molten glass on the other. A blob of hot glass in the required initial shape and viscosity was attached to the end of the iron tube, and then blown into shape by an artisan either freely in air or into a mold cavity. Other simple tools were utilized to add the stem and/or base to the object. The ancient Romans showed great skill in their use of various metallic oxides to color glass. Their technology is evident in the stained glass windows of cathedrals and churches of the Middle Ages in Italy and the rest of Europe. The art of glassblowing is still practiced today for certain consumer glassware; and automated versions of glassblowing are used for mass-produced glass products such as bottles and light bulbs (Chapter 12).

7.4.1 *CHEMISTRY AND PROPERTIES OF GLASS*

The principal ingredient in virtually all glasses is *silica* (SiO_2), most commonly found as the mineral quartz in sandstone and silica sand. Quartz occurs naturally as a crystalline substance; but when melted and then cooled, it forms vitreous silica. Silica glass has a very low thermal expansion coefficient and is therefore quite resistant to thermal shock. These properties are ideal for elevated temperature applications; accordingly, Pyrex and chemical glassware designed for heating are made with high proportions of silica glass.

In order to reduce the melting point of glass for easier processing, and to control properties, the composition of most commercial glasses includes other oxides as well as silica. Silica remains as the main component in these glass products, usually comprising 50% to 75% of total chemistry. The reason SiO_2 is used so widely in these compositions is because it is the best *glass former*. It naturally transforms into a glassy state upon cooling from the liquid, whereas most ceramics crystallize upon solidification. Table 7.4 lists typical chemistries for some common glasses. The additional ingredients are contained in a solid solution with SiO_2, and each has a function: (1) acting as flux (promoting fusion) during heating; (2) increasing fluidity in the molten glass for processing; (3) retarding *devitrification*—the tendency to crystallize from the glassy state; (4) reducing thermal expansion in the final product; (5) improving the chemical resistance against attack by acids, basic substances, or water; (6) adding color to the glass; and (7) altering the index of refraction for optical applications (e.g., lenses).

7.4.2 *GLASS PRODUCTS*

Following is a list of the major categories of glass products. The roles played by the different ingredients are examined in Table 7.4 as these products are discussed.

Window Glass   This glass is represented by two chemistries in Table 7.4: (1) soda-lime glass and (2) window glass. The soda-lime formula dates back to the glass-blowing industry of the 1800s and earlier. It was (and is) made by mixing soda (Na_2O) and lime (CaO) with silica (SiO_2) as the major ingredient. The blending of ingredients has evolved empirically to achieve a balance between avoiding crystallization during

TABLE • 7.4 Typical compositions of selected glass products.

Product	Chemical Composition (by weight to nearest %)								
	SiO_2	Na_2O	CaO	Al_2O_3	MgO	K_2O	PbO	B_2O_3	Other
Soda-lime glass	71	14	13	2					
Window glass	72	15	8	1	4				
Container glass	72	13	10	2[a]	2	1			
Light bulb glass	73	17	5	1	4				
Laboratory glass:									
Vycor	96			1				3	
Pyrex	81	4		2				13	
E-glass (fibers)	54	1	17	15	4			9	
S-glass (fibers)	64			26	10				
Optical glasses:									
Crown glass	67	8				12		12	ZnO
Flint glass	46	3				6	45		

Compiled from [4], [5] and [10], and other sources.
[a]May include Fe_2O_3 with Al_2O_3

cooling and achieving chemical durability of the final product. Modern window glass and the techniques for making it have required slight adjustments in composition and closer control over its variation. Magnesia (MgO) has been added to help re- duce devitrification.

Containers In previous times, the same basic soda-lime composition was used for manual glass-blowing to make bottles and other containers. Modern processes for shaping glass containers cool the glass more rapidly than older methods. Also, the importance of chemical stability in container glass is better understood today. Resulting changes in composition have attempted to optimize the proportions of lime (CaO) and soda (Na_2O_3). Lime promotes fluidity. It also increases devitrification, but since cooling is more rapid, this effect is not as important as in prior processing techniques with slower cooling rates. Soda reduces chemical instability and solubil- ity of the container glass.

Light Bulb Glass Glass used in light bulbs and other thin glass items (e.g., drinking glasses, Christmas ornaments) is high in soda and low in lime; it also contains small amounts of magnesia and alumina. The chemistry is dictated largely by the economics of large volumes involved in light bulb manufacture. The raw materials are inexpensive and suited to the continuous melting furnaces used today.

Laboratory Glassware These products include containers for chemicals (e.g., flasks, beakers, glass tubing). The glass must be resistant to chemical attack and thermal shock. Glass that is high in silica is suitable because of its low thermal expansion. The trade name "Vicor" is used for this high-silica glass. This product is very insoluble in water and acids. Additions of boric oxide also produce a glass with low coefficient of thermal expansion, so some glass for laboratory ware contains B_2O_3 in amounts of around 13%. The trade name "Pyrex" is used for the borosilicate glass

developed by the Corning Glass Works. Both Vicor and Pyrex are included in the listing as examples of this product category.

Glass Fibers Glass fibers are manufactured for a number of important applica- tions, including fiberglass reinforced plastics, insulation wool, and fiber optics. The compositions vary according to function. The most commonly used glass reinforcing fibers in plastics are E-glass. It is high in CaO and Al_2O_3 content, it is economical, and it possesses good tensile strength in fiber form. Another glass fiber material is S-glass, which has higher strength but is not as economical as E-glass. Compositions are indicated in the table.

Insulating fiberglass wool can be manufactured from regular soda-lime-silica glasses. The glass product for fiber optics consists of a long, continuous core of glass with high refractive index surrounded by a sheath of lower refractive glass. The in-side glass must have a very high transmittance for light in order to accomplish long distance communication.

Optical Glasses Applications for these glasses include lenses for eyeglasses and optical instruments such as cameras, microscopes, and telescopes. To achieve their function, the glasses must have different refractive indices, but each lens must be homogenous in composition. Optical glasses are generally divided into: crowns and flints. ***Crown glass*** has a low index of refraction, while ***flint glass*** contains lead oxide (PbO) that gives it a high index of refraction.

7.4.3 *GLASS-CERAMICS*

Glass-ceramics are a class of ceramic material produced by conversion of glass into   a polycrystalline structure through heat treatment. The proportion of crystalline phase in the final product typically ranges between 90% and 98%, with the remain- der being unconverted vitreous material. Grain size is usually between 0.1 and 1.0 mm (4 and 40 m-in), significantly smaller than the grain size of conventional ceramics. This fine crystal microstructure makes glass-ceramics much stronger than the glasses from which they are derived. Also, due to their crystal structure, glass-ceramics are opaque (usually gray or white) rather than clear.

The processing sequence for glass-ceramics is as follows: (1) The first step in-volves heating and forming operations used in glassworking (Section 12.2) to create the desired product geometry. Glass shaping methods are generally more economi- cal than pressing and sintering to shape traditional and new ceramics made from powders. (2) The product is cooled. (3) The glass is reheated to a temperature suf- ficient to cause a dense network of crystal nuclei to form throughout the material. It is the high density of nucleation sites that inhibits grain growth of individual crystals, thus leading ultimately to the fine grain size in the glass-ceramic material. The key to the propensity for nucleation is the presence of small amounts of nucleating agents in the glass composition. Common nucleating agents are TiO_2, P_2O_5, and ZrO_2. (4) Once nucleation is initiated, the heat treatment is continued at a higher temperature to cause growth of the crystalline phases.

Several examples of glass-ceramic systems and typical compositions are listed in Table 7.5. The Li_2O-Al_2O_3-SiO_2 system is the most important commercially; it includes Corning Ware (Pyroceram), the familiar product of the Corning Glass Works.

TABLE • 7.5 Several glass-ceramic systems.

Glass-Ceramic System	Typical Composition (to nearest %)						
	Li_2O	MgO	Na_2O	BaO	Al_2O_3	SiO_2	TiO_2
Li_2O-Al_2O_3-SiO_2	3				18	70	5
MgO-Al_2O_3-SiO_2		13			30	47	10
Na_2O-BaO-Al_2O_3-SiO_2			13	9	29	41	7

Compiled from [5], [6], and [10].

The significant advantages of glass-ceramics include (1) efficiency of processing in the glassy state, (2) close dimensional control over the final product shape, and (3) good mechanical and physical properties. Properties include high strength (stronger than glass), absence of porosity, low coefficient of thermal expansion, and high resistance to thermal shock. These properties have resulted in applications in cooking ware, heat exchangers, and missile radomes. Certain systems (e.g., MgO-Al_2O_3-SiO_2 system) are also characterized by high electrical resistance, suitable for electrical and electronics applications.

7.5 Some Important Elements Related to Ceramics

In this section, several elements of engineering importance are discussed: carbon, silicon, and boron. These materials are encountered occasionally in subsequent chapters. Although they are not ceramic materials according to the definition, they sometimes compete for applications with ceramics. And they have important applications of their own. Basic data on these elements are presented in Table 7.6.

7.5.1 *CARBON*

Carbon occurs in two alternative forms of engineering and commercial importance: graphite and diamond. They compete with ceramics in various applications: graphite in situations where its refractory properties are important, and diamond

TABLE • 7.6 Some basic data and properties of carbon, silicon, and boron.

	Carbon	Silicon	Boron
Symbol	C	Si	B
Atomic number	6	14	5
Specific gravity	2.25	2.42	2.34
Melting temperature	3727°C[a] (6740°F)	1410°C (2570°F)	2030°C (3686°F)
Elastic modulus, GPa (lb/in²)	240[b] (35 X 10⁶)[c] 10357[c] (150 X 10⁶)[c]	N.A.	393 (57 X 10⁶)
Hardness (Mohs scale)	1[b], 10[c]	7	9.3

[a]Carbon sublimes (vaporizes) rather than melt.
[b]Carbon in the form of graphite (typical value given).
[c]Carbon in the form of diamond.
N.A. = not available.

in industrial applications where hardness is the critical factor (such as cutting and grinding tools).

Graphite   Graphite has a high content of crystalline carbon in the form of layers. Bonding between atoms in the layers is covalent and therefore strong, but the parallel layers are bonded to each other by weak van der Waals forces. This structure makes graphite quite anisotropic; strength and other properties vary significantly with direction. It explains why graphite can be used both as a lubricant and as a fiber in advanced composite materials. In powder form, graphite possesses low frictional characteristics due to the ease with which it shears between the layers; in this form, graphite is valued as a lubricant. In fiber form, graphite is oriented in the hexagonal planar direction to produce a filament material of very high strength and elastic modulus. These graphite fibers are used in structural composites ranging from tennis rackets to fighter aircraft components.

Graphite exhibits certain high temperature properties that are both useful and unusual. It is resistant to thermal shock, and its strength actually increases with temperature. Tensile strength at room temperature is about 100 MPa (15,000 lb/in^2), but increases to about twice this value at 2500°C (4500°F) [5]. Theoretical density of carbon is 2.22 gm/cm^3, but apparent density of bulk graphite is lower due to porosity (around 1.7 gm/cm^3). This is increased through compacting and heating. It is electrically conductive, but its conductivity is not as high as most metals. A disadvantage of graphite is that it oxidizes in air above around 500°C (900°F). In a reducing atmosphere it can be used up to around 3000°C (5400°F), not far below its sublimation point of 3727°C (6740°F).

The traditional form of graphite is polycrystalline with a certain amount of amorphous carbon in the mixture. Graphite crystals are often oriented (to a limited degree) in the commercial production process to enhance properties in a preferred direction for the application. Also, strength is improved by reducing grain size (similar to ceramics). Graphite in this form is used for crucibles and other refractory applications, electrodes, resistance heating elements, antifriction materials, and fibers in composite materials. Thus, graphite is a very versatile material. As a powder it is a lubricant. In traditional solid form it is a refractory. And when formed into graphite fibers, it is a high-strength structural material.

Diamond   Diamond is carbon that possesses a cubic crystalline structure with covalent bonding between atoms, as shown in Figure 2.5(b). This structure is three- dimensional, rather than layered as in graphite carbon, and this accounts for the very high hardness of diamond. Single crystal natural diamonds (mined in South Africa) have a hardness of 10,000 HV, while the hardness of an industrial diamond (polycrystalline) is around 7000 HV. The high hardness accounts for most of the ap- plications of industrial diamond. It is used in cutting tools and grinding wheels for machining hard, brittle materials, or materials that are very abrasive. For example, diamond tools and wheels are used to cut ceramics, fiberglass, and hardened metals other than steels. Diamond is also used in dressing tools to sharpen grinding wheels that consist of other abrasives such as alumina and silicon carbide. Similar to graph- ite, diamond has a propensity to oxidize (decompose) in air at temperatures above about 650°C (1200°F).

Industrial or synthetic diamonds date back to the 1950s and are fabricated by heating graphite to around 3000°C (5400°F) under very high pressures (Figure 7.2). This process approximates the geological conditions by which natural diamonds were formed millions of years ago.
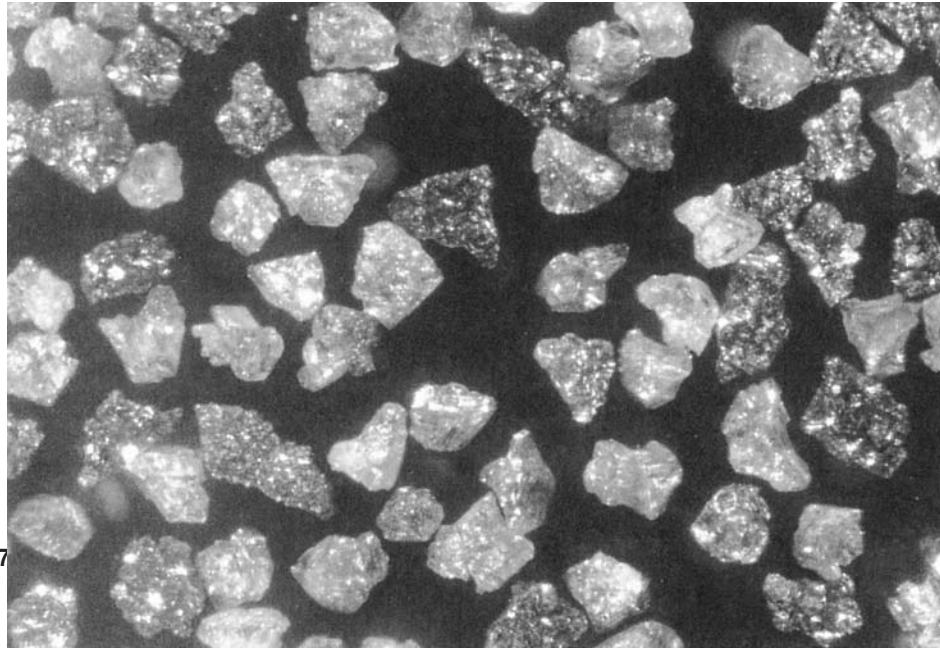
FIGURE 7
Synthetically produced diamond powders. (Photoc

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7.5.2   *SILICON*

Silicon is a semimetallic element in the same group in the periodic table as carbon (Figure 2.1). Silicon is one of the most abundant elements in the Earth's crust, com- prising about 26% by weight (Table 7.1). It occurs naturally only as a chemical com- pound—in rocks, sand, clay, and soil—either as silicon dioxide or as more complex silicate compounds. As an element it has the same crystalline structure as diamond, but its hardness is lower. It is hard but brittle, lightweight, chemically inactive at room temperature, and is classified as a semiconductor.

The greatest amounts of silicon in manufacturing are in ceramic compounds (SiO_2 in glass and silicates in clays) and alloying elements in steel, aluminum, and copper alloys. It is also used as a reducing agent in certain metallurgical processes. Of sig- nificant technological importance is pure silicon as the base material in semiconduc- tor manufacturing in electronics. The vast majority of integrated circuits produced today are made from silicon (Chapter 33).

7.5.3   *BORON*

Boron is a semimetallic element in the same periodic group as aluminum. It is only about 0.001% of the Earth's crust by weight, commonly occurring as the miner- als **borax** ($Na_2B_4O_7–10H_2O$) and **kernite** ($Na_2B_4O_7–4H_2O$). Boron is lightweight and very stiff (high modulus of elasticity) in fiber form. In terms of electrical properties, it is classified as a semiconductor (its conductivity varies with temperature; it is an insulator at low temperatures but a conductor at high temperatures).

As a material of industrial significance, boron is usually found in compound form. As such, it is used as a solution in nickel electroplating operations, an ingredient (B_2O_3) in certain glass compositions, a catalyst in organic chemical reactions, and as a nitride (cubic boron nitride) for cutting tools. In nearly pure form it is used as a fiber in composite materials (Sections 9.4.1 and 14.1).