CHAPTER TWO

CERAMICS INDUSTRY

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An important goal of this study was to identify key needs in the Industries of the Future and to explore ways that ceramics might meet these needs. As shown in Fig. 2.1, key needs that crosscut the Industries of the Future and that match the favorable characteristics of ceramics include wear resistance, corrosion resistance, temperature resistance, controlled surface behavior, dimensional stability, engineered behavior, heat recovery, and filtration. In some cases, only ceramics can simultaneously meet combinations of these needs. In other cases, the favorable characteristics of ceramics are often offset by cost considerations or by concerns that ceramics are weak and have poor durability and toughness. However, broad progress has been accomplished in the past 15–20 years to alleviate these negatives through material improvement, new ceramic materials, and improved design methods. This new generation of ceramics and design methods has the potential to help the Industries of the Future reach their visions of increased efficiency, decreased maintenance, optimized recycling, and decreased pollution.

Important advances have occurred in four ceramic material categories: monolithic ceramics, composite ceramics, coatings, and refractories. Some of the progress, especially in monolithic and composite ceramics, is described in the following sections. The emphasis is on reviewing what is new and different about these new ceramic materials (compared to perceptions industry individuals may have acquired using prior ceramic materials) and identifying the types of applications that have been successful.

2.1 KEY MONOLITHIC CERAMICS

The term *monolithic* has been applied to ceramic materials which are entirely ceramic, typically have low porosity, and comprise a complete component or a lining. Examples include dense forms of aluminum oxide (Al_2O_3), silicon nitride (Si_3N_4), silicon carbide (SiC), zirconium oxide (ZrO_2), transformation-toughened zirconia (TTZ), transformation-toughened alumina (TTA), and aluminum nitride (AlN).

Major progress has been accomplished in the past 20 years to increase the capability of monolithic ceramics for thermal, wear, corrosion and structural applications. In particular, the

Fig. 2.1. Ceramic materials can meet crosscutting needs of Industries of the Future.

strength and toughness have been dramatically improved to the degree that ceramics are now available that can compete with metals in applications previously thought impossible for ceramics. Figure 2.2 illustrates the level of increases in the key structural characteristics of strength, toughness, and Weibull Modulus. Strength is a measurement of the resistance to formation of a crack or structural damage in the material when a load is applied. Toughness is a measurement of the resistance of the material to propagation of a crack or extension of damage to the point of failure. The Weibull Modulus is a measurement of the uniformity in strength. The lower the Weibull Modulus, the higher the likelihood that the material will fail at a stress substantially below the average strength. Thus, high Weibull Modulus means better material reliability and greater ease in designing with the material.

Most ceramics prior to 1970 had strength well below 345 MPa (50,000 psi). Now Al_20_3 and SiC are commercially available with strength over 345 MPa, and Si_3N_4 and toughened zirconia are available with strengths above 690 MPa (100,000 psi). Strength at elevated temperatures also has been improved, as shown in Fig. 2.3 for Si_3N_4 materials. SiC ceramics retain strength to even higher temperatures.

One of the most significant advances in ceramics during the past 20 years has been to increase fracture toughness. Increased fracture toughness is important to industry because it reduces risk of fracture during installation and service, which has always been a concern with glass and traditional ceramics. Figure 2.4 compares the toughness of some of the new ceramic materials with typical ceramics and other key engineering materials. Glass has fracture toughness of about 1 $MPa{\cdot}m^{1/2}$, and conventional ceramics range from about 2–3 $MPa{\cdot}m^{1/2}$. Steel is around 40 $MPa{\cdot}m^{1/2}$. Some Si_3N_4 materials approach 10 $MPa{\cdot}m^{1/2}$, which is higher than cast iron. Some transformation-toughened ZrO_2 materials have toughness around 15 $MPa{\cdot}m^{1/2}$, which is higher than that of tungsten carbide–cobalt (WC-Co) cermet. These new tougher ceramics have demonstrated dramatically better resistance to impact, contact stress and handling damage and are providing high reliability and durability that users are accustomed to receiving with metals and WC-Co. New continuous fiber ceramic composites (CFCCs) are under development that provide further improvements in fracture toughness. These are discussed under Sect.2.4.

Silicon Nitride

Silicon nitride refers to an alloy family of ceramics whose primary constituent is Si_3N_4. The ceramics in this family have a favorable combination of properties that includes high strength over a broad temperature range, high hardness, moderate thermal conductivity, low coefficient of thermal expansion, moderately high elastic modulus, and unusually high fracture toughness for a ceramic. This combination of properties leads to excellent thermal shock resistance, ability to withstand high structural loads to high temperature, and superior wear resistance.

Si_3N_4 has been continuously under development in the U.S. since the late 1960s. Since the early 1980s, much of the development of Si_3N_4 materials has been cofunded by the Department of Energy (DOE) and industry and has been directed especially towards gas turbine engines and other heat engines. These developments have resulted in improved properties, increased reliability, complex shape fabrication capability, and some cost reduction.

Si_3N_4 has been successfully demonstrated in a variety of applications. In general, the issue has not been technical performance, but cost. As the cost has come down, the number of production applications is accelerating. Table 2.1 lists some of the applications, the kind of conditions that the silicon nitride is exposed to in each application, and the benefit that is perceived by the customer. The objective of the table is to provide to the Industries of the Future a baseline for comparison with their specific materials needs. To further achieve this objective, subsequent paragraphs provide additional details of the conditions silicon nitride is surviving in existing applications.

Although the driver for Si_3N_4 development has been gas turbine engine components, the first major application was cutting tool inserts. Grinding, milling, and boring of metals is a major cost of manufacturing. A study in the early 1970s estimated that there were 2,692,000 metal-cutting machine tools in the United States with an annual operating cost of $64 billion. The life of the cutting tool insert and the speed of cutting were the key factors identified in the study regarding the number of machines required and the operation cost.

Cutting hard metals such as cast iron and high-temperature alloys results in high temperature at the tool–work piece interface. WC-Co, the

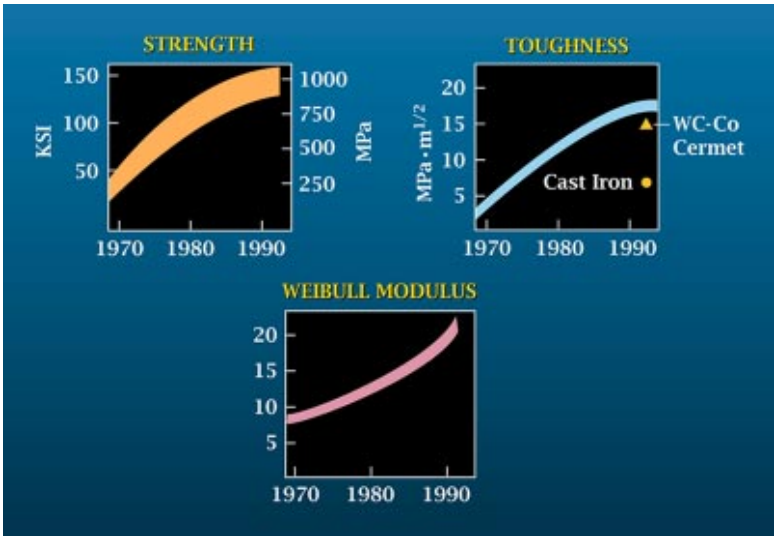
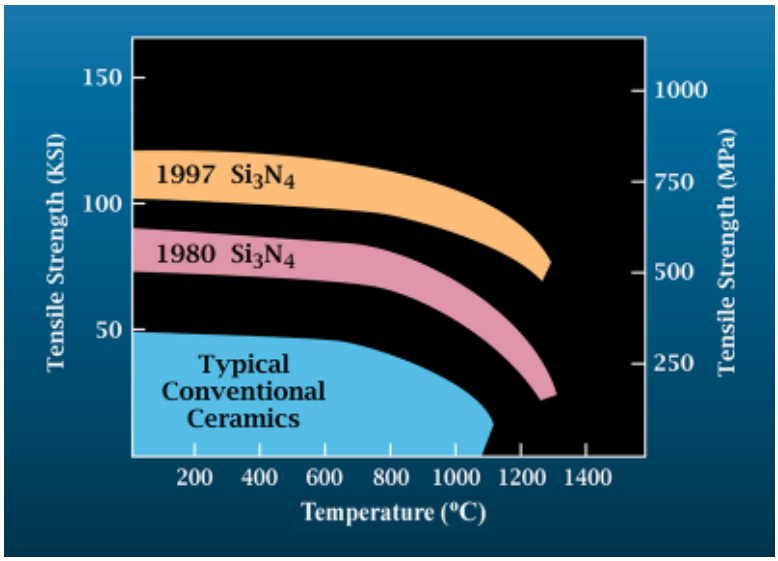


Fig. 2.2. Strength, toughness, and uniformity have been dramatically increased since 1960.

Fig. 2.3. Silicon nitride alloys have evolved from properties comparable to conventional ceramics to very high strength which is retained to high temperatures.



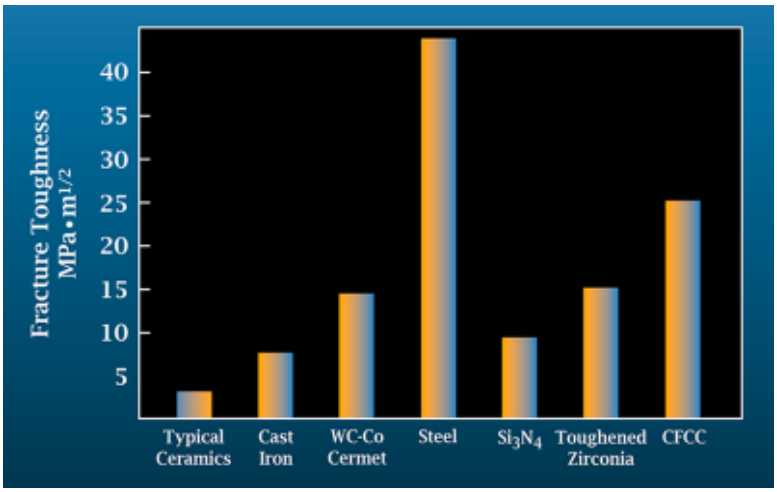


Fig. 2.4. Comparison of the fracture toughness of new ceramic materials with conventional ceramics and other key structural materials.

Table 2.1. Production applications of silicon nitride

Application	Conditions imposed on the silicon nitride	Benefits demonstrated or perceived by customers
Cutting tool inserts (introduced late 1970s)	High contact stress, severe physical and chemical erosion, temperatures to around 1100°C	75–90% reduction in machining time for cast iron, 5–10 times increase in the metal-removal rate, and increase in the number of parts machined per tool
Diesel cam follower rollers (introduced 1990s)	Highly concentrated rolling contact stress	Increased life at higher injection pressures, reduced frictional losses, improved engine performance
Bearings (introduced late 1980s)	High contact loads that can exceed 2 million psi (~13,800 MPa)	3–10 times life of best metal bearings, 80% lower friction, 80% higher speed, 60% lighter, higher operation temperature, ability to operate with lubrication starvation
Papermaking machine foils	Sliding contact, wet environment	Increased life, decreased maintenance
Wear parts for many applications	Depends on application, but typically abrasion, erosion, and some impact over a broad range of temperature	Dramatic increase in life and decrease in maintenance
Turbocharger rotors (introduced 1985)	Centrifugal and thermal stress at elevated temperature	Reduced inertia due to the low specific gravity of silicon nitride (about 40% that of turbo-charger rotor metals)
Manufacturing tooling (dies for aluminum can making, drawing dies, etc.)	Depends on application, but can include high stress, sliding erosion, and elevated temperature	Extended life, reduced maintenance, improved dimensional control of product
Aircraft engine seal (for man-rated gas turbine aircraft propulsion engine — introduced mid-1990s)	Sliding seal operating at engine shaft speed and elevated temperature	Much higher reliability and life than metals
Fuel injector link (for timing control— introduced 1989)	Sliding contact	>60% less wear
Diesel glow plug (tungsten heating element in a silicon nitride container — introduced 1981)	High temperature, thermal shock, combustion gas environment	Quicker starting, cleaner exhaust gases
Diesel prechamber (swirl chamber— introduced about 1983)	Elevated temperature, thermal shock	Improved power, reduced pollution
Check valve balls	Impact, abrasive particles erosion, adverse chemical environments, elevated temperature	Longer life, reduced maintenance
Slotted dewatering centrifuge liners for mining industry	Severe erosion, some impact	Longer life, decreased maintenance

traditional workhorse for metals machining, wears rapidly if the temperature gets too high, so the cutting speed must be limited to around 400 surface feet per minute (sfpm) (121.6 m / min.) and sometimes even down to around 80 sfpm. Because Si_3N_4 is much more resistant to temperature, cutting speeds as high as 5000 sfpm (1520 m / min.) have been demonstrated. At a depth of cut of 0.2 in. (5 mm) and feed rate of 0.015 in. (0.4 mm) per revolution, this speed represents a material removal rate each minute equivalent to a block of metal $3 \times 6 \times 10$ in. ($7.6 \times 15.2 \times 24.5$ cm). The Si_3N_4 is exposed to thermal shock, impact, contact stress, severe erosion, and temperatures around 1100° C. This gives an indication of the severe conditions that silicon nitride materials can survive.

The use of Si_3N_4 cutting tool inserts has had a dramatic effect on manufacturing output (see Fig. 2.5.) For example, face milling of gray cast iron gear-case housings with silicon nitride inserts doubled the cutting speed, increased tool life from one part to six parts per edge, and reduced the average cost of inserts by 50%. Outside grinding of diesel truck cylinder liners increased the number of parts machined per tool index from around 130 to 1200 and totally eliminated a prior problem with insert breakage. As a result, tool life was increased to achieve 9600 cylinders per cutter load of inserts compared to 450. Just the decreased downtime alone increased the output per shift 25%.

A more recent application for Si_3N_4 that is having revolutionary impact on many industries is bearings (see example in Fig. 2.6). Si_3N_4 was first demonstrated as a superior bearing in 1972 but did not reach production until nearly 1990 because of challenges associated with reducing the cost. Since 1990, the cost has been reduced substantially as production volume has increased. Although Si_3N_4 bearings are still 2–5 times more expensive than the best bearing steel, their superior performance and life are justifying rapid adoption. Around 15–20 million Si_3N_4 bearing balls were produced in the U.S. in 1996 for machine tools and many other applications. Growth is estimated at 40% per year, but could be even higher if ceramic bearings are selected for consumer applications such as in-line skates and computer disk drives.

Si_3N_4 balls similar to bearings are also in production for ball-and-seat check valves (see examples in Fig. 2.7). One severe application is for down-hole pumping of oil with a "sucker rod." Si_3N_4 is used for the ball and WC-Co for the seat. With each stroke of the sucker rod, oil-containing fluid at the bottom of the oil well is forced into the

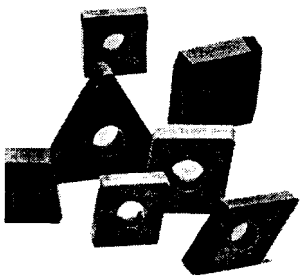


Fig. 2.5. Si_3N_4 can withstand the severe conditions of cutting metal and has resulted in dramatic improvements in the efficiency of machining cast iron. Photograph shows cutting tool inserts from Ceradyne, Inc., Costa Mesa, Calif.

Fig. 2.6. Si_3N_4 bearings, check valve balls and other high-strength, wear-resistant components from Saint-Gobain/Norton Advanced Ceramics, East Granby, Conn.

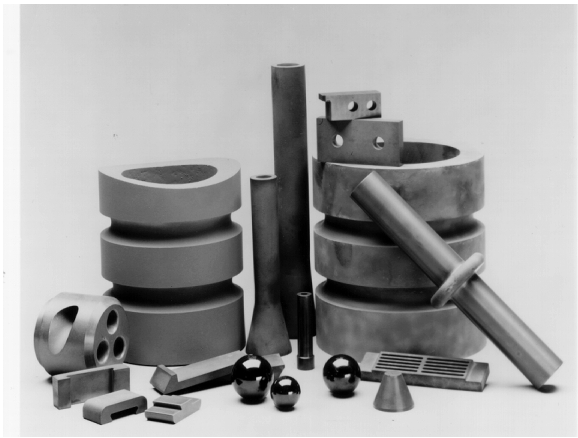


Fig. 2.7. Si_3N_4 components from Ceradyne, Inc., Costa Mesa, Calif. Includes grit-blast nozzle liners, wire-forming rolls and guides, papermaking dewatering foil segments, check valve balls, down-hole oil well parts, custom wear parts, a refractory ferrule, and a centrifugal dewatering screen and scraper blade for potash and coal dewatering.

rod and towards the surface of the well. At the end of the stroke, the ball drops back down to the seat to form a seal so the fluid does not flow back. This results in substantial impact on both the ball and seat under the weight of all the fluid in the well, which commonly is well over 2000 ft (608 m) deep. The fluid is a mixture of petroleum, water / steam, sand and other debris, hydrogen sulfide, and other chemicals—all at several hundred degrees temperature. The pump operates around 12 cycles / min, 24 h / day, 7 d / week.

The key message from the above examples is that the Si_3N_4 family is a new generation of ceramics that are much more durable and resistant to brittle fracture than traditional ceramics. In addition to the applications listed in Table 2.1, Si_3N_4 is being vigorously evaluated for diesel and auto engine valves, valve guides, stator vanes and rotors for turbines (Fig. 2.8), a variety of wear parts, tooling for aluminum processing (Fig. 2.9), and many other potential products. As additional production applications are achieved and current production levels increase, it is anticipated that the cost of silicon nitride will come down substantially, removing the primary barrier that has limited broad use of advanced silicon nitride materials. Within 10 years Si_3N_4 could be a commodity material similar to Al_2O_3.

Information on Si_3N_4 suppliers in the United States is included in the appendix to this report.

Aluminum Oxide

Al_2O_3 is the most mature high technology ceramic. It is the same composition as sapphire, which accounts for its high hardness and durability. Al_2O_3 ceramic is produced by compacting alumina powder into a shape and firing the powder at high temperature to allow it to densify into a solid, polycrystalline, nonporous part. About 5 million metric tons were produced in 1995 for wear, chemical, electrical, medical, and other applications. Table 2.2 lists some of the applications of Al_2O_3, the use conditions, and the advantages over alternate materials.

Al_2O_3 is used in these applications because of its high hardness and wear resistance, chemical resistance, and smooth surface (see examples in Fig. 2.10). Al_2O_3 also is used extensively for electrical applications due to its good electrical insulating characteristics. Examples are spark plug insulators, substrates for electronics modules (such as in automobiles), and packages for integrated circuits. Other applications of Al_2O_3 include radomes, medical components, orthodontic brackets, sodium vapor lamp arc tubes,

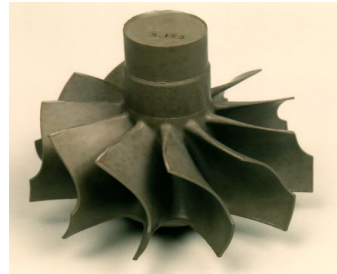


Fig. 2.8. Si_3N_4 gas turbine engine radial rotor from AlliedSignal Ceramic Components. *Source:* AlliedSignal Ceramic Components, Torrance, Calif.

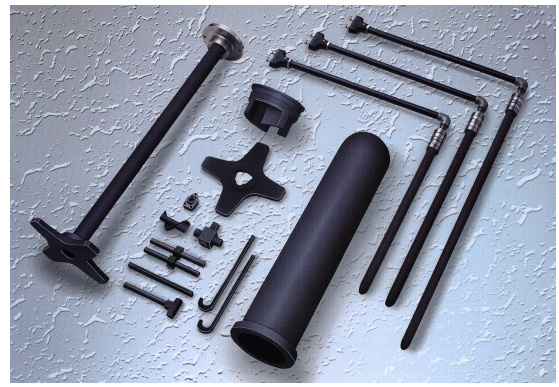


Fig. 2.9. Silicon nitride tooling designed for immersion in molten aluminum. *Source:* Kyocera Corporation, Kyoto, Japan.

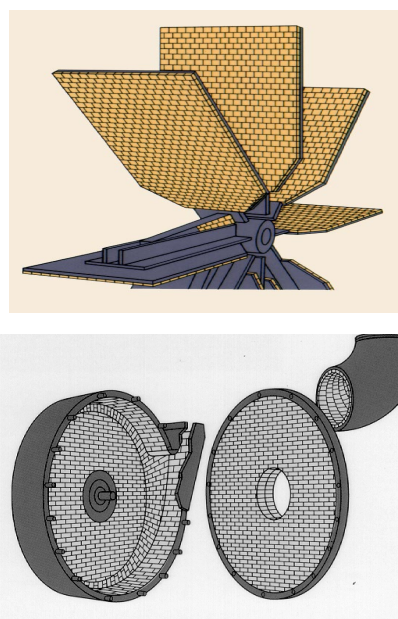


Fig. 2.10. Al_2O_3 tiles provide reliable wear-resistant surfaces on chutes, fans, housings, pipes, and cyclones in handling systems for pulverized coal, grain, ore, and other flowing abrasive materials. *Source:* Coors Wear Products, Inc. brochure, Coors Ceramics Company, Golden, Colo.