Review

Recent Advances in Microstructural Tailoring of Silicon Nitride Ceramics and the Effects on Thermal Conductivity and Fracture Properties

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ABSTRACT

Tailoring the microstructure and the composition of silicon nitride ceramics can have profound effects on their properties. Here it is shown that the grain growth behavior, in particular its anisotropy, is a function of the specific additives, which allow one to tune the microstructure from one consisting of more equiaxed grains to one with very elongated grains. Recent studies are discussed that provide an understanding of the atomic level processes by which these additives influence grain shapes. Next the microstructural (and compositional) parameters are discussed that can be used to modify the thermal conductivity, as well as fracture toughness of silicon nitride ceramics. As a result of the open <0001> channels in β-Si_3N_4, the c-axis conductivity can be exceptionally high. Thus, the formation of elongated c-axis grains, particularly when aligned can result in conductivity values approaching those of AlN ceramics. In addition, the controlled formation of elongated grains can also be used to significantly enhance the fracture toughness. At the same time, both properties are shown to be affected by the composition of the densification additives. Utilizing such understanding, one will be able to tailor the ceramics to achieve the properties desired for specific applications.

Key words : Silicon nitride, Microstructure, Thermal conductivity, Mechanical properties

1. Introduction

A review of the progress made in the development of silicon nitride based ceramics would be an overwhelming task considering the efforts of just the last 30 or so years. Furthermore, there are a number of excellent reviews that address the realm of processing, properties and characteristics of silicon nitride ceramics. For instance, the extended article by Petzow and Herrmann provides an excellent overview on the development of silicon nitride ceramics.[1] The Gmelin Handbook Inorganic and Organometallic Chemistry series, which include extensive references, is a must source for those interested in detailed reviews on each of the above topics.[2-4] For a review of the progress made in the development of silicon nitride gas turbine components, the reader is referred to a recent two-volume review edited by van Roode, Ferber and Richerson.[5,6] In addition, the reader is encouraged to examine the summary by Wiederhorn and Ferber on the issues of creep and fracture resistance and corrosion due to water vapor in silicon nitride ceramics.[7]

In the present paper, the focus will be on more recent advances in our understanding of anisotropic grain growth, which can be used to form self-reinforced microstructures and can influence properties like thermal conductivity, together with developments in high thermal conductivity and toughened self-reinforced silicon nitride ceramics.

2. Evolution of Elongated Grain Structures

A variety of additives are employed to promote the densification of silicon nitride ceramics, which begins to decompose at temperatures in excess of 1700°C. These additives include oxides (e.g., alumina, magnesia, yttria, rare earth oxides), which along with the native oxide present in Si_3N_4 powders form minor phases that have low viscosities at temperatures over 1200°C and induce liquid-phase sintering mechanisms. In addition, anisotropic grain growth, which can yield long c-axis grains (Fig. 1), is strongly affected by the choice of additives, especially the rare earth (RE) and Group III elements.[8-11] Similar effects of additives on grain aspect rations occur in α-SiAlON ceramics.[12,13] While these trends are informative, the size of the additive cation provides no insight into the mechanism(s) that control grain growth. Understanding grain growth behavior becomes significant in the quest to form elongated reinforcing grains that can bridge the crack and increase the crack tip stress necessary for crack growth (e.g., Fig. 1) in the development of toughened Si_3N_4-based ceramics.[14,15]

Grains in both Si_3N_4 and SiAlON ceramics have hexagonal cross-section rod-like shapes with curved end caps. The growth in the c-axis (i.e., rod length) is generally fast and is considered to be a diffusion-controlled process (e.g., ref. 16). Diametrical (i.e., a-axis) growth rates are slower in compar-

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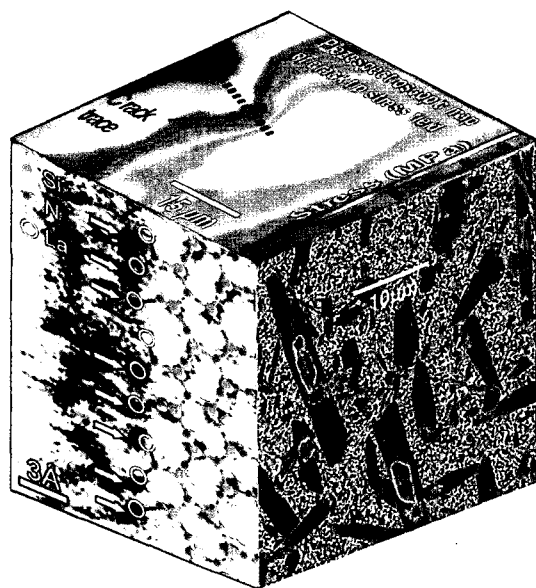
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Fig. 1. Elongated reinforcing Si_3N_4 grains in fine grained matrix (right panel) can bridge crack and raise the crack tip stress required to advance the crack (upper panel). Growth of the grain diameters is impeded by the use of certain additive elements such as La, which adsorb strongly to prismatic surfaces of the grains (i.e., indicated by high contrast regions in scanning transmission electron microscopy image with corresponding open circles of theoretical predicted La adsorption positions in left panel).[a]

ison and are found to depend upon the specific rare earth or Group III element present, suggesting an attachment limited process.[10,11,17,18] Studies of Si_3N_4 grain clusters embedded in Si-RE-Al oxynitride glasses have shown that greater anisotropic grain growth occurred in the presence of La is accompanied by a concentration of La in the intergranular film between prismatic surfaces of the silicon nitride grains.[9] Yb, on the other hand, did not concentrate in the intergranular film and the grain growth anisotropy was significantly reduced.

Theoretical models have now been developed that predict the segregation and adsorption behavior of various additive elements, and these predictions are confirmed by unique atomic resolution scanning transmission electron microscopy (STEM) observations. First the differential binding energy (DBE) model defined the chemical preference of additive elements compared to that of silicon for both nitrogen-rich (i.e., grain surfaces) and oxygen-bearing (i.e., in the midst of the intergranular film and/or near the triple point pockets) regions that are present in the Si_3N_4 microstructure.[19] The model provides insight into the binding energies for RE's and Si with oxygen and nitrogen. From these first-principles calculations, one finds that the preference for segregation to a nitrogen-rich region should decrease across the lanthanide series in the order from La to Gd to Lu.

Additional calculations address the specifics of interfacial RE binding based on a N-terminated Si_3N_4 prism plane sur-

face.[20,21] For La, Gd, and Lu adsorption on the nitrogen-terminated prismatic plane, there are two stable sites for each of the repeating Si_3N_4 surface units. These sites can be occupied by each of the RE's as they have higher binding energies with nitrogen than those for Si. For La, there is also a third site, with weaker binding energy but still larger than that for Si. The DBE theory suggests that differences in the occupation of these sites can be expected as Lu should prefer to reside in oxygen containing regions rather than at the nitrogen rich grain surfaces resulting in fewer of the less energetic second adsorption sites being occupied by Lu. Because it has a strong preference for nitrogen, La would occupy not only the two most stable adsorption sites but also many of the less energetic third sites. STEM images (e.g., Fig. 1) confirm the predicted adsorption sites for La, Gd, and Lu.[21-23]

The picture that emerges is that the degree of segregation of the additive cation to the grain surfaces is determined by the chemical bond preference of the RE, as compared to Si, for oxygen versus nitrogen as silicon competes for bonding with these anions. As such the DBE model explains the observed trend for the increase in RE segregation to the interfacial region as one goes from Lu to La. The local density calculations of the adsorption behavior provide specific information on the RE/interface coordination and relative stabilities of RE surface occupancies. At the same time the DBE results also show that the extent to which predicted sites are occupied depends upon the preference of the RE to migrate to the grain surface region.

Experimentally, it is clear that diametrical growth is slowed, but not halted, by the larger RE elements. Thus, the key issue is how difficult it is for silicon to displace the additive element from the grain surface. It is necessary to also assess how readily the RE desorbs from the grain surface as grain growth at high temperatures is dependent on desorption kinetics. These depend exponentially on the energy for the RE to desorb from the interface into the adjacent glassy film. The desorption rate of the RE versus kT thus is sensitive to the RE/interface bond strength, as well as the bond strength of the RE within the glass. The DBE theory compares the energy preference of each RE for N versus O referenced against that of Si for N or O. This provides at least a semi-quantitative determination of how readily the RE at the nitrogen-terminated surface can be displaced into the oxygen-bearing intergranular film by Si. From this one notes that Lu prefers oxygen while Gd and La have increasing preference for nitrogen. As such, desorption occur more readily in the order La to Gd to Lu, which yields increasing ease for the attachment of Si to the nitrogen-terminated prismatic plane in that same order. It is the respective increase in interfacial binding energy from Lu to Gd to La that dominates the respective diminishment in the diametrical grain growth and the resultant increase in the anisotropy in grain shape.

3. Thermal Conductivity

There is considerable need for advanced refractory ceram-

Table 1. Survey of General Properties of Ceramics and Silicon

Property	Al_2O_3	BeO	AlN	α-SiC	Self-Reinforced β-Si_3N_4	Si crystal
Theoretical density (g/cc)	3.98	3.01	3.26	3.2	3.25	2.33
Flexure strength (MPa)	350	200	350	420	$\geq$1000	
Fracture toughness (MPa$\sqrt{m}$)	3	4	3	3	6 – 10$^+$	$\leq$1
Young's modulus (GPa)	390	360	330	410	320	165
Thermal conductivity (W/m K)	20	250	70 – 200	40 – 80	70 – 150	130
Thermal expansion coefficient (10^{-6}/°C)	7.5	7.2	4.6	3.7	3.4	4.7
Dielectric constant (@ 1 MHz)	9.5	6.7	8.8	9.7	9.0	12.1
Dissipation factor (10^{-4})	2	2	10		9	
Electrical resistivity (ohms/cm)	>10^{14}	>10^{14}	>10^{14}	up to 100	>10^{14}	

ics with high thermal conductivity to serve as substrates for microelectronic devices (where they must also be electrical insulators) in the rapidly expanding automotive applications and in devices where increasing power levels generate considerable heat. Stresses imposed by vibrations and the service environment will also require substrate materials with increased fracture strength and toughness as compared to high thermal conductivity ceramics such as berylia or aluminum nitride. A similar critical need exists for advanced refractory ceramics for high temperature heat exchange and combustion system components. The focus has been on SiC ceramics for heat exchangers. However as seen in Table 1, these materials (and aluminas currently used as substrates) exhibit modest (at best) strength and low fracture toughness values as compared to the self-reinforced silicon nitride ceramics.[14,15] The high conductivity ceramics typically are subject to time dependent failure that is accelerated with increase in the relative humidity of the environment; these include alumina, BeO, and AlN ceramics. On the other hand, silicon nitride ceramics generally are highly resistant to time-dependent failure due to environmentally assisted slow crack growth. The combination of low thermal expansion (comparable to silicon) and lower elastic modulus with high fracture strength and toughness of the self-reinforced silicon nitrides provides excellent resistance to failure induced by thermal transients and gradients. This will be an important factor when considering the thermal loads that can be generated in both high power devices and high temperature applications, especially those experiencing thermal cycles.

One had typically thought of silicon nitride ceramics as having thermal conductivities comparable to those of alumina ceramics. However, early calculations had indicated that the thermal conductivity of silicon nitrides could be much higher; the crystal structure of β-Si_3N_4 consists of open channels aligned with the [0001] axis. Recent measurements of individual large β-Si_3N_4 grains confirm a high thermal conductivity value (180 W/m K) is achieved in the c-axis direction, and, as expected, this reduces to ~70 W/m K in a direction normal to the c-axis.[24] On the other hand, the solute content (e.g., aluminum content in β'-SiAlON), amorphous phase and porosity levels each must be minimized or eliminated to optimize the conductivity of the ceramics.[25]
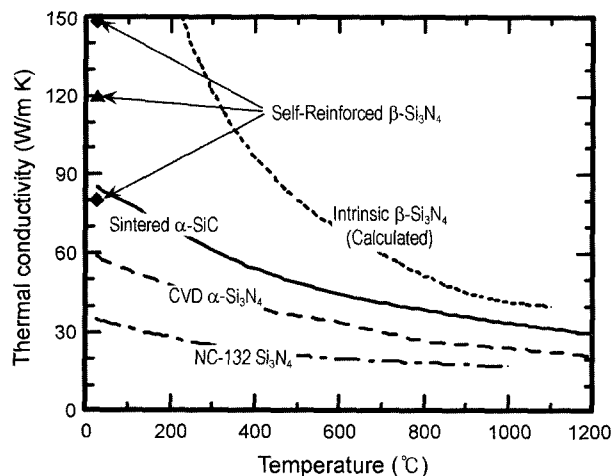

Fig. 2. Recent studies have suggested the potential for developing β-self-reinforced silicon nitride ceramics with high thermal conductivity. The calculation of the intrinsic values for silicon nitride were described in ref. 28.

Expanding upon these guidelines, recent experimental studies have revealed some startling potential for developing high thermal conductivity silicon nitride ceramics, Fig. 2.[26-28] Studies revealed that the thermal conductivity was a function of the volume fraction of large elongated grains in tape cast β-Si_3N_4 where the large elongated grains were oriented by tape casting.[27] The conductivity as a function of content of large elongated grains obtained by the inclusion of beta seeds is illustrated in Fig. 3 together with the cross section microstructure. Subsequent analysis of the degree of preferred orientation in these ceramics clearly shows the increase in alignment of the elongated beta grains with increase in their content, Fig. 4.

Note that the above ceramics[27] were sintered using an addition of alumina plus yttria, which results in the growth of an epitaxial β-SiAlON on individual silicon nitride grains, especially noticeable on larger elongated grains (e.g., ref. 14). Thus, further increases in conductivity would be achieved by eliminating the Al solute. Experiments based on sintering of mixtures of beta and alpha silicon nitride powders to manipulate the microstructure revealed a trend of increasing conductivity with increased grain size.[29] Sub-
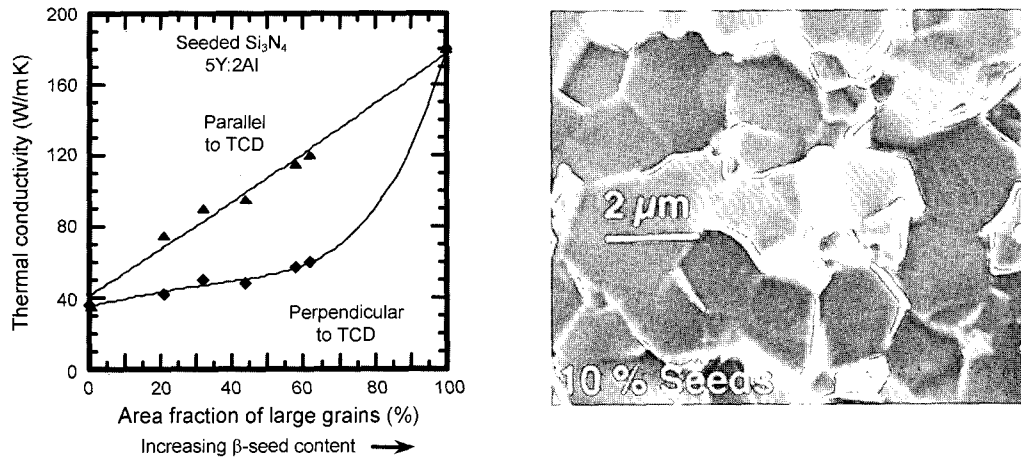
Fig. 3. The thermal conductivity of tape cast silicon nitride ceramics processed with slurries containing elongated β-seeds increases with seed content (a). There is a directional dependence of the conductivity with the highest values obtained for measurements where the heat flow is in the tape casting direction (data from ref. 27). Microscopy observations reveal a degree of alignment of the large elongated grains generated by the β-seeds with a substantial increase in the large grains as the seed content increases. Fracture surface normal to the tape casting direction reveals mainly the cross-sections normal to the length of large elongated grains in the ceramic made with 10% seeds (b).
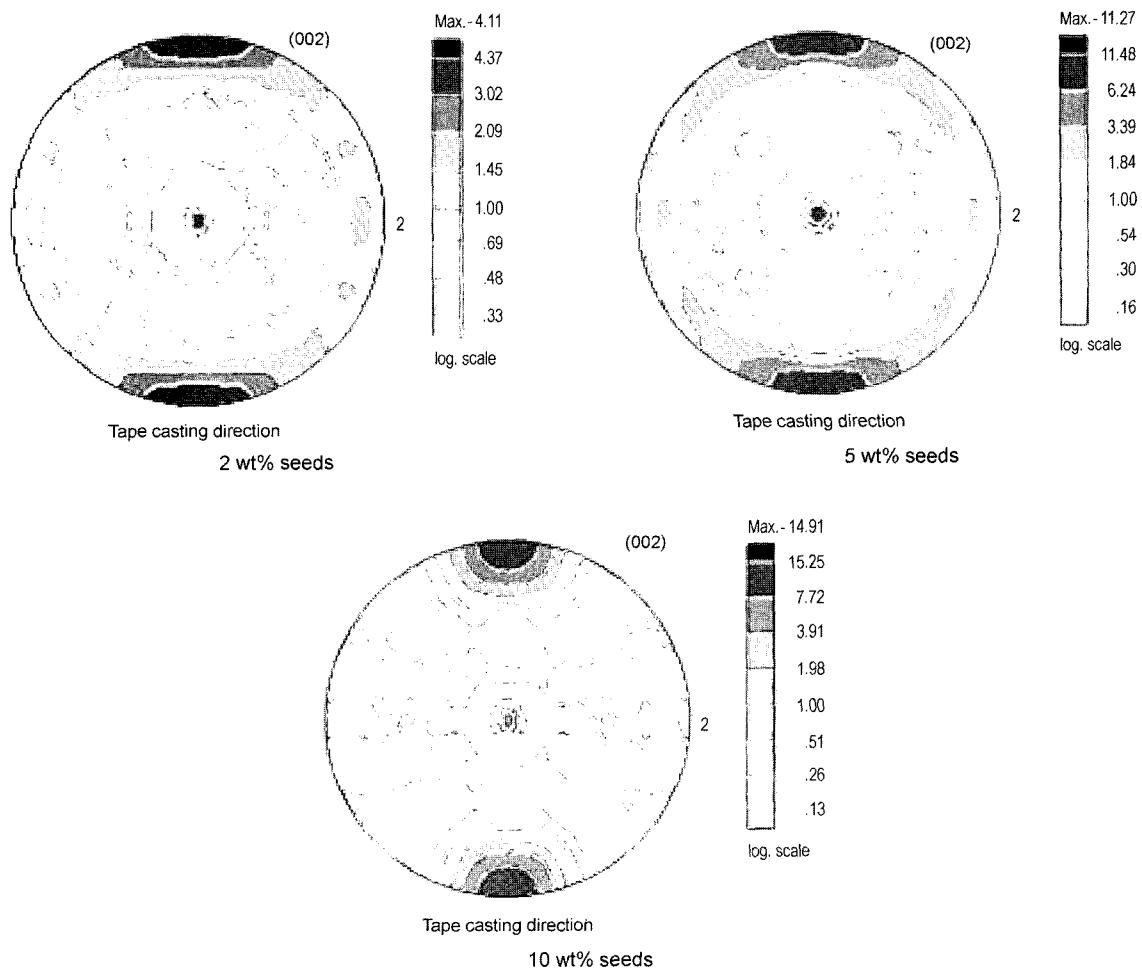

Fig. 4. A substantial increase in the alignment of the c-axis of the β-grains with the tape casting direction is confirmed by pole figure analysis. Increasing the β-seed content results in further increasing the alignment of the c-axis grains in the tape casting direction (the N-S axis of the pole figures) as reflected by increase in <0001> intensities (given in log scale) at the N and S poles.

sequent research indicated that larger rare earth additives affected a similar increase in conductivity, which was again related to increase grain size, but was also accompanied by a decrease in lattice oxygen content.[30] Additional observations confirmed the increase in conductivity with decrease in lattice oxygen in silicon nitride, which is similar to the effect in AlN.[31] It was further pointed out that one might use the crystallization of secondary phases as these typically take up oxygen and deplete the oxygen content of the silicon nitride grains.[31]

Early work had shown that amorphous intergranular phases had deleterious effects on the conductivity (e.g. ref. 25). Indeed amorphous intergranular phases are essentially ubiquitous in silicon nitride ceramics due to the presence of oxygen associated with silicon nitride powders and the additives needed to densify silicon nitride. However, studies have shown that the thermal conductivity and the refractive index of oxides and glasses are closely related. A search of the literature demonstrates that the refractive index of the rare earth oxides is raised as the cation size increases.[32] Similar effects are suggested to occur in oxynitride glasses typically present at Si_3N_4 grain boundaries in preliminary studies.[33] Clearly, significant opportunities exist for developing high conductivity silicon nitride ceramics that will have capability of performing under more severe conditions than possible with the ceramics currently considered for high power electronic devices (e.g., electrical insulating substrates[34]) and heat exchanger components.

4. Fracture Properties

Over the last 30 years, a number of programs in the United States have sought to introduce monolithic ceramic components into gas turbines with the goals of increasing efficiency and lowering emissions. High-performance silicon nitride and silicon carbide ceramics typically have been leading candidates for use in these applications. In spite of their potential, ceramic components for turbine applications have met with limited success. Recent programs at Solar Turbines, Rolls-Royce and Pratt & Whitney UTRC have done much to identify key technological barriers. For example, in early field tests conducted under Solar Turbine's Ceramics for Stationary Gas Turbine Program,[35] silicon nitride first-stage blades failed after 948 h due to impact damage from a metallic locating-pin from the inner combustor liner. A subsequent impact study showed[36] that the low toughness values of the silicon nitride used were a major factor in their limited impact resistance.

This interest in structural applications of silicon nitride ceramics has focused primarily on research aimed at material characterization, design methodology development (life prediction), and machining parameter optimization in order to manufacture dependable complex ceramic components for engine applications. A major lesson learned from this research is that current silicon nitride ceramics do not exhibit the necessary reliability due largely to their limited
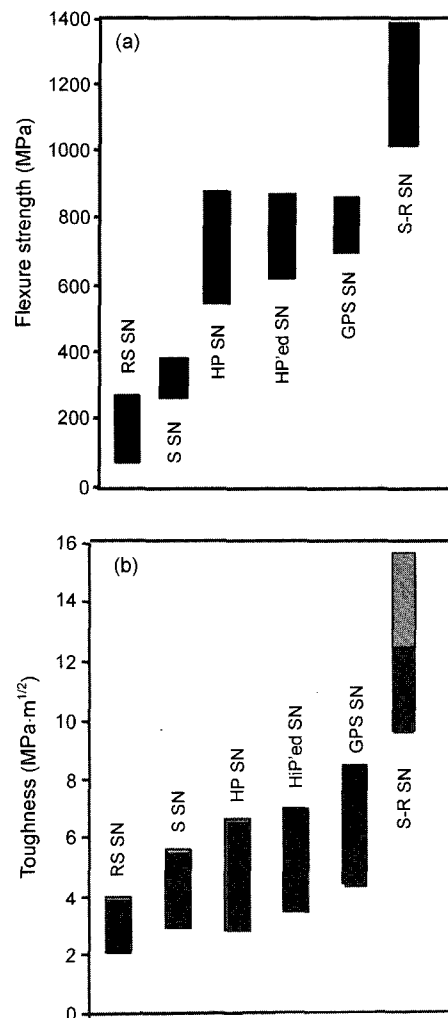
Fig. 5. A progressive improvement in both the fracture strength (a) and toughness (b) values achieved in silicon nitride ceramics fabricated by a variety of processing methods including: reaction sintered Si_3N_4 (RS SN) and sintered Si_3N_4 (S SN), hot pressed Si_3N_4 (HP SN), hot isostatically pressed Si_3N_4 (HIPed SN), gas pressure sintered Si_3N_4 (GPS SN), and self-reinforced β-Si_3N_4 (S-R SN) ceramics.

fracture toughness and to some extent by strength. The progression that has taken place in silicon nitride ceramics with respect to strength and toughness can be seen in Fig. 5(a), which highlights the advances in the recent self-reinforced silicon nitride ceramics.

The recent advances in toughening silicon nitride ceramics are based on the controlled incorporation of elongated microscopic reinforcing grains together with the tailoring of the sintering additive composition.[14,15] The elongated grains serve as the reinforcing elements much like whiskers in whisker-reinforced ceramics[37] or fibers in fiber-reinforced ceramics.[38] Results using these principles show that self-reinforced silicon nitride (S-RSN) ceramics can have high strengths (1 to 1.4 GPa, Fig. 1) combined with high fracture toughness (e.g., over $10\,MP \cdot am^{1/2}$ or at least two to three

times that of commercial materials), Fig. 5(b). However, these findings also reveal that simply the presence of larger elongated grains in silicon nitride is not a sufficient condition for achieving high strength with high toughness. Control of the microstructure and composition are key here as the toughening achieved by crack bridging processes is dependent upon the size and volume fraction of these larger elongated grains and debonding of these reinforcing grains during fracture.

In self-reinforced ceramics, the reinforcements are generated during the sintering of the ceramic, which greatly simplifies the processing and avoids the use of expensive ceramic fibers or whiskers. Such elongated beta-phase grains form in silicon nitride ceramics and larger grains form due to the presence of some beta phase in the alpha phase silicon nitride powders typically used. Unfortunately in this case, it is difficult to obtain the desired fraction of reinforcing grains nor uniform size and spatial distribution of them. Both factors must be satisfied in order to achieve both high toughness and high strength. Control of the size and distribution of reinforcing grains is one of two major factors that has limited the achievement of high toughness, high strength self-reinforced silicon nitride ceramics. Recent studies have shown that this can be overcome by the incorporation of a small fraction of rice-like beta seeds into the silicon nitride powder. The "beta-rice" seeds used to date are typically 3 to 4 μm long by ~1 μm in diameter; however, the optimum size and shape of such seeds have not been determined as yet. These "beta-rice seeds" serve as the nuclei for generating well dispersed elongated reinforcing grains with controlled size(s).[14,39] Recent studies suggest that toughening by self-reinforcing grains can be also developed in α-SiAlON ceramics using a similar seeding approach.[40]

Both the growth of the reinforcing grains during sintering and their subsequent ability to act as reinforcements are controlled by the additives, which impact the composition of intergranular material typical found in silicon nitride ceramics as noted earlier. These intergranular films (typically <2 nm thick) are a result of the reaction between the native oxygen in silicon nitride powders and the specific chemical additives used to promote sintering. This reaction results in the formation of a viscous glass that allows liquid phase sintering to occur and acts as a media for the growth of the elongated reinforced beta grains. In addition, the resultant Intergranular Films (IGFs) effect the debonding of the reinforcing grains from the matrix material in the crack tip region. This debonding process prevents the crack from cutting through the reinforcing grains and allows them to bridge across the crack. This is similar to what occurs in fiber-reinforced ceramics. Recent studies are revealing that the composition of the sintering additives and, hence, the IGF can be tailored to optimize the toughening effects of the elongated reinforcing grains in silicon nitride ceramics. These studies revealed that the fracture toughness of SRSN ceramics with ~7 wt% additives of yttria plus alumina could be raised by ~50% simply by substituting more yttria in

place of the alumina.[24] The tailoring of the additive composition plus the microstructure are now recognized as the critical factors in obtaining both high fracture toughness and high fracture strength.

5. Summary

Microstructure tailoring of silicon nitride ceramics offers new approaches to improve their properties. The formation of larger elongated grains can be promoted by seeding the starting powders (e.g., larger beta particles in the case of Si_3N_4 that are typically alpha phase) and by careful selection of the densification additives. The judicious selection of additives cannot be overlooked as it allows one to tailor the grain aspect ratios, and the thermal conductivity and fracture properties. Combined theoretical and unique microscopy studies are finally providing fundamental under- standing of the role of additive elements in the anisotropic grain growth process. Because of the high thermal conductivity along the c-axis, one can now combine seeding processes and selective additives to enhance silicon nitrides thermal conductivity, which to date have reached ~150 W/m K in some instances. While the conductivity is not isotropic, much can yet be done to improve these levels as witnessed by studies addressing the effects of lattice oxygen level and tailoring the composition of the secondary phases and intergranular films.

Finally, the generation of large elongated grains in a fine grained matrix through selection of rare earth sintering additives and seeding techniques have lead to high fracture toughness combined with high fracture strengths. We have seen some evidence of the effects that additives can have on the process of debonding these reinforcing grains to allow them to bridge cracks and toughen the ceramic. However, we have yet to explore the role of additives in promoting (or inhibiting) the reinforcing mechanisms in significant detail, which is the next challenge in advancing the design of the next generation of silicon nitride-based ceramics.

Acknowledgements

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