4 Introduction

We usually consider metals 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.

The importance of ceramics as engineering materials 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 semimetal) 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 ranging from abrasives to artificial bones; and more complex compounds such as hydrous aluminum silicate ($Al_2Si_2O_5(OH)_4$), 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 4.1.

TABLE 4.1 *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%

The group includes many additional compounds, 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 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 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:

a. *Clay construction products*, such as bricks, clay pipe, and building tile
b. *Refractory ceramics*, which are capable of high temperature applications such as furnace walls, crucibles, and molds
c. *Cement* used in concrete, used for construction and roads (concrete is a composite material, but its components are ceramics)
d. *Whiteware products*, including pottery, stoneware, fine china, porcelain, and other tableware, based on mixtures of clay and other minerals
e. *Glass* used in bottles, glasses, lenses, window panes, and light bulbs
f. *Glass fibers* for thermal insulating wool, reinforced plastics (fiberglass), and fiber optics communications lines
g. *Abrasives*, such as aluminum oxide and silicon carbide
h. *Cutting tool materials*, including tungsten carbide, aluminum oxide, and cubic boron nitride
i. *Ceramic insulators*, which are used in applications such as electrical transmission components, spark plugs, and microelectronic chip substrates

For purposes of organization, we classify ceramic materials into three (3) 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 non silicates 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 non-crystalline 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.

4.1 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, 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 andAl_2O_3.Bothof 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. 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 that have a crystal structure use the glassy phase as a binder for their crystalline phase.

4.1.1 Mechanical Properties

Ceramic materials are rigid and brittle, exhibiting a stress-strain behavior best characterized as perfectly elastic. As shown in Table 4.2, hardness and elastic modulus for many of the new ceramics are greater than those of metals. 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, 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 applied 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.

TABLE 4.2: *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	NA	95	14×10^6	2.3	NA	NA
Cement, Portland	NA	50	7×10^6	2.4	NA	NA
Silicon carbide (SiC)	2600 HV	460	68×10^6	3.2	27,007[a]	48,927[a]
New ceramics						
Alumina (Al_2O_3)	2200 HV	345	50×10^6	3.8	2054	3729
Cubic boron nitride (cBN)	6000 HV	NA	NA	2.3	30,007[a]	54,307[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]

NA = 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 140^{0}C (255^{0}F).

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 learnt 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.

4.1.2 Physical Properties

Most ceramic materials are lighter than metals and heavier than polymers. 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 different regions of the same part. The terms thermal shock and thermal cracking are used in connection with such failures.

4.2 Traditional Ceramics

These materials are based on mineral silicates, silica, and mineral oxides. The primary 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. Glass is also a silicate

4.2.1 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 KAlSi3O8. 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^{o}C (4000^{o}F), so that the resulting chemical reaction forms SiC and carbon monoxide.

4.2.2 Traditional Ceramic Products

The minerals discussed above are the ingredients for a variety of ceramic products. We organize our coverage here 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 4.3.

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.

Earthenware: It 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 as silica and alumina, to make the product less pervious to moisture and more attractive to the eye.

Stoneware: It 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.

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 relatively 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 we have mentioned, alumina is often used as a refractory ceramic, together with silica. Other refractory materials include magnesium oxide (MgO) and calcium oxide (CaO).

Abrasives: Traditional ceramics used for abrasive products, such as grinding wheels and sandpaper, are alumina and silicon carbide. Although SiCis the harder material (hardness of SiC is 2600 HV vs. 2200 HV for alumina), the majority of grinding wheels are based on.

TABLE 4.3: S*ummary 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

4.3 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 noncrystalline, 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 crystalline structure to form. It turns out that all three categories of engineering materials (metals, ceramics, and polymers) can assume the glassy state, although the circumstances 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.

4.3.1 Chemistry and Properties of Glass

The principal ingredient in virtually all glasses is silica, 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 SiO2 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.

4.3.2 Glass Products

Following is a list of the major categories of glass products. We examine the roles played by the different ingredients in Table 4.4 as we discuss these products.

Window Glass: This glass is represented by two chemistries in Table 4.4: (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 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 reduce 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 glassmore 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 solubility 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 containsB2O3 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 our listing as examples of this product category.

Glass Fibers: Glass fibers are manufactured for a number of important applications, 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 our 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 inside 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.

4.3.3 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 remainder 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 involves heating and forming operations used in glassworking to create the desired product geometry. Glass shaping methods are generally more economical than pressing and sintering to shape traditional and new ceramics madefrom powders.

(2)The product is cooled.

(3) The glass is reheated to a temperature sufficient 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.

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., $MgO\text{-}Al_2O_3\text{-}SiO_2$ system) are also characterized by high electrical resistance, suitable for electrical and electronics applications.