

Ceramics

Ceramics are compounds between metallic and nonmetallic elements; they are most frequently oxides, nitrides, and carbides. For example, common ceramic materials include aluminum oxide (or alumina, Al_2O_3), silicon dioxide (or silica, SiO_2), silicon carbide (SiC), silicon nitride (Si_3N_4), and, in addition, what some refer to as the traditional ceramics, those composed of clay minerals (e.g., porcelain), as well as cement and glass. With regard to mechanical behavior, ceramic materials are relatively stiff and strong, stiffnesses and strengths are comparable to those of the metals. In addition, they are typically very hard.

Historically, ceramics have exhibited extreme brittleness (lack of ductility) and are highly susceptible to fracture. However, newer ceramics are being engineered to have improved resistance to fracture; these materials are used for cookware, cutlery, and even automobile engine parts.

Furthermore, ceramic materials are typically insulative to the passage of heat and electricity, and are more resistant to high temperatures and harsh environments than are metals and polymers. With regard to optical characteristics, ceramics may be transparent, translucent, or opaque, and some of the oxide ceramics (e.g., Fe_3O_4) exhibit magnetic behavior.

Types of Ceramics

There is a significant disparity between the physical characteristics of metals and ceramics. Consequently, these materials are used in completely different kinds of applications and, tend to complement each other and also the polymers. Most ceramic materials fall into an application-classification scheme that includes the following groups: glasses, structural clay products, white wares, refractories, abrasives, cements, carbons, and the newly developed advanced ceramics. Figure 1 presents a taxonomy of these several types.

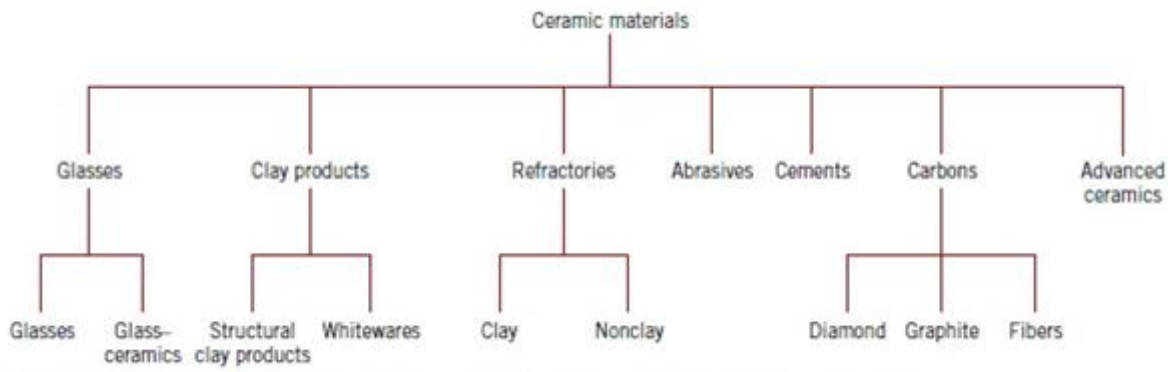


Figure 1. Classification of ceramic materials on the basis of application.

GLASSES

The glasses are a familiar group of ceramics; containers, lenses, and fiberglass represent typical applications, they are non-crystalline silicates containing other oxides, notably CaO , Na_2O , K_2O , and Al_2O_3 , which influence the glass properties. A typical soda–lime glass consists of approximately 70 wt% SiO_2 , the balance being mainly Na_2O (soda) and CaO (lime). Possibly the two prime assets of these materials are their optical transparency and the relative ease with which they may be fabricated.

GLASS-CERAMICS

Most inorganic glasses can be made to transform from a non-crystalline state into one that is crystalline by the proper high-temperature heat treatment. This process is called devitrification, and the product is a fine-grained polycrystalline material that is often called a glass-ceramic. A nucleating agent (frequently titanium dioxide) must be added to induce the crystallization or devitrification process. Desirable characteristics of glass–ceramics include a low coefficient of thermal expansion, such that the glass–ceramic ware will not experience thermal shock; in addition, relatively high mechanical strengths and thermal conductivities are achieved. Some glass–ceramics may be made optically transparent; others are opaque. Possibly the most attractive attribute of this class of materials is the ease with which they may be fabricated; conventional glass-forming techniques may be used conveniently in the mass production of nearly pore-free ware.

Glass–ceramics are manufactured commercially under the trade names of Pyro-ceram, Corningware, Cericor, and Vision. The most common uses for these materials are as ovenware

and tableware, primarily because of their strength, excellent resistance to thermal shock, and their high thermal conductivity. They also serve as electrical insulators and as substrates for printed circuit boards, and are utilized

CLAY PRODUCTS

One of the most widely used ceramic raw materials is clay. This inexpensive ingredient, found naturally in great abundance, often is used as mined without any upgrading of quality. Another reason for its popularity lies in the ease with which clay products may be formed; when mixed in the proper proportions, clay and water form a plastic mass that is very amenable to shaping. The formed piece is dried to remove some of the moisture, after which it is fired at an elevated temperature to improve its mechanical strength.

Most of the clay-based products fall within two broad classifications: the structural clay products and the whitewares. Structural clay products include building bricks, tiles, and sewer pipes—applications in which structural integrity is important.

The whiteware ceramics become white after the high-temperature firing. Included in this group are porcelain, pottery, tableware, china, and plumbing fixtures (sanitary ware). In addition to clay, many of these products also contain other ingredients, each of which has some role to play in the processing and characteristics of the finished piece.

REFRACTORIES

Another important class of ceramics that are utilized in large tonnages is the refractory ceramics. The salient properties of these materials include the capacity to withstand high temperatures without melting or decomposing, and the capacity to remain unreactive and inert when exposed to severe environments. In addition, the ability to provide thermal insulation is often an important consideration. Refractory materials are marketed in a variety of forms, but bricks are the most common.

Typical applications include furnace linings for metal refining, glass manufacturing, metallurgical heat treatment, and power generation.

Of course, the performance of a refractory ceramic, to a large degree, depends on its composition. On this basis, there are several classifications, namely, fireclay, silica, basic, and special refractories. For many commercial materials, the raw ingredients consist of both

large (or grog) particles and fine particles, which may have different compositions. Upon firing, the fine particles normally are involved in the formation of a bonding phase, which is responsible for the increased strength of the brick; this phase may be predominantly either glassy or crystalline. The service temperature is normally below that at which the refractory piece was fired.

Porosity is one microstructural variable that must be controlled to produce a suitable refractory brick. Strength, load-bearing capacity, and resistance to attack by corrosive materials all increase with porosity reduction. At the same time, thermal insulation characteristics and resistance to thermal shock are diminished. Of course, the optimum porosity depends on the conditions of service.

ABRASIVES

Abrasive ceramics are used to wear, grind, or cut away other material, which necessarily is softer. Therefore, the prime requisite for this group of materials is hardness or wear resistance; in addition, a high degree of toughness is essential to ensure that the abrasive particles do not easily fracture. Furthermore, high temperatures may be produced from abrasive frictional forces, so some refractoriness is also desirable.

Diamonds, both natural and synthetic, are utilized as abrasives; however, they are relatively expensive. The more common ceramic abrasives include silicon carbide, tungsten carbide (WC), aluminum oxide (or corundum), and silica sand.

Abrasives are used in several forms; bonded to grinding wheels, as coated abrasives, and as loose grains. In the first case, the abrasive particles are bonded to a wheel by means of a glassy ceramic or an organic resin. The surface structure should contain some porosity; a continual flow of air currents or liquid coolants within the pores that surround the refractory grains will prevent excessive heating.

Coated abrasives are those in which an abrasive powder is coated on some type of paper or cloth material; sandpaper is probably the most familiar example.

Wood, metals, ceramics, and plastics are all frequently ground and polished using this form of abrasive.

Grinding, lapping, and polishing wheels often employ loose abrasive grains that are delivered in some type of oil- or water-based vehicle. Diamonds, corundum, silicon carbide, and rouge (an iron oxide) are used in loose form over a variety of grain size ranges.

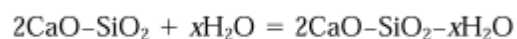
CEMENTS

Several familiar ceramic materials are classified as inorganic cements: cement, plaster of paris, and lime, which, as a group, are produced in extremely large quantities.

The characteristic feature of these materials is that when mixed with water, they form a paste that subsequently sets and hardens. This trait is especially useful in that solid and rigid structures having just about any shape may be expeditiously formed. Also, some of these materials act as a bonding phase that chemically binds particulate aggregates into a single cohesive structure. Under these circumstances, the role of the cement is similar to that of the glassy bonding phase that forms when clay products and some refractory bricks are fired. One important difference, however, is that the cementitious bond develops at room temperature.

Of this group of materials, Portland cement is consumed in the largest tonnages. It is produced by grinding and intimately mixing clay and lime-bearing minerals in the proper proportions, and then heating the mixture to about 1400° (2550°F) in a rotary kiln; this process, sometimes called calcination, produces physical and chemical changes in the raw materials. The resulting “clinker” product is then ground into a very fine powder to which is added a small amount of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) to retard the setting process. This product is Portland cement. The properties of Portland cement, including setting time and final strength, to a large degree depend on its composition.

Several different constituents are found in portland cement, the principal ones being tricalcium silicate ($3\text{CaO} \cdot \text{SiO}_2$) and dicalcium silicate ($2\text{CaO} \cdot \text{SiO}_2$). The setting and hardening of this material result from relatively complicated hydration reactions that occur between the various cement constituents and the water that is added. For example, one hydration reaction involving dicalcium silicate is as follows:



where x is variable and depends on how much water is available. These hydrated products are in the form of complex gels or crystalline substances that form the cementitious bond. Hydration reactions begin just as soon as water is added to the cement. These are first manifested as setting (i.e., the stiffening of the once-plastic paste), which takes place soon after mixing, usually within several hours. Hardening of the mass follows as a result of further hydration, a relatively slow process that may continue for as long as several years. It should be

emphasized that the process by which cement hardens is not one of drying, but rather, of hydration in which water actually participates in a chemical bonding reaction.

Portland cement is termed a hydraulic cement because its hardness develops by chemical reactions with water. It is used primarily in mortar and concrete to bind, into a cohesive mass, aggregates of inert particles (sand and/or gravel); these are considered to be composite materials. Other cement materials, such as lime, are nonhydraulic; that is, compounds other than water (e.g., CO_2) are involved in the hardening reaction.

DIAMOND AND GRAPHITE

DIAMOND

The physical properties of diamond make it an extremely attractive material. It is extremely hard (the hardest known material) and has a very low electrical conductivity; these characteristics are due to its crystal structure and the strong interatomic covalent bonds. Furthermore, it has an unusually high thermal conductivity for a nonmetallic material, is optically transparent in the visible and infrared regions of the electromagnetic spectrum, and has a high index of refraction. Relatively large diamond single crystals are used as gem stones. Industrially, diamonds are utilized to grind or cut other softer materials (Section 13.8). Techniques to produce synthetic diamonds have been developed, beginning in the mid-1950s, that have been refined to the degree that today a large proportion of the industrial-quality materials are man-made, in addition to some of those of gem quality.

Over the last several years, diamond in the form of thin films has been produced. Film growth techniques involve vapor-phase chemical reactions followed by the film deposition. Maximum film thicknesses are on the order of a millimeter. Furthermore, none of the films yet produced has the long-range crystalline regularity of natural diamond. The diamond is polycrystalline and may consist of very small and/or relatively large grains; in addition, amorphous carbon and graphite may be present.

The mechanical, electrical, and optical properties of diamond films approach those of the bulk diamond material. These desirable properties have been and will continue to be exploited so as to create new and better products. For example, the surfaces of drills, dies, bearings, knives, and other tools have been coated with diamond films to increase surface hardness; some lenses and radomes have been made stronger while remaining transparent by the application of

diamond coatings; coatings have also been applied to loudspeaker tweeters and to high-precision micrometers. Potential applications for these films include application to the surface of machine components such as gears and bearings, to optical recording heads and disks, and as substrates for semiconductor devices.

GRAPHITE

In the structure of graphite, the electron bonding between the layers of hexagonally arranged carbon atoms is of the van der Waals type. As a consequence of these weak interplanar bonds, interplanar cleavage is facile, which gives rise to the excellent lubricative properties of graphite. Also, the electrical conductivity is relatively high in crystallographic directions parallel to the hexagonal sheets.

Other desirable properties of graphite include the following: high strength and good chemical stability at elevated temperatures and in nonoxidizing atmospheres, high thermal conductivity, low coefficient of thermal expansion and high resistance to thermal shock, high adsorption of gases, and good machinability. Graphite is commonly used as heating elements for electric furnaces, as electrodes for arc welding, in metallurgical crucibles, in casting molds for metal alloys and ceramics, for high-temperature refractories and insulations, in rocket nozzles, in chemical reactor vessels, for electrical contacts, brushes and resistors, as electrodes in batteries, and in air purification devices.