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# ALUMINA REINFORCED TETRAGONAL ZIRCONIA (TZP) COMPOSITES

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Department of Materials Science
University of Utah
Salt Lake City, Utah 84112

Dinesh K. Shetty
Professor Dinesh K. Shetty
Principal Investigator
[redacted]
Phone : (801) 581-6449

Office of Sponsored Projects
University of Utah

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# Abstract

This progress report / continuation proposal summarizes the significant research results obtained during the period February 16, 1994 through February 15, 1995 in the DOE-supported research project entitled, " Alumina Reinforced Tetragonal Zirconia (TZP) Composites ", and outlines research proposed for the period July 1, 1995 through June 30, 1996. The objective of the research is to develop high-strength and high-toughness ceramic composites by combining mechanisms of platelet, whisker or fiber reinforcement with transformation toughening. The approach being used includes reinforcement of ceria- or yttria-partially-stabilized zirconia (Ce-TZP or Y-TZP) with platelets, whiskers or continuous filaments of alumina. The important results obtained during the reporting period were the following : (a) Critical stresses for extension of filament-bridged matrix cracks were measured as a function of crack length in a model composite system, SiC (filament)-reinforced epoxy-alumina (matrix). The crack-length dependence of the crack-extension stress at short crack lengths followed the prediction of a fracture-mechanics analysis that employed a new force-displacement law for the crack-bridging filaments developed in this study. At large crack lengths, the measured matrix-cracking stress was close to the prediction of the steady-state theory of Budiansky, Hutchinson and Evans[1]. (b) An optical fluorescence technique was employed to measure stresses in crack-bridging sapphire filaments and assess interfacial properties in a model sapphire-epoxy composite. (c) Composites of yttria-partially-stabilized zirconia (Y-TZP) matrix dispersed with either single crystal $Al_2O_3$ platelets or particulates were fabricated by a hybrid suspension/powder processing route to densities greater than 99.0 % of theoretical. (d) Both transformation toughening and platelet reinforcement were shown to contribute to the high fracture toughness ($K_{Ic} \approx 8$ MPa$\sqrt{m}$) of the $Al_2O_3$ (platelet)-Y-TZP composites. The research proposed for the continuation period, July 1, 1995 through June 30, 1996, will include the following topics : (a) The fluorescence technique will be employed to measure in situ crack-closure forces in crack-bridging sapphire filaments in epoxy-alumina (matrix) composites. The closure force-crack-opening displacement relation assessed in these experiments will be compared with the new shear-lag model developed in this project. (b) The measurements of critical stress for extension of fiber-bridged matrix cracks will be extended to composites with increased volume fraction of SiC filaments and/or increased interfacial sliding resistance in the epoxy-alumina matrix. (c) The effects of increased platelet content and post-sinter hot-isostatic pressing on strength and fracture toughness of alumina-Y-TZP composites will be studied.

## Introduction

A research project entitled, " Alumina-Reinforced Tetragonal Zirconia Polycrystal (TZP) Composites " is being conducted at University of Utah under the research sponsorship of the Department of Energy, Basic Energy Sciences Division. Prof. Dinesh K. Shetty is the principal investigator of the project. The project objectives are to develop high-strength, high-toughness composites by combining mechanisms of platelet, whisker or fiber reinforcement with transformation toughening. The approach being used includes reinforcement of ceria- or yttria-partially-stabilized zirconia (Ce-TZP or Y-TZP) with single crystal platelets, whiskers or filaments of alumina. Alumina was chosen as the reinforcement phase for TZP ceramics based on considerations of chemical, phase and thermal expansion compatibility and elastic modulus difference. In platelet-reinforced composites, the research aims to develop pressureless sintering of the composites and to optimize the platelet volume and the stabilizer oxide contents to maximize the contributions of platelet toughening via crack deflection and transformation toughening in the TZP matrix. In whisker or filament-reinforced TZP composites, the research focusses on combining crack-bridging and pullout mechanisms with the transformation toughening. Theoretical studies of the mechanics of crack bridging and matrix cracking and experimental studies of the critical stress for extension of fiber-bridged cracks in model composites are important components of the research. The following paragraphs summarize the significant results obtained during the period February 16, 1994 through February 15, 1995. These research results are discussed in greater detail in reprints or preprints of technical papers that are attached to this progress report/proposal as appendices. A proposed plan of research to be conducted during the continuation period (July 1, 1995 through June 30, 1996) will follow the progress report.

## Progress Report

The following paragraphs briefly describe significant research accomplishments in the respective areas :

### *(1) Critical Stresses for Extension of Filament-Bridged Matrix Cracks in SiC (Filament)-Reinforced Epoxy-Alumina (Matrix) Composites.*

The principal investigator (Prof. Dinesh K. Shetty) and one of his former graduate students (Dr. Sawai Danchaivijit) have developed a new theoretical analysis for calculating the critical stress for extension of fiber-bridged matrix cracks in brittle-matrix composites[2]. The technical paper that describes the theoretical analysis is attached to this progress report as Appendix A. In summary, the theory models the critical stress for extension of fiber-bridged matrix cracks by calculating the effective stress intensity under combined far-field applied stress and crack-closure tractions of the bridging fibers. The crack-closure traction was modeled for the case of unbonded fiber-matrix interface characterized by a constant sliding friction stress using a shear-lag analysis.

An experimental study was undertaken during the reporting period to test the validity of the theoretical model using a model composite system : SiC (filament)-reinforced epoxy-bonded alumina. This particular system was chosen because unidirectional composite test coupons (5 x 25 x 100 mm) with controlled, fiber-bridged through cracks could be fabricated by a novel, two-step casting process. Details of this technique are described in a technical paper currently in press with the Journal of the American Ceramic Society. The paper is attached to this report as Appendix B. In summary, the technique involved low-temperature bonding of a composite specimen with a matrix crack with two new uncracked sections cast with the epoxy/alumina matrix in SiC filament preforms. The fiber surface was coated with a releasing agent to ensure unbonded, frictional interface. The alumina filler reduced the volume shrinkage of the epoxy, thus reducing both the tensile residual stress in the matrix as well as the clamping stress on the fibers.

Figure 1 summarizes the measurements of the critical stresses for extension of filament-bridged cracks in 4 v% SiC (filament)-reinforced epoxy/alumina composite as a function of the crack size (filled circles). Critical extension stresses for cracks in the unreinforced matrix are also shown on the figure (open circles). These data were used to estimate a matrix fracture toughness, $K_{cm} = 0.86$ MPa$\sqrt{m}$. The prediction of the stress-intensity analysis, solid line in Figure 1, showed good agreement with the experimental measurements on the composite specimens. The theoretical prediction required independent estimates of the sliding friction stress at the interface, $\tau$, and the residual stress in the matrix, $\sigma_m{}^I$, in addition to $K_{cm}$. The sliding friction stress and the matrix residual stress were measured by a filament pushin test technique described by Marshall and Oliver[3]. These experiments were conducted in collaboration with J. Eldridge at NASA Lewis Research Center. Also shown on Figure 1 is the prediction of the Budiansky, Hutchinson and Evans theory (BHE)[1]. It is evident that the BHE theory, being based on a steady-state energy balance analysis, gives a good lower-bound estimate of the crack-extension stress for long fiber-bridged cracks.

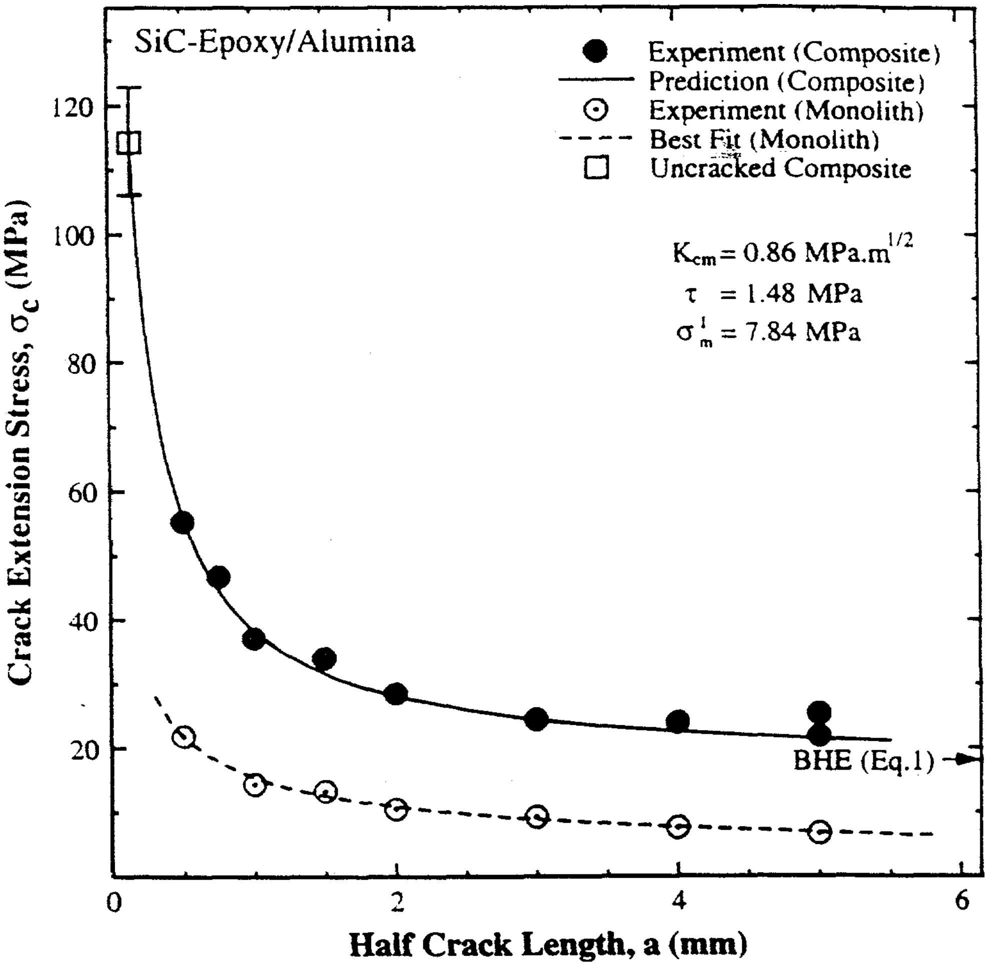

Figure 1. Crack-extension stresses for center cracks in uniaxial tension test specimens of the epoxy-alumina monolith and SiC(filament)-reinforced epoxy-alumina composite.

### *(2) Application of Fluorescence Spectroscopy in Micromechanics Studies of Brittle-Matrix Composites .*

The central element of the new theory of matrix cracking described in Appendices A and B is the development of a new crack-closure force-crack-opening displacement relation for crack-bridging fibers in composites with unbonded, frictional interfaces. The specific force-displacement relation was developed using a shear-lag theory that assumes unbonded interfaces characterized by constant sliding friction stress. An experimental study was initiated to examine the validity of this shear-lag analysis. The objective of this study was to measure stresses in a crack-bridging fiber as a function of position relative to the crack plane, i.e., examine the stress transfer problem, as well as measure stresses in fibers at different locations on the crack surface, i.e., examine the closure traction distribution. For this purpose, an optical fluorescence technique was applied to composites reinforced with single crystal sapphire filaments[4]. Sapphire crystals exhibit characteristic fluorescence lines due to chromium impurity (see Figure 2). The frequency of these fluorescence lines shift on application of a stress as demonstrated in the data of Figure 3. Fluorescence spectroscopy can be implemented with an optical microprobe and a laser source. The frequency shift in Figure 3 was calibrated by applying known amounts of force in a filament loading device. The advantage of the technique is its high spatial resolution made possible with the small laser probe (~ 5 μm) and the high intensity of the fluorescence peaks.

Figure 4 shows a plot of the stress in a crack-bridging sapphire filament in an epoxy-matrix composite as a function of distance from the crack plane in a steady-state crack specimen (i.e., a specimen with a matrix crack extending completely through the cross section). The measurements were made on a uniaxial tension specimen subjected to a far-field stress of 20.5 MPa. The solid line through the data points corresponds to the following equations derived from shear-lag analysis (see BHE[1]) for the case of constant sliding friction stress along a sliding interface length, $l_s >> R$, the filament radius :

For $0 < z < l_s$,

$$\sigma_f(z) = \frac{\sigma}{V_f} - 2\tau\frac{z}{R} \tag{1}$$

and for $z > l_s$,

$$\sigma_f(z) = \sigma\frac{E_f}{E_c} + \sigma_f^I \tag{2}$$

In Eqs.(1) and (2), $\sigma_f(z)$ is the stress in the filament at a distance z from the crack plane, $\sigma$ is the far-field applied stress, $V_f$ is the volume fraction of the filaments, R is the fiber radius, $E_f$ and $E_c$ are the filament and the composite modulus and $\sigma_f^I$ is the initial residual stress in the filament in the composite. $l_s$, the sliding length of the filament is defined by the following equation :

$$l_s = \frac{\left|\left\{\sigma - \sigma_f^I\left(\frac{E_c V_f}{E_m V_m}\right)\right\}R\right|}{2(1+\eta)\tau V_f} \tag{3}$$

where $\eta = (E_f V_f / E_m V_m)$ and $E_m$ and $V_m$ are the elastic modulus and the volume fraction of the matrix in the composite, respectively. The 'best fit' values of $\tau$ and $\sigma_f^I$ estimated by fitting Eqs.(1) through (3) to the data of Fig.4 were $\tau = 1.33$ MPa and $\sigma_f^I = -70$ MPa, respectively. This research task has proven the feasibility of employing fluorescence spectroscopy for micromechanics studies in brittle-matrix composites.

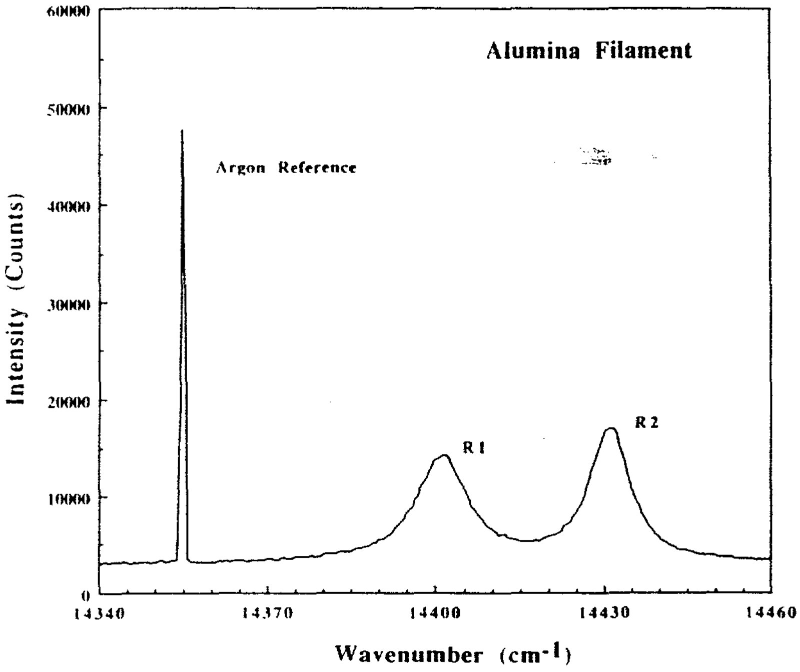

Figure 2. Chromium fluorescence lines from a sapphire single crystal filament activated with a laser microprobe.

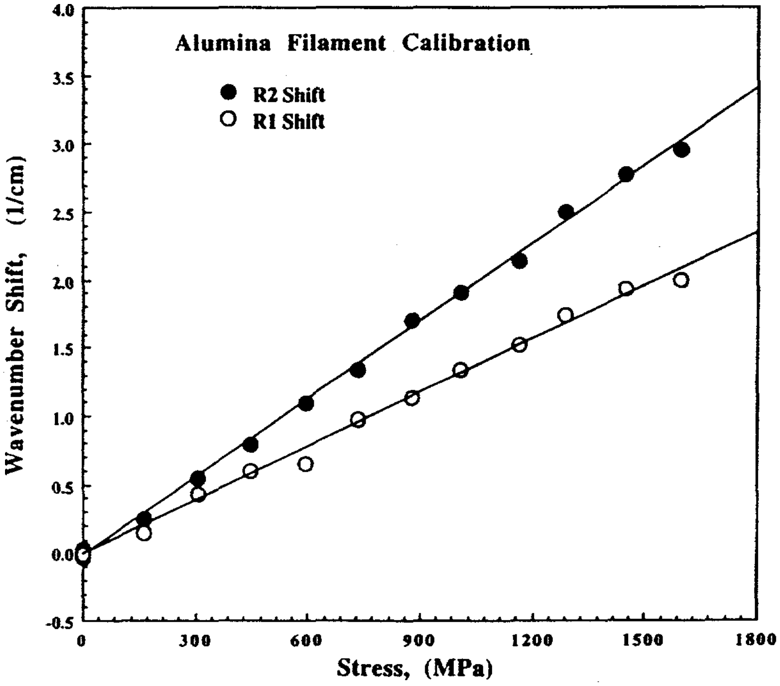

Figure 3. Shift in the frequency of the chromium fluorescence lines with stress applied to a single crystal sapphire filament.

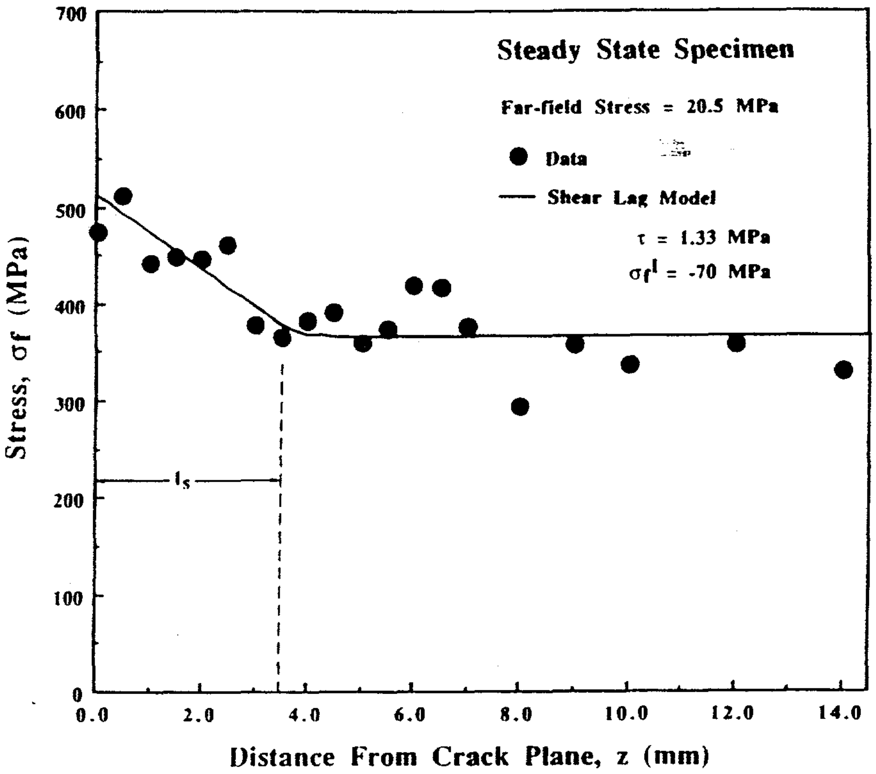

Figure 4. Stress in a crack-bridging filament as a function of distance from a steady-state crack in a sapphire (filament)-reinforced epoxy (matrix) composite.

*(3) Processing and Optimization of the Alumina (Platelet)-Reinforced Y-TZP (Matrix Composites.*

The recent availability of $Al_2O_3$ in the form of single crystal platelets has generated interest in their use as reinforcement for ceramic matrices, particularly oxide ceramics[5-7]. Theoretical considerations of toughening by such mechanisms as crack deflection indicate that dispersed phases in the form of platelets are not as effective as whiskers with high aspect ratio, but they can be more effective than equiaxed particles[8]. Use of platelets as reinforcing phase is also motivated by the lower cost and less concern for adverse health effects as compared to whiskers.

The challenge in the processing of platelet-reinforced ceramic composites, as it is in whisker-reinforced composites, is to achieve high density by pressureless sintering. This was accomplished in the present study by a hybrid suspension/powder processing route that was based in part on recent developments in colloidal processing of $Al_2O_3$-$ZrO_2$ composites[9,10]. The processing steps included dispersing the Y-TZP powder (mixtures of grades HSY-2.6 and DK-I, Zirconia Sales (America), Inc., Marietta, GA) and α-$Al_2O_3$

platelets (Grade T1, Elf Atochem, France) or particulates (Grade Baikalox CR-30, Baikowsky International, Charlotte, NC) separately in deionized water (60 w % of solids) at a low pH (~ 2.5) by ball milling, separating large, hard agglomerates in the Y-TZP powder by settling and decanting, mixing the two suspensions and final ball milling for 2 hours. The milled suspension was sieved through 75 μm screen, the pH raised to 5.5 and then allowed to settle. The clear water was decanted and the sediment was dried first in air at room temperature (23 °C) and then in an oven. The dry sediment was crushed, sieved through 75 μm screen, uniaxially die pressed to form compacts at 50 MPa pressure and isostatically cold pressed at 200 MPa. The compacts were, then, sintered in air at 1450 °C for 2 hours.

The research during the reporting period was focussed on resolving two issues : (a) Are single crystal $Al_2O_3$ platelets superior to alumina particulates in toughening and/or strengthening Y-TZP matrix ? (b) Is there an optimum $Y_2O_3$ content in Y-TZP to realize the maximum benefit of combined toughening from platelet reinforcement and transformation toughening ?. To address these two issues three classes of materials with varying $Y_2O_3$ content were processed using the above-described procedure : monolithic Y-TZP, Y-TZP+10v% $Al_2O_3$ platelets and Y-TZP+10v% $Al_2O_3$ particulates. The $Y_2O_3$ content was varied in the range 1.8 to 2.6 m% by mixing appropriate amounts of pure $ZrO_2$ and 2.6 Y-TZP powders. The thickness and in-pane dimension of the single crystal $Al_2O_3$ platelets were in the ranges 0.5-1 and 5-10 μm, respectively. Most of the crystals had a hexagonal shape. The $Al_2O_3$ particulates had a median particle size between 0.4 and 0.5 μm. The sintered monolithic Y-TZPs and the Y-TZP/$Al_2O_3$ composites were characterized for density, microstructure, initial phase content, mechanical properties (fracture toughness, $K_{Ic}$, and fracture strength, $\sigma_f$) and phase content on the fracture surface.

Figures 5A through 5C show representative microstructures of 2.2Y-TZP monolith, 2.2Y-TZP+10v% $Al_2O_3$ particulate composite and 2.2Y-TZP+10v% $Al_2O_3$ platelet composite, respectively. The properties of the three materials are listed in Table 1. All the three materials sintered to high densities at the modest sintering temperature of 1450 °C. The grain sizes were comparable with only the particulate composite showing a moderate grain-growth inhibition due to the dispersed phase. An interesting result in Table 1 is the initial phase contents of the materials. Monolithic Y-TZP was 100 % tetragonal. In the particulate composite, the initial tetragonal content dropped to 93 v%. In the platelet composite, the tetragonal content was significantly lower at 77 v%. Thus, the platelets promoted the tetragonal to the monoclinic transformation of zirconia.

Figure 5. Microstructures of (A) 2.2 Y-TZP monolith, (B) 2.2Y-TZP+10v% $Al_2O_3$ (particulates) and (C) 2.2Y-TZP+10v% $Al_2O_3$ (platelets) sintered at 1450 °C for 2 hours.

Table 1. Properties of 2.2Y-TZP monolith, 2.2Y-TZP+10v% $Al_2O_3$ (particulate) composite and 2.2Y-TZP+10v% $Al_2O_3$ (platelet) composite sintered at 1450 °C for 2 hours.

| Property | 2.2Y-TZP | 2.2Y-TZP+10v% $Al_2O_3$ Particulates | 2.2Y-TZP+10v% $Al_2O_3$ Platelets |
|---|---|---|---|
| Density (% Theoretical) | 99.5 | 99.2 | 98.5 |
| Grain Size (μm) | 0.74 | 0.65 | 0.73 |
| Phase Content (v% tetragonal) | 100 | 93 | 77 |
| Fracture Strength | | | |
| $\sigma_\theta$ (MPa) | 1212 | 954 | 923 |
| m | 13.6 | 9.6 | 17.3 |
| Fracture Toughness (MPa√m) | 6.59 ± 0.03 | 6.17 ± 0.07 | 7.52 ± 0.08 |

Table 1 also shows that the platelet composite had the highest fracture toughness and a fracture strength comparable to that of the particulate composite. To understand the origin of this toughness enhancement the fracture toughness of both the monolith and the composites were assessed as functions of $Y_2O_3$ content in the Y-TZP matrix. These results are summarized in Figure 6. The fracture toughness of all three material classes increased with decreasing $Y_2O_3$ content beginning at 2.6 m%. In the composition range 2.2 to 2.6 m% of $Y_2O_3$, the platelet composites had roughly the same increase in fracture toughness of about 1 MPa√m relative to the Y-TZP monoliths. The particulate composites had lower fracture toughness as compared to the monoliths. The optimum $Y_2O_3$ contents for maximum fracture toughness were, however, different for the three material classes. The platelet composite had the highest fracture toughness at 2.2 m% $Y_2O_3$ and the fracture toughness decreased at lower $Y_2O_3$ content. For the particulate composites, the optimum $Y_2O_3$ content was lower at 2.0 m%. The Y-TZP monoliths had the highest fracture toughness at even lower $Y_2O_3$ content of 1.9 m%. These trends reflect the different amounts of the stabilizer required for optimum stability of the tetragonal phase in the presence of destabilizing dispersed $Al_2O_3$.

A critical issue in this study was the origin of the fracture toughness of the platelet composites; i.e., whether it was entirely due to transformation toughening or a second mechanism contributed to the fracture toughness. Since the contribution of transformation toughening is governed by the stress-induced change in the volume fraction of the monoclinic $ZrO_2$ phase, the fracture toughnesses of the platelet composites and of the Y-TZP monoliths were correlated with $\Delta V_m$, the difference in the monoclinic contents on the fracture surface and in the as-sintered condition in the bulk. Such correlations for the platelet composites and for the Y-TZP monoliths are shown in Figure 7. It is interesting to note in Figure 7 that the $K_{Ic}$ versus $\Delta V_m$ plot for the platelet composites is shifted to higher toughness as compared to the plot for the Y-TZP monoliths. This is a strong indication that a secondary mechanism was operating in the platelet composites. In fact, at the same $Y_2O_3$ content the platelet composites had smaller stress-induced change in the monoclinic content than the Y-TZP monoliths. In other words, at the same $Y_2O_3$ content the platelet composites had smaller contribution of transformation toughening. Thus, the platelets suppressed transformation toughening, but increased the contribution of a secondary mechanism of toughening. A technical paper entitled, " Processing and Characterization of Alumina (Platelet) Reinforced Y-TZP (Matrix) Composites " was published in Ceramic Transactions, Volume 38, pp.461-71(1994). A reprint of this paper is attached to this progress report/proposal as Appendix C.

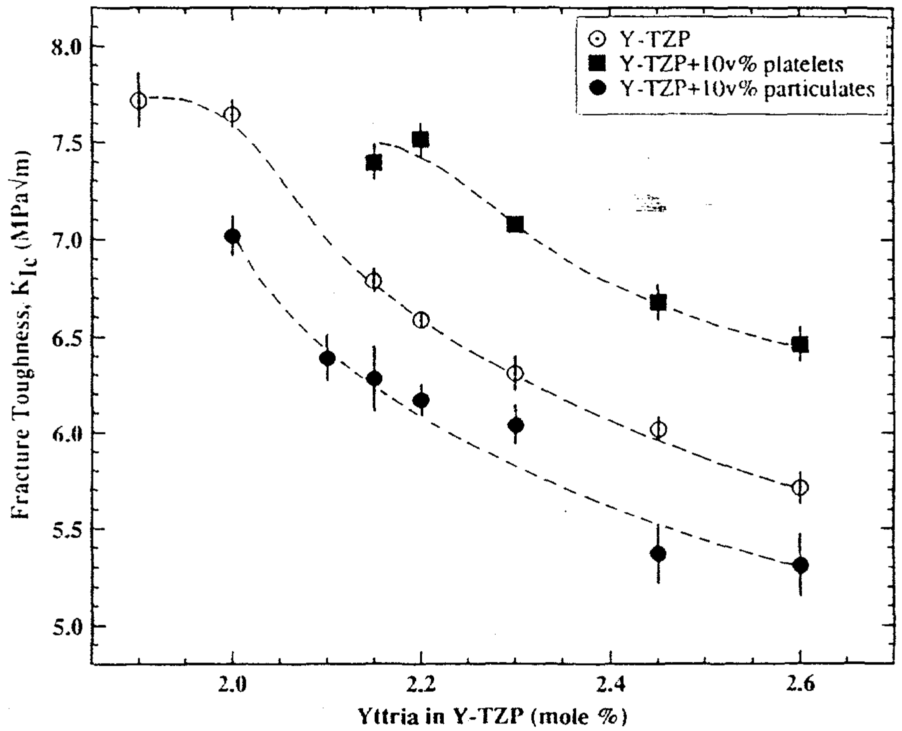

Figure 6. Effect of $Y_2O_3$ content on the fracture toughness of Y-TZP monoliths, Y-TZP+10v% $Al_2O_3$ (platelet) composites and Y-TZP+10v% $Al_2O_3$ (particulate) composites.

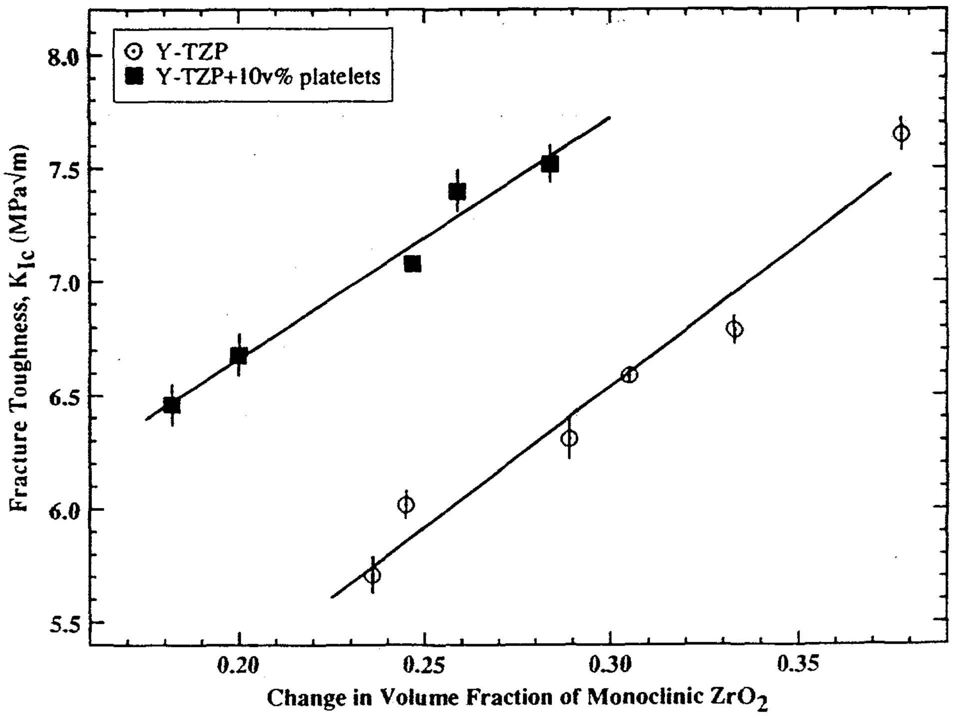

Figure 7. Correlations of fracture toughness and change in monoclinic content on the fracture surface for Y-TZP monoliths and Y-TZP+10v% $Al_2O_3$ (platelet) composites.

## List of Publications

The following publications have resulted so far from research supported by this project :

1. D. K. Shetty, " Shear-Lag Analysis of Fiber Pushout (Indentation) Tests for Estimating Interfacial Friction Stress in Ceramic-Matrix Composites ", *J. Am. Ceram. Soc.*, **71** [2] C-107-C-109 (1988).
2. D. K. Shetty and J. S. Wang, " On Crack Stability and Strength Distribution of Ceramics That Exhibit Rising Crack-Growth-Resistance (R-Curve) Behavior ", *J. Am. Ceram. Soc.*, **72** [7] 1158-62 (1989).
3. J. D. Bright, D. K. Shetty, C. W. Griffin and S. Y. Limaye, " Interfacial Bonding and Friction in Silicon Carbide (Filament)-Reinforced Ceramic- and Glass-Matrix Composites ", *J. Am. Ceram. Soc.*, **72** [10] 1891-98 (1989).
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5. J. S. Wang, D. K. Shetty and A. V. Virkar, " Effect of MnO on the Microstructures, Phase Stability and Mechanical Properties of Ceria-Partially-Stabilized Zirconia (Ce-TZP) and Ce-TZP-$Al_2O_3$ Ceramics ", *J. Mater. Res.*, **5** [9] 1948-57 (1990).
6. S. Gochnour, J. D. Bright, D. K. Shetty and R. A. Cutler, " Solid Particle Erosion of SiC-$Al_2OC$ Ceramics ", *J. Mater. Sci.*, **25**, 3229-35 (1990).
7. J. D. Bright, S. Danchaivijit and D. K. Shetty, " Interfacial Sliding Friction in SiC-Borosilicate Glass Composites : A Comparison of Pullout and Pushout Tests ", *J. Am. Ceram. Soc.*, **74** [1] 115-22 (1991).
8. C-H. Hsueh, J. D. Bright and D. K. Shetty, " Interfacial Properties Of SiC-Borosilicate Glass Composites Evaluated From Pushout and Pullout Tests ", *J. Mater. Sci. Lett.*, **10**, 135-38 (1991).
9. J. F. Tsai, C. S. Yu and D. K. Shetty, " Role of Autocatalytic Transformation in Zone Shape and Toughening of Ceria-Tetragonal-Zirconia-Alumina (Ce-TZP/$Al_2O_3$) Composites ", *J. Am. Ceram. Soc.*, **74** [3] 678-81 (1991).
10. N. Ramachandran and D. K. Shetty, " Rising Crack-Growth-Resistance (R-Curve) Behaviors of Toughened Alumina and Silicon Nitride ", *J. Am. Ceram. Soc.*, **74** [10] 2634-41 (1991).

11. J. F. Tsai, U. Chon, N. Ramachandran and D. K. Shetty, " Transformation Plasticity and Toughening in $CeO_2$-Partially-Stabilized Zirconia-Alumina (Ce-TZP/$Al_2O_3$) Composites ",*J. Am. Ceram. Soc.*, 75 [5] 1229-38 (1992).
12. N. Ramachandran, L. Y. Chao and D. K. Shetty, " R-Curve Behavior and Flaw Insensitivity of Ce-TZP/$Al_2O_3$ Composite ", *J. Am. Ceram. Soc.*, **76** [4] 961-69 (1993).
13. N. Ramachandran and D. K. Shetty, " Prediction of Indentation Load Dependence of Fracture Strengths From R-Curves of Toughened Ceramics ", *J. of Mater. Sci.*, **28**, 6120-126 (1993).
14. S. Danchaivijit and D. K. Shetty, " Matrix Cracking in Ceramic-Matrix Composites ", *J. Am. Ceram. Soc.*, **76** [10] 2497-504 (1993).
15. S. Dey and D. K. Shetty, " Processing and Characterization of Alumina (Platelet) Reinforced Y-TZP (Matrix) Composites ", *Ceramic Transactions*, Vol.38, pp.461-71 (1994).
16. D. K. Shetty, " Overview of Design Methodology for Ceramic-Matrix Composites ", Chapter 13, Handbook on Continuous Fiber Reinforced Ceramic Matrix Composites, DoD Ceramics Information Analysis Center (1994).
17. S. Danchaivijit, D. K. Shetty and J. Eldridge, " Critical Stresses for Extension of Filament-Bridged Matrix Cracks in Ceramic-Matrix Composites : An Assessment With A Model Composite With Tailored Interfaces " (In Press) *J. Am. Ceram. Soc.*, January (1995).
18. S. Danchaivijit, L-Y. Chao and D. K. Shetty, " Matrix Cracking in Model Brittle-Matrix Composites With Tailored Interfaces "; pp. in *Ceramic Matrix Composites*, R. A. Lowden, J. R. Hellman, M. K. Ferber, S. G. DiPietro and K. K. Chawla (Eds.), Materials Research Society Symp., (In Press) (1995).