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The Influence of Microstructure on the Mechanical Behavior of Silicon Nitride Ceramics

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BACKGROUND

Mechanisms such as crack bridging (with and without interfacial friction) and pullout that operate in the crack tip wake, Figure 1, can significantly toughen ceramics and greatly improve their overall mechanical performance. The relative contributions of each of these crack wake mechanisms are dependent upon the interface properties, thermo-mechanical properties of matrix and reinforcing phases, and the amount, size, and geometry of the reinforcing phase. The degree of toughening achieved depends upon the energy dissipated by each mechanism as follows:

$$K = [E_c (\Delta J^m + \Delta J^{cb})]^{1/2} \qquad 1$$

where K is the fracture toughness of the composite system, E_c is its Young's modulus, ΔJ^m is the energy dissipated by crack extension in the matrix and ΔJ^{cb} is the energy dissipated by one of the crack wake bridging processes.[1]

Debonding of the interface between the matrix and the reinforcing phase is, of course, a necessary condition to achieve the toughening effects. One way to describe this condition is that the energy required for interfacial debonding γ_i must be less than the fracture energy of the reinforcing phase γ_r. However, this does not require that the debond energy or the stress to debond the interface equal or approach zero. In the SiC whisker reinforced alumina system, the radial compressive stresses imposed on the whisker-matrix interfaces due to the thermal expansion mismatch is quite high. This will most likely preclude a very low value of either the interfacial debonding or

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pullout shear resistance. However, this system exhibits toughening by pullout of the reinforcement. Therefore, one does need to be able to tailor the interface to promote pullout (and debonding).

Note that here we have used the debonding relationship of Budiansky et al.[2]:

$$\gamma_r/\gamma_i = Al_{db} / d \qquad 2$$

where l_{db} is the length of the debonded interface, γ_r/γ_i is $\propto \sigma_f^r/\tau_{db}$. Additionally, σ_f^r, d, and γ_r, are the tensile strength, diameter, and fracture energy of the reinforcing phase, respectively, γ^i and τ_{db} are the debonding energy of and the shear stress to debond the interface, respectively, and A is a constant with a value of two to three. For a constant γ_r/γ_i ratio (e.g., consistent with that for a composite where only the reinforcing phase dimensions are changed), the amount of debonding increases as the diameter of the reinforcing phase increases. For each mechanism, the toughening contribution increases as the diameter of the reinforcing phase increases (this assumes that the matrix, interface, and reinforcing phase characteristics do not change when the size of the reinforcing phase is changed).

There are a number of examples that reveal that such crack wake processes occur in monolithic ceramics including alumina[3] and silicon nitride[4], as well as in ceramics reinforced with whisker[1] or platelet[5] second phases. Therefore, it is consistent with the theme of this symposium to consider how the microstructure of silicon nitride ceramics might influence the fracture resistance, as well as the other mechanical properties.

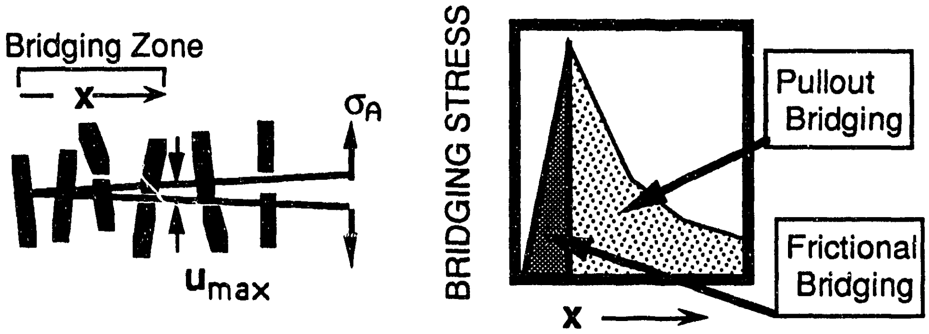


Figure 1. Crack wake processes can increase the fracture resistance by imposing bridging stresses that act to impede crack opening and propagation.

First, let us review the micromechanics descriptions appropriate to ceramics toughened by the actions of such discontinuous reinforcements (e.g., elongated or large grains) in the crack wake. The contribution of the various crack wake bridging mechanisms to the fracture resistance are as follows:[1]

1. Crack Bridging (Frictional Interface) by Elongated Grains

$$\Delta J^{fb} = [A_r(\sigma_f^{\,r})^2\, l_{db} / 9E_r] = [A_r(\sigma_f^{\,r})^2\, (\gamma_r/\gamma_i)/ 9E_r]\, d \tag{3}$$

where A_r and E_r are the areal fraction and Young's modulus of the reinforcing phase, respectively.

2. Grain Rotation[6]

$$\Delta J^{gr} = [\pi\, A_{gr}\, \mu\ \sigma_f^{\,r} /2]\, d \tag{4}$$

3. Grain Pullout

$$\Delta Jpo = [A_{po}\, (\sigma_f^{\,r})^3 /12\, E\, \tau_i]\, d \tag{5}$$

where τ_i [$\propto \mu\sigma_r$ where τ_i is the sliding resistance of the interface, μ is the coefficient of friction, and σ_r is the radial (compression) stress imposed on the interface] and A_{gr} and A_{po} are the areal fraction of grains on the crack surface that rotate and pullout, respectively (i.e., $\propto$ volume fraction of elongated grains).

These simplified relationships reveal the basic contributing parameters. With each mechanism, apparently the size and shape of the grains can significantly affect the fracture toughness of silicon nitride ceramics provided that the grain boundary phase promotes debonding. The following concerns, however, need to be clarified. How significant is the size of the elongated grains in the toughening effect, what effect does this have on strength and strength distribution, and how might the presence of silicate-based phases at the grain boundaries coupled with grain size influence fatigue resistance? To this end, observations of the influence of microstructure on the mechanical behavior of silicon nitrides containing elongated grains are discussed in hope of stimulating research on approaches to tailor the microstructure and composition of silicon nitrides to optimize various combinations of mechanical properties.

OBSERVATIONS

Fracture Toughness

Various experimental studies show that the toughening response in silicon nitrides with elongated grains can be described in terms of crack wake mechanisms. Bridging of the crack by intact elongated grains is often observed behind the crack tip. Evidence of pullout of these grains further behind the crack tip is also observed. Most importantly, the observed toughening contribution associated with the introduction of quite large diameter elongated grains is, indeed, found to scale with (diameter of elongated grain)$^{1/2}$, Figure 2. Thus, the toughening behavior observed in silicon nitrides containing elongated grains is consistent with the predictions based on crack wake mechanisms. Other types of toughening processes (e.g., crack deflection) would not result in this dependence of the toughness upon the diameter of the reinforcing phase.

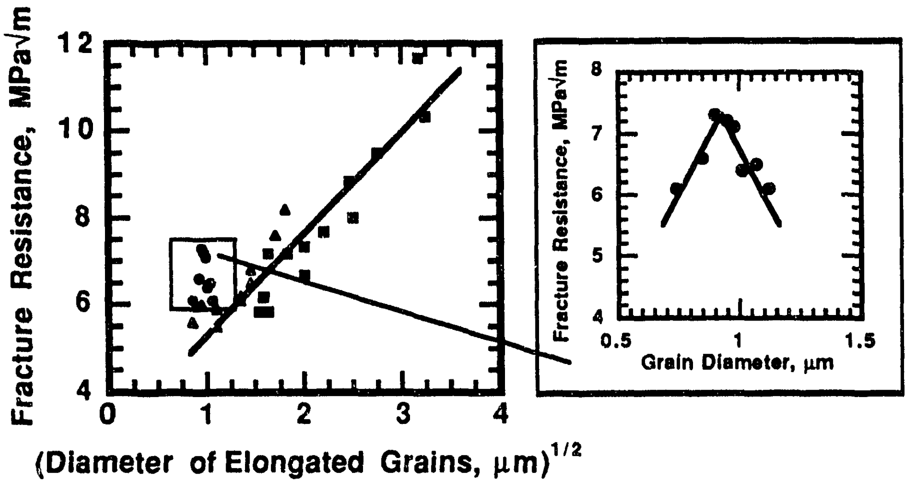


Figure 2. The steady-state fracture toughness of Si_3N_4 ceramics having elongated grain structures increases with increase in grain diameter, d, consistent with various crack bridging models (refs. 7 and 8). Insert illustrates grain size response observed in some materials containing smaller diameter elongated grains (ref. 9).

However, several characteristics that should affect crack wake processes remain to be tested. Note that the descriptions of the contribution of each mechanism indicate that the toughness should increase with an increase in the volume fraction of the larger elongated grains. Yet studies to date have documented the effect of changing the volume content. Another observation suggests that a maximum in the toughness occurs for submicron diameter grains for silicon nitrides fabricated with somewhat different levels of yttrium and aluminum, Figure 2 (insert). These results raise the question why a maximum in toughness might occur with certain additives and/or microstructures.

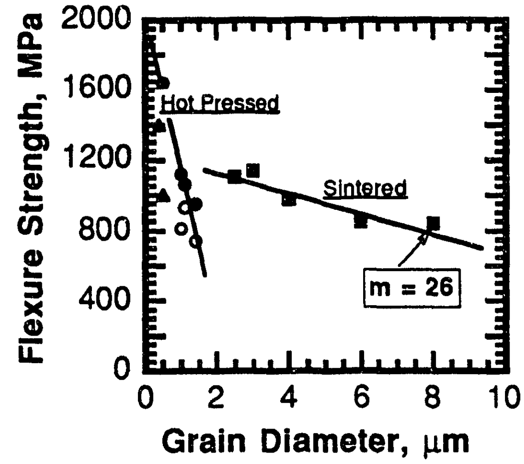
Finally, Tajima observed that the presence of larger elongated grains was not sufficient to ensure a toughening effect.[10] He found that in the case of two silicon nitrides exhibiting similar elongated grain microstructure but employing different additives that in one the crack propagated through the elongated grains while leaving bridging grains in the crack tip wake in the other. This points out the importance of interface debonding (e.g., intergranular fracture versus transgranular fracture) in crack wake processes. One can speculate that the properties of the intergranular phase(s) (e.g., thermal expansion, fracture resistance, or chemical bonding with silicon nitride) would alter the stress state at the interfaces and the conditions for interfacial debonding. However, very little is known about the properties of the oxynitride glasses that are present. It is known that the cations present in the sintering additives can modify the equilibrium thickness of two grain junctions in silicon nitride,[11] but it is not clear how this might effect debonding. Thus, several questions remain as to how to optimize the toughening effects resulting from the presence of elongated grains in silicon nitrides.

Fracture Strength

Another very significant attribute of the toughened large grained material described in the previous figure is the very modest decrease in fracture strength with increase in grain diameter.[7] Both equiaxed grained ceramics and the Si_3N_4 having much smaller diameter elongated grains (and different additives)[12] exhibit a very substantial loss in strength with increase in grain size. To achieve strengths in the range of $\geq$ 1000 MPa in dense alumina ceramics grain sizes must be much < 1 µm and the strengths decrease to 500 MPa for grain sizes of ~ 2 µm.[13] Similar behavior is shown for the hot pressed Si_3N_4 ceramic in Figure 3. On the other hand, strengths of 800 MPa or greater can be achieved in the sintered Si_3N_4 having elongated grains with diameters of up to ~ 9 µm! These materials also can exhibit quite high Weibull moduli, e.g., m = 26 as shown in Figure 3.

Note that often the larger elongated grains are observed at the fracture origin; this suggests that they might act as flaws. This is not inconsistent with the toughening effect as relatively easy debonding at the silicon nitride interfaces is required for toughening. A large partially debonded elongated grain interface could then contribute to the formation of a larger flaw and a reduction in strength versus that achieved in the less tough finer grained material. This is born out by the strength versus grain diameter behavior as shown in Figure 3. Nonetheless, the toughening effect achieved minimizes the strength reduction.

One might, then, expect that clusters of the larger elongated grains may generate larger defects to further lower the fracture strength. If such clusters are randomly distributed throughout the microstructure, a much broader strength distribution could result. Evidence for such can be seen in the strength distributions for two silicon nitrides prepared with the same additives and sintering schedule but from two different powders, Figure 4. Both materials exhibit the same level of fracture toughness, but ceramic A exhibits a slightly higher strength (~ 900 MPa) and a much higher Weibull modulus (m > 40) versus ~ 810 MPa and 18, respectively, for material B. The main difference in these two materials is the presence of elongated grain clusters in material B often found at the fracture origins. Thus, simply increasing the size of the elongated grains without controlling the volume fraction and the distribution of the largest elongated grains could prove to be quite detrimental to the mechanical performance, especially when a narrow strength distribution along with toughening effects is crucial for the intended application.



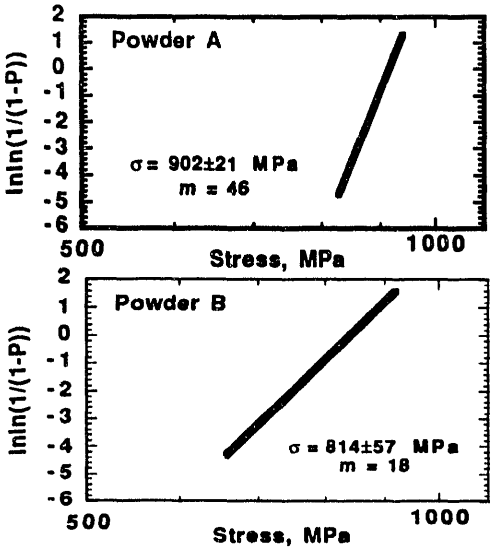


Figure 3. The grain size dependence of the fracture strength of Si_3N_4 can be substantially reduced in some of the systems toughened by the formation of elongated grain structures. Such materials also exhibit quite high Weibull moduli.

Figure 4. Narrow strength distributions attained with well-dispersed large grains are degraded when the large elongated grains tend to form clusters.

Evaluation of the two powders used reveals nearly identical size distributions, phase contents, and contents of oxygen and other impurities. In the case of powder A, the large powder particles consist of friable agglomerates of submicron particles. However, in the case of powder A, the number of larger β-particles in the starting powder is smaller in comparison to powder B. Detailed grain growth experiments show that these large β-particles act as nuclei for the growth of large elongated grains (lengths > 100 μm) during isothermal sintering after completion of the α to β transformation.[14] Thus, attention needs to be given not only to the effects of additives and sintering conditions on the formation of elongated grain microstructures but also, not surprisingly, to the powder characteristics.

R-Curve Response

High fracture toughness coupled with high strengths and narrow strength distributions that can be achieved in certain silicon nitrides suggests that the rise in the fracture resistance with initial extension of a crack (e.g., R-curve response) may be an important factor. However, little information is available on the R-curve behavior of these materials particularly regarding the influence of microstructure. Figure 5 illustrates the R-curves for several

Si_3N_4 ceramics having elongated grains but containing different additives. Materials with larger diameter elongated grains tend to exhibit a steeper initial portion of the R-curve in the limited materials studied. The reader is cautioned that these R-curves cannot be compared directly to the results in the proceeding figures due to differences in additives and processing and thus microstructures. However, if we assume that their microstructures are quite similar, as suggested by preliminary examinations, one could suggest that differences in second phase and grain boundary phase chemistry and content may play a role. Both the microstructural and chemistry and phase content aspects in the toughness, strength, and R-curve behaviors need to be systematically explored.

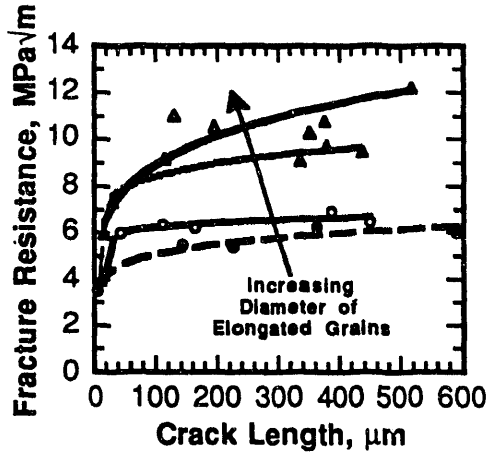


Figure 5. The R-curve behavior of four different Si_3N_4 ceramics illustrate that the initial rate of rise of the fracture resistance with crack length can increase with increase in the diameter of the elongated grains.

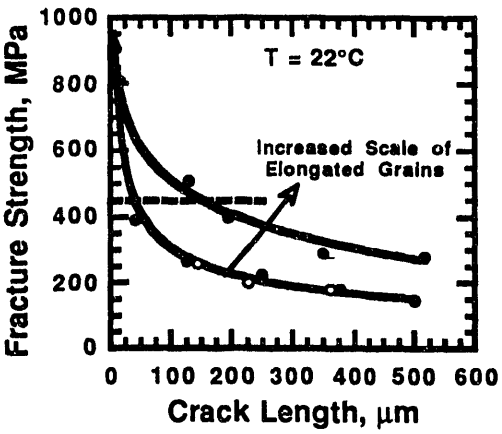


Figure 6. High strengths are retained for larger crack sizes in material with the most rapid rise in the R-curve response as compared to the material with both the lower toughness and slower rise in the R-curve (see Figure 5).

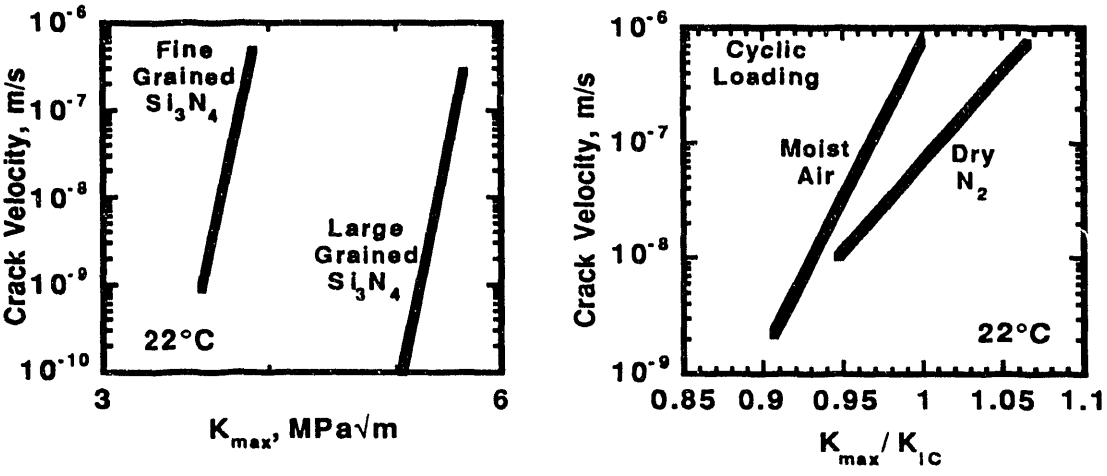
To obtain some insight into the influence that the R-curve might have, it is informative to consider the strength-flaw size response of two materials representing the extremes in the R-curve response shown in Figure 5. The importance of the details of the R-curve behavior is indicated by the strength-crack size response in these materials, Figure 6. While the strength of each decreases with increase in crack size, the rate of decrease is reduced as the rate of initial rise in the R-curve and the magnitude of the toughness plateau. In other words, materials with R-curves that rapidly rise to high levels are more damage resistant. This can be seen in Figure 6 where, for example, the strength level can be maintained ≥ 500 MPa for crack sizes up to 125 μm in the material that has the steepest and highest R-curve. While in the material with the poorest R-curve response, the same levels of strength can only be maintained for crack lengths of < 50 μm. It is obvious from the findings to date that understanding what factors control the crack bridging mechanisms and related R-curve behavior can also be of significant engineering importance in meeting the demands of various applications.

Fatigue Resistance

With a microstructure consisting of amorphous and crystalline silicate grain boundary phases, one should consider the resistance of these toughened silicon nitride ceramics to fatigue in the form of slow crack growth under static and cyclic loading. It is well documented that silicates and, in particular, glasses are quite susceptible to crack growth at applied stress intensities that are substantially lower than those required for catastrophic fracture.[15] On the other hand, nonoxides with no oxide additives, as typified by sintered silicon carbide containing boron and carbon, can be extremely resistant to slow crack growth.[16] In addition, toughening achieved by crack bridging and pullout may exhibit somewhat poorer crack growth resistance under cyclic versus static loading due to damage of the bridging elements during crack closure on unloading.[17] Also, the presence of amorphous silicate grain boundary (interfacial) phases may substantially alter the elevated temperature response due to softening and viscous flow of the amorphous phases.

At room temperature, slow crack growth is observed in silicon nitrides containing elongated grains and silicate grain boundary phases under static loading, Figure 7a. However, two features should be noted. First, the dependence of the crack velocity on the applied stress intensity is quite strong and the exponent of the stress intensity derived from a power law crack growth description is quite large (e.g., $n > 50$). Second, the high resistance to slow crack growth is maintained when the grain size is increased to further toughen the ceramic. When cyclic loading is applied, crack growth in the toughened silicon nitride is promoted in chemically active environments, Figure 7b, as happens in glasses and oxides.[15] Thus, one can state that the use of glass phases to promote the growth of elongated grains in silicon nitride ceramics may lower their resistance to slow crack growth and make them susceptible to environmental effects at room temperature. While these static fatigue effects may not be very strong, attention should be paid to regulating the amount and the composition of the grain phases to avoid promoting cyclic fatigue.

Besides room temperature fatigue, the presence of silicate grain boundary phases suggests that the fatigue response at elevated temperatures may be a concern as softening of these phases may alter the crack bridging behavior. Static and low cycle fatigue of the silicon nitride with the large elongated grains as shown in Figure 8 at 1400°C in air reveals that slow crack growth is inhibited under cyclic versus static loading. Observations of the crack path indicate that bridging of the crack can be enhanced under cyclic loading. Lin et al. noted similar effects at elevated temperatures in a commercial silicon nitride containing elongated grains where the time to failure increased and the strain rates decreased with cyclic versus static tensile loading.[18]



a b

Figure 7. Slow crack growth is observed at room temperature in elongated grain structured silicon nitrides due to the presence of silicate phases (a. static loading; b. cyclic loading in various environments).

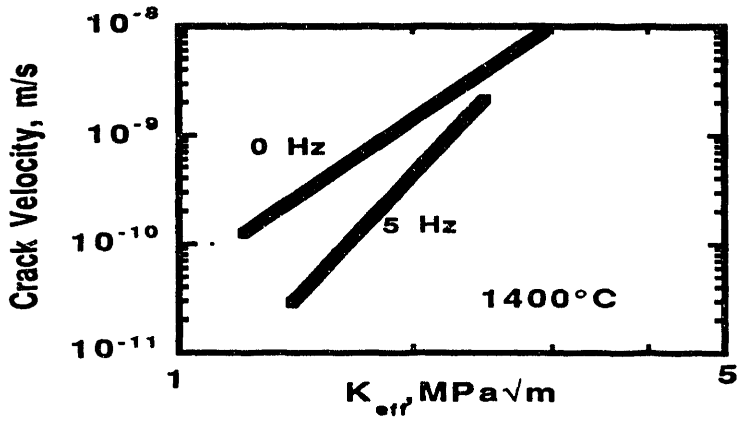


Figure 8. Slow crack growth resistance is enhanced at 1400°C under cyclic loading.

While it is not known why certain mechanisms are activated or suppressed in cyclic loading, it is observed in the experiments by Lin et al. that cavitation is less prevalent.[17] Combined with the observed increase in the contribution of crack bridging mechanisms under cyclic loading, this suggests that stress relaxation during unloading could be a contributing factor. How this depends on the viscous behavior of the grain boundary phase that must influence both bridging and cavitation remains to be resolved.

SUMMARY

The introduction of elongated silicon nitride grains during densification in the presence of a liquid phase can impart considerable improvement to the fracture toughness. This toughening is not universally attained but depends on the activation of intergranular rather than transgranular fracture. This is reminiscent of the requirement of interfacial debonding in whisker-reinforced ceramics. In fact, additional observations such as bridging in the crack wake by elongated grains and pullout of some of these grains further suggest that the crack wake mechanisms that contribute to the toughening of whisker-reinforced ceramics can also operate in silicon nitrides containing elongated grains. Various investigators have found that, consistent with crack wake mechanisms, the fracture toughness of silicon nitrides increases with increase in the diameter of the larger elongated grains. However, little is known about the effects of the grain boundary phase(s) and their properties on the interfacial debonding/intergranular fracture in such silicon nitrides. This is critical as observations show that crack propagation in some systems exhibiting larger elongated grains occurs transgranularly and no toughening occurs.

The fracture strengths of these toughened silicon nitrides containing larger elongated grains are quite impressive, reaching levels of 900 MPa or so. Large grains are frequently found at the fracture origins; this is not surprising if debonding of their interfaces is required for toughening (i.e., the debonding of a large grain surface should act to increase the flaw size). However, some observations reveal that the accompanying improvements in toughness act to minimize the reduction in fracture strength as the size of the larger elongated grains increases. Even with diameters of the larger elongated grains approaching 9 μm, strengths > 800 MPa have been achieved along with high Weibull moduli. However, care must be taken to avoid clustering of these larger elongated grains (i.e., either maintain lower volume fractions or uniform spatial distributions) as such clusters can reduce the strength and the Weibull modulus. The strength-damage response in such materials must also reflect their R-curve behavior where the fracture resistance increases as the crack extends through the microstructure and develops a bridging zone behind the crack tip. The details of how the grain boundary phase(s) and scale of the microstructure influence the R-curve response need to be addressed. Preliminary studies only indicate that large differences in the plateau toughness values can alter the initial rising portion of the R-curve.

The fatigue behavior of these toughened silicon nitrides is influenced by the silicate grain boundary phases. Slow crack growth behavior is observed at room and elevated temperatures. At room temperature, the slow crack growth-environment response is similar to those seen in glasses and oxides indicating moisture-assisted crack growth in the silicate grain boundary phase. At elevated temperatures, cyclic loading appears to enhance the fatigue resistance in several toughened silicon nitride ceramics with evidence for both enhanced crack bridging and reduced cavitation as compared to that under static loading. Obviously, design of such toughened silicon nitrides must consider the effects of the silicate phase(s) composition and content on the fatigue and creep response as well. Further attention to the various microstructural characteristics should provide an approach to designing high strength silicon nitride ceramics with further improvements in toughness and mechanical reliability.

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