OXIDE FIBER-COATINGS FOR CONTROLLED FRACTURE IN ROBUST CERAMIC COMPOSITES

R. J. Kerans, T. A. Parthasarathy*, R. S. Hay, E. E. Boakye*,
K. A. Keller*, T. Mah* and M. K. Cinibulk

Air Force Research Laboratory, Materials and Manufacturing Directorate
AFRL/MLLN, Wright-Patterson AFB, OH 45433-7817
(*UES Inc., Dayton OH under AFRL contract)

ABSTRACT

There has been significant recent progress in the development of new fiber coatings to promote crack deflection and distributed damage mechanisms in ceramic composites. There is now definitive proof that oxide coatings can provide good composite behavior in real composites. Research to deduce viable approaches to the controlled-fracture-coating problem has uncovered other intriguing aspects of fracture behavior of constituents and composites. The evaluation of oxide based approaches required developing viable coating processes and solving pervasive problems with fiber degradation apparently due to previously unknown stress-corrosion effects. Microcomposite testing revealed interesting, potentially revealing and useful effects on fracture statistics. Finally, evidence of the desired crack deflection and beneficial effects on composite behavior are presented, and the surprising role of plasticity is briefly discussed.

KEYWORDS

coating, oxide, fiber, interface, interphase, pullout, fracture, composite

INTRODUCTION

The development of tough composites made of brittle constituents necessitates a higher degree of control of fracture processes than generally required. Fracture is most often an event to be avoided by all possible means, and once it happens the details are not so important. In other cases, while the fracture is to be avoided, it is desirable for a failure to occur in a relatively benign fashion, and design effort is devoted to that end. Examples include safety glass, containment of turbine engines, and shear connections on road signs. There are also examples of designed fracture behavior, such as perforated sheets, tamper resistant plastic and metal screw tops, pull tabs openers, snap-off knife blades, and a variety of forms of tamper-resistant medicinal packages. However, the design of structural materials such that the sequence of fracture events and crack paths are predetermined on a microstructural level pushes hard on the limits of our understanding of the details of crack initiation and propagation.

The basic requirement for a tough composite comprising brittle constituents is that cracks that initiate in the matrix not propagate into fibers but bypass them by deflecting into fiber-matrix debonding cracks. This requires that something in the fiber-matrix interfacial region -- an interface, a fiber coating, or the near-fiber-surface region of the matrix -- be sufficiently weak to fail before the fiber fails. It is important to note the "sufficiently weak" means sufficiently weak relative to the fiber in the finished composite. This is important because virtually all processes have some effect on the strength of the fiber. The actual crack path is the result of a competition between fracture in the fiber, coating and matrix. C and BN have unusual combinations of properties that make them ideal choices for fiber coatings, except for oxidation resistance. The design of oxide substitutes is a significant challenge. See Refs. [1] and [2] for reviews.

The development of new fiber coatings has been greatly complicated by effects of processes on fiber properties, both in terms of direct process constraints and in terms of interpretation of composite behavior. Of the two coatings discussed here, monazite ($LaPO_4$) appears to be practically useful, while hibonite ($XAl_{12}O_{19}$) can not be processed at sufficiently low temperature to avoid damaging currently available, compatible polycrystalline fibers. Three interesting facets of fracture behavior in constituents and composites are briefly addressed. The first of these involves severe fiber degradation during coating, apparently by a stress-corrosion mechanism, and the eventual successfully modified process. The second involves fracture statistics of monofilament fibers with and without coatings and matrices applied. Finally, an example of successful use of oxide coatings in actual composites, with considerable improvement in high temperature life, is presented. The surprising discovery of low temperature plasticity in the oxide coatings is briefly discussed.

FIBER STRENGTH DEGRADATION

The strengths of monazite coated fibers were found to be highly dependant on the characteristics of the monazite precursor used for coating (Table 1). The sol eventually found to be benign to the fiber, Precursor 3, was purified by centrifugal separation of the sol particles from nitric acid solution and re-dispersed in deionized water. The pH of the purified sol was 3. A continuous vertical coater was used in all the coating experiments. [3]

Table 1

MONAZITE PRECURSORS USED FOR FIBER COATINGS

Precursor Number	Lanthanum Source	Phosphate Source
1. Aqueous solution	$La(NO_3)_3$	$(OCH_3)_3PO_4$
2. Aqueous sol	$La(NO_3)_3$	$(NH4)_4HPO_4$
3. Aqueous sol	$La(NO_3)_3$	H_3PO_4

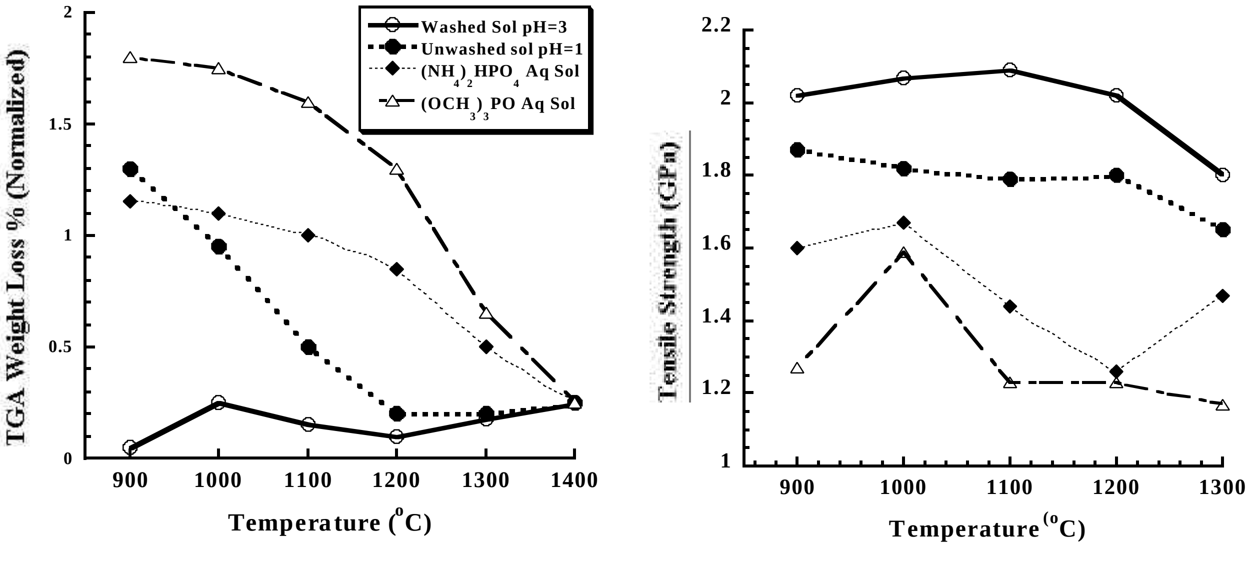

Fig. 1 a) TGA weight loss from different precursors. b) Effect of monazite precursors on fiber strength.

Evidence for stress corrosion comes from comparison of weight loss in different monazite precursors to the strengths of fibers coated with these precursors (Fig. 1). [4, 5] Fibers coated with precursors with high weight loss had low strength (Precursors #1 and #2). Fibers coated with precursors with low weight loss (Precursor #3) had the highest strengths. Filament strengths were also high after Nextel^{TM} 610, Tyranno-SA, Hi-Nicalon, Hi-Nicalon-S and Sylramic were coated with precursor #3.

Degradation at a particular temperature correlated with the amount of gas-phase decomposition products that remained in the coating at that particular temperature. [4] Partial pressures of precursor decomposition products in coating pores may be significantly higher than atmospheric pressure, and therefore enhance the activity of a corrosive species if the coating is hermetic. Coatings with high pore volume fraction will generally not be hermetic; the open porosity will provide escape pathways for the out-gassing species. Coatings made from precursor #3 were also the most porous; this may also account for higher coated fiber strength.

MICROCOMPOSITE FRACTURE TESTS

Axisymmetric cylinders of oxide/oxide microcomposites were fabricated and tested in tension to evaluate the effectiveness of monazite ($LaPO_4$) and hibonite ($CaAl_{12}O_{19}$) as interlayers (0.3 to 0.5 μm) in sapphire monofilament-reinforced alumina matrix composites. [6]

Fractography

The fractured surfaces of the control specimens (uncoated fiber in a matrix) showed that the fracture in the matrix and in the fiber are coplanar. Fracture surfaces of the hibonite-coating-microcomposites reveal short deflections in the coating resulting in steps to the fiber surfaces. The step is attributable to the easy-cleaving hibonite deflecting the crack, but there is no indication of a dominant debond crack; multiple deflections occur within the hibonite coating. The fracture surfaces of the monazite containing composites showed extensive evidence for crack deflection. The matrix cracks were periodic along the length of the fiber, with spacing in the neighborhood of a millimeter. When the exposed interface region was examined at higher magnifications, it was found that the debonding occurred at the matrix/monazite interface

Strengths and Weibull Moduli of Fibers, Coated Fibers and Microcomposites

All the specimens tested exhibited a linear load-displacement relationship until failure. The only quantitative parameter that can be used for evaluation is the reference stress and Weibull modulus of the ultimate failure load of the fibers and microcomposites. All loads were divided by the fiber cross-sectional area for comparison and the strengths thus calculated were plotted on a Weibull distribution. Figure 2a shows the strength of the control and monazite-coated microcomposites compared with each other and the respective fiber strengths. Figure 2b is the same plot for fibers and microcomposites with hibonite as the coating or interlayer. All of the fiber strength results are for fibers that were tested after they were given a heat treatment at 1450°C for 2 hrs to simulate the heat treatment used to sinter the matrix. Hibonite appears to degrade the fiber slightly while monazite has little effect; however in both coated fibers the Weibull modulus is much enhanced. From Fig. 2a, it is seen that the strengths of both composites are lowered after the matrix processing and the average strengths are not significantly different. However the monazite-coated composites have much-improved Weibull modulus. Essentially the same result was obtained for the hibonite coated composites, Fig. 2b. Since the monazite composites showed significant debonding, the lack of difference in strength between the control and monazite-coated composite is puzzling. To determine if this is due to having a poor matrix density, a second set of control and monazite-coated samples were sintered at 1500°C for 2 hrs to improve the matrix density. There was only a marginal improvement in the matrix density and essentially the same result was obtained (Fig. 2c) with some loss in strength, which can be easily rationalized as due to loss of fiber strength following the 1500°C heat treatment.

Discussion of Microcomposite Behavior

In the case of monazite, microstructures of fractured microcomposites show clear evidence for debonding at the coating/matrix interface confirming that the interface between monazite and the matrix alumina is sufficiently weak to debond under axial loading of the composite in tension. Fractographs of hibonite-containing composites show evidence for crack deflection but the debond crack is not sustained beyond a few micrometers.

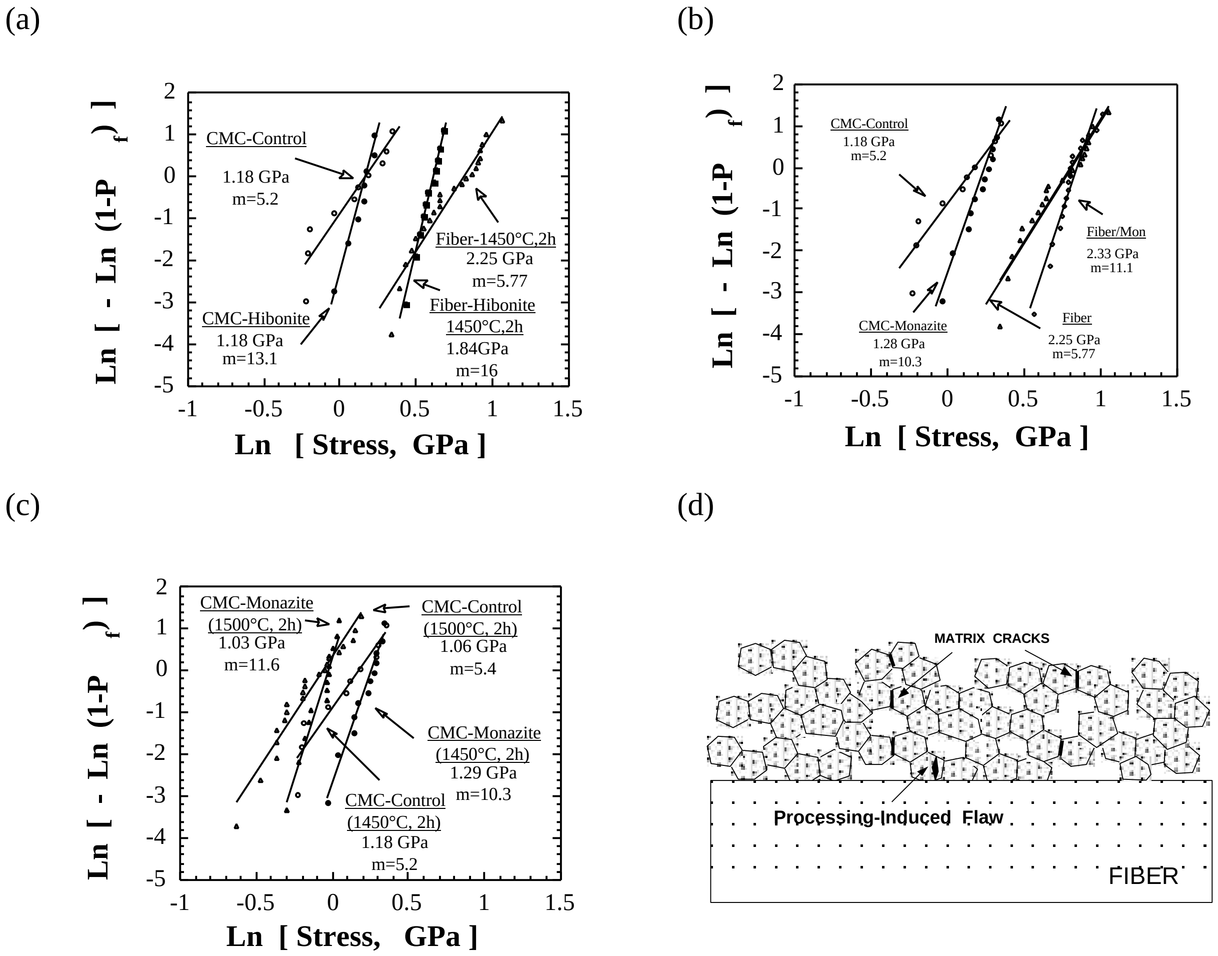

Figure 2: Weibull plot of the fracture stresses of monofilaments, and monofilaments with matrices around them (micro-CMCs) are shown for the cases of (a) hibonite and (b) monazite as interlayers. Uncoated filaments and control micro-CMCs are shown for comparison. (c) The same experiments as in (b) but with the matrix fired at higher temperature shows that the results are essentially the same. (d) A schematic of a plausible mechanism for the protection of a fiber from cracks in a porous matrix. [6]

The only positive indication in either case relative to the control specimens was a substantial increase in Weibull modulus and its retention in the final microcomposites. The effects on Weibull modulus and mean strength of both coating and matrix are not simply resolvable with a definitive model; an extensive discussion appears in Ref. [6]. Nevertheless, the beneficial effect of the coating on the strength statistics (in the monazite case) combined with the fractographic evidence is postulated to support earlier work [7] in indicating proper functioning of the coating. The scenario imagined is that mode I cracks deflect into debonding cracks in the desired fashion and that the coating serves to bridge the larger fiber flaws by way of the same mechanism in reverse, leading to the observed increase in Weibull modulus.

OXIDE COATINGS IN COMPOSITES

The effectiveness of monazite coatings in actual composites was evaluated using a Nextel™ 610 reinforced alumina system. [8] Composites containing either uncoated or monazite-coated fiber displayed satisfactory strengths after sintering at 1100°C/5 hours in air. At this degree of consolidation, the matrix is quite porous (composite porosity ~30 – 35%) and the control composites behave as porous-matrix composites that do not require a fiber coating to deflect cracks; the debond occurs via matrix failure at the fiber surface. (See for example [9]) The control specimens (uncoated fiber) exhibited an average strength of 168 MPa, while specimens reinforced with monazite-coated fibers displayed a much higher average strength of 230 MPa. The fracture surfaces of both the uncoated and monazite-coated samples sintered at 1100°C showed “woody” type failures, with some bundle pullout.

After sintering for a short time (5 hours) at 1200°C, there was a distinct difference between the behavior of the uncoated and the monazite-coated composites (Table 2). The samples containing uncoated fibers displayed drastic strength losses of >70%, resulting in an average strength of 45 MPa, with approximately 0.03% strain. Such a decrease is typical of porous-matrix composites and is generally attributed to sintering of the matrix to a degree that suppresses debonding via matrix failure. [9] Conversely, the samples containing monazite-coated fiber showed a strength decrease of only ~14% to an average of 198 MPa. Stress-strain curves for the monazite-containing specimens revealed strain-to-failure values ranging from 0.25 – 0.4%. This indicates that there is a definite advantage to incorporating monazite coatings in the composite. The samples containing uncoated fiber exhibited brittle-type fracture surfaces, while the monazite-containing samples showed distinct fiber pullout, along with woody-type fracture.

Table 2

MEASURED COMPOSITE STRENGTHS AFTER NORMALIZING TO 20 VOL.% FIBER COMPOSITE

Sample Nextel™610//Alumina	**1100°C/5 h (initial process)**	**1200°C/5 h**	**1200°C/100h**
Control (no coating)	168 (±33)	45 (±20), 0.03%	-
Monazite	230 (±18)	198 (±12), 0.27%	143 (±7), 0.22%

The fracture surfaces of the monazite-coated samples indicated that debonding occurred in the region bounded by the matrix surface and the fiber surface. Preliminary indications suggest that the debonding crack tends to run in the coating near the fiber surface or at the coating/fiber interface, though this has not been thoroughly examined. Figure 3 shows a back-scattered image of the fracture surface of a specimen sintered at 1200°C/5 h. The bright areas visible in the fiber trough and on the fiber surface are the monazite coatings.

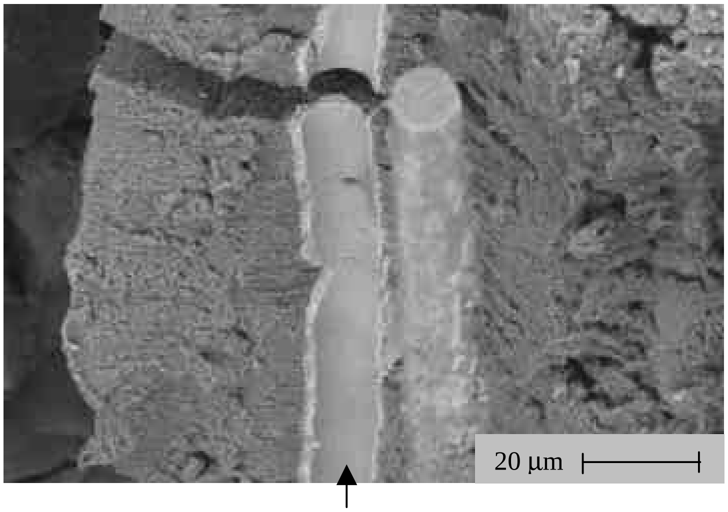

Figure 3: Back-scattered image of a fiber trough on the fracture surface of Nextel™ 610/monazite/alumina composite. Bright areas are monazite coatings. Coatings evident both in the trough and on the fiber surface in the foreground of the image.

Similar features were seen on the fracture surfaces of monazite-containing samples after heat treatment at 1200°C for 100 hours. There appeared to be a decrease in the amount and length of fiber pullout on the fracture surface. The strength decreased 38% from the as-processed value bringing the average strength to 143 MPa, with ~0.22% strain. This is markedly superior to control specimens exposed for only 5 hours at 1200°C. It is apparent that the monazite coating performs the crack deflection–debonding function and truly provides protection for the fibers in an actual composite. Manipulation of the monazite coating characteristics, such as thickness and uniformity, will allow for optimization of composite properties.

Grain growth in Nextel™ 610 fiber in composites has been observed to change with the presence of monazite coatings. The coatings serve to inhibit grain growth, or more likely to suppress accelerated grain growth, as compared to control composites. The loss in strength of the composites containing uncoated fiber can be attributed, in part, to grain growth in the Nextel™ 610 fiber. Neither the mechanisms involved nor the degree of contribution to composite strength retention have yet been determined.

It has become clear, though certainly surprising, that plasticity plays a substantial role in the crack-deflection and sliding behavior of monazite, even in room temperature composite tests. Early reports of apparent smearing of monazite in the wear tracks resulting from fiber sliding led to TEM confirmation of sufficient dislocation activity and deformation twinning, though in a very limited volume, to produce dynamic recrystallization. [10]

CONCLUSIONS

The search for oxide coatings to perform the crack deflection function in ceramic composites has not only led to an enhanced understanding of composite behavior, but has uncovered several surprising aspects of constituent and composite fracture behavior. Three interesting facets have been briefly addressed here. Each of these has implications broader than the immediate question of composite behavior. The vulnerability of high strength fibers to apparent stress-corrosion issues raises the question of the degree of ubiquity and importance of such processes. The interesting behavior of the failure statistics of microcomposites challenges our interpretation of fracture statistics and perhaps will provide a directly measurable parameter that answers the qualitative question “good composite or bad composite?” Finally, successful use of oxide coatings in actual composites, with considerable improvement in high temperature life, definitively confirms that the “long shot” substitution of oxides for C and BN is viable. It is thought provoking to consider that success of the first of these coating systems was predicated on their unanticipated low temperature plasticity.

References:

1. Kerans, R. J., Hay, R. S. & Parthasarathy, T. A. (1999) *Current Opinion in Solid State and Materials Science* 4**,** 445-451.
2. Faber, K. T. (1997) *Annu. Rev. Mater. Sci.* 27**,** 499-524.
3. Hay, R. S. & Hermes, E. E. (1993) Patent No. 5,217,533 USA
4. Boakye, E. E., Hay, R. S., Mogilevsky, P. & Douglas, L. M. (2000) *Submitted to J. Am. Cer. Soc* .
5. Hay, R. S. & Boakye, E. E. (2000) *Submitted to J. Am. Ceram. Soc* .
6. Parthasarathy, T. A., Boakye, E., Cinibulk, M. K. & Petry, M. D. (1999) *J. Am. Ceram. Soc.* 82**,** 3575-3583.
7. Morgan, P. E. D. & Marshall, D. B. (1995) *J. Am. Cer. Soc.* 78**,** 1553-63.
8. Keller, K. A., Mah, T., Parthasarathy, T. A., Boakye, E. E. & Cinibulk, M. K. (2001) *Ceram. Eng. Sci. Proc., in press* .
9. Levi, C. G., Yang, J. Y., Dalgleish, B. J., Zok, F. W. & Evans, A. G. (1998) *J. Am. Ceram. Soc.* 81**,** 2077-2086.
10. Hay, R. S. (2000) *Cer. Eng. Sci. Proc.* 21**,** 203-218.