

CERAMICS

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Engineers traditionally consider metals to be the most important class of engineering materials. However, it is interesting to note that ceramic materials are actually more abundant and widely used. Included in this category are clay products (bricks, tile, pottery, and chinaware), glass, cement, and concrete. (Concrete is a composite material, but its two components are both ceramic.) Also included are modern ceramic materials such as tungsten carbide and cubic boron nitride.

The importance of ceramics as engineering materials is based on 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 semimetal) and one or more nonmetals. 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 ranging from abrasives to artificial bones; and more complex compounds such as hydrous aluminum silicate ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$).

known as *kaolinite*, the principal ingredient 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 compounds, some of which occur naturally, while others are manufactured.

Ceramic raw materials are generally formed into solid products by the action of heat, such as the firing of clay or the heating of glass for blowing or molding. The word *ceramic* traces from the Greek *keramos*, meaning potter's clay or wares made from fired clay. Thus the modern word describes both the material itself and many of the products made of it.

The general properties that make ceramics useful in engineered products are high hardness, good electrical and thermal insulating characteristics, chemical stability, 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 performance of the ceramic products.

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 the following:

- > **Clay construction products**, such as bricks, clay pipe, and building tile
- > **Refractory ceramics**—ceramics capable of high temperature applications such as furnace walls, crucibles, and molds
- > **Cement** used in **concrete**, used for construction and roads
- > **Whiteware products**, including pottery, stoneware, fine china, porcelain, and other tableware, based on mixtures of clay and other minerals
- > **Glass**—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**—applications include 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**, such as artificial teeth and bones

For purposes of organization, we classify ceramic materials 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 traditional 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, we have **glass ceramics**—glasses that have been transformed into a largely crystalline structure by heat treatment.

Also included in this chapter is coverage of several elements that are related to the ceramics because they are used in similar applications and are often competitive materials. These elemental materials are carbon, silicon, and boron.

7.1 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; in fact, some ceramics decompose rather than melt at high temperature.

Ceramics usually 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 $(\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4)$, 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. Chemically, most glasses consist of fused silica. Variations in properties and colors are obtained by adding other glassy ceramic materials such as oxides of aluminum, boron, calcium, and magnesium. In addition to these pure glasses, many ceramics possessing 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(a)). As seen in Table 7.2, hardness and elastic modulus for many of the new ceramics are greater than those of metals (compare 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 because 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, interstitials, 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 applied stress much more

(S) 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 stronger in compression than in tension. For engineering and structural applications, designers have learned to use ceramic components so that they are loaded in compression 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 (1) making the starting materials more uniform; (2) decreasing grain size in polycrystalline ceramic products; (3) minimizing porosity; (4) introducing compressive surface stresses; for example, through application 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 (see [6]).

Physical Properties

(1) Several of the physical properties of ceramics are presented in Table 7.3. Most ceramic materials are lighter than metals and heavier than polymers (refer to Table 4.1). Melting temperatures are higher than for most metals, some ceramics preferring to decompose rather than melt.

(2) 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 different 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

POLYMERS

plastics
Rubbers

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Of the three basic types of materials, polymers are the newest and at the same time the oldest known to man. A polymer is a compound consisting of long-chain molecules, each molecule made up of repeating units connected together. There may be thousands, even millions of units in a single polymer molecule. The word is derived from the Greek words poly, meaning many, and meros (reduced to mer), meaning part. Most polymers are based on carbon and are therefore considered organic chemicals. However, the group also includes a number of inorganic polymers.

Polymers form the living organisms and vital processes of all life on Earth. To ancient man, biological polymers were the source of food, shelter, and many of his implements. However, our interest in this chapter is in materials other than biological polymers. With the exception of natural rubber, nearly all of the polymeric materials used in engineering are synthetic—they are made by chemical processing.

Polymers can be separated into plastics and rubbers. As engineering materials, they are relatively new compared to metals and ceramics, dating only from around the mid-1800s (Historical Notes 8.1 on plastics, and 8.2 and 8.3 on rubbers). For our purposes in covering polymers as a technical subject, it is appropriate to divide them into the following three categories, where (1) and (2) are the plastics and (3) are the rubbers:

- ✓ (1) ***Thermoplastic polymers***, or ***Thermoplastics*** (TP), as they are often called, are solid materials at room temperature, but they become viscous liquids when heated to temperatures of only a few hundred degrees. This characteristic allows them to be easily and economically shaped into products. They can be subjected to this heating and cooling cycle repeatedly without significant degradation of the polymer.
- ✓ (2) ***Thermosetting polymers***, or Thermosets (TS) cannot tolerate repeated heating cycles as thermoplastics can. When initially heated, they soften and flow for molding; but the elevated temperatures also produce a chemical reaction that hardens the material into an infusible solid. If reheated, thermosetting polymers degrade and char rather than soften.
- ✓ (3) ***Elastomers***. These are the rubbers. Elastomers (E) are polymers that exhibit extreme elastic extensibility when subjected to relatively low mechanical stress. Some elastomers can be stretched by a factor of 10 and yet completely recover to their original shape. Although their properties are quite different from thermosets, they share a similar molecular structure that is different from the thermoplastics.

Thermoplastics are commercially the most important of the three types, constituting around 70% of the tonnage of all synthetic polymers produced. Thermosets and elastomers share the remaining 30% about evenly, with a slight edge for the former. Common TP polymers include polyethylene, polyvinylchloride, polypropylene, polystyrene, and nylon. Examples of TS polymers are phenolics, epoxies, and certain polyesters. The most common example given for elastomers is natural (vulcanized) rubber; however, synthetic rubbers exceed the tonnage of natural rubber.

Although the classification of polymers into TP, TS, and E categories will suit our purposes quite adequately for organizing the topic in this chapter, we should note that the three types sometimes overlap: certain polymers that are normally thermoplastic can be made into thermosets; some polymers can be either thermosets or elastomers (we indicated that their molecular structures are similar); and some elastomers are thermoplastic. However, these are exceptions to the general classification scheme.

The growth in applications of synthetic polymers is truly impressive. On a volumetric basis, current annual usage of polymers exceeds that of metals. There are several reasons for the commercial and technological importance of polymers:

- ✓ ➤ Plastics can be formed by molding into intricate part geometries, usually with no further processing required. They are very compatible with *net shape* processing.
- ✓ ➤ Plastics possess an attractive list of properties for many engineering applications where strength is not a factor: (1) low density relative to metals and ceramics; (2) good strength-to-weight ratios for certain (but not all) polymers; (3) high corrosion resistance; and (4) low electrical and thermal conductivity.
- ✓ ➤ On a volumetric basis, polymers are cost competitive with metals.
- On a volumetric basis, polymers generally require less energy to produce than metals. This is generally true because the temperatures for working these materials are much lower than for metals.
- ✓ ➤ Certain plastics are translucent and/or transparent, which makes them competitive with glass in some applications.
- Polymers are widely used in composite materials (Chapter 9).

On the negative side, polymers in general have the following limitations: (1) strength is low, relative to metals and ceramics; (2) modulus of elasticity or stiffness is also low—in the case of elastomers, of course, this may be a desirable characteristic; (3) service temperatures are limited to only a few hundred degrees because of the softening of thermoplastic polymers or degradation of thermosetting polymers; (4) some polymers degrade when subjected to sunlight and other forms of radiation; and (5) plastics exhibit viscoelastic properties (Section 3.5), which can be a distinct limitation in load bearing applications.

In this chapter we examine the technology of polymeric materials. The first section is devoted to an introductory discussion of polymer science and technology. Subsequent sections survey the three basic categories of polymers: thermoplastics, thermosets, and elastomers.

Thermoplast

Mechanical PPs of Thermoplastic Polymers

- much lower stiffness
- _____ hardness
- greater ductility
- lower tensile strength, about 10% of metals

Physical PPs

- lower density than metals or ceramics
- much higher coefficient of thermal expansion
(5 times of metals, 10 times of ceramics)
- much lower melting temp
- higher insulating PPs

Thermosets

- more rigid
- brittle in nature
- less soluble
- capable of higher service temperature
- not capable to being remelted

COMPOSITE MATERIALS

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- 9.5 Guide to Processing Composite Materials

In addition to metals, ceramics, and polymers, a fourth material category can be distinguished: composites. In some ways, these are the most interesting of the engineering materials because their structure is more complex than the other three types. Although general agreement on a definition of composite materials is elusive, let us use the following for now: a composite material is a materials system composed of two or more physically distinct phases whose combination produces aggregate properties that are different from those of its constituents.

The technological and commercial interest in composite materials derives from the fact that their properties are not just different from their components but are often far superior. Some of the possibilities include

Properties

- > Composites can be designed that are very strong and stiff, yet very light in weight, giving them strength-to-weight and stiffness-to-weight ratios several times greater than steel or aluminum. These properties are highly desirable in applications ranging from commercial aircraft to sports equipment.
- > Fatigue properties are generally better than for the common engineering metals. Toughness is often greater, too.
- > Composites can be designed that do not corrode like steel; this is important in automotive and other applications.

- With composite materials, it is possible to achieve combinations of properties not attainable with metals, ceramics, or polymers alone.
- Better appearance and control of surface smoothness is possible with certain composite materials.

Along with the advantages, there are disadvantages and limitations associated with composite materials. These include: (1) properties of many important composites are anisotropic; the properties differ depending on the direction in which they are measured; (2) many of the polymer-based composites are subject to attack by chemicals or solvents, just as the polymers themselves are susceptible to attack; (3) composite materials are generally expensive, although prices may drop as volume increases; and (4) certain of the manufacturing methods for shaping composite materials are slow and costly.

We have already encountered several composite materials in our coverage of the three other material types. Examples include cemented carbides (tungsten carbide with cobalt binder), plastic molding compounds that contain fillers (e.g., cellulose fibers, wood flour), and rubber mixed with carbon black. We did not always identify these materials as composites; however, technically, they fit the above definition. It could even be argued that a two-phase metal alloy (e.g., Fe + Fe₃C) is a composite material, although it is not classified as such. Perhaps the most important composite material of all is wood.

In our presentation of composite materials, we first examine their technology and classification. There are many different materials and structures that can be used to form composites; we survey the various categories, devoting the most time to fiber-reinforced plastics—commercially the most important type. In the final section, we provide a guide to the manufacturing processes for composites.

9.1 TECHNOLOGY AND CLASSIFICATION OF COMPOSITE MATERIALS

As noted in our definition, a composite material consists of two or more distinct phases. The term phase indicates a homogeneous material, such as a metal or ceramic in which all of the grains have the same crystal structure, or a polymer with no fillers. By combining the phases, using methods yet to be described, a new material is created with aggregate performance exceeding that of its parts. The effect is synergistic.

Composite materials can be classified in various ways. One possible classification distinguishes between (1) traditional and (2) synthetic composites. Traditional composites are those that occur in nature or have been produced by civilizations for many years. Wood is a naturally occurring composite material, while concrete (Portland cement plus sand or gravel) and asphalt mixed with gravel are traditional composites used in construction. Synthetic composites are modern material systems normally associated with the manufacturing industries, in which the components are first produced separately and then combined in a controlled way to achieve the desired structure, properties, and part geometry. These synthetic materials are the composites normally thought of in the context of engineered products. Our attention in this chapter is focused on these materials.

9.1.1 Components in a Composite Material

In the simplest manifestation of our definition, a composite material consists of two phases: a primary phase and a secondary phase. The primary phase forms the matrix within which

the secondary phase is imbedded. The imbedded phase is sometimes referred to as a reinforcing agent (or similar term), because it usually serves to strengthen the composite. The reinforcing phase may be in the form of fibers, particles, or various other geometries, as we shall see. The phases are generally insoluble in each other, but strong adhesion must exist at their interface(s).

The matrix phase can be any of three basic material types: polymers, metals, or ceramics. The secondary phase may also be one of the three basic materials, or it may be an element such as carbon or boron. Possible combinations in a two-component composite material can be organized as a 3×4 chart, as in Table 9.1. We see that certain combinations are not feasible, such as a polymer in a metallic matrix. We also see that the possibilities include two-phase structures consisting of components of the same material type, such as fibers of Kevlar (polymer) in a plastic (polymer) matrix. In other composites the imbedded material is an element such as carbon or boron.

The classification system for composite materials used in this book is based on the matrix phase. We list the classes here and discuss them in Sections 9.2 through 9.4:

1. **Metal Matrix Composites** (MMCs)—These composites include mixtures of ceramics and metals, such as cemented carbides and other cermets, as well as aluminum or magnesium reinforced by strong, high stiffness fibers.
2. **Ceramic Matrix Composites** (CMCs)—This is the least common composite matrix. Aluminum oxide and silicon carbide are materials that can be imbedded with fibers for improved properties, especially in high temperature applications.
3. **Polymer Matrix Composites** (PMCs)—Thermosetting resins are the most widely used polymers in PMCs. Epoxy and polyester are commonly mixed with fiber reinforcement, and phenolic is mixed with powders such as wood flour. Thermoplastics are also reinforced, usually with powders (Section 8.1.5). Virtually all elastomers are reinforced with carbon black.

The classification can be applied to traditional composites as well as synthetics. Concrete is a ceramic matrix composite, while asphalt and wood are polymer matrix composites.

The matrix material serves several functions in the composite. First, it provides the bulk form of the part or product made of the composite material. Second, it holds the imbedded phase in place, usually enclosing and often concealing it. Third, when a load is applied, the matrix shares the load with the secondary phase, in some cases deforming so that the stress is essentially born by the reinforcing agent.

TABLE 9.1 Possible combinations of two-component composite materials.

Secondary phase, reinforcement:	Primary Phase, Matrix		
	Metal	Ceramic	Polymer
Metal	Infiltrated powder metallurgy parts	Cermets	Plastic molding compounds Steel-belted radial tires
Ceramic	Cermets ^a Fiber-reinforced metals	SiC whisker-reinforced Al ₂ O ₃	Plastic molding compounds Fiberglass-reinforced plastic
Polymer	NA	NA	Plastic molding compounds Kevlar-reinforced epoxy
Elements (C, B)	Fiber-reinforced metals	NA	Rubber with carbon black B or C fiber-reinforced plastic

NA = not applicable currently.

^a Cermets include cemented carbides.