

ADVANCED CERAMICS, STRUCTURAL CERAMICS

Advanced structural ceramics are those ceramics intended for use as load-bearing members. They are materials that combine the properties and advantages of traditional ceramics (qv), such as chemical inertness, high temperature capability, and hardness, with the ability to carry a significant mechanical stress. Like all ceramics, they are inorganic and nonmetallic; in addition, they are often multicomponent and/or multiphased materials having complex crystal structures. These materials are usually intended to be fully dense and to have tight dimensional tolerances. In addition to being designed to withstand substantially higher levels of mechanical and thermal stress, there are other important features which make advanced structural ceramics different from traditional ones. Starting powders, compositions, processing, and resulting microstructure must be carefully controlled to provide required levels of performance. Consequently, advanced structural ceramics are more expensive than traditional ceramics.

Most of the advanced structural ceramics under development today are based on silicon nitride [12033-89-5], Si_3N_4 ; silicon carbide [409-21-2], SiC ; zirconia [1314-23-4], ZrO_2 ; or alumina [1344-28-1], Al_2O_3 . In addition, materials such as titanium diboride [12045-63-5], TiB_2 ; aluminum nitride [24304-00-5], AlN ; silicon aluminum oxynitride [52935-33-8], SiAlON ; and some other ceramic carbides and nitrides are often classified as advanced or high tech ceramics because of processing methods or applications. Ceramic matrix composites are also receiving increasing attention as advanced structural ceramics (see Composite materials, Ceramic-matrix). Monolithic silicon nitride, silicon carbide, and zirconia each represent a family of materials rather than a single species. A wide range of microstructures and properties can be tailored within each family, through compositional or processing modifications, in order to optimize materials performance for specific applications.

1. Physical Properties

Advanced structural ceramics typically possess some combination of high temperature capabilities, high strength, toughness or flaw tolerance, high hardness, mechanical strength retention at high temperatures, wear resistance, corrosion resistance, thermal shock resistance, creep resistance, and long term durability. Figure 1 shows the typical stress and temperature ranges of application for SiC , Si_3N_4 , ZrO_2 . Zirconia ceramics, which find application under conditions of high stress and moderately high (up to 600°C) temperatures, have the highest low temperature strength. Although the low temperature strength of silicon nitride is less than that for zirconia, silicon nitride maintains these strength properties up to approximately 1200°C . Silicon carbide is somewhat weaker than silicon nitride over the entire temperature range, but maintains good strength and creep resistance at even higher (1500°C) temperatures.

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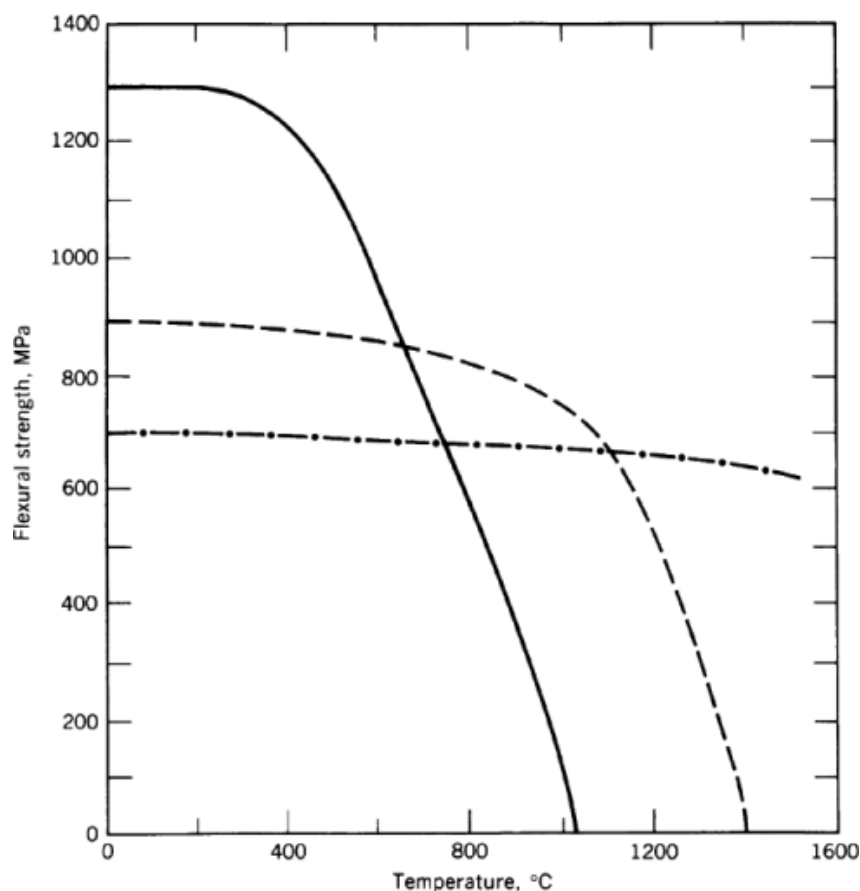


Fig. 1. Stress and temperature ranges of application for ZrO₂ (—), Si₃N₄ (---), and SiC (— · —) advanced structural ceramics. To convert MPa to psi, multiply by 145.

2. Processing and Fabrication Technology

The relationship between processing and properties is especially critical for advanced structural ceramics because subsequent successful operation in severe environments often requires carefully controlled compositions and microstructures. Fabrication generally takes place in four steps: powder processing, consolidation/forming, densification, and finishing. Starting powders must be chemically pure and fine grained. Then, depending on the forming and densification processes to be used and the final properties and microstructure desired, the powders may be mixed with various additives. For example, additives can be used to improve the flowability of dry powders to make mold filling easier. Plasticizers may be added to improve the formability of powder blends for some shape forming operations. Binders are almost always added to powder blends, especially those intended for dry forming, in order to improve adherence of the fine powder particles and impart strength to the green part. (Green refers to powder compacts, formed by any process, which have not yet been subjected to a densification operation.) Sintering additives are also necessary for covalent materials, particularly nonoxides, to enhance densification rates.

Once the powder has been processed and the composition set, several techniques, including dry pressing (uniaxial or isostatic), slip casting, plastic forming (extrusion or injection molding), and tape casting, can be

used for forming. In a dry pressing operation, powders are fed into a die or cavity and compacted under pressure. In general, pressure may be divided into two categories: uniaxial (unipressing) and isostatic (isopressing). For unipressing the powder is fed into a die and pressure is externally applied along a single axis, which limits this technique to relatively simple shapes. For isopressing, powder is fed into a compressible mold or bag and pressure is applied uniformly from all directions by a liquid or gas medium. Slip casting involves adding the ceramic powder to a liquid medium that is typically aqueous to produce a slurry which is then poured into a porous mold. In time, water from the slurry is absorbed by the mold and a solid ceramic results. This technique is most suitable for low volume production of relatively simple shapes and traditionally has been used for hollow or tubular components. Advances in slurry compositions, mold materials, and mold design have resulted in faster casting times however, permitting thicker cross-section parts and more complex shapes.

For plastic forming techniques the ceramic powder is combined with plasticizers such as thermoplastic resins and other additives to make a mixture which is deformable under pressure. This mixture is then heated slightly, facilitating plasticity, and either forced through dies (extrusion) or into molds (injection molding). Extrusion is a continuous, high volume process, but is limited to shapes having a constant cross section, eg, rods and tubes. Injection molding is a high volume process capable of producing complex shapes, but tooling costs for molds can be very high.

Regardless of the consolidation method used, the formed or green part must generally undergo a burn-out step prior to densification in order to remove the binders, plasticizers, and other decomposable additives which were added in the forming step. In the case of dry pressing usually only small amounts (several volume percent) of binders are added, whereas for injection-molded components, the additives can comprise 30–40 vol % of the green part. Additives are typically organic compounds that decompose at temperatures less than 700°C. However, in order to ensure complete removal of additives without disruption to the part, eg, swelling or cracking, burn-out must be done slowly and under carefully controlled conditions. Burn-out may be a separate step or it may be incorporated in the early stages of the densification procedure.

High temperature consolidation techniques such as conventional sintering, reaction sintering, hot-pressing, and hot isostatic pressing, are generally necessary for advanced structural ceramics. Sintering involves subjecting a powder compact to high temperature without application of pressure and, especially in the case of nonoxides, usually requires additives to promote densification and/or to inhibit grain growth. Achieving full density may be more difficult than in pressure-assisted methods and the composition and quantity of densification aids required may degrade the material's high temperature properties. Reaction sintering or reaction bonding involves the infiltration of a powder bed by the appropriate gaseous constituent or molten material at elevated temperatures to produce the desired composition. Complex shapes can be formed using the starting powder and little or no shrinkage occurs during the reaction. However, residual unreacted starting material and/or residual porosity in the final product can be a problem.

Hot-pressing is the simultaneous application of uniaxial high pressure and temperature to the powder. Fully dense materials can be formed, often having high strength, but the application of uniaxial pressure limits this technique to simple shapes. In the case of hot isostatic pressing (HIP), pressure is applied to the powder compact equally in all directions through the use of a compressed gas. Fabrication of more complex shapes, not possible using hot-pressing, can be accomplished, and densities approaching theoretical are often achieved. However, this technique requires that the material be either sintered to closed porosity prior to application of isostatic pressure or encased in a compressible can of metal or molten glass.

Microwave sintering of powders, a relatively new technique, has the advantage of providing more uniform heating of the component, because it does not rely on conduction and convection. Other routes to forming and densification which avoid traditional powder processing are also under development. Sol-gel processing, chemical vapor deposition (CVD) and organometallic polymer pyrolysis are examples.

Although some postforming grinding and machining are often necessary, the intrinsic hardness of advanced structural ceramics makes them difficult and costly to machine. In addition, grinding can introduce surface flaws which may serve as failure sites. Thus, forming processes producing near net-shape components,

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such as injection molding and hot isostatic pressing, are desirable because their usage reduces the amount of postforming machining required.

3. Applications

Throughout the development of structural ceramics the focus has been on applications for gas turbine, diesel, and spark-ignited engines. The ability of ceramics to function at higher temperatures than superalloys, and to do so without cooling, has been a particularly important driving force. Ceramics utilization in heat engines can lead to reduced fuel consumption and increased performance through higher engine operating temperatures, the elimination of mechanical losses resulting from cooling, lower inertia, and reduced friction. In addition to the properties critical to mechanical performance, advanced structural ceramics have the significant advantage of not requiring imported, strategic metals (eg, Ni, Co, Cr) for their fabrication.

Advanced structural ceramics are also under investigation for use in numerous other high performance applications including antifriction roller and ball bearings, metal-cutting and shaping tools, hot extrusion and hot forging dies, industrial wear parts (eg, sand-blast nozzles, pump seals, thread guides, chute liners), and various military applications (eg, armor, radomes, ir domes, gun barrel liners). More comprehensive works on the processing, properties, and applications of advanced ceramics are available (1–4).

4. Silicon Carbide Structural Ceramics

Silicon carbide (see Carbides, Silicon carbide) has been a candidate material for structural ceramic applications far longer than other materials. Properties such as the relatively low thermal expansion, high strength-to-weight ratio, high stiffness, high thermal conductivity, hardness, erosion and corrosion resistance, and most importantly, the maintenance of strength as high as 1650°C, have led to a wide range of applications. Additionally, it is possible to produce both large quantities of pure silicon carbide powders and required component shapes. An in-depth review of SiC structural ceramics is available (5).

4.1. Material System

Silicon carbide occurs in a variety of polymorphic crystalline forms, generally designated β -SiC for the cubic form and α -SiC for the hexagonal and rhombohedral varieties. The alpha form appears most stable at temperatures above 2000°C, whereas the cubic β -SiC is the most common product when silicon carbide is produced at lower temperatures (4). Most silicon carbide powder is produced by the Acheson process involving the reduction of high purity silica sand surrounding an electrically heated core of petroleum coke or anthracite coal (6). The reaction is carried out at about 2400°C in the core for as long as 36 h where the higher temperature α -SiC is formed. The product is separated based on purity (determined by crystal color) and ground. For structural ceramic applications this material must be milled, often to submicrometer sizes, and chemically cleaned of impurities. The large scale of this process leads to a relatively low cost for such a high purity raw material.

α -SiC can also be produced directly in the desired purity by the plasma gas-phase reaction of species such as silane [7803-62-5], SiH_4 , and methane [74-82-8], CH_4 (7). β -SiC powders can be produced by the same gas-phase reaction at lower temperature (1500–1600°C) or by polymer decomposition reactions (8).

4.2. Fabrication Technology

Silicon carbides for structural application can be classed as reaction-bonded, liquid-phase sintered, and solid-state sintered. Reaction-bonded SiCs are actually a composite of a continuous SiC matrix having 5 to 20% silicon

[7440-21-3], metal filling the remaining volume (9). To form this material, a preform of powder containing carbon [7440-44-0] added either as a powder or as the decomposition product of a carbon source resin, is infiltrated with silicon at about 1500°C either through direct contact or using silicon vapor. The silicon reacts with the carbon preform to form a bridging structure of more SiC. Excess silicon remains, filling the residual pore space and giving a fully dense product having structural integrity to 1370°C. Silicon melts at 1410°C. The preform can be fabricated by any of the traditional ceramic shaping processes (5, 10). The silicon carbide powder utilized for the preform does not require the submicrometer particle sizes and the purity of other forms of dense SiC, although finer sized SiC preforms tend to give a stronger product (11). Reaction bonding also leads to little dimensional change (<1%) from the preform, allowing large shapes and complex shapes having tight dimensional tolerances to be fabricated. Moreover, the low (1500°C) temperatures employed during reaction bonding, combined with the flexibility in powder size and purity, provide a good quality product at a reasonable cost.

A desire for a higher strength form of dense SiC suitable for applications at temperatures above 1300–1400°C led to the development of liquid-phase sintered material. This process involves reaction of an oxide additive (typically 1 to 2% Al_2O_3) and the silica present on the surface of SiC grains to create a melt during densification above 2000°C. A simultaneous application of pressure through hot-pressing is often required to achieve a dense product and the resultant hot-pressed SiC exhibits excellent room temperature strength and wear resistance. However, the hot-pressing process is limited to the production of simple shapes, and the presence of the aluminosilicate phase tends to decrease elevated temperature strength and oxidation resistance (12). Liquid-phase sintered SiC usage has therefore been limited for applications requiring complex shapes and long term exposure to high temperatures.

A new type of liquid-phase sintered SiC using yttria [1314-36-9], Y_2O_3 , as the oxide additive and submicrometer SiC powder for enhanced densification, produces a material which can be densified without the application of pressure (13). This material, sintered from cold isostatically pressed billets, appears to be comparable to silicon nitride in strength and fracture toughness.

Two forms of dense high purity SiC resulted from a discovery (14) that simultaneous additions of carbon and boron [7440-42-4] allow silicon carbide densification without the application of pressure. One is a sinterable material based on β -SiC raw materials and about 1% carbon and 0.5% boron (15). Control of powder reactivity and densification conditions is critical because densification temperatures approach the region for transformation to the alpha form of SiC resulting in excessive grain growth rates and resultant lowering of final strength. The other product results from the same additive system, but is based on the more readily available α -SiC (16). Ultrafine SiC powder is utilized both to increase the driving force for densification and to minimize diffusion distances (17). There has been extensive analysis of the role of these two additives in densification (18–21). The carbon appears to react with surface oxygen present on the SiC grains, forming volatile CO and thereby purifying the surfaces. The role of boron is more difficult to define, but it is believed to promote both volume diffusion and grain boundary diffusion.

Both α - and β -sintered silicon carbides have been fabricated by all of the available ceramic forming methods. Sintering is performed in vacuum or in an argon atmosphere (22). Shrinkages during densification are typically 15 to 20 linear percent. The resultant material is about 98% dense having small isolated porosity and residual carbon particles. Analysis indicates no presence of second phases along the grain boundaries. This leads to a material with excellent retention of strength at temperatures in excess of 1500°C and superior resistance to elevated temperature oxidation (23, 24).

A postsintering HIP treatment has been used to further improve the strength of sintered silicon carbide (25). The component is sintered until all surface porosity is closed, about 95% dense or higher, then subjected to a combination of temperature and argon gas pressure to achieve final densification. Finer grain sizes are achieved in the final body because sintering temperatures tend to be lower. The resultant material shows good density uniformity, even in thick cross-section components, and density levels over 99% of theoretical density. If densification is performed properly, a significant increase and improved uniformity in strength results (26).

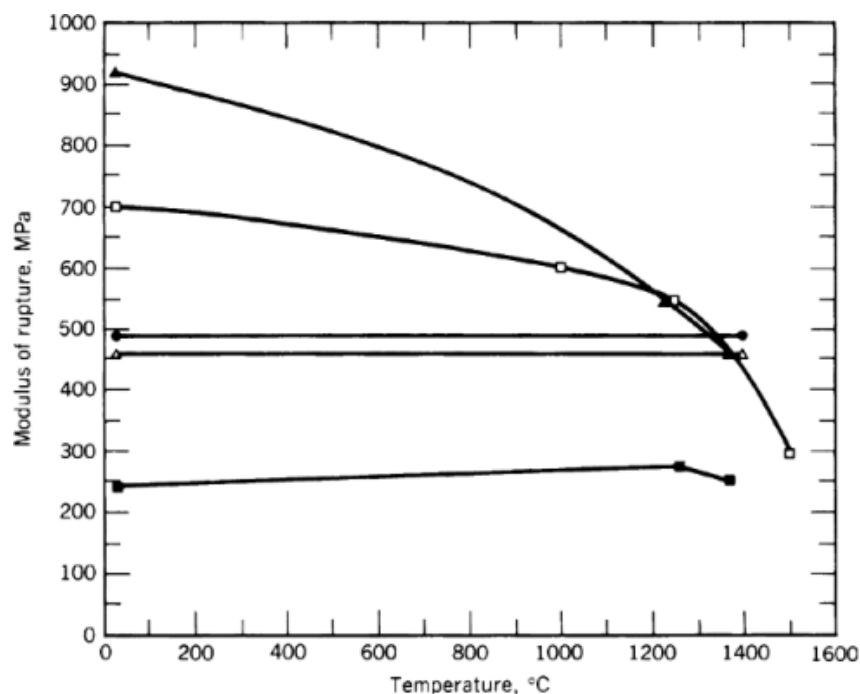


Fig. 2. Strength as a function of temperature for representative SiC structural ceramics: ▲, sintered (Y₂O₃ added); □, hot-pressed (2% Al₂O₃); ●, sintered beta; △, sintered alpha; and ■, reaction-bonded. To convert MPa to psi, multiply by 145.

4.3. Properties of Dense Silicon Carbide

Properties of the SiC structural ceramics are shown in Table 1. These properties are for representative materials. Variations can exist within a given form depending on the manufacturer. Figure 2 shows the flexure strength of the SiC as a function of temperature. Sintered or sinter/HIP SiC is the preferred material for applications at temperatures over 1400°C and the liquid-phase densified materials show best performance at low temperatures. The reaction-bonded form is utilized primarily for its ease of manufacture and not for superior mechanical properties.

Flexural stress SiC rupture curves are shown in Figure 3 (27). All the forms tend to be fairly resistant to time-dependent failure by elevated temperature creep. In addition, SiC shows outstanding resistance to oxidation even at 1200°C as a result of formation of a protective high purity silica surface layer (28).

The elastic modulus and thermal expansion properties are dominated by the characteristics of the SiC crystal itself and the thermal conductivity or thermal diffusivity of silicon carbides tends to be substantially higher than those of other structural ceramics. Thermal diffusivity as a function of temperature is shown in Figure 4 (29). These values tend to be sensitive to the form of silicon carbide, but all values drop significantly as temperature increases. The combination of a high elastic modulus and moderate thermal expansion coefficient result in SiC being susceptible to damage by thermal shock. Resistance to thermal shock is significantly lower than that of silicon nitride, but higher than that of the high expansion zirconia structural ceramics. Thermal shock behavior is also very application-dependent. For example, very rapid temperature changes can lead to a preference of Si₃N₄ over SiC, whereas during moderate rates of temperature change the high thermal conductivity of SiC can lead to a superior performance.

Table 1. Properties of Silicon Carbide Ceramics

Property	Material densification mode				
	Reaction-bonded	Sintered alpha ^a	Sintered beta	Hot-pressed (Al ₂ O ₃) ^b	Sintered (Y ₂ O ₃) ^c
density, kg/m ³	3.1	3.1	3.0	3.3	3.2
hardness, kg/mm ²	1620	2800		2400	
flexure strength, MPa ^d at 25°C	245	460	490	702	917
Young's modulus, GPa ^e	383	410	372	446	
Poisson's ratio, GPa ^e	0.24	0.14	0.16	0.17	
thermal expansion coeff, $\times 10^{-6}/^{\circ}\text{C}$	4.8	4.02	4.4	4.6	
thermal conductivity, W/(m.K) at 25°C	135	126	71	80	

^aMaterial subjected to a postsintering HIP treatment; sinter/HIP alpha SiC has a density of 3.2 g/mL and a flexural strength of 530 MPa at 25°C.

^bContains about 2% alumina.

^cContains some yttria, see text.

^dTo convert MPa to psi, multiply by 145.

^eTo convert GPa to psi, multiply by 145,000.

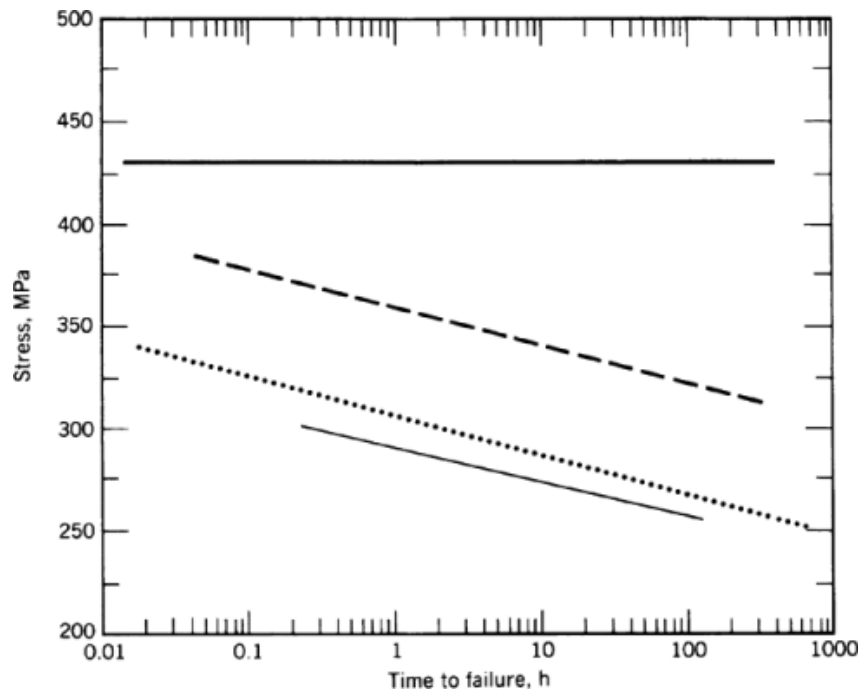


Fig. 3. Stress rupture behavior in air at 1200°C for SiC structural ceramics:—, hot-pressed; — — —, reaction-bonded; ····, sintered alpha;—, sintered beta. To convert MPa to psi, multiply by 145.

Fracture toughness of SiC tends to be lower than that of other structural ceramics leading to some concern about the application of SiC in certain heat engines, such as turbine rotors which may be susceptible to impact from foreign objects (30). The yttria liquid-phase sintered SiC is, however, reported to be comparable to other structural ceramics in fracture toughness. Erosion and corrosion characteristics have not been measured as

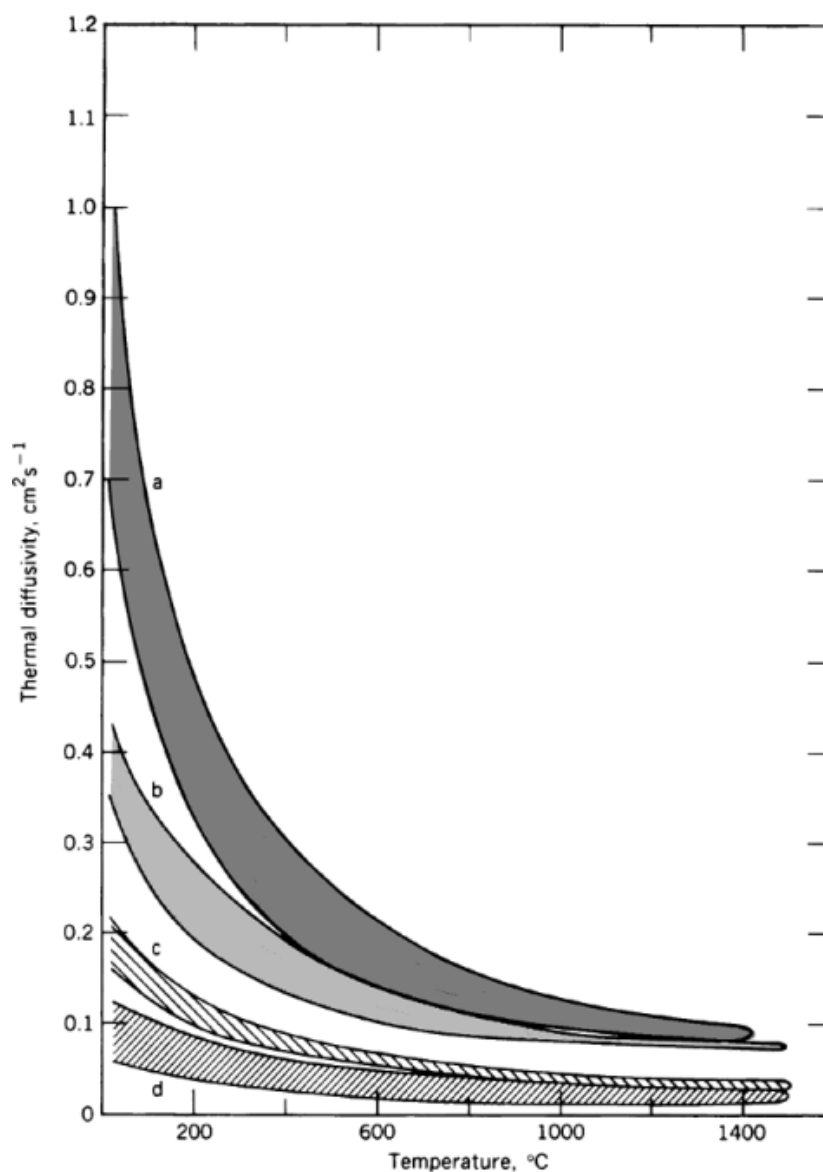


Fig. 4. Thermal diffusivity of silicon-based structural ceramics: (a) reaction-bonded SiC; (b) hot-pressed and sintered SiC; (c) hot-pressed Si_3N_4 (1% MgO, 8% Y_2O_3); (d) RS- Si_3N_4 (density is 2.1–2.9 g/mL).

extensively as other mechanical properties. Wear and coefficient of friction measurements have mostly been application specific, but point out the importance of surface preparation and characterization. Published erosion results show good resistance to angular particle or slurry erosion. Reaction-bonded SiC tends to be the most susceptible to erosive wear because of preferential wear of surface connected free silicon grains (31). Reaction-bonded SiC also appears much less resistant to acids, alkali, and high temperature combustion products than the single-phase sintered material (32). In contact with sodium sulfate, or acidic or basic coal slags from coal gasification, SiC tends to corrode slightly in a pitting reaction. In basic coal slag reactions at temperatures from

1000 to 1300°C, the reaction involves dissolution of the protective silica oxidation layer followed by reaction with Fe or Ni to form low-melting point silicides (33). Sintered silicon carbide has also been shown to corrode at elevated temperature in hydrogen-containing atmospheres. The reaction appears to be a decarburization of the SiC, particularly at grain boundaries, resulting in silicon rich regions and some grain fallout (34). Corrosion from sodium silicate glass vapors and particulates has demonstrated that both sintered and reaction-bonded SiC corrode through passive oxidation followed by dissolution of the oxide coating. The silicon component in reaction-bonded SiC was oxidized more rapidly than the SiC phase (35).

4.4. Applications of Silicon Carbide

Silicon carbides are used more for the low temperature wear properties than for the high temperature behavior. Applications such as sand blasting nozzles, automotive water pump seals, bearings, pump components, and extrusion dies utilize the high hardness, abrasion resistance, and corrosion resistance of silicon carbide (4, 5, 32). Elevated temperature structural applications range from rocket nozzle throats to furnace rollers and the combination of high thermal conductivity and high temperature strength and stability make silicon carbide heat exchanger tubes and diffusion furnace components feasible.

Most engine applications involve auxiliary components such as turbo-charger rotors, valve train parts to reduce friction losses, piston wrist pins, and precombustion chambers. Application of SiC for pistons and cylinder liners has been demonstrated, but the high thermal conductivity makes SiC use more difficult than that of other structural ceramics. However, high thermal conductivity and strength at high temperatures make SiC the material of choice for combustors. Well-developed fabrication technology and lower raw material cost have also resulted in the use of SiC for many hot path stationary gas turbine components. SiC turbine rotors and vanes have also been demonstrated, but material strength considerations have often resulted in the selection of Si_3N_4 .

Future applications may involve use of SiC as substrates for silicon chips, making use of the high thermal conductivity of SiC and its close thermal expansion match to silicon. The low density and high stiffness of silicon carbides may also result in applications in space. One such application is for space-based mirrors, making use of the high degree of surface polish possible on dense SiC.

5. Silicon Nitride Structural Ceramics

Silicon nitride (see Nitrides) is a key material for structural ceramic applications in environments of high mechanical and thermal stress such as in vehicular propulsion engines. Properties which make this material uniquely suitable are high mechanical strength at room and elevated temperatures, good oxidation and creep resistance at high temperatures, high thermal shock resistance, excellent abrasion and corrosion resistance, low density, and, consequently, a low moment of inertia. Additionally, silicon nitride is made from abundant raw materials.

5.1. Material System

There are two basic techniques for the industrial synthesis of Si_3N_4 powder, although other methods are available (36). The older and most widely used method is the nitridation of silicon. Silicon is heated in a nitrogen [7727-37-9] atmosphere at temperatures of 1100–1450°C in the presence of an iron catalyst (37). The purity of the product depends on the purity of the starting materials, the amount of catalyst used, and the extent to which the catalyst is removed (38). The other commercial process is a type of ammonolysis where silicon tetrachloride [10026-04-7] or a silane reacts with liquid ammonia [7664-41-7] at low temperatures. The silicon compound is dissolved in an aromatic solvent such as toluene and silicon imide is formed at the interface

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between the liquid ammonia and the organic phase. The silicon imide is separated and thermally converted to crystalline silicon nitride (34) resulting in a powder of high purity.

Silicon nitride exists in two hexagonal crystallographic modifications designated as the α - and β -phases (40). The latter is prevalent at high temperatures. Metallic impurities are deleterious to Si_3N_4 thermomechanical properties and in the purest powders their total concentration does not exceed 100 ppm. Tolerance levels for the various metals vary, but any contaminant must be homogeneously dispersed in the powder rather than present in discrete particles. Alkalies and metals forming low melting glasses are wholly unacceptable because they may cause failure at high temperatures; Al and Mg are not as problematic because they are frequently used as sintering aids; transition metals such as Fe, Ni, or Cr can adversely affect the material strength (36).

5.2. Fabrication Technology

A variety of simple and complex-shaped dense parts are made from Si_3N_4 powders by ceramic processing techniques. Inasmuch as silicon nitride is a covalently bonded compound having a low diffusion coefficient, sintering aids are used to achieve complete densification. Aids are typically oxides such as Al_2O_3 , Y_2O_3 , ZrO_2 , MgO , lanthanide oxides, and, at times, AlN as well. They are added singly or in combinations in amounts of several weight percent and may reach as high as 15 wt % of the matrix. The α - Si_3N_4 crystallites, which typically comprise over 90% of the starting powder material, dissolve in the liquid phase formed by the reaction of the sintering additives with the silica layer present on the surface of the silicon nitride particles, then reprecipitate as β - Si_3N_4 (41). This α - to β -phase transformation is facilitated by the presence of liquid phase as well as β -crystal nuclei (42). It does not appear to be reversible. The strongest ceramics are realized when all the pores are eliminated and full conversion to β - Si_3N_4 takes place. A dense crystalline matrix consisting of rodlike grains characteristic of the β -phase is formed (43). The crystallites are surrounded by a thin intergranular amorphous or crystalline phase which forms upon cooling (44).

Both composition and the quantity of sintering additives profoundly affect the properties of silicon nitride ceramics (43). Additives facilitate densification, serve as the strength limiting factor at high temperatures, and may also adversely affect oxidation resistance. Thus sintering additives are kept to a minimum. The specific additive used depends on the ceramic's ultimate application. For uses at lower (up to 1000°C) temperatures, magnesia–magnesia/alumina combinations are frequently employed; in the intermediate (up to 1200°C) range yttria–alumina formulations are usually preferred; for the applications in which structural integrity and performance are required at temperatures up to 1400°C , yttria alone is used.

Si_3N_4 powder is typically mixed with the appropriate amount of sintering additives and an organic binder. This mixture then undergoes extensive comminution, generally by milling, often using silicon nitride grinding media. Powder processing for the most critical applications is frequently done in clean room environments.

The shaping of these fine, submicrometer powders into complex components and their subsequent consolidation into dense ceramic parts of ideally zero porosity is a major technological challenge. The parts formed need to be consolidated to near-net shape because Si_3N_4 machining requires expensive diamond grinding. Additionally, Si_3N_4 dissociates at or near the typical densification temperatures used in the fabrication of structural ceramics and, therefore, special measures have to be taken to preserve the compositional integrity of the material.

Parts of simple geometries can be readily made by uniaxial die pressing or cold isostatic pressing and densified by sintering or hot isostatic pressing (HIP). Typical sintering temperatures are in the range of 1700 – 2000°C , depending on the composition and concentration of the sintering aid, and in order to prevent silicon nitride decomposition, the parts are usually embedded in a protective powder such as boron or silicon nitride and/or placed in a closed vessel (45). An overpressure of 0.1–10 MPa (15–1500 psi) of nitrogen is usually maintained during sintering. Satisfactory products can be obtained at atmospheric pressures, particularly using silicon nitride formulations designed for applications at lower temperatures. Parts having densities over

99% of theoretical can be made by this technique and shrinkage can be controlled to achieve near net shape fabrication.

Using hot-pressing, shaping and densification occur in a single process step. The temperatures are in the range of 1650–1800°C and applied pressures are from 30–40 MPa (4000–6000 psi) (45), resulting in parts of high quality. This method is limited to simple shapes and low production volumes, however, and the process may also impart anisotropic characteristics to the material (46).

There are two operational variations in the HIP process as applied to silicon nitride parts. In one, shaped specimens are encapsulated in a glass and then hot pressed isostatically (46, 47); in the other, called sinter-HIP, the parts are first presintered to closed porosity (<7%) and then hot isostatically pressed directly, without encapsulation (45, 48–50). The latter technique, although a two-step process, offers the advantage of eliminating both the risk of the diffusion of deleterious glass components into the work pieces and the need for a post-HIP decapsulation step. Process conditions for both variations are similar: temperatures range from 1700–2000°C and pressures from 100–200 MPa (45). The quality of the resulting products is high. Densities approach theoretical values and mechanical properties are comparable to those of hot-pressed components.

Injection molding and slip casting are used for making complex-shaped silicon nitride structural ceramic components. Injection molding is a high volume production technique (51). To impart the appropriate rheological characteristics the powder is mixed with significant (10–15 wt %) amounts of organic binder components which then need to be removed from the part prior to densification. This process requires careful time-temperature control and may take from a few days to even weeks (52). Complex parts such as turbine rotors and turbochargers have been fabricated having adequate green strength and the requisite microstructure for densification by HIP processing into high quality ceramics (53–57).

Slip casting, used increasingly for silicon nitride parts, has the advantage that only small amounts of chemical additives are employed and therefore, binder burn-out problems are basically eliminated (46). The biggest disadvantage is the time it takes for the part to form. Tens of hours may be required to cast a gas turbine engine rotor and during that time the stability of the slip suspension may change (58). Therefore, pressure-assisted casting is being used to accelerate part formation (58, 59) reducing the casting time to about an hour. After removal from the mold, the part needs to be dried carefully and slowly to prevent crack formation (58). Automated process methodology is used to shape tens of thousands of silicon nitride turbochargers per month by pressure-assisted slip casting. These are then densified either by HIP or gas overpressure sintering.

An alternative technique for the fabrication of complex Si_3N_4 parts is reaction bonding. A shape is formed from silicon powder by any of the aforementioned methods and the resulting green compact, having a typical density that is 60–70% of the theoretical value of Si, is then nitrided by reaction with nitrogen at 1300–1400°C to form reaction-bonded silicon nitride (RBSN). The reaction, carried out over a 3 to 10 day period, is exothermic and needs to be carefully controlled so as not to exceed, even locally, the melting point of silicon (1410°C). The final product is not fully dense; it has a residual connected porosity of about 12–30% (45, 49). This process allows for real net shape fabrication of complex components because the part does not shrink during the reaction. Precise dimensional tolerances can be obtained without postfabrication machining. Another advantage is that no sintering aids are used so that RBSN parts retain their strength even at high temperatures and they are resistant to creep. However, the low density of RBSN materials results in typical strength values that are only a fraction of fully dense silicon nitride ceramics. The high porosity RBSN materials also have lower oxidation resistance and are more brittle than dense silicon nitride (45, 46, 49, 60). Modifications to the reaction-bonding process material density include postsintering (SRBSN) (45) or post-HIP (HIPRBSN) (48). Property improvements have been realized, but this approach does not appear to offer quality advantages over the more direct processes.

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Table 2. Properties of Silicon Nitride Ceramics

Property	Material densification mode			
	Reaction-bonded ^a	Sintered ^b	Hot-pressed isostatically ^c	Hot-pressed ^d
density, kg/m ³	2.5	3.26	3.23	3.2
elastic modulus, GPa ^e	180	300	310	310
hardness, kg/mm ²	1350	1370	1620	1800
flexure strength, MPa ^f at ambient temperature	340	700	900	700
1000°C		600		610
1200°C		480		570
1370°C		210	580	310
fracture toughness, MPa√m	3–4	4.6	4.7–5.5	4.9
thermal expansion coeff, 25–1000°C, 10 ^{–6} /°C	3	3.9	3.9	3.5
thermal conductivity, W/(m·K) at 25°C	12	32	38	32

^aCoors Ceramics Company, Bulletin #980.

^bGTE Laboratories AY-6, 6 wt% yttria +2 wt% alumina (43).

^cNorton NT154, 4 wt % yttria (61).

^dNorton NC 132, 1 wt % magnesia (46).

^eTo convert GPa to psi, multiply by 145×10^3 .

^fTo convert MPa to psi, multiply by 145.

5.3. Properties

Properties of structural silicon nitride ceramics are given in Table 2. These values represent available, well-tested materials. However, test methodology and the quality of the specimens, particularly their surface finish, can affect the measured values. Another important material property is tensile strength. Values obtained on Norton's NT154 material are: 750 MPa at RT, 500 MPa at 1200°C, and 350 MPa (50,000 psi) at 1400°C (62).

As noted, the oxidation resistance of silicon nitride ceramics depends on the type and concentration of the sintering aids. In materials designed for high temperature applications the specific weight gain resulting from oxidation upon a 500-h air exposure at 1200°C and 1350°C is about 1–2 g/m² and 2–4 g/m², respectively. The kinetics of the oxidation process have been investigated (63, 64) as has the corrosion resistance (65). Corrosion resistance is also dependent on material formulation and density.

5.4. Applications

Silicon nitride is the leading material for components in advanced automotive, diesel, and gas turbine engines. The range of potentially useful ceramic parts includes both static structural components and dynamic ones such as turbocharger rotors, gasifier turbine rotors, valves, valve guides, valve seats, piston components, cam followers, fuel injector links, and bearings. Some of these parts have been commercialized, others are being evaluated.

The first commercial use of silicon nitride ceramics for automotive applications was in glow plugs to reduce engine startup wait times for light duty diesel engines. More recently, Si₃N₄ hot plugs have been installed in similar engines. These plugs also reduce engine emissions and noise (66). Silicon nitride turbocharger rotors are being used (67, 68) in Japanese production cars sold in Japan. 1990 production rates were about 20,000/month and are projected to reach 30,000/month in 1991. A limited production run of a U.S. model was also equipped with a ceramic turbocharger (60). The primary advantage is the low density of the material and a consequent

lower moment of inertia leading to faster engine response and to a decrease in turbocharger lag. Introduction of such turbo-chargers into Japanese light duty diesel engines is probable (66). Silicon nitride cam followers are being introduced into heavy-duty diesel engines in the United States because of their superior wear performance (69); an additional advantage is a reduction or even elimination of the need for forced lubrication and for costly lubrication channels. Ceramic fuel injector links are being incorporated into heavy-duty diesel engines, also because of superior wear resistance (70). A silicon nitride exhaust port liner is being used in sports cars because it results in faster heat up of the catalytic converter and consequent reduction in hydrocarbon and oxide emissions (70). A Si_3N_4 rocker arm wear pad has been introduced (67).

The lower inertia of silicon nitride valves allows them to follow the valve-lifting cam more closely resulting in a more stable operation which could increase the engine speed by up to 1000 rpm (68). This advantage was utilized effectively in stock car racing in which engines equipped with silicon nitride valves out-performed standard engines in many competitions (71). In conventional applications the use of ceramic valves offers the potential for increased fuel efficiency by reducing the spring load resulting in a lower camshaft torque. Large silicon nitride components, including valves about 50 cm in diameter and 50 cm high, have been fabricated and are being evaluated in coal gasification plants in Japan (72).

The emerging field of gas turbine engines is a technology in which silicon nitride ceramics serve as enabling materials. The automotive version of this engine is designed to provide the powertrain for the next generation of passenger cars (73). Car manufacturers in the United States, Germany, and Japan are actively involved in the development of such engines and there are several variations in its design; one of the common features is that the engine is intended to operate at a gas inlet temperature of 1375°C . The only suitable materials for rotating components under these conditions are silicon nitride ceramics. Gas turbine rotors which successfully passed spin tests at maximum speed both at room temperature and at 1395°C have been developed (73).

A car powered with a gas turbine engine having ceramic rotors has been undergoing successful road tests in Germany for several years (74) and a similar engine of larger capacity is being developed in Japan for stationary use for co-generation of electric power. Another application for silicon nitride rotors is in auxiliary power unit (APU) engines (75).

In other useful applications, silicon nitride bearings have been found to offer excellent performance; silicon nitride cutting tool inserts are a commercial product; wear parts such as sand blast nozzles, seals, and die liners are also commercially produced; the superior performance of heat exchangers has been demonstrated and there are also military applications.

6. Zirconia Structural Ceramics

Zirconia ceramics represent a fairly new class of advanced structural materials (see Zirconium and zirconium compounds). Their potential use in structural applications was first realized in the mid-1970s. Since then numerous publications have appeared devoted entirely to these materials (76–81).

6.1. Material System

Pure zirconia at atmospheric pressures exhibits three well-defined crystalline polymorphs: the monoclinic, tetragonal, and cubic phases. The monoclinic phase is stable up to about 1170°C where it transforms to the tetragonal phase. At 2370°C the tetragonal phase transforms to the cubic phase which exists up to 2680°C , the zirconia melting point (82). On cooling through the tetragonal-to-monoclinic transformation temperature, a large volume increase (3–5%) occurs. This change is sufficient to cause cracking. Thus, fabrication of large components of pure zirconia is not possible. The transformation volume expansion can be used to advantage, however, by the addition of cubic stabilizing oxides, most commonly magnesia, calcium oxide [1305-78-8], CaO , and yttria. These oxides can stabilize the relatively weak cubic form down to room temperature. Moreover, if

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insufficient stabilizing oxide is added, and the material is properly processed, zirconia particles can be retained in the metastable tetragonal form at room temperature. These materials are referred to as partially stabilized zirconia (PSZ) ceramics.

During application of stress, eg, in the region of a propagating crack, metastable tetragonal particles transform to the stable monoclinic phase. The resulting volume expansion places the region around these particles, ie, adjacent to the crack, in compression and crack propagation is retarded until the applied stress is increased. The extra work required to move the crack through the matrix can lead to increases in strength, toughness, and resistance to thermal shock. The phases present in these ceramics, their amount, size, and distribution, can be controlled to produce materials having a range of properties tailored for specific applications.

The transformation is believed to occur by a diffusionless shear process (83). It is often referred to as martensitic transformation, having a thermal hysteresis between the cooling and heating cycles. The transformation is dependent on particle size; finer particles transforming at a lower temperature than coarser particles. Transformation toughening can also result upon incorporation of fine zirconia particles into another matrix such as Al_2O_3 (84). These materials are called zirconia toughened ceramics (ZTC). A third type of transformation-toughened ceramic material is formed using a low concentration of yttria in zirconia and a very fine grain size (85–87). An approximately 100% tetragonal zirconia polycrystalline (TZP) ceramic results.

6.2. Fabrication Technology

Stabilizing additives must be uniformly distributed within the starting powders for zirconia ceramics. Homogeneous distribution can be attained by controlled coprecipitation of hydroxides which are then decomposed by calcination yielding powders of fine particle sizes. Active sinterable powders are produced commercially, usually by hydrolysis of a mixture of ZrOCl_2 and YCl_3 to precipitate the mixed hydroxide. The method produces a powder having a very fine (about $0.3\ \mu\text{m}$) particle size. Alternative methods of fabricating fine active powders include CVD and hydrothermal oxidation. Preparation of zirconia powders is covered in the literature (78, 88–90).

Zirconia powders may be shaped using techniques such as slip casting, dry pressing, and injection molding. The ceramics may be densified by sintering, hot pressing, or hot isostatic pressing, provided the thermal treatment of the material is appropriate to develop the desired microstructure. Other fabrication methods, such as microwave sintering, are also under investigation. Reaction sintering has been used to produce microstructures of zirconia particles in various ceramic matrices as well (91, 92).

6.2.1. Partially Stabilized Zirconia

PSZ is comprised of a cubic zirconia matrix having a fine dispersion of tetragonal particles. Stabilizing additives are on the order of several weight percent of MgO , CaO , or Y_2O_3 to produce the appropriate microstructures. Powders are first sintered at an appropriate temperature, solution annealed in the single-phase cubic region of the zirconia phase diagram, and then heat-treated (aged) in the two-phase tetragonal + cubic region to nucleate and grow tetragonal precipitates within the cubic matrix. A critical size range, submicrometer to several micrometers, exists for stress-induced transformation of tetragonal zirconia particles. If the material is aged too long and the precipitates grow larger than the critical size, particles spontaneously transform to the monoclinic phase upon cooling to room temperature; if the particles are smaller than the critical size, transformation does not occur. The critical size limit depends on the matrix constraint and the composition of the zirconia. As the stabilizing oxide content is increased, the chemical free energy associated with the phase transformation decreases and hence larger particles can be induced to remain in the metastable tetragonal form.

6.2.2. Tetragonal Zirconia Polycrystal

TZP ceramics may be produced from compositions stabilized using Y_2O_3 (2–4 mol %) or cerium(IV) oxide [1306-38-3], CeO_2 (9–14 mol %) by sintering in the single-phase tetragonal region of the phase diagram (87, 93). In order to retain the tetragonal phase to room temperature, the grain size must be kept very small (usually $<1\text{ }\mu\text{m}$). Each grain is restrained by surrounding grains from transforming to the stable monoclinic form. TZP materials exhibit exceptionally high fracture strength values and high toughness. Yttria TZP, however, exhibits a serious decrease in strength when aged in air between 150° and 300°C (94–97). Because of fine grain size and the presence of a grain boundary phase, TZP ceramics exhibit pseudosuperplasticity at 1200°C with extension of $>100\%$ measured in tension (98, 99). This feature provides opportunities for shape forming of this material.

6.2.3. Zirconia Toughened Ceramics

Zirconia particles can be embedded in host matrices to form a variety of transformation-toughened ceramics (100). Hosts include Al_2O_3 (84, 101), β'' -alumina (102), mullite [55964-99-3] (103, 104, 91), Si_3N_4 (105–109), SiAlON (110), cordierite [12182-53-5] (111), glass ceramics (112), TiB_2 (113, 114), MgO (115), and molybdenum silicide [12136-78-6] MoSi_2 (116). Requirements are that the host matrix not react with the ZrO_2 and that the matrix have a sufficiently high elastic modulus to retain the ZrO_2 in the tetragonal state. The zirconia particles can then transform as they do in PSZ or TZP materials. Optimum toughness and strength result using very fine (usually $<1\text{ }\mu\text{m}$) zirconia. ZTC are generally formed by either mixing powders of zirconia and the matrix and sintering or chemically preparing powders of mixed composition by coprecipitation. Mixed powder synthesis yields intergranular particles whereas the chemical route yields intragranular ones. Mechanical properties are optimized by maintaining a very well dispersed zirconia phase and avoiding particle growth during sintering. However, sintering temperatures must be high enough to achieve full density.

6.2.4. Toughening Mechanisms

The mechanics of tetragonal-to-monoclinic transformation can effect the strength and toughness of the ceramic.

6.2.4.1. Stress-Induced Transformation Toughening. The stress field of a crack can initiate martensitic transformation (117–121); the transformed particles expand against the matrix, resulting in compressive stress on the crack surface. This stress acts to reduce the eventually stop propagation of the crack. The particles which have transformed in the vicinity of the crack comprise what is called a process zone. This zone tends to shield the crack tip from applied stress.

6.2.4.2. Compressive Surface Layers. Spontaneous tetragonal-to-monoclinic transformation of zirconia particles may take place at or near the surface of a macroscopic part as a result of the absence of the hydrostatic constraint near the free surface. The particles expand and induce a compressive strain. This compressive surface layer leads to high fracture strength and in some cases the strength may be doubled. Surface grinding has been found to be the most effective method of inducing this transformation.

6.2.4.3. Microcrack Toughening. Toughening can result from both residual and stress induced microcracks. Residual microcracks are formed when the retained tetragonal particles are larger than some critical size causing them to spontaneously transform on cooling. The stresses generated around the transformed particles induce microcracks between the particles and the matrix. The microcracks may extend in the stress field of the propagating crack, or deflect the propagating crack, thereby absorbing or dissipating fracture energy and, hence, increasing the toughness of the ceramic. However, although *fracture toughness* is increased, the presence of either stress-induced or residual microcracks can result in a significant reduction in the *fracture strength*. Because of increased fracture toughness, microstructures having residual microcracks are useful in situations requiring resistance to thermal shock. These materials must be carefully processed to produce particles large enough to transform but small enough to cause only limited microcrack development.

The microstructure of zirconia materials can be designed to yield optimum combinations of fracture strength and toughness by controlling the relative amount of stress-induced transformation toughening and

Table 3. Properties of Zirconia Ceramics

Property	PSZ ^a	TZP ^b	ZTA ^c
density, kg/m ³	5.7	6.0	4.2
hardness, kg/mm ²	1000	1300	1600
flexural strength, MPa ^d	300–700	1000–2500	400–900
fracture toughness, MPa√m	4–8	5–15	5–10
elastic modulus, GPa ^e	200	200	340
thermal expansion coeff, $\times 10^{-6}/K$	9–10	10–11	8–9
thermal conductivity, W/(m·K)	2.0–2.5	2.7	7–10
maximum service temperature, °C	950	500	1700

^aProperties of PSZ depend on whether CaO, MgO, or Y₂O₃ is used as the stabilizing agent.

^bProperties of TZP depend on whether CeO₂ or Y₂O₃ is used as the stabilizing agent.

^cProperties of zirconia toughened alumina, ZTA, depend on the specific microstructure and the proportions of zirconia and alumina.

^dTo convert MPa to psi, multiply by 145.

^eTo convert GPa to psi, multiply by 145×10^3 .

microcracking (122). The temperature dependence of mechanical properties is also correlated with different toughening mechanisms. Transformation toughening provides high strength and toughness at low and intermediate temperatures but its effectiveness decreases as temperature increases. Microcrack toughening is a less effective toughening mechanism but it is essentially temperature-independent.

6.2.4.4. Crack Deflection. Crack deflection can result when particles transform ahead of a propagating crack. The crack can be deflected by the localized residual stress field which develops as a result of phase transformation. The force is effectively reduced on the deflected portion of the propagating crack resulting in toughening of the part.

6.3. Properties

Transformation toughened ceramics have excellent strength and toughness at low and intermediate temperatures. Compared to SiC and Si₃N₄, ZrO₂-toughened ceramics can withstand significantly higher applied stress at room temperature (see Fig. 1), but SiC and Si₃N₄ have much greater high temperature potential. Zirconia ceramics have limited high (>800 – 1000°C) temperature capability for two reasons: creep rates are high compared to nonoxide ceramics; and the contribution from the transformation toughening mechanism decreases as the temperature increases. That is, as the tetragonal phase becomes more stable, the driving force for the transformation decreases. Table 3 lists the properties of zirconia ceramics each of which is a family of materials. Specific properties are a function of amount and type of stabilizing agent, processing conditions utilized, and resulting microstructure.

TZP materials have exceptionally high fracture strength values: strengths greater than 1000 MPa are consistently achieved and values over 2000 MPa have been reported. Toughness is generally greater than 5 MPa√m (123). Yttria TZP, however, exhibits a serious decrease in strength when aged in air between 150° and 300°C (94–97). The effect appears to be related to water vapor in the air reacting with the Y₂O₃-ZrO₂ at the ceramic surface, promoting the tetragonal-to-monoclinic transformation, and forming microcracks. There are indications that this problem can be avoided or at least minimized by achieving a suitably fine grain size (0.2–0.6 μm), by adding finely dispersed alumina to the yttria–zirconia (124), or by substituting CeO₂ for Y₂O₃ as the stabilizing oxide (125). Addition of alumina (~20 wt % Al₂O₃) to Y–TZP inhibits grain growth and transformation of the tetragonal particles. The toughness of Ce–TZP (>30 MPa√m) can be higher than that of Y–TZP (15 – 20 MPa√m) but the strength is relatively low, 500–1000 MPa for Ce–TZP vs 1500–2000 MPa for Y–TZP (125). A limiting factor in the application of zirconia ceramics is the decrease in properties that result

as temperatures increase. Several possible strategies exist for improving the high temperature capabilities of zirconia ceramics (126). SiC whisker reinforced zirconia ceramics have also been investigated (127–129).

6.4. Applications

One of the most demanding applications for zirconia ceramics is in automotive engine parts, particularly for the diesel engine (130). Applications attempt to exploit its low thermal conductivity and/or the wear-resistance characteristics. One approach utilizes ceramic liners or inserts (eg, piston crowns, head face plates, and piston liners) attached to metal engine components. PSZ is a favored material for this approach, not only because it has low thermal conductivity and is a good insulator, but more importantly, because its high thermal expansion coefficient is close to that of cast iron. This compatibility facilitates attachment and reduces the possibility of failure during engine cycling. Other engine applications for zirconia include components which are limited by wear, particularly in the valve train, such as cams, cam followers, tappets, and exhaust valves.

Alumina–zirconia ceramics have superior strength, toughness, and wear resistance when compared to conventional alumina and these composite ceramics have found use as cutting tool tips and abrasion wheels. Applications include scissors and shears for cutting of difficult materials such as Kelvar, and cutting and slitting of industrial materials, such as magnetic tape, plastic film, and paper items. The fracture toughness and thermal shock resistance of transformation-toughened PSZ has made it a leading candidate for both wire drawing and hot extrusion dies. Seals in valves, chemical pumps, and abrasive slurry pumps and impellers are being made of zirconia ceramics. In some applications involving abrasive slurries, PSZ materials can be more wear resistant than silicon carbide. Components requiring long life under low load conditions, such as thread guides and bearings and guides for dot matrix printers can also be made successfully from zirconia. MgO–PSZ has found the widest commercial use because of the range of tailored microstructures which can be produced.

Zirconia also has suitable properties for thermal barrier coatings, for turbine rotors for example, because of its high thermal expansion coefficient, low thermal conductivity, good chemical stability, and thermal shock resistance (131–133). Plasma-sprayed zirconia compositions have been investigated and the most durable coatings were found to be formed from a partially stabilized zirconia composition. A major problem encountered with such coatings is corrosive attack by the mineral constituents in fuel oil leading to destabilization of the tetragonal zirconia to give the monoclinic form.

In all applications involving zirconia, the thermal instability of the tetragonal phase presents limitations especially for prolonged use at temperatures greater than $\sim 1000^{\circ}\text{C}$ or uses involving thermal cycling. Additionally, the sensitivity of Y–TZP ceramics to aqueous environments at low temperatures has to be taken into account. High raw material costs have precluded some applications particularly in the automotive industry.

7. Environmental Aspects

Exposure limits for silicon carbide and powders of zirconium compounds (including zirconium dioxide) have been established by ACGIH. TLV–TWA's are 10 mg/m^3 and 5 mg/m^3 , respectively. OSHA guidelines for zirconium compounds call for a PEL of 5 mg/m^3 . There are no exposure limits for silicon nitride powder, but prudent practice suggests a TLV–TWA of 0.1 mg/m^3 . The solid ceramics present no apparent health hazard. In machining such ceramics, however, care should be taken to prevent inhalation of respirable particles in amounts in excess of established limits. Disposal should be in approved landfills; the materials are inert and should pose no danger to the environment.

Table 4. Producers of Structural Ceramics

Location, company	Ceramic type
Australia	
Nilcra	ZrO ₂
Europe	
ASEA	Si ₃ N ₄
ESK	SiC, Si ₃ N ₄
Feldmühle ^a	ZrO ₂
Japan	
Kyocera Corp. ^a	SiC, Si ₃ N ₄ , ZrO ₂
NGK Insulators	SiC, Si ₃ N ₄
NTK Technical Ceramics	Si ₃ N ₄
United States	
Carborundum Co.	SiC
Ceramatec	ZrO ₂
Coors ^b	ZrO ₂
Corning	ZrO ₂
Dow Chemical	ZrO ₂
WR Grace	ZrO ₂
GTE	Si ₃ N ₄
Norton Co.	SiC, Si ₃ N ₄ , ZrO ₂
Zircoa ^b	ZrO ₂

^aKyocera Corp. licenses Feldmühle and Max Planck Institute zirconia technology.

^bLargest U.S. suppliers of ZrO₂ ceramics.

8. Economic Aspects

The production of advanced ceramic mechanical and wear components in Japan in 1989 is estimated at one billion U.S. dollars. Silicon nitride powder production amounted to about ten million U.S. dollars, about one tenth of the total nonoxide ceramic powder production. It is projected that in the year 2000 the market for these ceramic components will be in the \$2.7–4.2 billion range (134). In Western Europe the market for mechanoceramics in 1989 was estimated at \$200 million U.S. dollars and projected to grow modestly in the near future. The amount of silicon nitride and silicon carbide sold was \$32 and \$21 million, respectively (135). It is projected that in the United States the market for structural ceramics in automotive applications will grow in the year 2000 to \$820 million (in 1990 dollars) from the current estimate of \$81 million for 1990. In the same time interval the market for wear parts and other industrial advanced ceramics (excluding cutting tools) is expected to grow to \$720 million from its 1990 value of \$150 million. The corresponding figures for the aerospace and defense-related advanced ceramics market are \$445 and \$80 million, respectively (136). Structural ceramics producers are given in Table 4.

Premium zirconia powders cost from U.S. \$55 to \$100/kg. Suppliers include Ferro and Z-Tech (a subsidiary of ICI); Japanese sources of powders include Toyo Soda Manufacturing Company (now Tosoh) and Daichi Kigenso.

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