The Effects of Intergranular Films on the Mechanical Behavior of Self-Reinforced Ceramics

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Abstract
Self-reinforced silicon nitride ceramics exhibiting high toughness and strength are obtained by tailoring the size and number of the bridging grains. In each material, bridging mechanisms rely on debonding of the reinforcing grains from the matrix to increase toughness. Interfacial debonding can be influenced by the nature of the intergranular films, whose composition and properties are a function of the sintering aids. In silicon nitride ceramics that use alumina as one of the sintering aids, the amorphous intergranular films surround β-Si_3N_4 grains on which epitaxial β-SiAlON layers form. In this case, interfacial debonding is dependent on the composition of the SiAlON layer, becoming more difficult as the Al (and O) content of the SiAlON increases. This appears to be a result of the formation of strong Si-O, Si-N and Al-O bonds across the glass-crystalline interface. Observations by others also reveal that the interfacial debonding conditions required in the toughening process can be altered in the presence of amorphous Si-O-N intergranular films and in "special" grain boundaries.

In addition to its influence on fracture, the amorphous intergranular films containing Si, Al, O, N and RE (i.e., rare earth elements) will also influence the temperature dependent viscosity of the amorphous phase. Measurements of softening temperature (T_g) reveal that T_g decreases with increase in oxygen to nitrogen ratio and with the substitution of larger rare earth ions in the film. These reductions in the T_g of the amorphous intergranular films lower the creep resistance of the ceramic and limit its life at elevated temperatures. It is apparent that sintering additives used to promote the densification of self-reinforced ceramics can play an important role in improving their fracture and creep resistances. However, greater understanding at the basic level is needed for further insight into how their chemistry controls the structure/bonding and properties of the amorphous films and interfaces in self-reinforced polycrystalline ceramics.

Background

Additives to promote densification are commonly employed to produce monolithic ceramic components. In a number of cases, these additives result in the formation of amorphous intergranular films; a feature that is further promoted when lower purity raw materials are used to reduce costs. These intergranular films can degrade the mechanical behavior of ceramics both at room and elevated temperatures. Thus, considerable effort has been made to produce ceramics where such films are eliminated by use of more sophisticated processing and/or high purity raw materials, adding to cost. In addition, one can modify the additives in an attempt to crystallize the amorphous films after densifying the body. Typically, the material in triple points can be crystallized, however crystallizing that between grain faces is far more difficult, often impossible, to achieve. As an alternative, one should consider whether or not the properties of these amorphous intergranular films can be tailored to actually enhance both the fracture and creep resistances of the ceramics and, if so, to understand how the film composition can be used to achieve this.

Such issues abound in silicon nitride ceramics where sintering additives are required to promote densification and also influence the development of a self-reinforced microstructure wherein elongated grains can serve to toughen the ceramic. Densification proceeds in the presence of an oxynitride glass that serves as a liquid sintering agent in which growth of the elongated grains also occurs. The result is a microstructure of larger elongated grains in an often finer grained matrix, where all grains are surrounded by the amorphous intergranular film when the energy of the unwetted "special" boundary is greater than the sum of the energies of the two interfaces formed when the boundary is wetted. As summarized by Ernst et al., the film thickness between two grains can reach an equilibrium thickness which is a function of the specific constituents of the film in silicon nitride ceramics.[1,2] However as these authors point out, this film thickness does not appear to depend on the amount of a specific composition amorphous phase. A numerous observations are reported which demonstrate that silicon nitrides contain continuous amorphous intergranular films.

The growth of elongated grains in silicon nitride ceramics provides a means to increase the fracture toughness, as observed by a number of researchers. The toughening mechanism involves the formation of elongated grains that bridge the crack in the region behind the crack tip, which imposes a closure stress on the crack. Bridging grains can be partially debonded but still intact close to the crack tip and, then with continued advance of the crack tip, pull out of the matrix on one side of the crack plane. Both types resist opening of the crack and dissipate strain energy by frictional processes such that the toughening contribution can be enhanced by the presence of larger diameter elongated grains.[3,4] A distinctly bimodal microstructure consisting of larger (1-2 μm diameter) elongated grains dispersed in a matrix with a submicron grain size was one approach to achieve both high strength and toughness, Table I. Additional studies indicate that similar toughening could be obtained by introducing a strong degree of alignment of the reinforcing grains where the matrix and reinforcing grain sizes were similar.[5]

Table I. Effect of Microstructure on the Mechanical Properties of Silicon Nitride Containing 6.25 wt. % Y_2O_3 plus 1 wt. % Al_2O_3.[4]

Material Description	Average Grain Diameter	Fracture Toughness MPa√m	Fracture Strength MPa
Large elongated grains in fine grain matrix	0.3 µm / 2 µm Distinctly Bimodal	10.6	1144 ± 126
Medium sized reinforcing grains and matrix grains	~ 1 µm Broad Monomodal	6.3	850 ± 75
Small elongated grains in fine grained matrix	~0.2 µm / ~0.5 µm Distinctly Bimodal	4.4	925 ± 75
Fine equiaxed grains	~0.4 µm Monomodal	3.5	165

However, the process of forming bridging grains requires that the crack tip be diverted around a potential bridging grain rather than cutting through it. This can be accomplished if the crack tip is deflected when it reaches the interface between the intergranular film and the elongated grain and the grain separates from the film (i.e., debonds).[6] Earlier evidence indicated that the composition of this intergranular phase may be a factor in the interfacial debonding/toughness process where it was found that transgranular fracture and low toughness were associated with an amorphous SiO_xN_y intergranular film.[7] Additional analytical studies have indicated that interface strength can be weakened when larger lanthanide ions are present in the intergranular films.[8] These observations and the fact that a variety of sintering aids have been used to develop toughened silicon nitrides with mixed results stimulated studies of the effects the intergranular film composition could have on the interfacial properties and the mechanical behavior of self-reinforced ceramics.

Results and Discussion

Interfacial Debonding Associated with Intergranular Films

The influence of the intergranular film composition on interfacial debonding has been examined using β-Si_3N_4 whiskers embedded in oxynitride glasses. This allows one to control the glass composition and alter the radial compressive thermal expansion mismatch stresses imposed on the interfaces to assess its role on debonding. The experimental technique involves the generation of a crack in the glass by indentation that intercepts the prism plane of the whisker.[9] The angle between the crack and prism planes can be varied allowing one to characterize the energy required to debond the interface. Basically, the minimum angle at which the crack tip begins to deflect up along the interface will increase as the interface becomes weaker. This minimum angle is known as the critical angle for debonding and large critical angle values are sought to promote interface debonding in the ceramics. As seen in Table II, the largest critical debond angles are associated with the absence of the formation of an epitaxial β-SiAlON layer on

the β-Si_3N_4 whiskers. In glasses containing aluminum, this occurs when the nitrogen content of the glass is low, but can also be retarded by significantly lowering the aluminum content of the glass. By decreasing the aluminum content, the viscosity of the glass increases, which lowers the rate of SiAlON formation. The current results also indicate that residual stresses acting on the interface have a more limited effect as compared to that due to the formation of the epitaxial SiAlON layer. One then wonders if the amount of aluminum could not be lowered sufficiently to promote debonding while still having a sufficient amount to effectively promote densification.

Thus, three silicon nitrides with the same bimodal microstructures were prepared using different ratios of the yttria and alumina sintering aids to selectively reduce the alumina content of the epitaxial SiAlON layers.[11] Quantitative analysis confirmed that the same microstructural characteristics were maintained in each composition: average diameter of matrix grain 0.3 µm, average diameter of reinforcing grains - 2 µm, distribution of grain diameters maintained, and area fraction of intergranular glass phase same - ~ 0.04. As shown in Table III, the aluminum (and oxygen) content of the epitaxial SiAlON layers on the β-Si_3N_4 grains does decrease as yttria was substituted for alumina in the sintering aids. This is accompanied by an increase in critical debond angle and, more importantly, by an increase in the toughness for the same reinforcing microstructural characteristics. One can, then, by tailoring the sintering aids, enhance the interfacial debonding required to cause crack deflection and the formation of bridging grains, which are critical to the toughening process.

Table II. Debonding Conditions for β-Si_3N_4 Whiskers Embedded in Oxynitride Glass [9,10]

Sample	Compressive Stress on Interface, MPa [a]	z-Value of Epitaxial Beta $Si_{6-z}Al_zO_zN_{8-z}$ Layer	Critical Debond Angle, Degrees
Glass Composition, Eq. %			
55Si25Al20Y10N90O	~ 350	0	~ 70
55Si10Al35Y10N90O	~ 515	0	~ 70
57Si43La20N80O	~ 590	0	~ 68
55Si10Al35Y20N80O	~ 530	0	~ 72
55Si10Al35Y20N80O After annealing	~ 530	0.15	~ 50
55Si25Al20Y20N80O	~ 320	1.0	~ 55
41Si30Al29Yb23N77O	~ 455	1.6 – 2.0	~ 55
46Si27Al27La27N73O	~ 555	1.6 – 2.0	~ 50

[a] Calculated stress based on measured values of thermal expansion coefficients, softening temperatures, and Young's modulus of the glasses and silicon nitride (e.g., ref. 9,10).

Table III. Characteristics of Self-Reinforced β-Si_3N_4 with an Amorphous Intergranular Film.[11]

Sintering Additive Composition, wt. %	z-Value of Epitaxial Beta $Si_{6-z}Al_zO_zN_{8-z}$ Layer	Critical Debond Angle, Degrees	Areal Fraction Glass, %	Areal Fraction Large Grains, %	Steady-State Fracture Toughness, MPa√m
$6.25Y_2O_3+1Al_2O_3$	0.01	~ 75	4.7	32	10.5 - 11.0
$5Y_2O_3+2Al_2O_3$	0.03	~ 70	3.4	29	8.5 - 9.0
$4Y_2O_3+2.8Al_2O_3$	0.06	~ 60	3.7	29	7 - 7.5

Recent first principles cluster calculations have addressed the strength of the interface between the amorphous intergranular film and the grains by characterizing the strength within and between Si- and Al-based tetrahedral clusters centered along the interface.[12,13] Such tetrahedral clusters are common to both the crystalline and amorphous phases. The calculation reveal that the binding energies of the SiN_4 tetrahedra increase as oxygen replaces the nitrogen with SiO_4 exhibiting very high binding energies. In the case of the formation of $Si_{6-z}Al_zO_zN_{8-z}$, where Al replaces some of Si, the binding energies of the Al-based tetrahedra exhibit the same increase with oxygen substitution for nitrogen. In fact, the AlO_4 tetrahedron has only slightly lower binding energy than does the SiO_4 tetrahedra. The combination of Si- and Al-based tetrahedra on either side of the interface will cause the SiAlON-glass interface to be stronger than a Si_3N_4-glass interface. In the presence of an epitaxial layer, the calculations reveal that the interface strength will also increase with the Al and O content of the SiAlON layer, consistent with the observations in Tables I and II.

Viscous flow of amorphous intergranular phase

The dilatometric softening temperature(T_g) of SiREAl oxynitride glasses decreases significantly when nitrogen in the glass network is replaced by oxygen. This occurs due to loss of strength of network bonding as three-fold coordination of nitrogen is replaced by the two-fold coordination of oxygen. This would result in shifting the viscosity-temperature curve of the intergranular oxynitride glass phase to lower temperatures as nitrogen is replaced by oxygen. This is reflected in the lowering of the temperature to reach a specific viscosity (the softening point) as the nitrogen content of the glass decreases, Figure 1. While the viscosity of an amorphous film under the constraint of neighboring rigid grains may well be higher than a bulk glass of the same composition, the *trends* in viscosity with compositional changes will be quite similar.

One can sense that in oxidizing environments the glass phase and hence the ceramic can exhibit creep rates that increase with time due to an increase in the oxygen content of the intergranular glass phase. In fact, it is possible with some intergranular glass compositions for the viscosity to be diminished sufficiently in this manner for creep to occur at temperatures below 1000°C. This effect would be localized to the sample region and expand into the interior as oxygen was able to diffuse inward along the intergranular glass phase. As the viscosity of the glass decreases, the diffusion rates at a given temperature within the glass will also increase, raising the rate of oxygen penetration. After creep testing at 1370°C, observations reveal the development of a surface/subsurface layer where the intergranular phase is enriched in oxygen and the promotion of

intergranular cavitation within this region consistent with a lowering of the amorphous phase viscosity.[14] Additional support for losses in the glass viscosity in silicon nitride ceramics due to oxygen enrichment are indicated failure that originate in the surface/sub-surface region due to viscous flow of the glass phase observed as ligaments in the fracture origin region after tensile testing in air at temperatures as low as 850°C .[15]

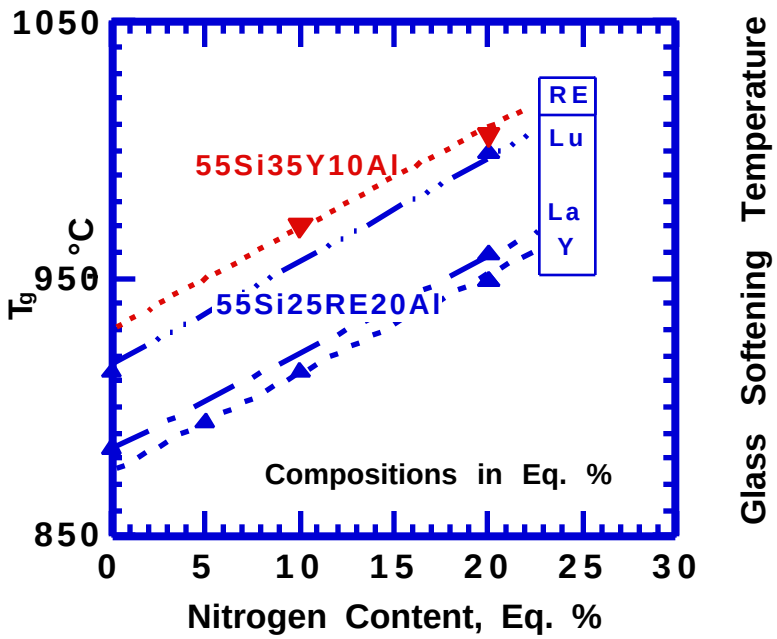

Figure 1. The softening temperatures of SiREAl oxynitride glasses increase as oxygen is replaced by nitrogen, as aluminum is replaced by yttrium, and as the yttrium is replaced by smaller sized lanthanide series ions.

These processes can, then, markedly influence the lifetime of ceramics. However, the viscosity (as well as other properties) of intergranular amorphous phases can be controlled by the judicious selection of the sintering additives (e.g., rare earth oxides, aluminum oxide, etc.). For example, substituting yttrium for aluminum in the glass phase substantially increases the softening temperature over the range of nitrogen contents, Figure 1. As one recalls from the debonding and toughening results, substitution of yttrium for aluminum in the intergranular glass produced a substantial increase in the fracture resistance of the self-reinforced silicon nitrides. Thus, procedures are available to significantly improve the fracture and creep resistance of silicon nitride by tailoring compositions. Finally, in glasses with fixed cation ratios, replacing yttrium by rare earth ions in the lanthanide series raises the glass softening temperature, especially with the substitution of smaller ions such as lutetium, Figure 1. If a trend similar to that seen with yttrium follows, substitution of lutetium for aluminum should raise the softening point further. Thus, careful selection of rare earth additives in combination with Si:Al ratios offers the potential for further improvements in creep resistance in sinterable self-reinforced silicon nitride ceramics.

Concluding Thoughts

It is clear that intergranular films can influence the toughening response and the creep resistance of self-reinforced silicon nitrides. To promote densification, additives such as alumina and yttria are employed, resulting in a fluid amorphous phase that promotes sintering processes and grain growth. The presence of aluminum (and oxygen from the silicon nitride powder) results in the formation of an epitaxial SiAlON layer on the silicon nitride grains. The initial studies revealed that the presence of an epitaxial SiAlON layer was detrimental to the interfacial debonding process, which is required to obtain toughening by crack deflection and grain bridging. However, interfacial debonding is promoted when the aluminum (and oxygen) content of the SiAlON layer is diminished. Thus, one can make compromises between enhancing the densification and increasing the toughening effects by tailoring the Al:Rare Earth ratio in the additives.

The intergranular glass properties are also a function of the densification additive composition. The glass softening temperature (hence viscosity) can be increased by raising its nitrogen content, substituting smaller lanthanide series ions for yttrium, increasing the silicon level, or by increasing the RE: Al ratio. By raising the glass softening temperature, one increase the viscosity at maximum use temperature. This has two effects. First, the rates of diffusion of species into and out of the ceramic will be lowered as the viscosity increases. This will limit the penetration of any reaction zones due to environmental effects. Second, limiting flow of the intergranular glass phase will increase the creep resistance of the ceramics, which is obviously desirable for elevated temperature applications. The results suggest that by understanding the influence of additive chemistry one can tailor self-reinforced ceramics with both high strength and toughness at room temperature and creep resistance and prolonged life at elevated temperatures.

Still other issues regarding the tailoring of grain boundaries and amorphous intergranular films in these systems require our attention. As noted earlier, transgranular fracture occurs in silicon nitrides containing Si-O-N intergranular films.[7] However, molecular orbital calculations{ref,13} indicate the strengths of the interfaces associated with this system may exhibit a maximum at an intermediate O:N ratio and be lowest when oxygen is absent. Recent observations indicate that debonding occurs accompanied by toughening effects in self-reinforced silicon nitrides composed of large elongated grains having a highly fibrous texture.[16] This material is produced with sintering additives of 5 wt. % yttria with 2 wt. % alumina and the elongated grains exhibit a thick SiAlON epitaxial layer. In this case however, initial analysis of this material suggests that the grain boundaries between aligned prism surfaces are “special” boundaries with no amorphous film present. Furthermore, Pezzotti and Kleebe have begun to address the important issue of the effects of the stresses created by crystallized triple point phases, which cannot be neglected in the interfacial debonding process.[17] Therefore these studies suggest that additional questions remain as to the role of the structure and composition of the grain boundary on the ability to obtain fracture resistance (and creep resistance).

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