ROLE OF INTERGRANULAR FILMS IN TOUGHENED CERAMICS

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ceramics where rod- or whisker-like grains were generated.[4] Initial success along these lines was achieved in silicon nitride.5

One first needs to determine how these elongated grains can act as reinforcements. Figure 1 shows a large elongated silicon nitride grain that is still intact and bridges the crack ~ 20 microns behind the tip of the crack. This grain holds the crack together and requires much greater applied strain energy to extend the crack. Note that an amorphous (white) network surrounds all the silicon nitride (gray) grains. A key feature here is the breaking of the bond between the elongated bridging grain and the surrounding amorphous network along a portion the grain-glass interface. This interface fracture/debonding has allowed the crack tip to pass without cutting through the reinforcement. This illustrates the key mechanisms required to toughen this ceramic: (1) the formation of strong elongated grains and (2) debonding along the interface between these grains and the intergranular amorphous network to form a crack bridging reinforcement.

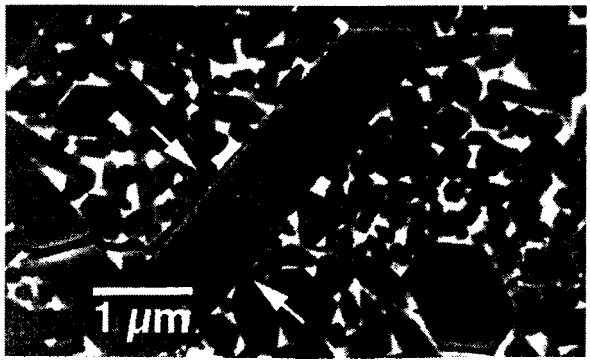

Figure 1. A larger elongated grain in a silicon nitride ceramic bridges across a crack behind its tip. Note the interface between the grain and the matrix has separated/debonded along a portion of the grain's length (arrows). A glass network (white) surrounds all the silicon nitride grains as well.

II. Role of Microstructure

In using these microscopic reinforcements, we need to ask what is needed in terms of these microscopic reinforcements. First, the length of the reinforcing grain must meet the conditions for efficient transfer of load to the reinforcement when the crack passes it (e.g., the length to diameter ratio must be > 4: 1 based on the mechanics of the silicon nitride system). Second, frictional motion of the debonded reinforcement against the matrix is a significant toughening contribution. This is enhanced with increase in the reinforcement's diameter, as well as the length of the debonded interface over which frictional sliding occurs. The frictional contribution to the toughening process depends not on the size but also on the number fraction of reinforcements.[6,7] Theoretically the toughness obtained with a given number of one micron diameter reinforcements per unit volume could also be achieved by using twice as many half micron diameter reinforcements.

One can see the effects of reinforcing grains on the fracture toughness of silicon nitride by carefully changing the microstructure of the ceramics in which the amount and composition of the intergranular glass phase were kept constant.* The number and size of the reinforcing grains generated during the sintering of silicon nitride powder compacts was controlled either by the silicon nitride powder used and the sintering temperature and time,

or by the addition of microscopic rice-shaped β-Si_3N_4 seeds.[9,a] By characterizing the resistance to the growth of small cracks in these ceramics, one can assess two very important toughening features: (1) the maximum toughness achieved and (2) how rapidly the toughness/resistance increases as the crack grows. In ceramics, we are most often concerned with the role of small cracks (i.e., 10's of microns in length) that result in failure. Thus, we are searching for materials not only with high fracture toughness but also for toughening effects that increase quickly with very small crack extensions. One observes that the silicon nitride with only fine, equiaxed grains, Figure 2 bottom micrograph, has little resistance to the growth of a crack regardless of the crack length. The lack of toughness is not surprising considering the absence of elongated reinforcing grains; note also the low fracture strength in this material. When larger elongated grains are generated but with little control of their number and size (Figure 2, middle micrograph), there is a modest toughening effect which rises rapidly for even small amounts of crack growth and the fracture strength increases to 850 MPa.

Figure 2. The fracture resistance curves reveal that the toughness increases with the controlled introduction of reinforcing grains. The ceramic with no reinforcing grains (lower micrograph) exhibits a toughness of 3 - 3.5 MPa$\sqrt{m}$. The ceramic with the uncontrolled introduction of reinforcing grains (middle micrograph) exhibits a toughness of 6 - 6.5 MPa$\sqrt{m}$. With selective generation of reinforcing grains (upper micrograph) a toughness of ~ 11 MPa$\sqrt{m}$ is obtained.

If instead we control the generation of larger elongated grains in a fine grained matrix (Figure 2, upper micrograph), a very high fracture toughness, representing a nearly four-fold increase, is achieved characterized by a rapid rise in resistance as a small crack attempts to grow. This combination results in a very high strength (up to 1400 MPa)

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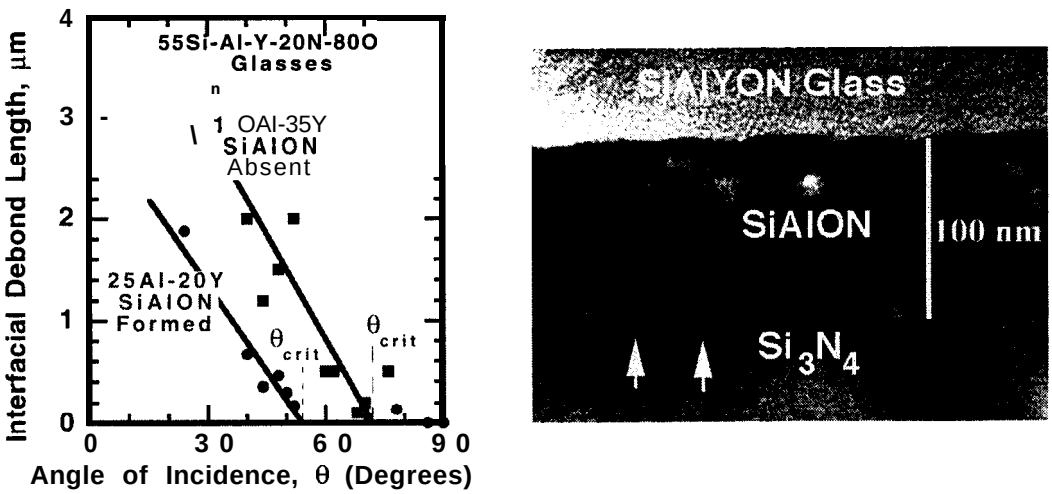
[a] These samples were fabricated at the NIRI-Nagoya ceramics laboratory by Dr. K. P. Plucknett, who was an ORNL Postdoctoral Fellow at the time. His research activitives there with Drs. K. Hirao and M. Brito were also supported by a Japanese Agency for Industrial Science and Technology Fellowship.

material that is very resistant to fracture. These results are a clear demonstration that simply introducing larger elongated grains in the matrix is not sufficient to obtain the desired toughening effects. These observations emphasize that one must control the size and number of elongated grains in self-reinforced ceramics, e.g., silicon nitride.

III. Influence of Interface Characteristics

As pointed out in Figure 1, these microscopic reinforcements only work when interfacial debonding process occurs and allows the reinforcement to survive as a growing crack reaches and passes it. Thus, the glass network appears to play an important role in the debonding and toughening processes in silicon nitride ceramics. These intergranular films result from the reaction between the chemical additives used to promote densification and the native silicon-oxygen species on the silicon nitride powders during sintering. The resultant glass formation serves as a viscous media for the growth of the elongated grains, as well as promoting the formation of a dense silicon nitride. Historically, researchers have used different amounts and types of sintering additives; thus, one might suspect that the resultant composition of this glass phase might influence the ease of interfacial debonding and, thus, the toughening effects.

An indentation cracking method was used to examine interfacial debonding involving such microscopic reinforcements employing silicon nitride whiskers dispersed in oxynitride glasses.10 The technique allows one to systematically determine the length over which the interface is debonded (l_{db}) [created when the crack is deflected at and extends up the interface] for a variety of angles (θ) of incidence between the crack plane and the whisker's prism surface. Because it is difficult to cause a crack to deflect up out of plane, cracks will deflect up along only the weaker interfaces when the angle of incidence is high. Thus, the interface strength (and energy to debond the interface) will decrease as the angle for the onset of debonding (θ_{crit}) increases.



(a) (b)

Figure 3. Observations of the conditions for the onset of interfacial debonding reveal that the composition of the Si-Al-Y oxynitride glass (composition in equivalent %, Eq. %) altered the angle for the onset for debonding (a), hence the interface strength. In the case of the stronger interface (smaller θ_{crit} value), an epitaxial SiAlON layer formed on the silicon nitride (b). The interface between these two crystalline phases exhibited a low density of misfit dislocations (see arrows).

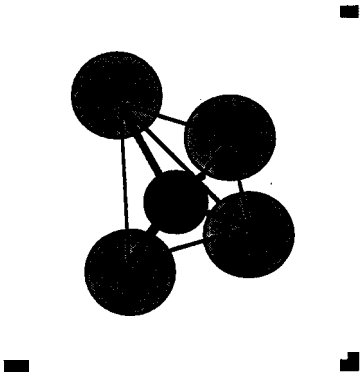
Let us examine, the debonding conditions associated with Si-Al-Y-O-N glasses as these form, in silicon nitride ceramics from the often used yttria plus alumina sintering additives. Here it was found that simply changing the composition of the Si-Y-Al oxynitride glass modified the interfacial debonding conditions significantly. By decreasing the ratio of Al to Y in the glass, the interfacial strength was reduced as indicated by the increase in the critical angle for the onset of debonding (θ_{crit}), Figure 3. Subsequent transmission electron

substituted for Yttrium in the SiAlRe oxynitride glass with a significant increase in the critical debond angle when an epitaxial SiAlON layer forms on the silicon nitride. Interestingly, there is no correlation between the critical debond angle and the magnitude of compressive residual stress imposed on the interface by the glass matrix. Clearly, some factor other than the residual stress is dominating the debonding response for the whisker-glass system. Finally, we note that the there is a rapid reduction in the critical debonding angle with increase in the Al (and 0) content (z-value) of the epitaxial layer in both silicon nitride ceramics and the glasses containing dispersed whiskers.

Finally, one then had to address how the glass composition effected the toughness of the self-reinforced silicon nitride ceramics with identical microstructures. Again in collaboration with our colleagues at NIRI-Nagoya, self-reinforced silicon nitride ceramics, each with the same amount and size of larger elongated grains in a fine grained matrix and amount of intergranular glass were fabricated with specific yttria to alumina ratios.[11] Analytical electron microscopy observations showed that (1) an epitaxial $Si_{6-z}Al_zO_zN_{8-z}$ layer was formed on the elongated reinforcing Si_3N_4 grains in each ceramic and (2) the Al and 0 content (or z-value) of this layer decreased as the yttria to alumina ratio of the original additives increased. The observed toughening effect due to self-reinforcement increased very significantly with decrease in the z-value of the epitaxial $Si_{6-z}Al_zO_zN_{8-z}$ layer formed in each of the Si_3N_4 ceramics, Table II. Thus, changing the additive composition and, thus, enhancing the strength of the interface between the reinforcing grains and the glass network is a powerful method for tailoring the properties. With the exception of thick film resistors, few such graphic examples of the important positive contribution of an intergranular glass phase to the behavior of ceramics are known to exist.

Table II. The Steady-State Toughness of Self-Reinforced β-Si_3N_4 Ceramics with Fixed Microstructure (See Figure 2, upper micrograph).

Additive Composition, wt. %	z-Value of Epitaxial SiAlON Layer	Fracture Toughness, MPa√m
6.25 Y_2O_3/1.0 Al_2O_3	0.01	10.6
5.0		



V. Summary

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