IN CONTRAST TO METALS, high-performance ceramics have higher hardness, lower ductility, and a basically brittle nature. Other general properties to note are: excellent high-temperature performance, good wear resistance and thermal insulation (low thermal conductivity), as well as high resistance to corrosion and oxidation. However, the full advantage that these materials can provide is strongly dependent on composition and microstructure.

Most high-performance ceramics are based on high-purity oxides, nitrides, carbides, and borides with carefully controlled compositions. Ceramic engineering components are usually produced by powder metallurgical methods. The required properties of a specific part are optimized by selecting parameters associated with the powder mixture and the pressing and sintering operations to obtain the desired microstructure.

High-performance ceramics can be divided into two main categories; structural and functional ceramics. While optimization of structural ceramics is directed toward improved mechanical properties, the performance of components produced from functional ceramics is controlled by electrical, magnetic, dielectric, or optical properties. Therefore, restrictions with respect to mechanical properties can be tolerated. Typical structural ceramics are aluminum oxide (Al$_2$O$_3$), zirconium dioxide (ZrO$_2$), silicon nitride (Si$_3$N$_4$), and silicon carbide (SiC). However, Al$_2$O$_3$, ZrO$_2$- and SiC-based ceramics are also often used as functional ceramics. Other functional ceramics of technological interest are barium titanate (BaTiO$_3$) and lead zirconate titanate (Pb(Ti,Zr)O$_3$).

Due to the large variations in microstructure, different ceramographic preparation techniques are applied to achieve the surface quality desired so structural details are revealed under the microscope. For ceramographic preparation, it is necessary to polish the surface. For ceramographic preparation of TZP and CSZ is quite different. The tough, fine-grained TZP requires longer polishing times for the fine-polishing step with 1 and 0.25 μm diamond, while CSZ needs longer polishing times for the coarser polishing with 6 and 3 μm diamond compounds.

Depending on the type of ceramic or ceramic component, the mechanical properties (e.g., fracture toughness and strength) may vary considerably, and therefore the ceramographic preparation procedures have to be adjusted accordingly.

**Specimen Preparation**

Similarly to metallographic preparation, sequential steps have to be performed to prepare ceramics for microstructural investigations (Ref 1–3). Careful selection of sectioning, mounting, grinding, polishing, and etching procedures is re-

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**Fig. 1** Tetragonal zirconia polycrystals (TZP) with 2 mol% Y$_2$O$_3$ thermally etched in air at 1300 °C (2370 °F). The scanning electron micrograph shows a fine-grained microstructure. Pores appear black.

**Fig. 2** Light micrograph of a cubic stabilized zirconia (CSZ) with 12 mol% Y$_2$O$_3$ thermally etched in air at 1300 °C (2370 °F). The large cubic grains show interand intragranular porosity.
quired, and each step must be optimized for each type of ceramic. However, due to the brittleness, porosity, and chemical resistance of ceramics it is quite often difficult to polish them in the same way as metals. Automated sample preparation is recommended. The capability to adjust polishing pressure and the use of special grinding disks with diamond as the abrasive material is also preferred. With this equipment, a flat surface that displays an undistorted “true” microstructure may be prepared in a reasonable time.

**Sectioning.** Generally, ceramics are cut with a lubricated (water or a special cutting fluid), rotating diamond cutting wheel on a bench-type lab machine or on a precision cutting machine. The cutting speed (low-speed cutting machine: 25 to 500 rpm; high-speed cutting machine: 500 to 5000 rpm) and the cutting pressure should be optimized for the properties of a given material. A slow cutting speed and low pressure produce less cutting and surface damage for most ceramics, although some ceramic materials require the opposite (e.g., TZP-ZrO₂). Diamond cutting wheels are either metal bonded or resin bonded, and normally metal-bonded cutting wheels are selected. However, for very brittle and sensitive ceramics, resin-bonded cutting wheels are recommended. These wheels are softer and will generally produce a better cut-surface finish than a metal-bonded diamond wheel, but their weaker bond shortens service life. Additional criteria for selection of cutting wheels also include: the concentration of abrasive, the grain size of abrasive, and the wheel thickness. Generally, low abrasive concentration blades are used, because the lower the abrasive loading, the higher the contact stress on each abrasive particle and therefore the higher the cutting rate. The grain size of a diamond blade is usually 94 µm, but for delicate samples, it may be advisable to cut with a diamond blade of a finer grit to avoid unnecessary damage to the material. The thickness of the diamond cutting wheel is dependent on the thickness of the sample. For samples with limited dimensions it is advisable to use a thinner wheel.

**Mounting.** For automatic sample preparation, specimens can be mounted or may be glued directly onto a sample holder. The two possibilities for metallographic mounting are hot mounting, with compression and heat, and cold mounting. It should be noted that sensitive, small, and very brittle ceramics specimen are susceptible to damage and cracking when using hot mounting, because of the high pressure and temperature that is needed for this process. The mounting material should be either very hard or have good abrasion resistance. Additionally, before the sample is mounted consideration must be given to the etching technique that is to be used. This will guide the selection of a mounting material most suited to the complete sample preparation. For example, when using thermal etching techniques or molten-salt etching techniques the sample should be removed from the mount before etching. When etching in a boiling chemical solution, the mount should be of a material that will not be attacked by the acid mixture.

**Mechanical Preparation (Grinding and Polishing).** It is preferable to perform the grinding and polishing procedures with an automatic or semiautomatic machine. The procedure of each and every ceramic product has been specifically adjusted to exhibit required properties, and thus each material will exhibit a unique behavior during preparation. Table 1 contains preparation standards for structural ceramics (e.g., Si₃N₄ and Al₂O₃) as well as AlN, and Table 2 provides the preparation standards for functional ceramics (e.g., BaTiO₃ and PZT). These tables should be used as a rough guide only; the parameters will need to be adjusted according to the preparation requirements of specific ceramics.

In general, resin-bonded diamond disks are employed for grinding. In individual cases, silicon carbide paper is used. For example, this type of paper would be selected for the functional ceramics.

The surface damage generated during sectioning and grinding has to be removed during fine grinding, or lapping and polishing. Fine grinding and/or lapping retains the plane of the specimen surface, and no further damage is introduced. Complete removal of the damaged surface must therefore be achieved by subsequent polishing steps. Polishing should be performed on hard cloths. The highest removal rates will occur during steps with the application of 6 and 3 µm diamond grain sizes. Polishing with 1 µm diamond removes a minimal amount of material. All breakouts and scratches should be removed during these steps. In general, fine polishing with a SiO₂ suspension is only applied if small and fine scratches have to be removed. In some cases, this final step can also produce a slight relief on the sample surface, which may be beneficial for microscopy.

**Microscopic Examination.** For the investigation of ceramic microstructures and the identification of flaws and defects, the use of light optical microscopy (LOM) or scanning electron microscopy (SEM) are most common. Since most of the ceramics are electrical insulators, samples for SEM investigations have to be coated by an electrical conductive layer such as carbon, gold, or gold-palladium alloys. Metals are used for simple microstructural analysis, while carbon is used for simultaneous chemical analysis, for example, energy-dispersive x-ray (EDX) analysis. Standard scanning electron microscopes are normally equipped with different detectors. The backscatter detector is useful for multiphase materials, when the different phases reveal a strong mass contrast. In this case, no etching is required. Secondary electron detectors are sensitive to small differences in height of a polished and etched surface. The microscopic examination of ceramic specimens in the as-polished state has proved useful. An evaluation of the number of pores, their distribution, and possible pullouts can only be assessed in this state. Evaluation of inclusions, contamination, and cracks should also be made before etching.

In order to reveal grain boundaries, phases, and other microstructural details, ceramic specimens have to be etched. Ceramic microstructures, examined under the LOM (>200×) will show a low contrast and a milky image. Ceramics permit light rays to penetrate the surface where scattering and internal reflection occurs. To eliminate light scattering and to improve the reflectivity, coating the surface with a reflective layer is recommended. Such a layer should be.

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**Table 1** Standard preparation conditions for structural ceramics (e.g., Si₃N₄, AlN, SiC and Al₂O₃), semiautomatic preparation

<table>
<thead>
<tr>
<th>Process</th>
<th>Diamond grade, µm</th>
<th>Lubricant</th>
<th>Speed, rpm</th>
<th>Pressure(a)</th>
<th>Time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grinding</td>
<td>Diamond disk</td>
<td>65</td>
<td>Water</td>
<td>300</td>
<td>~180–40</td>
</tr>
<tr>
<td>Fine grinding</td>
<td>Diamond disk</td>
<td>20</td>
<td>Water</td>
<td>300</td>
<td>~180–40</td>
</tr>
<tr>
<td>Polishing</td>
<td>Composite disk</td>
<td>6</td>
<td>Alcohol-based</td>
<td>300</td>
<td>~100–23</td>
</tr>
<tr>
<td>Polishing</td>
<td>Pellan cloth</td>
<td>6</td>
<td>Alcohol-based</td>
<td>150</td>
<td>~150–34</td>
</tr>
<tr>
<td>Polishing</td>
<td>Hard synthetic cloth</td>
<td>3</td>
<td>Alcohol-based</td>
<td>150</td>
<td>~120–27</td>
</tr>
<tr>
<td>Fine polishing</td>
<td>Hard silk cloth</td>
<td>1</td>
<td>Alcohol-based</td>
<td>150</td>
<td>~90–20</td>
</tr>
<tr>
<td>Fine polishing</td>
<td>Short napped, fiber cloth</td>
<td>SiO₂ suspension</td>
<td>150</td>
<td>~50–11</td>
<td>0.5–5</td>
</tr>
</tbody>
</table>

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**Table 2** Standard preparation conditions for functional ceramics (e.g., BaTiO₃, PZT, and ZnO), semiautomatic preparation

<table>
<thead>
<tr>
<th>Process</th>
<th>Diamond grade, µm</th>
<th>Lubricant</th>
<th>Speed, rpm</th>
<th>Pressure(a)</th>
<th>Time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grinding</td>
<td>Siliccon carbide paper</td>
<td>320</td>
<td>Water</td>
<td>300</td>
<td>~150–34</td>
</tr>
<tr>
<td>Lapping</td>
<td>Hard synthetic cloth</td>
<td>6</td>
<td>Lubricant</td>
<td>150</td>
<td>~100–23</td>
</tr>
<tr>
<td>Polishing</td>
<td>Hard synthetic cloth</td>
<td>3</td>
<td>Lubricant</td>
<td>150</td>
<td>~120–27</td>
</tr>
<tr>
<td>Polishing</td>
<td>Hard silk cloth</td>
<td>1</td>
<td>Lubricant</td>
<td>150</td>
<td>~90–20</td>
</tr>
<tr>
<td>Fine polishing</td>
<td>Short napped, fiber cloth</td>
<td>SiO₂ suspension</td>
<td>150</td>
<td>~50–11</td>
<td>0.5–1</td>
</tr>
</tbody>
</table>
between 5 and 10 nm thick and can be applied by sputter coating with either gold or aluminum.

**Thin-Section Polarized Light Microscopy.**

In general, all nonmetallic materials are suitable for examination by transmission polarized light microscopy, including the high-performance ceramics (Ref 4). The only limitations are the grain size of the material and its mechanical behavior. Many ceramics have a very small grain size (<1 μm), which makes LOM examination impossible. Because resolution depends on the wave-length of light, the smallest particle size that can be observed is 1 μm. In order for a thin section to be mechanically stable it needs to be about 5 to 30 μm thick. At this thickness, however, the grains in fine-grained materials lie over one another, and this multilayering results in formation of a diffuse image. This can cause difficulty in differentiating between certain optical effects. It is for this reason that a grain size of at least 5 μm is preferred.

The preparation of thin sections requires the use of precision cutting, grinding, and polishing machines. It should be remembered that several square centimeters of specimen must be removed by cutting, grinding, and polishing to achieve a specimen of uniform 5 to 30 μm thickness with a smooth, polished surface on either side, free of surface breakouts.

In the first stage of preparation, the specimens are treated in the same way as polished sections for incident light microscopy. The ceramic is cut and mounted and then ground and polished using a semiautomatic grinding and polishing machine. A roughened glass slide is then bonded to the polished surface of the specimen with a drop of epoxy resin (Fig. 3). To prevent the formation of pores and air bubbles between the specimen and the glass slide, this operation should be carried out in a vacuum infiltration chamber. Once the specimen has fully hardened, which generally takes about two days, the specimen is sliced off to a thickness of about 500 μm. Thereafter, the specimen is ground down to a thickness of about 80 to 100 μm using a diamond grinding disk. Because there is always a danger of deep pullouts and cracking, which then have to be eliminated by the following stages of preparation, the specimen should not be ground any thinner than 80 μm. Depending on the material being prepared, the specimen is either manually or semiautomatically fine ground and then polished. As the thin section nears the end of its preparation, it must be handled extremely carefully and must be repeatedly checked with the microscope under polarized light. When the target thickness is achieved—that is, when all the grains, depending on their double refraction, exhibit the colors gray, yellow-brown, or blue-green—a thin cover glass is bonded to the surface of the specimen for protection, using thinned epoxy resin.

**Ceramographic Etching**

Figure 4 presents a review of ceramographic etching methods (Ref 1, 5). Three etching methods can be distinguished: optical, electrochemical, and physical contrasting. The most frequently used etching methods for high-performance ceramics are solution etching, thermal etching, and plasma etching. Plasma etching works only in case of silicon-base ceramics (SiC, Si3N4). Details of the etching procedure are described below. Thermal etching is mostly used for oxide ceramics. Typical etching temperatures are 150 °C (270 °F) below sintering temperature in air. Etching time can vary between 15 min and some hours, depending on the structure and composition of the grain boundary that evaporates during the heat treatment. Thermal etching of nonoxide ceramics requires an inert atmosphere or an encapsulation of the sample in a quartz tube. Due to the chemical resistance of many ceramics, solution etching of polished specimens was applied to the preparation of very aggressive chemical solutions at elevated temperatures, or the application of molten-salt reagents. For the etchants given in Table 3, only general details can be given in regard to the concentration and etching time required for a given sample. The desired level of etching on a sample must be determined by trial and error.

**Oxide Ceramics.** Apart from etching with very aggressive chemical solutions, thermal etching in air is also an important method for developing the microstructures of Al2O3 and ZrO2 ceramics (Ref 6, 7). The polished and “de-mounted” samples are placed in an air furnace. Exposure temperature and time are selected so that the heat treatment does not alter the microstructure. The temperature should be approximately 100 to 150 °C (180 to 270 °F) below the sintering temperature. Temperatures that are too high or etching times that are too long may result in grain growth.

Generally, chemical solutions are used to develop microstructures, grain boundaries, and the domain structure of other oxide ceramics such as BaTiO3 and PZT (see Table 3). Thermal etching in air can also be used to show the grain boundaries, but it will not develop the domain structure. If the grain size exceeds 5 μm, the microstructure of the ceramic material can also be revealed with a thin section under polarized light. An example is shown in Fig. 19 for BaTiO3.

**Nitride Ceramics.** When Si3N4 is prepared with solutions containing concentrated phosphoric acid or molten NaOH, the intergranular grain-boundary phase between the Si3N4 grains is dissolved away by chemical attack (Fig. 5–7) (Ref 8). One disadvantage of these two etchants is their poor reproducibility. This is because the optimal etching time is extremely dependent on both the microstructure and the composition of the glass phase, which varies with the composition of the additives used.

In contrast to solution etching for Si3N4 materials, plasma etching attacks the ceramic-matrix grains and not the grain-boundary phase (Fig. 8 and 9) (Ref 9). Plasma etching is carried...
out inside a special chamber, which produces a gaseous mixture of CF4 and O2. A radio frequency generator emits high-frequency electromagnetic oscillations and thus produces fluorine radicals inside the reaction chamber. These radicals then react with the silicon contained in the matrix of the ceramic (Si3N4). The intergranular grain-boundary phase remains unattacked by the plasma etching process. The etchants for AlN, given in Table 3, are proven for chemical solution etching and give reproducible results (Ref 10).

Carbide Ceramics. Several suitable etchants for different SiC materials exist (Table 3). Molten salt, thermal etching, hot chemical etchants, and a number of Murakami solutions with different modifications reveal the microstructure by attacking the grain-boundary phases (Ref 11). For SiC with 5 to 15% oxide additions, the plasma etching technique (see above for Si3N4) can be successfully applied. In this case the SiC grains are attacked, leaving the grain-boundary phase untouched.

Classification and Microstructure of Frequently Used Ceramics

Details of the microstructure of common structural and functional ceramics along with typical applications follows.

**Aluminum oxide (Al2O3)** is the most common ceramic and, depending on the adjusted properties, is either used as a structural or a functional ceramic material (Ref 12). Applications of high-temperature-resistant alumina are crucibles, tubes, and rods for furnaces. Sealing disks, insulators, and as a structural component in many prosthetic devices are either made from alumina or contain alumina components.

The densification of alumina powder compacts is achieved by a sintering process, which controls density and grain size (Ref 12). These parameters determine the strength characteristics of the final product. Figure 10 shows a cross section of a fluorescent tube with isotropically grown grains. For Si3N4 with 15 μm average grain size and a porosity of less than 0.5%, Figure 11 illustrates a microstructure characterized by anisotropically grown grains with an average size of 2 to 4 μm. The resulting texture is caused by a preferred orientation of alumina seed crystals during injection molding. The microstructure of a ceramic sealing disk with a typical residual porosity of 3 to 4%, a bimodal grain size distribution, and a glassy phase at the grain boundaries (liquid-
phase sintering) is given in Fig. 12. Figure 13 shows the microstructure of a spark plug with anisotropic grains, a glassy grain-boundary phase, and large pores. The effect of different etching techniques is demonstrated in Fig. 14 and 15. After thermal etching of the magnesium-doped sample at 1500 °C (2730 °F) in air, equiaxed grains with black gaps along the grain boundaries can be seen. The gaps are pores and voids formed by an evaporated spinel phase (MgAl2O4) (Fig. 14). The microstructure shown in Fig. 15 is from the same material, but chemically etched in phosphoric acid at 270 °C (520 °F). The spinel phase is dissolved, and the grain boundaries look broader.

Zirconium dioxide (ZrO2) based ceramics belong to those materials that are characterized by having both good mechanical properties and exceptional electrical properties (Ref 14, 15). The thermomechanical and electrical properties have led to a wide range of applications. Tough, wear-resistant, and refractory ZrO2 is being developed for applications as extrusion dies, machinery wear parts, and piston heads. Zirconium dioxide is a good ion conductor and, as a solid electrolyte, is used in oxygen sensors and in solid oxide fuel cells (SOFC). Zirconium dioxide is also used for furnace elements. The low thermal conductivity of ZrO2 makes it important as a thermal barrier coating in aerospace engine components and land-based gas turbines. The different kinds of application require different properties that are realized by four basic types of microstructure: cubic stabilized zirconia (CSZ), partially stabilized zirconia (PSZ), tetragonal zirconia polycrystals (TZP), and zirconia toughened ceramics (ZTC).

The CSZ microstructure is a solid solution of ZrO2 and a stabilizing oxide such as Y2O3, MgO, or CaO. These additives maintain the cubic structure down to room temperature. Cubic sta-
bibilized zirconia is manufactured from powder mixtures or prealloyed powders and homoge-

nized completely during sintering in the homo-
geneous cubic region at temperature between
1600 and 1800 °C (2910 and 3270 °F). The mi-
crostructure of stabilized ZrO₂ consists of cubic
grains together with an intergranular glassy
phase (Fig. 2). As a result of the high processing
temperatures, a comparatively large grain size in
the range 10 to 150 μm is formed. The inter-
granular glassy phase contains various impuri-
ties originating from the manufacturing process
and the raw materials, but these are mainly SiO₂.

Partially stabilized zirconia is a ceramic with
5 to 15 mol% of stabilizer additives (Y₂O₃,
MgO, CaO). It is sintered in the cubic homo-
geinity range. The PSZ microstructural develop-
ment requires a special program of sintering. Ini-
tially, the ceramic is compacted at high
temperatures (>1700 °C) in the cubic solid-so-
lution region. A coarse microstructure with cubic
grains and an intergranular glassy phase forms.
By heat treating in the two-phase field (tetrago-
nal and cubic), small lenticular particles of the
tetragonal phase are precipitated. These particles
are not resolved in the LOM. They are coherent
with the cubic {100} planes. The precipitates are
shown in the electron microscope image insert
in Fig. 16.

Tetragonal zirconia polycrystals contain only
2 to 3 mol% Y₂O₃ (or 10 to 20 mol% CeO₂) as
stabilizer and crystallizes in a metastable tetrag-
onal form. However, due to the high activation
energy of the transformation, the tetragonal
structure is retained down to room temperature
and can be activated for a strain-induced trans-
formation to the stable monoclinic structure. The
tetragonal and monoclinic crystallites (grains)
both have the same morphology and cannot be
distinguished by LOM or SEM, but require x-
ray diffraction. An example of the TZP micro-
structure, taken in the SEM, is shown in Fig. 1.

Zirconia toughened ceramics consist of a ce-
ramic matrix (e.g. Al₂O₃) in which 3 to 15 vol%
of ZrO₂ particles are embedded (Fig. 17). The
difference between the thermal expansion coef-
ficients of the matrix and the ZrO₂ particles
causes stresses during cooling, which is essential
to the stability of the dispersoid. The increase in
toughness results from the strain-induced trans-
formation and microcrack formation (Ref 16).

Piezoelectric Ceramics. BaTiO₃ and PZT
(Pb( Ti, Zr)O₃) are the most widely used piezo-
electric materials, in electronic devices. The
properties can be varied over a wide range by
donor or acceptor dopants to achieve the re-
quired properties for a given application. BaTiO₃
is mainly used in capacitors because of its high
dielectric strength as well as the ability to have
a positive or negative temperature coefficient of
the dielectric by dopant addition and process
procedures. Pb( Ti, Zr)O₃ exhibits a high piezo-
electric constant and is used for sensors and ac-
tuators and for ultrasonic wave generation (Ref
17, 18).

The starting powders with the corresponding
dopants are usually prepared by a mixed-oxide
process. The required oxides and/or carbonates
are first milled and subsequently calcined to obtain a single-phase powder. Consolidation of the prereacted powders is achieved by either pressing or tape casting. Sintering is performed in air or in an oxygen atmosphere at a temperature range of 1000 to 1350 °C (1830 to 2460 °F). Both BaTiO₃ and Pb(Ti,Zr)O₃ crystallize above the Curie temperature in the cubic perovskite structure and transform into a lower symmetry structure during cooling. The phase transformation is accompanied by lattice distortion, typically about 1% for BaTiO₃ and 1.0 to 2.5% for Pb(Ti,Zr)O₃, depending on the zirconium-to-titanium ratio. The lattice distortion generates internal stresses, which are reduced by the formation of domains.

The phase transformation from the paraelectric cubic phase to the tetragonal ferroelectric phase occurs for BaTiO₃ at 130 °C (265 °F). Below 0 °C (32 °F) other phase transformations occur, but they have no technological interest. The domain configuration consists of 90° and 180° domains based on the different possibilities for the orientation of the spontaneous polarization vector. The domain structures can be readily observed by chemical etching of polished BaTiO₃ ceramics samples (Fig. 18) or by using the thin-section technique (Fig. 19).

Paraelectric PZT is a solid solution between lead zirconate and lead titanate with a cubic crystal structure. Below the Curie temperature it transforms into a ferroelectric tetragonal phase for titanium-rich PZT and ferroelectric rhombohedral phase for zirconium-rich PZT. The Curie temperature is not well defined and depends on the zirconium-to-titanium ratio and the amount of additives. The maximum piezoelectric constants and coupling factors are achieved for compositions with approximately equal volume fractions of tetragonal and rhombohedral PZT (morphotropic PZT). The domain structures of these materials are more complex than in BaTiO₃ because both crystallographic modifications can coexist within one grain, and they have different possible directions for the spontaneous polarization vector. Tetragonal PZT forms have only 90° and 180° domains, but rhombohedral PZT also has 71° and 109° domains. A typical microstructure of a PZT ceramic is shown in Fig. 20. After chemical etching, the grain boundaries, as well as the domain structures within the grains, are revealed in this SEM image.

Aluminum Nitride (AIN). High-purity AlN has a high thermal conductivity of more than 200 W/m · K together with a low thermal expansion coefficient. These, and other useful properties, make AlN a very suitable material for application as a substrate in the electronics industry. Aluminum nitride has a hexagonal crystal structure. Pressureless sintering is impossible for pure AlN powder, because of its covalent bonding. Densification is achieved by liquid-phase sintering with additives. Commonly used additives are Y₂O₃ (Fig. 21), rare earth oxides (Fig. 22), or fluorides such as CaF₂ and YF₃. The thermal conductivity of AlN is affected by the presence of both secondary phases and impurities at the grain boundaries.
Silicon nitride (Si$_3$N$_4$) is a structural ceramic with excellent mechanical properties, good oxidation resistance, and good thermal shock behavior at ambient and high temperatures (Ref 19, 20). Si$_3$N$_4$ ceramics can be processed by two different methods: reaction-bonded silicon nitride (RBSN) and (pressureless) sintered silicon nitride (SSN). Other variants of the latter are known by the following abbreviations, according to their method of manufacture: gas-pressure sintered, GPSN; hot-pressed, HPSN; and hot isostatically pressed silicon nitride, HIPSN.

Porous Si$_3$N$_4$ ceramics produced from inexpensive raw materials are used as refractories. Dense materials with high strength in combination with a high wear resistance are developed for cutting tools to machine cast iron. The high-temperature-resistant Si$_3$N$_4$ ceramics are used as heating elements for furnaces, as parts in gas turbines, and components for pumps. Other types of applications include kiln supports, heat exchangers, or burner nozzles. Electrically conductive SiC ceramics are used as heating elements for furnaces for operation up to 1400 °C (2550 °F) in air.

Four types of SiC ceramics can be produced: recrystallized SiC (RSiC), silicon-infiltrated SiC (SiSiC), sintered SiC (SiSiC), and liquid-phase sintered SiC (LPS-SiC). They have significantly different manufacturing routes and therefore different microstructures and properties. Recrystallized SiC is produced by a powder compact with a bimodal grain size distribution. During heat treatment, the fine-grained powder evaporates and condenses at the points of contact with the large SiC particles. Because no densification occurs during heat treatment, a higher volume fraction of porosity remains, and this results in a relatively low strength. Figure 26 shows a typical microstructure of an RSiC ceramic.

Silicon-infiltrated SiC is produced by an infiltration of a SiC/C powder compact with liquid silicon. Part of the silicon reacts with the carbon to form fine-grained secondary silicon carbide. A larger volume fraction of silicon remains unreacted and reduces the oxidation and corrosion resistance of SiSiC, but increases the strength in comparison to RSiC.

Figure 23 Light micrograph of a reaction-bonded Si$_3$N$_4$ (RBSN). The unetched specimen contains iron silicide (arrow) and characteristic high porosity (black).

Figure 24 Light micrograph of an unetched sintered Si$_3$N$_4$ (GPSN) specimen. The white inclusions are iron silicide, and porosity is black. The porosity is much lower compared to Fig. 23 (RBSN).

Figure 25 Scanning electron micrograph of hot isostatically pressed Si$_3$N$_4$ (HIPSN) after plasma etching, shown at a magnification sufficient to reveal micro-porosity.

Figure 26 Light micrograph of an RSiC ceramic. Gray areas are α-grains on which β-SiC has recrystallized, dark areas are pores, and white areas are silicon. Etchant: modified Murakami’s solution.

Fig. 23 Light micrograph of a reaction-bonded Si$_3$N$_4$ (RBSN). The unetched specimen contains iron silicide (arrow) and characteristic high porosity (black).

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Fig. 25 Scanning electron micrograph of hot isostatically pressed Si$_3$N$_4$ (HIPSN) after plasma etching, shown at a magnification sufficient to reveal micro-porosity.

Fig. 26 Light micrograph of an RSiC ceramic. Gray areas are α-grains on which β-SiC has recrystallized, dark areas are pores, and white areas are silicon. Etchant: modified Murakami’s solution.
the multiphase ceramic SiSiC with the primary and secondary SiC and the unreacted silicon is shown Fig. 27.

Densification of SiC ceramics can be achieved by solid-state sintering with boron, B, or al-

Fig. 27 Light micrograph of an SiSiC microstructure with large α-SiC grains and a fine-grained fraction of the β modification. The bright phases represent infiltration silicon, which densifies the material but also impairs its corrosion resistance. Etchant: Murakami’s solution

Fig. 28 Light micrograph of an SSiC ceramic, pressureless sintered with boron as additive. The microstructure shows fine equiaxed grains and pores (dark). Etchant: modified Murakami’s solution

Fig. 29 Light micrograph of a pressureless-sintered SSiC ceramic with a pronounced bimodal platelet microstructure consisting of α-SiC grains. The large dark spherical particles, approximately 50 μm in diameter, are graphite (arrow). The smaller dark spots within the SiC grains are intragranular pores. Etchant: modified Murakami’s solution

Fig. 30 Light micrograph of a pressureless-sintered SSiC ceramic with a pronounced bimodal grain size distribution and 3.5% porosity. Etchant: modified Murakami’s solution

Fig. 31 Scanning electron micrograph of a liquid-phase sintered SiC ceramic (LPS-SiC) after plasma etching. The central and edge zones of the gray SiC matrix grains differ in their chemical composition, which causes a different etching attack. The light constituent is the grain-boundary phase, formed by the sintering additives.

REFERENCES


