CONF-9605168--1

THE *R*-CURVE RESPONSE OF CERAMICS WITH MICROSCOPIC REINFORCEMENTS: REINFORCEMENT AND ADDITIVE EFFECTS

P. F. Becher, E. Y. Sun, K. P. Plucknett, and C. H. Hsueh
Metals and Ceramics Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6068

ABSTRACT

Using direct observations with the scanning electron and optical microscopes, simultaneous measurements of fracture resistance versus crack length (*R*-curve behavior) and crack interactions with microstructural features at the crack tip and in its wake were made. Selecting whisker-reinforced aluminas and self-reinforced silicon nitrides, one can examine the effects of systematic modifications of microstructure and composition on the *R*-curve response and the mechanisms giving rise to it. Specifically, increases in whisker content and size can increase the *R*-Curve response, even for short crack lengths. In the self-reinforced silicon nitrides, changes in alumina:yttria additive ratios also modify the *R*-curve. Modeling of the *R*-curve response allows one to verify toughening mechanisms and, with experimental studies, to optimize the *R*-curve behavior in ceramics containing microscopic reinforcements, e.g., whiskers and elongated grain structures.

INTRODUCTION

Earlier studies revealed that the steady-state toughness of SiC whisker-reinforced aluminas could be increased by raising the whisker content and by incorporating whiskers of larger diameters.[1,2] Recently, it was shown that the *R*-curve response was also influenced by these same factors.[3] Constitutive models, based on crack-bridging mechanisms, agree well with experimental results;[1,4,5] however, more recent studies reveal that contributions from crack deflection by the whiskers must also be considered.[6] These findings provide very useful insights into how the fracture resistance behavior of both whisker- and self-reinforced ceramics can be tailored.

A possible analogue to the whisker-reinforced ceramics exists in the self-reinforced ceramics, specifically the self-reinforced beta silicon nitrides. Beta-silicon nitride ceramics typically incorporate amorphous phases, which can often also be partially crystallized, and exhibit elongated grain structures, even in very fine grained materials. Promotion of the growth of a portion of these elongated grains can be accomplished by the addition of beta particles to the starting powders, which are primarily alpha phase. A refinement of this approach is to use elongated beta seeds,[7] rather than "equiaxed" beta particles. This refinement can enhance the formation of large elongated beta grains and, to some extent, serve to control the content of these larger elongated grains. Under the proper conditions, these elongated beta grains act as a reinforcing phase resulting in an increase in the fracture resistance with extension of a crack. As shown earlier, the plateau or steady-state value of the toughness can increase with increase in the diameter of the larger elongated beta grains;[8,9] the increase in alignment of these larger elongated grains that can be achieved with the use of elongated beta seeds appears to further enhance this effect.[7]

However, the presence of large elongated beta grains apparently is not sufficient to generate strong *R*-curve effects or toughening. Indeed, there are examples of silicon nitride ceramics containing larger elongated grains that exhibit negligible improvements in toughness.[10] In these silicon nitrides, the crack is not deflected by the large elongated grains, but rather propogates through these grains. Thus, the elongated grains do not act as a reinforcement; similar behavior is observed in some SiC whisker-reinforced aluminas. The latter has been attributed to either much stronger interfacial bonding between the whisker and matrix and/or to surface topological features or internal defects that tend to weaken the whiskers.[2,5] There is evidence in whisker-reinforced aluminas that oxygen enrichment combined with carbon depletion in the whisker surface region[11] is one factor in reducing the reinforcement effect, suspected to be related to the formation of a strong interfacial bond. Assuming this is the case, could a similar phenomenon occur in silicon nitride ceramics? It has been shown in studies of beta-silicon nitride whiskers embedded in oxynitride glass matrices that interfacial debonding can be influenced by the composition of the oxynitride glass.[12] As interfacial debonding becomes more difficult, crack deflection and crack bridging by the elongated beta grains should diminish the toughening effects due to the presence of such grains. Thus, the present study seeks to determine the influence on the *R*-curve response of the reinforcing phase in SiC whisker-reinforced ceramics and the composition of the densification additives in self-reinforced silicon nitrides.

EXPERIMENT PROCEDURE

Two groups of fully dense SiC whisker-reinforced alumina composites were fabricated by hot pressing whisker-powder mixtures.[3] The first group included fine grained (1-2 μm) alumina composites containing 4, 10, and 20 vol. % whiskers prepared from one source of ~ 0.8 μm diameter SiC whiskers.[a] The second group was also based on a fine grained alumina matrix with 20 vol. % whiskers but used two different whisker sizes (i.e., the average diameters were ~ 0.4 μm [b] and ~ 2 μm [c]).

The self–reinforced silicon nitride ceramics were prepared combining 2 wt. % elongated beta-silicon nitride seeds with a mixture of Ube E-10 silicon nitride matrix powder and alumina plus yttria densification aids. Three different amounts of densification additives were added to the silicon nitride matrix: 1 wt. % alumina plus 6.25 wt. % yttria, 2 wt. % alumina plus 5 wt. % yttria, and 2.8 wt. % alumina plus 4 wt. % yttria. The three final mixtures were each used separately to form a slurry which was then tape cast, cut, stacked, pressed and dried. The pieces were then gas pressure sintered at 1850°C at a nitrogen

---

[a] SC-9 whiskers (α phase plus some β phase) with an average diameter of ~0.8 μm and length of ~30 μm, Advanced Composite Materials Corporation, Greer, SC.

[b] SCW-300 grade whiskers with average diameter of ~ 0.4 μm and length of 20-50 μm, ALCAN International, Ltd., Jonquiere, Canada.

[c] Whiskers with average diameter of ~ 2 μm and length of 40 to several hundred microns, Los Alamos National Lab., Albuequerque, N. M.

overpressure of 1 MPa for 6 hours. The beta seeds served to nucleate elongated beta silicon nitride grains, that act as the self-reinforcement phase, embedded in a fine grained matrix. The tape casting process combined with the use of elongated beta seeds provides a preferred orientation with the long axis of the elongated grains lying nearly parallel to the surface of the finished plates (e.g., see Ref. 7).

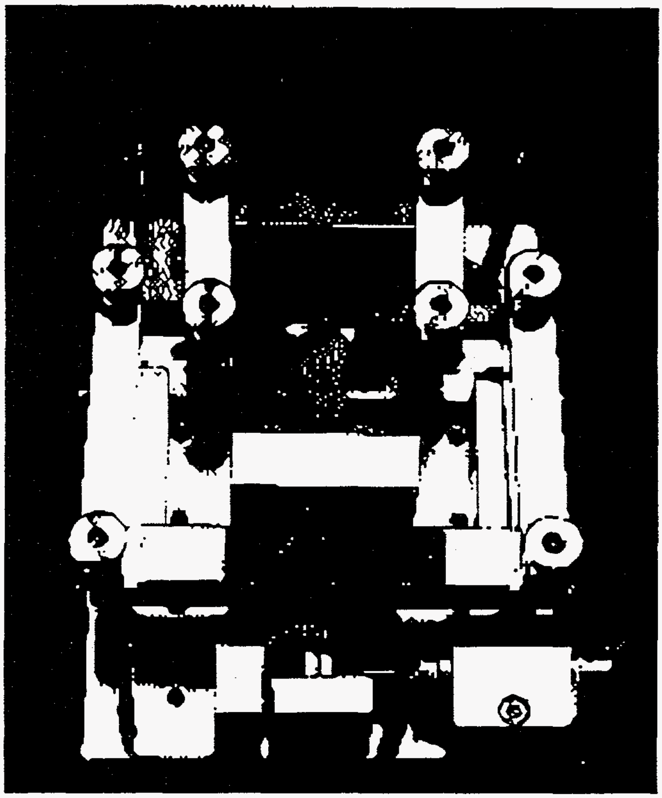

Figure 1. Applied moment DCB test module with sample under load. The testing stage can be placed on an optical microscope stage or housed in the chamber of an SEM. Companion module allows samples to be tested in three or four point flexure.

The *R*-curve responses of the above materials were investigated using an applied moment double cantilever beam (DCB) geometry[13] with the crack plane oriented normal to the plane containing the length of the SiC whiskers or the elongated beta-silicon nitride grains. The DCB samples were precracked with the wake of the precrack removed using a low speed diamond saw, and the loading arms attached with epoxy adhesive. Using direct stereo microscopy observations during back cutting of the crack wake, it is possible to routinely produce initial crack lengths of 50 to 100 µm. The DCB samples were, then, tested using a module[d] that fits on the stage of either an optical microscope[e] or

---

[d] Applied Moment DCB Module, Raith USA, Inc., Farmingdale, N.Y.

[e] Model 11B Optical Microscope, Nikon Inc., Melville, N.Y.

a scanning electron microscope[f] , as shown in Figure 1. Details of sample preparation and testing procedures are reported in Reference 3. Both digital images and video images were acquired during the tests to monitor crack advancement, crack opening displacements, and interactions with microstructural features.

R-CURVE DEPENDENCE ON WHISKER CONTENT AND SIZE IN SiC_W REINFORCED ALUMINAS

With the alumina composites, it was possible to investigate the influence of whisker content on the *R*-curve response using a single whisker source. The typical results, shown in Figure 2, reveal that the fracture resistance for cracks > 100 µm long increases significantly with whisker content. When only 4 vol. % whiskers are present, the fracture resistance increases insignificantly as a crack extends from 100 to 2000 µm in length. On the other hand, the fracture resistance rises by 3 to 5 MPa√m with same amount of crack extension at whisker contents of 10 and 20 vol. %.

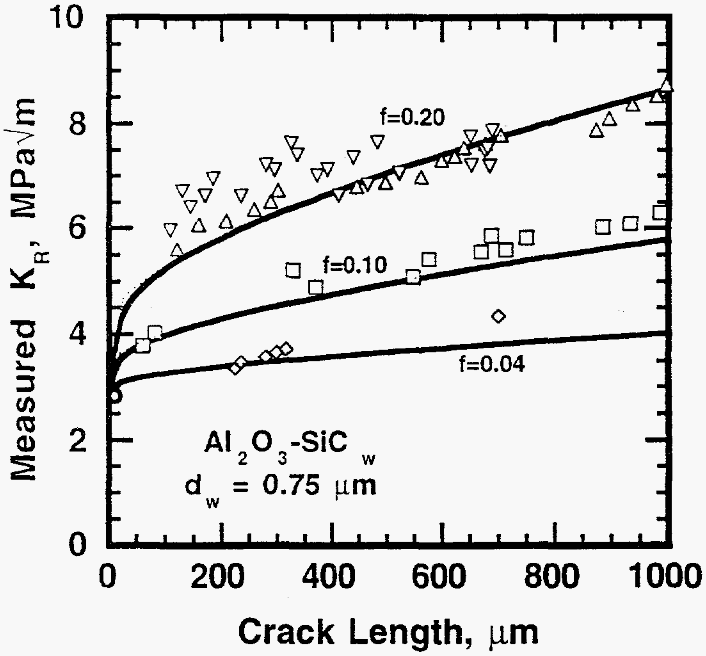

Figure 2. Both the initial rate of rise and the plateau value of the *R*-curve increase with addition of 0.75 µm diameter SiC whiskers to the fine (~2 µm) grained alumina matrix. Curves based on predictions of model of frictional bridging and pull out.[3]

A comparison of the *R*-curve response for alumina composites incorporating whisker lots of two different diameters is shown in Figure 3. This is not an ideal

---

[f] Model S-4100 Field Emission Gun Scanning Electron Microscope, Hitachi Scientific Instrucments, Gaithersburg, Md.

experiment as the distribution of whisker diameters is much broader in the case of the large diameter whiskers. Nonetheless, this does show that the fracture resistance can be improved even for short crack lengths by incorporating larger diameter reinforcements.

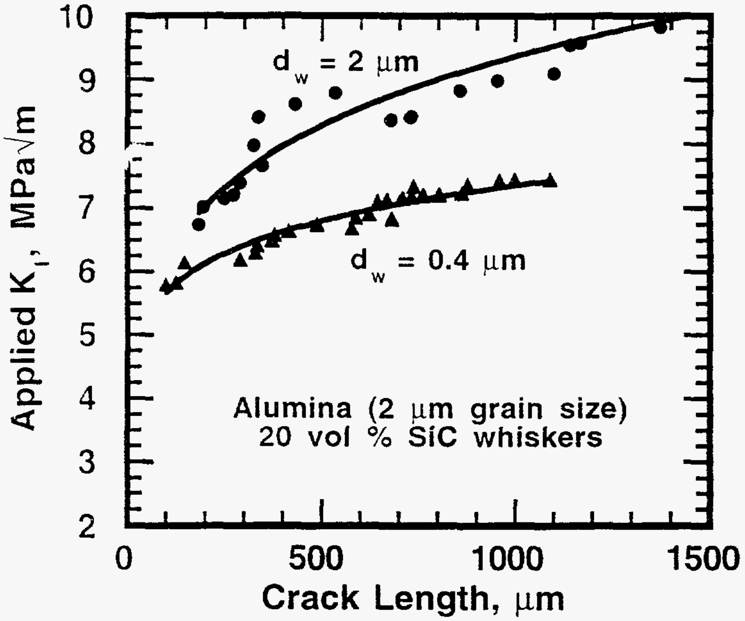

Figure 3. With increase in the average SiC whisker diameter, the *R*-curve response of the fine grained alumina matrix composite is enhanced.

Observations of crack propagation during the tests show that the crack tip is often deflected along one edge of a whisker and subsequently cut throught the whisker at a point away from where it intercepted the whisker, Figure 4a. At other times, the crack was arrested at the whisker until the applied stress intensity was increased, and then the crack tip apparently advanced around the circumference of the whisker and reappeared in the matrix ahead of the whisker. This process appears to generate a bridging whisker in the crack tip wake, see sequence in Figure 4 a and b. This example is considered to be representative of "frictional bridging" whiskers[3,4] which typical fail within the zone close behind the tip but give rise to a rapid increase in the *R*-curve during the initial extension of short cracks. Less frequently, the whisker-matrix interface completely debonds for a detectable distance from the main crack plane. As such they contribute to a further increase in the *R*-curve by either a frictional pull-out process (Figure 4c), or frictional processes involving bending and rotation against the matrix (Figure 4d). These direct observations[6] further support previous evidence for the crack wake processes of frictional bridging, whisker pullout, and rotation. More importantly, they also show that the deflection of the crack tip is also a contributing factor. The actual step of crack tip deflection modifies the initial (or intercept) value of the fracture resistance, e.g., similar to that due to increases in matrix toughness.

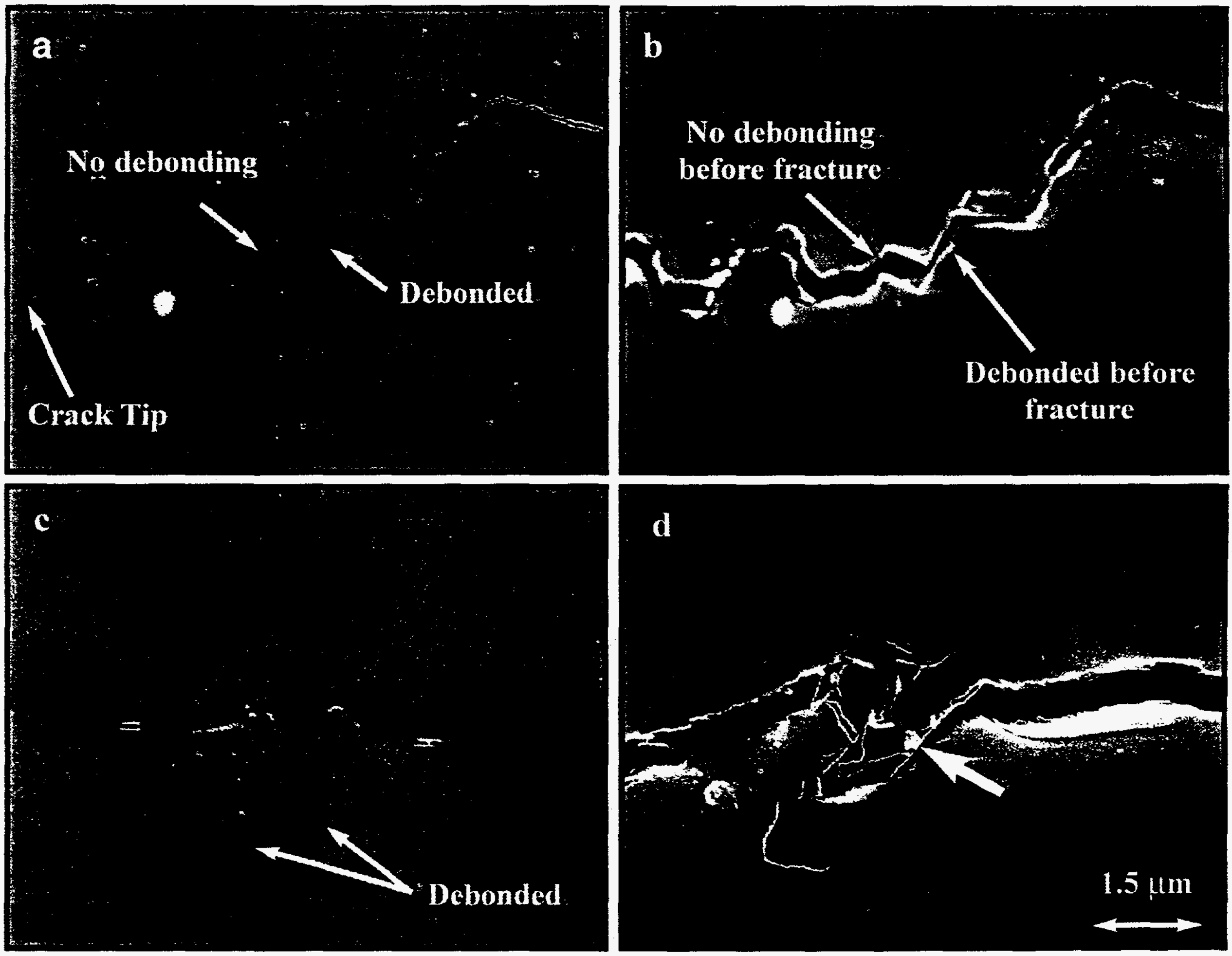

Figure 4. Fracture behavior of SiC whisker-reinforced alumina: (a) crack deflected and bridged by an intact whisker; (b) whisker fractured under higher applied stress; (c) crack-bridging via whisker pull-out; and (d) whisker subjected to bending stresses during pull-out. (Crack propagated from right to left in all pictures.)

From the in-situ observations, it can be concluded that crack deflection, "frictional bridging" and pull-out process are activated during crack extension in SiC whisker-reinforced alumina. However, it should be realized that among these three mechanisms, crack deflection increases the toughness of the material in the crack tip region rather than being a crack wake toughness contributor. Based on this interpretation, our previous bridging model for

R-curve was modified to include a crack-deflection contribution, see Figure 5. The *R*-curve for a 20 vol.% SiC whisker (0.75 μm diameter)-reinforced alumina was calculated using both the "deflection plus bridging" model and the "bridging" only model.[6] The K_0 value used in the "deflection plus bridging" model is 4.2 MPa√m instead of the 2.8 MPa√m used earlier in the "bridging" model.[3] Based solely on comparisons of the two predictions with the experimental data, it is still difficult to decide which model is correct. Obviously, thorough *in-situ* observations provide the necessary evidence to conclude that crack tip deflection is an important component of the toughening mechanisms in this case.

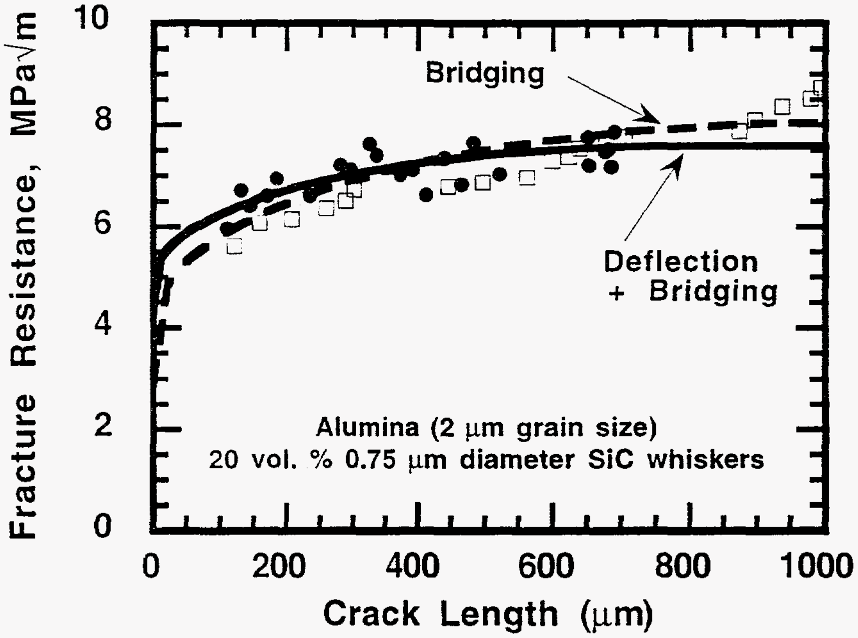

Figure 5. *R*-curve response of SiC whisker-reinforced alumina under dynamic loading. (Symbols are experimental data and curves represent calculations based on different toughening mechanisms described earlier: dashed line represents only bridging processes while solid line also includes crack deflection contribution.)

From these studies, we can see that increases in whisker content can result in a more rapid rise in the *R*-curve response and a greater steady-state toughness value. Use of larger diameter whiskers can have similar effects. With crack tip deflection by the reinforcing phase, the short crack fracture resistance can be substantially enhanced as well; a factor that, along with frictional bridging, could be significant in strength distributions and damage resistance. Each of these factors will be modified by the strength and shape or roughness of the whiskers and can be altered by the surface chemistry of the whiskers.[1,11]

INFLUENCE OF ELONGATED GRAIN SIZE AND ADDITIVE COMPOSITION ON THE *R*-CURVE RESPONSE IN SELF-REINFORCED SILICON NITRIDES

As with the whisker-reinforced aluminas, an increase in the diameter of the elongated grains can enhance the *R*-curve response and toughness of silicon nitrides, Figure 6. However as noted earlier, the presence of larger elongated beta grains does not ensure significant *R*-curve response or toughening. One area that must be addressed is the effect of the additive composition used to densify the silicon nitride. Specifically, could the composition of the additives modify the strength of the interface between the large elongated beta grains and the amorphous binder phase?

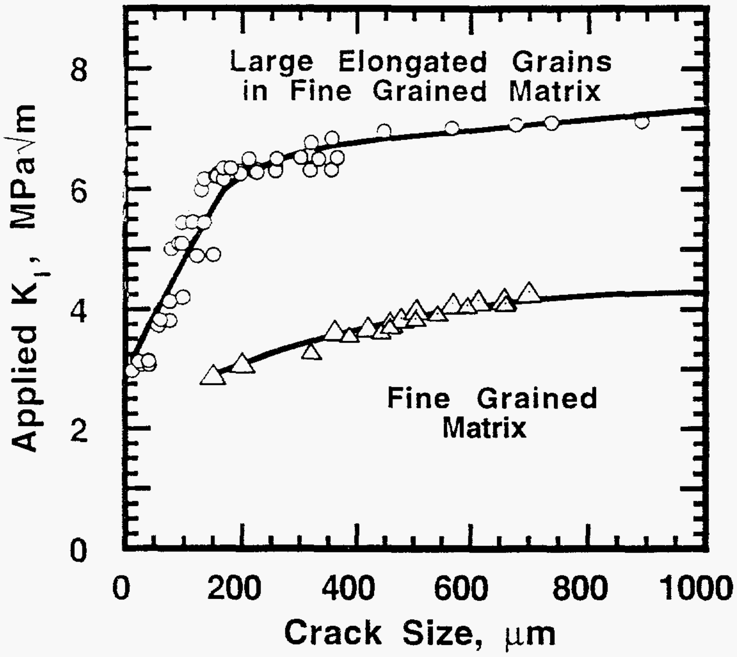

Figure 6. The incorporation of larger elongated beta grains can result in a significant increase in the *R*-curve response of silicon nitride ceramics.

Recent studies show that the formation of SiAlON layers on the Si_3N_4 grains inhibits the interfacial debonding that is required to produce the bridging grains and high toughness.[12,14] On the other hand, Peterson and Tien argue that thermal expansion mismatch stresses account for the differences in toughening effects observed with changes in additive chemistry.[15] At the same time, changes in additive composition (and processing conditions) can alter the microstructure (e.g., the number and size of the larger elongated grains). In fact, the data shown in Figure 6 represent a hot pressed, very fine grained Si_3N_4 using a MgO additive and a gas pressure sintered, self-reinforced ceramic using a Yb_2O_3 additive. Under these circumstances, it is impossible to determine the significance of each microstructural component (e.g., residual stresses in grain boundary phase, interface structure and strength, grain shape and size). A more fruitful approach is to systematically modify each of these, and Hirao *et al.* developed a process of using elongated beta seeds that allows one to control the size and fraction of the larger elongated grains in the self-reinforced ceramic.[7] Using 2 wt. % additions of the elongated seeds results in self-reinforced samples with 20-30 vol. % of the larger elongated grains with few impingements or clusterings of the larger grains.

Therefore, samples were prepared using the elongated beta seeds to regulate the volume content of larger elongated grains, where the ratio of alumina to yttria in the additive mixture was varied. The total amount of the weight fraction of additives was kept constant, while the yttrium to aluminum ratio was changed from 3:1 to 2:3 (based on equivalent percentages). The average diameter and content of the large elongated grains were similar in these three materials. The *R*-curve response in self-reinforced silicon nitrides fabricated with three different ratios of yttria to alumina additions is shown in Figure 7. These initial results indicate that the additive composition does indeed alter the *R*-curve response.

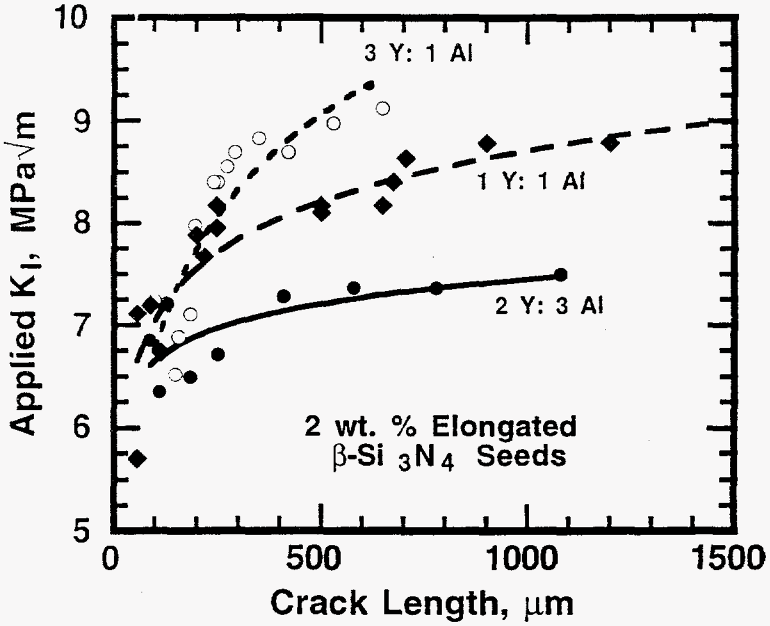

Figure 7. Self-reinforced silicon nitrides that use elongated beta seeds to control the fraction of large elongated grains exhibit *R*-curve responses that are dependent upon the ratio of yttria to alumina (in equivalent %) densification additives.

However, recent studies show that interfacial debonding is inhibited with the formation of a SiAlON growth layer on beta grains and that the initial SiAlON layer growth rate is simply decreased with increased Y:Al ratios. After the initial consolidation step at 1700°C for ~ 5 minutes, 0.2 μm SiAlON growth layer was detcted for whiskers embedded in a 1 Y:1 Al Oxynitride glass while no film was detected in the glass with a 3.5 Y: 1 Al ratio. However, an ~ 0.2 μm thick SiAlON layer was detected in the 3.5 Y: 1 Al ratio glass system after a subsequent anneal at 1600°C one hour. Therefore, a SiAlON shell should be (and indeed is) present on the larger elongated grains in the three ceramics used to generate the data in Figure 7 as they are processed at 1850°C for 6 h providing ample conditions for SiAlON formation. Thus, we can not attribute the increase in the *R*-curve responses in Figure 7 to the absence of SiAlON at the interface between the larger elongated β-Si$_3$N$_4$ grains and the boundary glasses.

Studies of the SiAlYON glasses reveal that the softening temperatures, thermal expansion coefficients, and Young's moduli increase with Y:Al ratio[16] such that the calculated thermal mismatch stresses would also increase. In the self-reinforced ceramic case, thermal expansion mismatch (TEM) stresses may be more important in interfacial debonding than was the case where the β-Si$_3$N$_4$ whisker is embedded in a glass matrix.[12] The interfacial residual stresses were addressed for the case of an elongated grain surrounded by a glass film embedded in a matrix comprised of fine grains and glass, Figure 8.

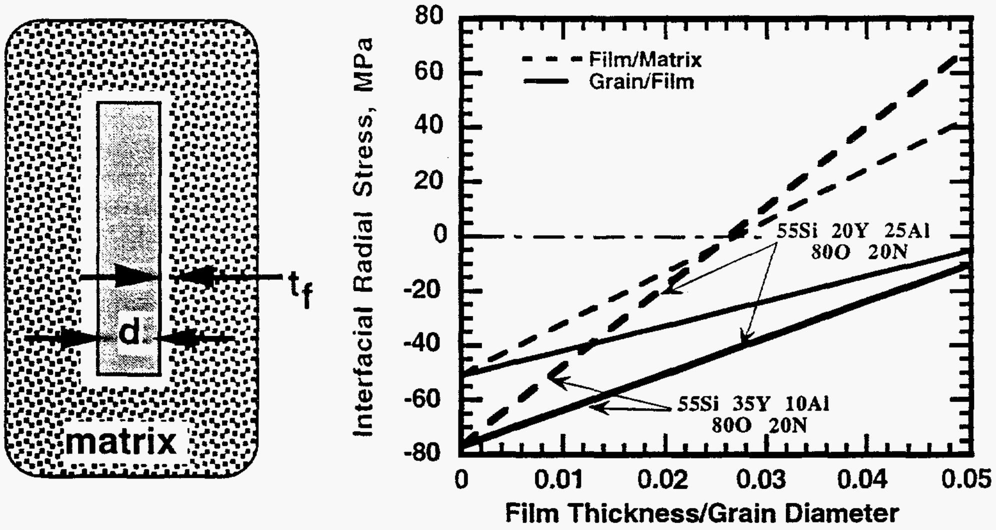

Figure 8. The radial residual TEM stress imposed on the interfaces was considered for a model system consisting of an elongated grain (diameter d) surrounded by a thin shell of glass of thickness t which were embedded in a matrix of silicon nitride with 8 % glass phase. For a very thin glass shell, the radial stress acting on both the elongated grain/shell and the shell/matrix interfaces is compressive in nature. With increase in the thickness of the glass shell surrounding the elongated grain, the radial residual stresses imposed on the interfaces become tensile.

Using just the mismatch in properties, one can see that the glass film will be subjected to a residual hydrostatic tensile stress which will increase with Y:Al ratio. However, the interface between the large elongated grain and its glass film will be subjected to radial compression as will the interface between this glass film and the "matrix." With increase in the Y:Al ratio in the additive, this stress increases and interfacial debonding ought to be more difficult. On the other hand, the compressive radial stress imposed on the interfaces decreases with increase in the thickness of the glass film around the elongated grain. In fact, they become tensile in nature as the film thickness continues to increase.

Increases in the thermal expansion mismatch (i.e., as with increase in Y:Al ratio) should result in a more rapid change in the radial stress acting on the interfaces with increase in the thickness of the glass film surrounding the elongated grain. Thus above a critical glass film thickness, the ceramics using the high Y:Al ratio would experience greater tensile interfacial radial stresses than those in the system incorporating the low Y:Al ratio glass. This would promote interfacial debonding and grain bridging in the silicon nitrides containing additives with increased Y:Al ratios.

The greater thermal expansion mismatch based on the properties of oxynitride glasses with greater Y:Al ratios could, then, be the major factor in the more rapid rise in the R-curve and the greater steady-state toughness observed in self-reinforced silicon nitrides prepared with the higher yttria to alumina additive ratios. We also find that the formation of SiAlON growth layer on the larger elongated grains does inhibit debonding; therefore, self-reinforced silicon nitrides that eliminate alumina as an additive might provide further improvements in the *R*-curve response.

CONCLUSIONS

Ceramics reinforced with microscopic rod-like phases can exhibit *R*-curves that rise rapidly with initial crack extension as well as high steady-state toughness values. Results show that the initial increase in the measured fracture resistance can become more substantial with increase in whisker content in SiC whisker-reinforced aluminas. In-situ observations indicate that the rising fracture resistance can be attributed to deflection of the crack tip and whiskers that bridge the crack tip wake. Both processes are enhanced with increase in whisker content resulting in the increase in fracture resistance for extension of small cracks. Increases in whisker diameter apparently generate similar effects probably by enhancing crack bridging.[9] The increase in fracture resistance with the extension of cracks beyond 300 μm in length with whisker content and diameter is dominated by frictional processes, e.g., pull-out and rotation.

Self-reinforced silicon nitride ceramics can also exhibit substantial *R*-curve behavior; however, this is not observed in all silicon nitrides containing larger elongated beta grains. Observations reveal that changes in the composition of the densification additives can modify the *R*-curve response. Specifically, increases in the yttria to alumina ratio are found to promote the initial rise in the fracture resistance as well as the resistance for continued crack extensions. Initial considerations indicate that this is likely due to changes in the residual thermal expansion mismatch stresses with boundary glass phase composition. However, separate studies reveal that when a SiAlON layer is formed during the growth of the reinforcing elongated grains interfacial debonding is inhibited. On the other hand, glass, hence additive, compositions that eliminate the formation of SiAlON interface layers promote debonding of the glass-beta silicon nitride interface and should, therefore, increase the rising fracture

---

[9] One should also consider that the strength of the whisker and the whisker-matrix interface could influence the observed whisker diameter effect as different sources of whiskers were used and each factor would alter the extent of crack bridging.

resistance of self-reinforced silicon nitride ceramics. Such interfacial debonding is necessary to activate the crack deflection and bridging processes that enhance the *R*-curve response.

ACKNOWLEDGMENTS

The authors thank Drs. K. Hirao and M. Brito of the National Industrial Research Institute-Nagoya for their assistance and the MITI Agency for International Science and Technology Fellowship (Japan) for KPP which supported his processing studies at NIRI-Nagoya to produce the silicon nitride ceramics. Drs. M. K. Ferber and H. T. Lin are thanked for reviewing the manuscript. Research is sponsored by the U.S. Department of Energy, Division of Materials Sciences, Office of Basic Energy Sciences, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation.

REFERENCES

1. P. F. Becher, C. H. Hsueh, P. Angelini and T. N. Tiegs, "Toughening Behavior in Whisker Reinforced Ceramic Matrix Composites," *J. Am. Ceram. Soc.*, 71, 1050 (1988).
2. E. Yasuda, T. Akatsu, and Y. Tanabe, "Influence of Whisker Shape and Size on Mechanical Properties of SiC Whisker-Reinforced Al_2O_3," *J. Ceram. Soc. Jpn.*, 99: 51-57 (1991).
3. P. F. Becher, C. H. Hsueh, K. B. Alexander, and E. Y. Sun, "Influence of Reinforcement Content and Diameter on the R-Curve Response in SiC-Whisker-Reinforced Alumina," *J. Am. Ceram. Soc.*, 79(2) 298-304 (1996).
4. C. H. Hsueh and P. F. Becher, "Some Considerations of Bridging Stresses for Fiber-Reinforced Ceramics,"*Compos. Engng.*, 1 [3] 129-143 (1991)
5. P. F. Becher,, "Microstructural Design of Toughened Ceramics," *J. Am. Ceram. Soc.*, 74, 255 (1991).
6. E. Y. Sun, C. H. Hsueh, and P. F. Becher, "R-Curve Response of SiC Whisker-Reinforced Alumina: Microstructural Influence," presented at the MRS Fall Meeting, Boston, MA., 1995.
7. K. Hirao, T. Nagaoka, M. E. Brito, and S. Kanzaki, "Microstructural Control of Silicon Nitride by Seeding with Rodlike β-Silicon Nitride Particles," *J. Am. Ceram. Soc.* 77(7) 1857-62 (1994).
8. T. Kawashima, H. Okamoto, H. Yamamoto, and A. Kitamura, "Grain Size Dependence of the Fracture Toughness of Silicon Nitride Ceramics," *J. Ceram. Soc. Japan*, 99: 1-4, (1991).
9. M. Mitomo, "Toughening of Silicon Nitride Ceramics by Microstructural Control,"pp. 101-07 in Proc. Science of Engineering Ceramics, S. Kimura & K. Niihara, eds., Ceram. Soc. Jpn, Tokyo, 1991.
10. a. Y. Tajima, K. Urashima, M. Watanabe, and Y. Matsuo, "Fracture Toughness and Microstructure Evaluation of Silicon Nitride Ceramics," pp. 1034-41 in Ceramic Transactions, Vol. 1: Ceramic Powder Science-IIB, G. L. Messing, E. R. Fuller, Jr., and H. Hausner (editors), Am. Ceram. Soc., Westerville, OH, 1988. b. Y. Tajima, "Development of High Performance Silicon Nitride Ceramics and Their Application," pp. 189-96 in MRS Proc., Vol. 287 : Silicon Nitride Ceramics-Scientific and Technological Advances, I. W. Chen, P.

F. Becher, M. Mitomo, G. Petzow, and T. S. Yen (eds), Materials Research Society, Pittsburgh, PA, 1993.

11. a. K. B. Alexander, P. Angelini, and P. F. Becher, Electron Microscopy of Interfaces in Silicon Carbide Whisker-Reinforced Alumina Composites," pp. 273-78 in High Resolution Electron Microscopy of Defects in Materials, R. Sinclair, D. J. Smith, and U. Dahmen (eds), Mater. Res. Soc. Proc. Vol. 183, Pittsburgh, PA, 1990. b. D. N. Braski and K. B. Alexander, "Auger Electron Spectroscopy Analysis of SiC-Whisker Surfaces and SiC-Whisker/Alumina Interfaces", *J. Mater. Res.*, 10(4) 1016–23 (1995).

12. P. F. Becher, E. Y. Sun, C. H. Hsueh, K. B. Alexander, S. L. Hwang, S. B. Waters, and C. G. Westmoreland, "Debonding of Interfaces Between Beta-Silicon Nitride Whiskers and Si-Al-Y Oxynitride Glasses," *Acta Metall.*, in press.

13. S. W. Freiman, D. R. Mulville, and P. W. Mast, "Crack Propagation Studies in Brittle Materials," *J. Mater. Sci.*, 8(11) 1527-33 (1973).

14. E. Y. Sun, P. F. Becher, S. W. Waters, to be published.

15. I. M. Peterson and T. Y. Tien, "Effect of Grain Boundary Thermal Expansion Coefficient on Fracture Toughness of Silicon Nitride," *J. Am. Ceram. Soc.*, 78(9) 2345-52 (1995).

16. E. Y. Sun, P. F. Becher, S. L. Hwang, and S. B. Waters, "Properties of Silicon-Aluminum -Yttrium Oxynitride Glasses," *J. Non-Cryst. Solids*, in press.