

# Macro- to Atomic-Scale Tailoring of Si<sub>3</sub>N<sub>4</sub> Ceramics to Enhance Properties

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Keywords: Silicon nitride ceramics, microstructure, composition, fracture toughness, creep resistance, intergranular films, elongated grains

## Abstract

Silicon nitride ceramics are finding uses in numerous engineering applications because of their tendency to form whisker-like microstructures that can overcome the inherent brittle nature of ceramics. Studies now establish the underlying microscopic and atomic-scale principles for engineering a tough, strong ceramic. The theoretical predictions are confirmed by macroscopic observations and atomic level characterization of preferential segregation at the interfaces between the grains and the continuous nanometer thick amorphous intergranular film (IGF). Two interrelated factors must be controlled for this to occur including the generation of the elongated reinforcing grains during sintering and debonding of the interfaces between the reinforcing grains and the matrix. The reinforcing grains can be controlled by (1) seeding with beta particles and (2) the chemistry of the additives, which also can influence the interfacial debonding conditions.

In addition to modifying the morphology of the reinforcing grains, it now appears that the combination of preferential segregation and strong bonding of the additives (e.g., the rare earths, RE) to the prism planes can also result in sufficiently weakens the bond of the interface with the IGF to promote debonding. Thus *atomic-scale engineering* may allow us to gain further enhancements in fracture properties. This new knowledge will enable true atomic-level engineering to be joined with micro-scale tailoring to develop the advanced ceramics that will be required for more efficient engines, new electronic device architectures and composites.

## Background

The expanded applications of silicon nitride, as well as silicon carbide and Continuous Fiber Ceramic Composites (CFCCs), are basically limited by either low fracture toughness or low fracture strength. Gas turbine engine field tests showed that silicon nitride failures were most likely due to impact damage [1] where separate impact tests [2,3] revealed that low toughness values were a major factor. While CFCC composites

exhibit “graceful” rather than catastrophic failure, their fracture strengths are quite low (e.g., 150 MPa) and limit their use to low stress components (e.g., combustor liners, transition pieces and shrouds). On the other hand, silicon nitride ceramics are used in some very demanding commercial applications, such as high performance bearings, turbocharged rotors, fuel igniters and machine tool inserts. Furthermore, silicon nitride ceramics have also been successfully demonstrated as (1) hot section components for auxiliary power units produced by AlliedSignal for aircraft and industrial auxiliary turbo-power units and various components for aircraft turbine engines [4] and (2) valves in selected automotive diesel engines by Daimler-Benz [5].

Until the late 1960’s to early 1970’s, advanced structural ceramics were more or less a curiosity for such demanding applications. Two major advances have given rise to the evolution of modern engineering ceramics. The first of these involves the technological advances in our ability to fabricate complex components. The second centers on our understanding of the approaches to improve their mechanical behavior, which is now resulting in much tougher and more creep resistant ceramics. Depending on the application, the manner in which microstructure and composition influence performance and reliability for the specific end use have to be considered. Like the tailoring of steels, there is no one set of microstructural and compositional parameters that fits all applications despite the factor that the generic chemical name is often taken to represent the properties of all members of that chemical family (e.g., as with steels, not all aluminas are the same). Here we only consider some of those factors that can influence the fracture and creep responses of silicon nitride-based ceramics.

### **Toughening Response**

Earlier results have shown that tailoring the microstructure to produce well-dispersed large elongated grains within a fine grained matrix yields silicon nitride ceramics with both high fracture strengths (1 to 1.4 GPa) and high fracture toughness (up to 11 MPa $\sqrt{m}$ ) [6]. Such micro-reinforcing grains induce toughening by crack deflection and bridging processes similar to those in whisker-reinforced ceramics [7,8]. However, these findings also reveal that introducing elongated grains into silicon nitride is not sufficient; one must control their dispersion and volume content, as is the case of whisker-reinforced ceramics. Recent studies have shown that such control can be achieved by the incorporation of a small fraction of rice-shaped beta seeds, which act to form the larger reinforcing grain, into the silicon nitride powder [4,9]. Similar toughening effects via the seeding method have also be achieved in  $\alpha'$ -SiAlON ceramics [10].

In the case of the silicon nitride ceramics, it is also clear that control of the reinforcing grains is only one component to improving the mechanical behavior. In order for the large elongated grains to serve as active reinforcements, they must at least partially separate from the matrix to avoid being fractured by the advancing crack. Only then can they bridge the crack to substantially toughen the ceramic; similar debonding processes must also occur in whisker- and fiber-reinforced ceramics. Known as debonding, the process can be influenced by the character of the amorphous, < 2 nanometer thick intergranular film (IGF) that typically surrounds each grain in silicon nitride ceramics. The amorphous IGF forms as a result of the reaction between the sintering additives

(often oxides) and the native oxide present in the silicon nitride powders. During sintering this amorphous material serves to enhance densification via a liquid phase and also serves as the media for grain growth. During fracture, these amorphous IGFs can also influence the debonding of the reinforcing grains [11]. Using a fixed total amount of yttria plus alumina additives, Si-Y-Al oxynitride-based IGFs form and the toughness is found to rise as the yttria to alumina ratio in the additives increases [12]. In-situ high-resolution electron microscopy observations of debonding reveal a transition in the debond path from the interface to a mixture of interface debonding and crack advance in the IGF as the yttria to alumina ratio increases [13]. Atomic cluster calculations and experimental observations reveal that the debonding of the reinforcing grains can be enhanced both by modifying the SiAlON epitaxial surface layer compositions and a weakening of the amorphous intergranular film by replacing Al and Si by Y [13,14].

Understanding the effects of additives in multi-component materials at the atomic level has gained increasing importance in the search for improved control over macroscopic properties. In order to enhance the fracture toughness, elongated grains with high aspect ratios are desired as they act much like whiskers and fibers to reinforce the matrix. In fact, the  $\text{Si}_3\text{N}_4$  grain morphology is very sensitive to the particular additive used, especially in the case of the oxides of the rare earths (RE) and Group III elements [15]. This is reflected in a significant change in the aspect ratio of the elongated grains with different RE and Group III elements. The major factor appears to be the effect on the diametrical growth rate, Figure 1. The prism planes are extremely smooth and growth is seen to be reaction rate limited, likely by processes that hinder silicon (Si) attachment to the prism surface.

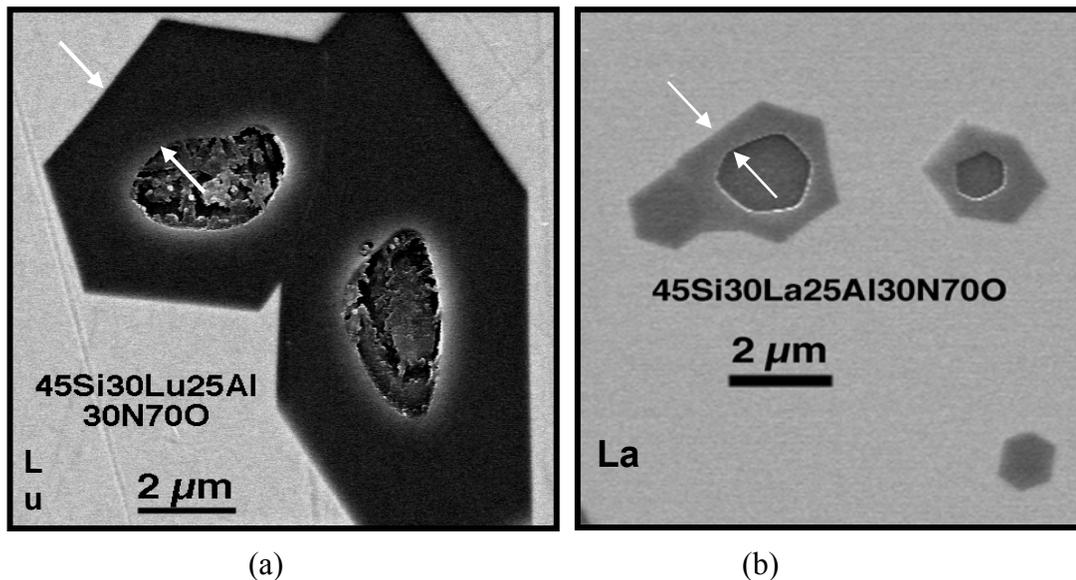


Figure 1. In the presence of lutecium (a), the diametrical growth of the silicon nitride grain is faster than when lanthanum (b) is present, resulting in low aspect ratio grains.

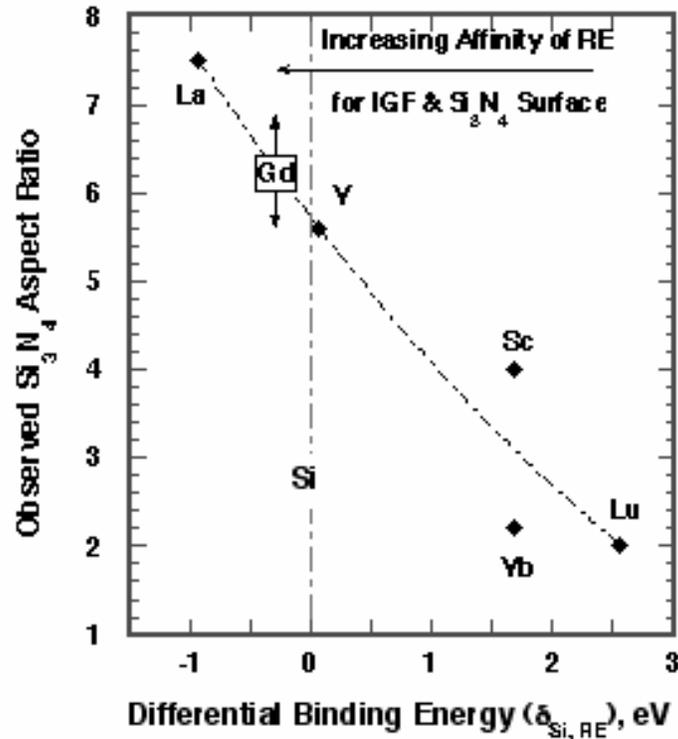


Figure 2. Theoretical calculations reveal this is a result of the greater affinity of lanthanum for the silicon nitride grain surfaces compared to silicon in an O-N chemical gradient.

Through a combination of theory and advanced microscopy, significant advances are being made towards our understanding of microstructural evolution with regard to the segregation and bonding of additive atoms to the grain surfaces. A first-principles model, the *differential binding energy* ( $\delta_{RE,Si}$ ), has been developed that characterizes the competition between RE and Si for migrating to the  $\beta$ - $Si_3N_4$  grain surface [16]. The first-principles cluster calculations derive the difference in the energy of the rare earth association with oxygen versus nitrogen, and these result is compared with a similar difference for silicon. In this regard, the preference of the rare earth for oxygen-rich versus nitrogen-rich environments is referenced against that of silicon. Thus the less positive the  $\delta_{RE,Si}$  value of the RE, the more likely it will attempt to migrate to the nitrogen-rich IGF and the surface of the silicon nitride grains. Many of these same elements bond very strongly to a nitrogen-terminated surface, which appears to be the case for nitrogen-terminated prism plane. As a result, the diametrical growth is impeded more strongly the greater the tendency for the RE/Group III element to migrate to the grain surface. As seen in Figure 2, lanthanum (La) is predicted have the strongest preferential segregation to the grain surfaces and thus leads to the formation of the highest aspect ratio grains by impeding the attachment of silicon. The preferential

migration of such rare earths as La is confirmed by unique atomic-resolution images that clearly show the segregation and the attachment of *individual* dopant atoms at specific grain surfaces [17]. Further explicit calculations of RE adsorption energies show that La attaches to more sites on the prism plane than does lutecium (Lu). Combined with the greater preference of La for residing at the silicon nitride grain surfaces, these can be taken as mechanisms for limiting diametrical grain growth resulting in high aspect ratio grains when La is one of the components of the sintering additives. The potential importance of this in the tailoring of the properties of silicon nitride ceramics is suggested by Satet's studies, which indicate an increase in toughness when Lu is replaced by La in the sintering additive [18].

### Elevated Temperature Response

In the case of silicon nitride ceramics, the creep and deformation behavior at elevated temperatures is often dominated by the response of the intergranular phase(s). Plastic deformation by dislocation motion is rare under these conditions in silicon nitride although dissolution and reprecipitation of the nitride grains can contribute to creep. On the other hand, the introduction of the elongated reinforcing grains can serve to inhibit the creep of silicon nitrides, much like SiC whiskers inhibit creep in aluminas [19]. Indeed, the creep resistance is found to increase as the fraction of reinforcing grains in the silicon nitride increases, Figure 3. The elongated grains are difficult to rotate and effectively form a disconnected rigid network. With increase in creep strain, one observes an increasing number of these elongated grains that either contain cracks or are fractured.

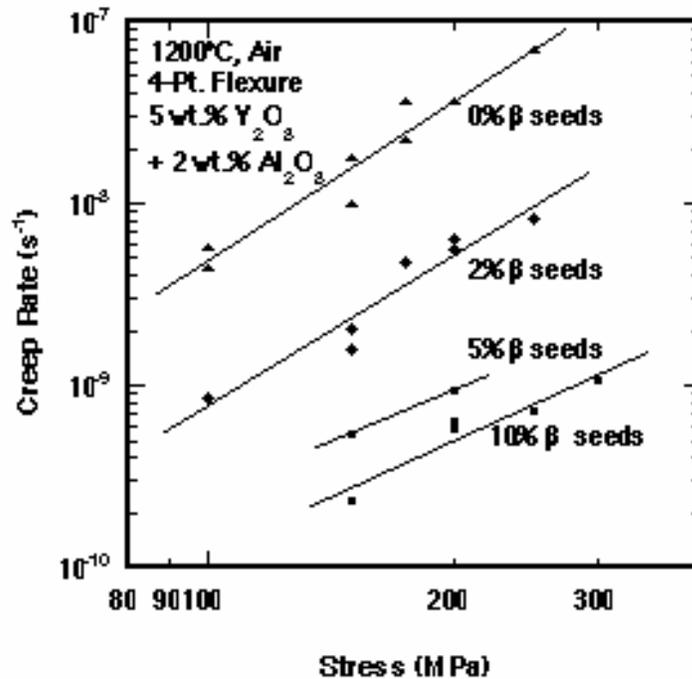


Figure 3. Greater creep resistance is achieved in a self-reinforced silicon nitride by increasing the fraction of large elongated grains by use of seeding.

Creep observations on a variety of silicon nitride ceramics have shown that their creep resistance is sensitive to the additives employed and that viscous flow of the intergranular phase is a primary contributor to the creep strain along with related cavitation processes [20,21]. This is noted in the increased creep resistance of silicon nitrides with the same self-reinforced microstructures and total additive content brought about by increasing the yttria to alumina ratio in the additives, Figure 4. In light of this, the effect of additives on the viscosity of the resultant amorphous intergranular phases becomes a critical factor. Studies reveal that the viscosity of oxynitride glasses increases substantially as the nitrogen content increases along with the use of smaller rare earth elements and cations that are stronger network formers ([22,23]. In the case of Si-Y-Al oxynitride glasses, raising the Y to Al ratio results in glasses with higher viscosities [22], which would account for the increase in the creep resistance of the ceramic associated with increase in yttria to alumina ratio in the densification additives, Figure 4.

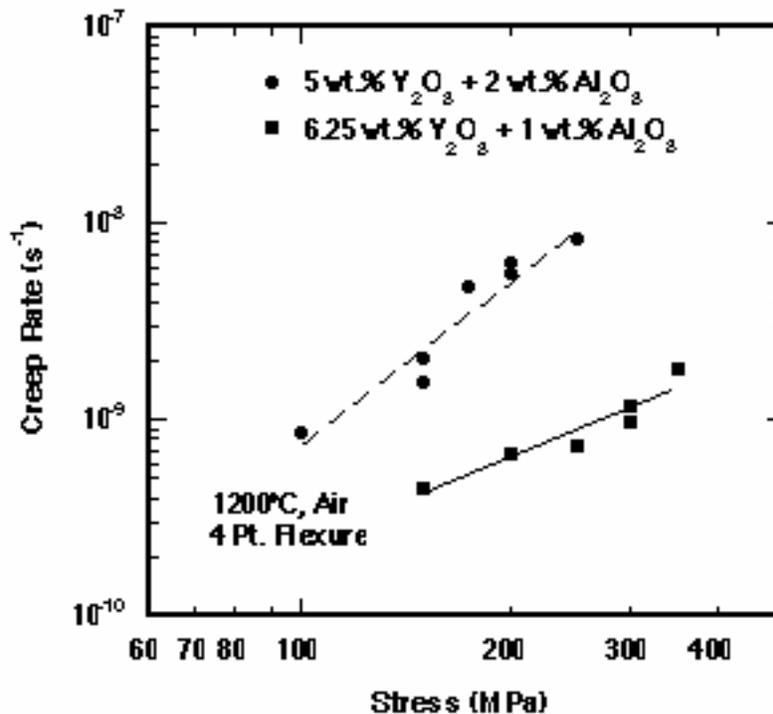


Figure 4. Partial replacement of alumina by yttria in the sintering additives improves the creep resistance of the self-reinforced silicon nitride ceramics fabricated by seeding.

A brick wall model is a convenient approach to characterize the creep of non-deformable Si<sub>3</sub>N<sub>4</sub> grains surrounded by a viscous intergranular film [24]. From this analysis and accounting for the decrease in the film thickness with decrease in rare earth size [25], projects that the effective creep resistance of the ceramic can be increased by several (~ 6) orders of magnitude by (1) increasing the nitrogen content, (2) using stronger

network forming cations, and (3) utilizing additions of smaller rare earths [22]. This would partially explain the exceptional creep resistance of commercial silicon nitrides containing a lutetium-bearing additive. However, an additional factor needs to be considered—the predicted low affinity of lutetium for the region of the IGF and grain surfaces. This implies that lutetium prefers to concentrate within the triple points and larger amorphous pockets in the microstructure. Indeed, it is noted that crystalline lutetium silicates form in these regions, which ought to leave the intergranular films between grains relatively depleted in oxygen and lutetium but richer in nitrogen and silicon. If this occurs, the IGF viscosity would be further increased as would the creep resistance of the ceramic.

### **Summary**

The design of toughened silicon nitride ceramics utilizes the mechanics approaches developed for whisker- (and fiber-) reinforcement wherein the formation of dispersed larger elongated grains serves as micro-reinforcements. In such self-reinforced systems it is essential that the reinforcements be well dispersed and their aspect ratios controlled. The use of seeding approaches has proven to be very effective in controlling both the dispersion and the fraction of reinforcing grains. Recent results show that the aspect ratio can be modified by the choice of densification additives where certain rare earth and Group III elements are more effective in promoting the growth of desirable high aspect ratio reinforcing grains. Theoretical studies reveal this is due to a combination of greater affinity of the sintering cation to migrate to the region adjacent to the silicon nitride grains and the degree of its bonding to the nitrogen-terminated prism planes of these grains. As a result diametrical grain growth is impeded and elongated grains, which are desired to toughen the ceramic, are formed.

The presence of larger elongated reinforcing grains in a fine-grained matrix is a necessary but not sufficient condition to achieve high fracture toughness in silicon nitride ceramics. The reinforcements must also separate or debond or else a crack will propagate through them eliminating any crack bridging effects. This debonding process appears to be significantly dependent upon the composition of the intergranular films, and hence the densification additives. Not only is the strength of the interface influenced by the composition of the additives, but also is the fracture resistance of the amorphous intergranular material. Both effects are significant as debonding of the reinforcing grains can occur by either interface fracture or fracture within the intergranular film. Thus, the densification additives play a role in both the formation of elongated reinforcing grains and the ease with which they debond from the matrix and toughen the ceramic.

For elevated temperature applications, both the microstructure and the choice of densification additives can also have a marked effect on the creep resistance of silicon nitride ceramics. Increasing the fraction of elongated grains can raise the creep resistance; however, additives that increase the viscosity of the resultant intergranular films also have a substantial impact on creep resistance of the ceramic. The use of small rare earth cations, increasing nitrogen levels and cations that are strong network formers are found to be beneficial to improving the creep resistance.

## Acknowledgements

The authors gratefully acknowledge Drs. S. J. Pennycook and R. L. Satet and Prof. M. J. Hoffmann for the technical contributions. The research was sponsored by the Division of Materials Sciences and Engineering, U. S. Department of Energy, under Contract No. DE-AC05-00OR22725 with UT-Battelle. Dr. Shibata is supported through a Japanese Society for the Promotion of Science Fellowship.

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