Section One

Fundamentals of Nature and Characteristics of Ceramics

Chapter 1

Ceramics: Definition and Characteristics

In this chapter, the general properties of ceramics are discussed in reference to other primary classes of materials. Further, the need for the development of high-toughness ceramics with high hardness, strength, and wear resistance are addressed. The development of ceramic materials for high-temperature applications are also discussed.

1.1 MATERIALS CLASSIFICATION

There is a general consensus that engineering materials can be classified into three primary classes: metals and alloys; ceramics and glasses; and polymers. Among these three primary classes, metals, metallic alloys, and polymers are, by far, more widely used than ceramics and glasses for various structural and engineering applications. Nevertheless, ceramics have attracted attention in the scientific community in the last three decades.[1–4] The widespread use of metallic materials is driven by their high tensile strength and high toughness (crack growth resistance) as well as their ability to be manufactured in various sizes and shapes using reproducible fabrication techniques. Similarly, polymers have distinct advantages in terms of their low density, high flexibility, and ability to be molded into different shapes and sizes. Nevertheless, polymeric materials have low melting point (less than 400°C) as well as very low strength and elastic modulus. Compared with ceramics, metals have much lower hardness and many commonly used metallic materials have a much lower melting point (<2000°C). From this perspective, ceramics and glasses have advantageous properties, including refractoriness (capability to withstand high temperatures), strength retention at high temperature, high melting point, and good mechanical properties (hardness, elastic modulus, and compressive strength). In view of such an attractive combination of properties, ceramics are considered as potential materials for high-temperature structural applications and various tribological applications requiring high hardness and wear resistance. Despite having such

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potential applications, the widespread use of ceramics has been limited, because of their brittleness (poor fracture toughness) and variability in mechanical properties.

To combine various advantageous properties of the three primary material classes, a derived material class—that is, composites—is being developed. The composites are generally defined as a class of materials that comprise at least two intimately bonded microstructural phases aimed to provide properties (e.g., elastic modulus, hardness, strength) tailored for specific applications; it is expected that a specific property of a composite should be higher than the simple addition of that property of the constituent phases. Depending on whether metals, ceramics, or polymers comprise more than 50% by volume of a composite, it can be further classified as a metal matrix composite (MMC), a ceramic matrix composite (CMC), or a polymer matrix composite (PMC) respectively. From the microstructural point of view, a composite contains a matrix (metal, ceramic, polymer) and a reinforcement phase. The crystalline matrix phase can have an equiaxed or elongated grain structure; the reinforcement phase can have different shapes, for example particulates, whiskers, and fibers. The reinforcement shapes can be distinguished in terms of aspect ratio: particulates can be spheroidal; whiskers have a higher aspect ratio (>10); fibers have the largest aspect ratio. It is widely recognized now that the use of fibers or whiskers can lead to composites with anisotropic properties (different properties in different directions). As far as nomenclature is concerned, it is a common practice to designate a composite as $M\text{-}R_p$, $M\text{-}R_w$, or $M\text{-}R_f$, where M and R are the matrix and reinforcement, respectively, and the subscripts (p, w, f) essentially indicate the presence of reinforcement as particulates, whiskers, or fibers, respectively. One widely researched MMC is $Al–SiC_p$ composite; $Mg–SiC_p$ is being developed as a lightweight composite; several MMCs are used as automotive parts and structural components. Some popular examples of CMCs include $Al_2O_3–ZrO_{2\,p}$ and $Al_2O_3–SiC_w$; these CMCs are typically used as wear parts and cutting-tool inserts. Various resin-bonded PMCs are used for aerospace applications.

1.2 HISTORICAL PERSPECTIVE; DEFINITION AND CLASSIFICATION OF CERAMICS

As far as the history of ceramics is concerned, the word "ceramics" is derived from the Greek word *keramikos*, literally meaning potter's earth. Historically, the use of burnt clay, commercial pottery, and the existing ceramic industries can be dated back to 14,000 BC, 4000 BC, and 1500 BC, respectively. Early evidence of the use of clay- or pottery-based materials has been found in Harappan, Chinese, Greek, and many other civilizations. A large number of traditional ceramics were produced using conventional ceramic technology. Early forms of color decorative glazes date back to 3500 BC. The potter's wheel, invented around 2000 BC, revolutionized pottery making; porcelain emerged in China circa 600 AD. Glazed tiles were used to decorate the walls of the famous Tower of Babel and the Ishtar Gate in the ancient city of Babylon (562 BC). Figure 1.1 indicates the growth in ceramic technology from prehistoric ages to the 20th century. It is clear that, with technological development,

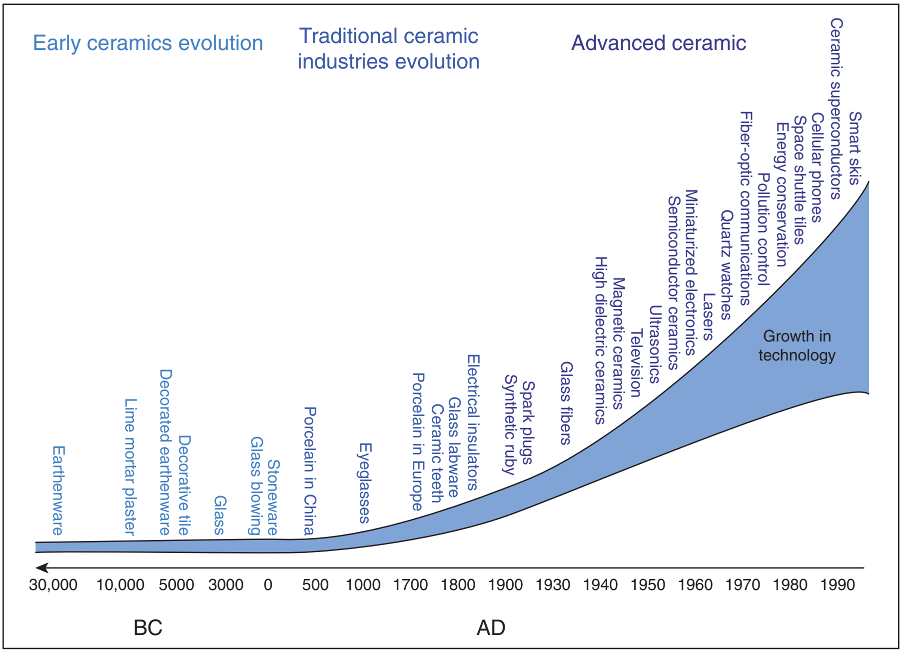


Figure 1.1 Historical evolution illustrating the growth of ceramic applications and industries.[30]

some newer applications in high-tech and important areas, for example the biomedical and electronics industries, are now possible.

A proper and exact definition of ceramics is very difficult. In general, ceramics can be defined as a class of inorganic nonmetallic materials[5] that have ionic and/or covalent bonding and that are either processed or used at high temperatures. Figures 1.1–1.4 illustrate two different aspects: (1) historical evolution of the development of ceramics right from traditional ceramics to the most advanced ceramics to composites and (2) illustration of various current uses of ceramics and their composites. For a layperson, the word “ceramic” means a coffee cup or sanitary ware—traditional ceramic products. Although the main use of ceramics in last few decades was centered on fields such as construction materials, tableware, and sanitary wares, the advancement of ceramic science since the early 1990s has enabled the application of this class of materials to evolve from more traditional fields to cutting-edge technologies, such as aerospace, nuclear, electronics, and biomedical, among others.[6] This is the reason that, in many textbooks, ceramics are classified as traditional ceramics and engineering ceramics. Traditional ceramics are largely silica or clay based and typically involve low-cost fabrication processes. A large cross section of people in the developing world is still familiar with the use of traditional ceramics. On the other hand, engineering ceramics are fabricated from high-purity ceramic powders, and their properties can be manipulated by varying process parameters and, thereby, microstructures. Also, engineering ceramics are, by far, more expensive

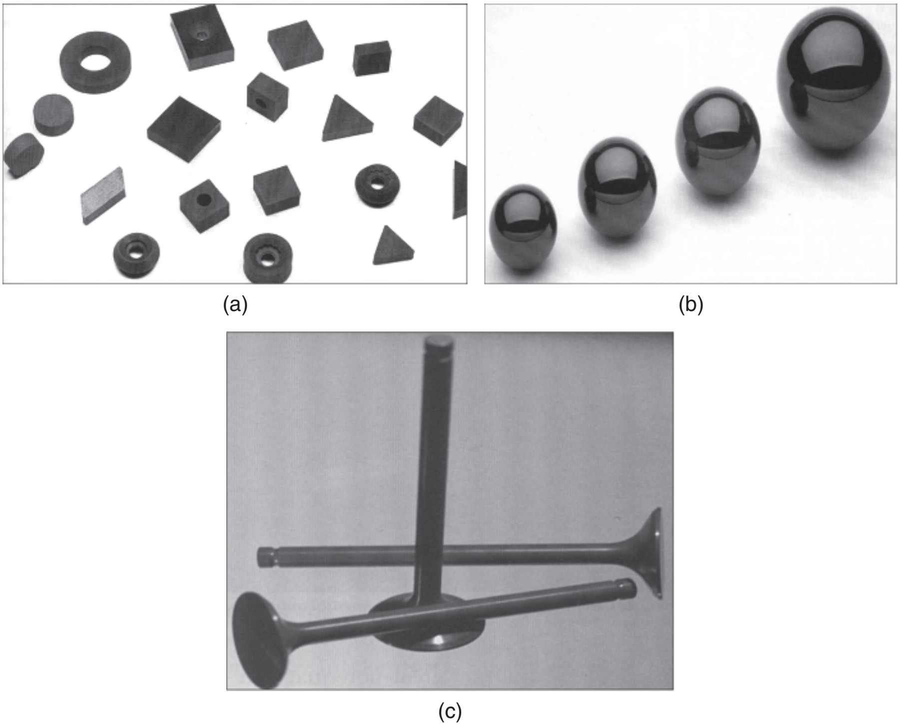
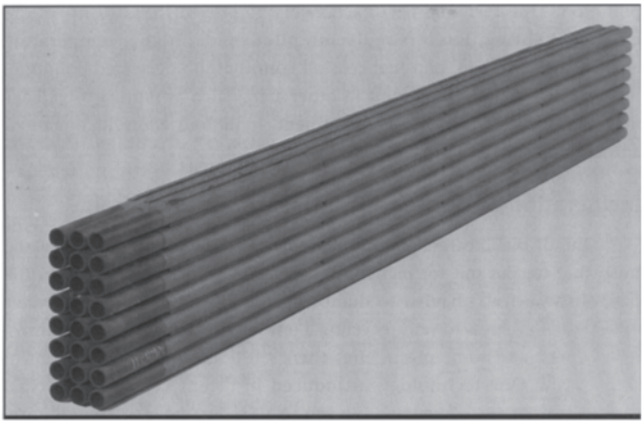
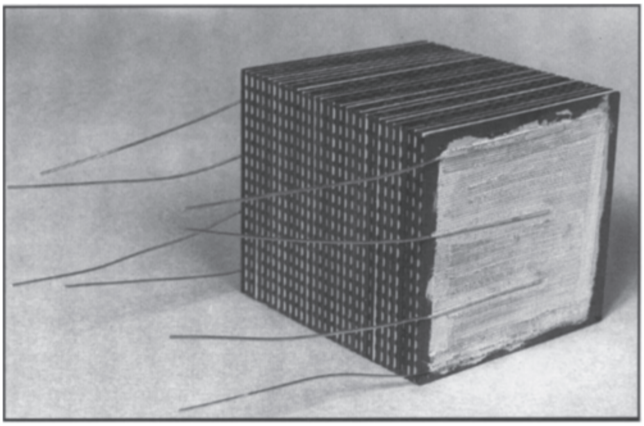


Figure 1.2 The illustrative examples of the use of engineering ceramics: silicon nitride (Si_3N_4) ceramic cutting tool inserts and components (a), silicon nitride check valve balls ranging from around 20 mm to around 40 mm in diameter (b) and silicon nitride–based experimental automobile valve (c).[30]

Figure 1.3 The use of silicon carbide seals as structural components.[30]



(a)



(b)

Figure 1.4 Another emerging area of oxide ceramics is shown: tubular solid oxide fuel cell module (a) and experimental planar SOFC module (b).[30]

than traditional ceramics. In this textbook, our focus is on discussing the structure, processing, properties, and applications of engineering ceramic systems, particularly on structure–property correlations. Based on their applications, engineering ceramics are usually classified into two major classes: structural ceramics and functional ceramics. While the applications of structural ceramics demands the optimization of mechanical strength, hardness, toughness, and wear resistance,[7] the performance of functional ceramics is controlled by electric, magnetic, dielectric, optical, and other properties.[6] In general, structural ceramics can be further classified into two classes: (1) oxide ceramics (Al_2O_3, ZrO_2, SiO_2, etc.) and (2) non-oxide ceramics (SiC, TiC, B_4C, TiB_2, Si_3N_4, TiN, etc.). Various chapters in this textbook focus only on several structural ceramics. Nevertheless, the crystal structure of some important functional ceramics is discussed in Chapter 2.

1.3 PROPERTIES OF STRUCTURAL CERAMICS

In general, ceramics have many useful properties, such as high hardness, stiffness, and elastic modulus, wear resistance, high strength retention at elevated temperatures, and corrosion resistance associated with chemical inertness.[7] The temporal progression of the development of advanced ceramics is presented in Figure 1.1. It has been reported that a flexural strength of more than 1 GPa can now be achieved in oxide ceramics and that a specific strength (strength-to-density ratio) of more than 2 can be obtained in some composites. Overall, a 50-fold increase in specific strength is now achievable in advanced ceramics, compared with that in primitive traditional ceramics. While various industries have still been mostly using high-speed tool steels, a 10-fold increase in cutting speed can be obtained with the use of ceramic- or cermet-based tool inserts. As far as the maximum operating temperature is concerned, Ni-based superalloys are typically used at 1000°C. In contrast, some nitride and some oxide ceramics can be used at temperatures of close to 1500°C. Although polymers have the lowest density, many of the ceramics (alumina, SiC) have half the density of steel-based materials. Therefore, high-speed turning or cutting operations are possible with ceramic- or cermet-based tool inserts. More often, density becomes a limitation or a requirement in selecting the ceramics for structural, defense, biomedical, and other applications: bone implants require density similar to that of bone; aerospace applications require minimal density with exceptional creep-resistance; and high-energy penetrators aim for high-density counterparts. In terms of elastic modulus or hardness, ceramics are much better than all the refractory metals. As an example of the hardness of commonly known ceramics, that of Al_2O_3 is around 19 GPa, which is close to 3 times the hardness value of fully hardened martensitic steel (~7 GPa). As is discussed in this book, many ceramics, such as TiB_2, can have hardness of around 28 GPa or higher. Also, the elastic modulus of Al_2O_3 is around 390 GPa, which is close to double that of steels (210 GPa). The higher elastic modulus of ceramics provides them with good resistance to contact damage. In addition, many ceramics, such as SiC and Si_3N_4, can exhibit high-temperature strength in the temperature range, where metallic alloys soften and cannot be used for structural applications. Many of these properties are realized in many of the hi-tech applications of ceramics, which include rocket nozzles, engine parts, bioceramics for medical implants, heat-resistant tiles for the space shuttle, nuclear materials, storage and renewable energy devices, and elements for integrated electronics such as microelectromechanical systems (MEMS).

Despite having many attractive properties, as just mentioned, the major limitations of ceramics for structural and some nonstructural applications is their poor fracture toughness. Over the years, it has been realized that an optimum combination of high toughness with high hardness and strength is required for the majority of the current and future applications of structural ceramics, including biomaterials (see Section Seven). To address this need, the development of ceramic composites with optimal combinations of mechanical properties is the major focus in the ceramics community.

1.4 APPLICATIONS OF STRUCTURAL CERAMICS

As mentioned earlier, ceramics are examples of high-temperature materials, which are used specifically for their high-temperature strength, hot erosion, and resistance to corrosion or oxidation at temperatures above 500°C. The need for high-temperature materials has been realized in different sectors of industry, including high-temperature machining, material production and processing, chemical engineering, high-temperature nuclear reactors, aerospace industries, power generation, and transportation, among others.

Typical examples of areas wherein engineering ceramics have found applications are illustrated in Figures 1.2–1.4. Figure 1.2 shows Si_3N_4-based materials as ball bearings, automobile valves, and cutting inserts; Figure 1.3 shows SiC used as bearing seals. In Figure 1.4, a solid oxide fuel cell (SOFC) module is shown; oxide ceramics, such as zirconia, are widely used in SOFCs. There exists a clear demand for materials that can withstand more than 1500°C; such applications include re-entry nozzles in rockets or hypersonic space vehicles. To this end, ultra-high-temperature ceramics (UHTCs) based on borides are being developed (see Section Five). Because of their high melting point, high hardness, electrical and thermal conductivity, and high wear resistance, the borides of transition metals, such as TiB_2, are used for a variety of technological applications.[8] Monolithic TiB_2, that is, without any second phase addition, has excellent hardness (≈25 GPa at room temperature), good thermal conductivity (≈64 W/m·°C), high electrical conductivity (electrical resistivity $\approx 13 \times 10^{-8}\,\Omega$ m) and considerable chemical stability.[9] Some of these attractive properties are ideally suited to be exploited for tribological applications. However, the relatively low fracture toughness ($\approx 5\,\mathrm{MPa\,m^{1/2}}$) and modest bending strength (≈500 MPa) coupled with poor sinterability of monolithic TiB_2 limits its use in many engineering applications.[10] In the materials world, TiB_2 is often used as reinforcement phase not only for ceramics, but also for metallic alloys such as stainless steel[11] and Al-alloys[12] to develop composites with improved abrasive wear resistance. The addition of TiB_2 to an Al_2O_3 or B_4C matrix increases its hardness, strength, and fracture toughness.[13] Furthermore, TiB_2 as well as TiN or TiC, is used not only to toughen Al_2O_3 and Si_3N_4 matrices, but also to obtain electroconductive materials with the incorporation of an optimum amount of an electroconductive phase.[14] These electroconductive toughened ceramics can be shaped by electrodischarge machining (EDM) to manufacture complex components, greatly increasing the number of industrial applications of these ceramic materials. The processing–property relationships of borides are discussed in one of the sections in this book, and the way sinter-aids and sintering conditions can be optimized to develop borides with high sinter density and a better combination of physical and mechanical properties is illustrated.

One application that has attracted much attention is ball bearings (see Fig. 1.2). Ceramic balls enclosed in a steel race, that is, hybrid bearings, are now used in turbopumps of the space shuttle main engine. The friction and wear properties of alumina, zirconia, and SiC in cryogenic environments are being investigated as such studies are relevant to cryotribological applications.[15–17] These ceramic balls are commercially available with diameters from 4 mm to as large as 20–30 mm and they are made from Al_2O_3, ZrO_2, SiC, Si_3N_4, or SiAlON ($Si_{6-z}Al_zO_zN_{8-z}$, with z being the substitution level). Commercial springs made of silicon nitride materials are also available. In one of the sections of this book, the microstructure and mechanical properties of such ceramics are discussed.

There is a tremendous industrial need for new tribological materials. This need is realized in metal-forming industries, bearings, gears, valve guides and tappets in engines, seals and bearings involving fluid and gas transport, often under corrosive conditions, and so on. The majority of these applications are currently served by hardened steels and WC-based hardmetals with or without surface coatings. However, new materials or improved existing materials are needed to meet the increasing demand in the tribological world. Ceramics, because of their ionic and/or covalent bonding, have a useful combination of physicomechanical properties (elastic modulus, hardness, and strength) and corrosion resistance. In many structural and tribological applications, ceramics are recognized as having great potential to replace existing materials for a series of rubbing-pairs, such as seal rings, valve seats, extrusion dies, cutting tools, bearings, and cylinder liners.[18] The materials of interest will have to combine high hardness, toughness, strength, elastic modulus, and wear resistance coupled with relatively low density, resulting in low inertia under reciprocating stresses. Furthermore, the fundamental understanding of the relationship between composition, microstructure, processing route, mechanical properties, wear behavior, and performance should be clarified in order to optimally use the engineered materials in tribological applications. The development of new tribological materials is proceeding in two main directions: the use of coatings on conventional metallic substrates and the use of monolithic ceramics and ceramic composites.

Coatings are frequently hard carbides, nitrides, or borides with recent development of diamond or diamondlike (C–H) films at the more exotic end of the hardness-versus-cost scale.[19] Coating thickness is normally between 1 and 50 μm, depending on the deposition process (physical vapor deposition [PVD], chemical vapor deposition [CVD], or electrolytic), which presents limitations in lifetime or property influence of the relatively soft substrate. Thicker coatings may be applied by thermal spraying (in the millimeter range) but are limited in chemistry, compatibility with substrate properties (thermal expansion etc.), and cohesion. An entire section of this textbook focuses on the discussion of processing and properties of coatings (Section Three).

Monolithic ceramics, especially those with improved strength and toughness, have been a focus of development in different research labs and industries since the 1970s.[20] However, monolithic ceramics are not optimal for all engineering applications. Ceramic composites such as metal matrix and PMCs are now the established approaches to designing structural materials.[21] Ceramic reinforcements are commercially available in different forms such as whiskers, platelets, particulates, and fibers. Two major classes of ceramic composites are fiber-reinforced and particle- or whisker-reinforced ceramic composites. A popular example of the first class of ceramic composites is silicon carbide fiber-reinforced glass-ceramics.[22] The alumina–silicon carbide whisker-reinforced composites are commercially fabricated for use as drilling components. Four major drawbacks normally restrict the widespread use of this material class for structural applications: high cost of ceramic fibers; the expensive composite production route; the chemical compatibility of the fiber with the matrix; and the oxidation of SiC fibers at high temperatures. To this end, particle-reinforced CMCs offer a viable and relatively cost-effective option for developing materials with improved and optimal combinations of mechanical properties (hardness, toughness, and strength).

In the world of ceramic materials, yttria-doped zirconia, in particular yttria-stabilized tetragonal zirconia polycrystalline (Y-TZP) ceramics, are regarded as a strong candidate for structural applications due to the excellent addition of strength (≈700–1200 MPa) and fracture toughness (2–10 MPa $m^{1/2}$) in addition to good chemical inertness.[23,24] The high toughness of the zirconia monoliths stems from the stress-induced transformation of the tetragonal (t) phase to the monoclinic (m) phase in the stress field of propagating cracks, a concept widely known as *transformation toughening*.[25] Basic microstructural requirements for the effective contribution from transformation toughening is the maximum retention of the tetragonal phase at the application temperature with sufficient transformability to m-ZrO_2 in the crack tip stress field. The concepts and microstructural parameters influencing transformation toughening are discussed in Section Four. Since the discovery of the concept of transformation toughening about two decades ago,[26] this approach has been successfully utilized to toughen several intermetallic,[27] glass,[28] and ceramic[29] microstructures. More recently, extensive efforts have been put into increasing the toughness of alumina by adding zirconia, a class of materials known as zirconia-toughened alumina (ZTA).[17,19]

The successful application of engineering ceramic components demands the careful selection and optimization of the initial material (i.e., powder purity, size, shape, etc.) followed by its optimal sintering (time, temperature, pressure, and environment to control grain size and densification) for achieving appropriate properties. These aspects necessitate that researchers consider the selection–processing–property–application tetrahedron, as shown in Figure 1.5.

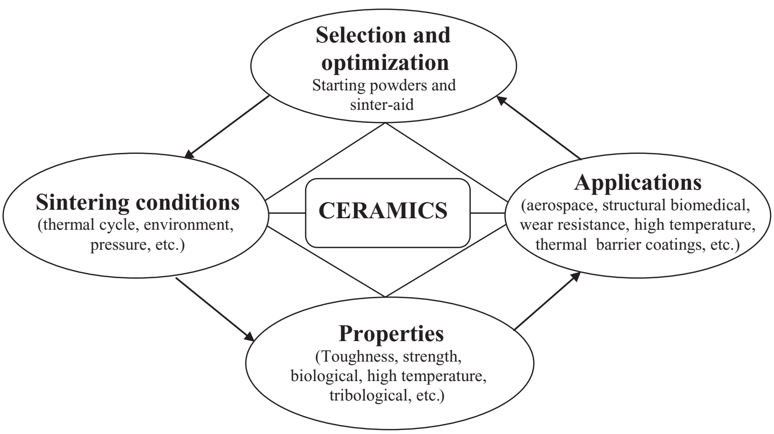


Figure 1.5 Selection–processing–property–application tetrahedron of ceramics.

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