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THE ROLE OF MONAZITE IN OXIDE CERAMIC MATRIX COMPOSITES

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ABSTRACT

Rare-earth orthophosphate (monazite and xenotime) fiber-matrix interphases allow debonding and sliding of fibers in oxide-oxide ceramic fiber-matrix composites (CMCs).[1-10] Rare-earth orthophosphates are refractory ($LaPO_4$ mp = 2072°C)[11] and compatible in high temperature oxidizing environments with many oxides that are available as reinforcing fibers.[2, 3] For refractory materials they are also relatively soft ($LaPO_4$ hardness of 5 GPa, Moh's scale hardness of 5).[1, 12] The most refractory of these, and the most thoroughly investigated, is $LaPO_4$ (La-monazite). Monazite has been demonstrated to enhance the performance of some porous matrix fiber-reinforced oxide composites. In addition, the use of a monazite interphase represents the most likely approach for a successful dense fiber-reinforced oxide composite. In this paper, the properties of monazite-containing composites will be reviewed and the role of monazite discussed.

KEYWORDS

monazite, fiber/matrix interphase, oxide composite, fiber debonding, damage tolerance

1. INTRODUCTION

The limited creep resistance and microstructural stability of fine-grained oxide fibers impose restrictions on composite processing conditions. Few refractory oxide materials can be sintered to full density at pressures and temperatures that do not degrade fiber properties. Consequently, all oxide composites developed so far have porous matrices (with the exception of hot-pressed composites containing very low volume fractions of single crystal fibers). In some cases, a virtue has been made of this necessity and porous matrices have been used to impart damage tolerance without the need for a weakly bonded interphase.[13, 14] Although matrix porosity provides the mechanism for decoupling matrix and fiber fracture, monazite interphases enhance the performance of some materials of this type. Specifically, monazite coatings have prevented fiber strength loss at high temperatures in some matrices and enhanced non-linear behavior.[6, 15] Furthermore, monazite-matrix composites have been developed with the requisite thermal stability and mechanical performance for use as constituents in durable thermal protection systems for spacecraft re-entry.[16, 17]

Although porous matrix composites are suitable for some applications, composites with strong, dense matrices are still needed, especially for service in erosive and chemically corrosive environments (e.g., high gas flow rates with salt spray and H_2O vapor). In composites with strong or fully dense matrices, a weak interface or interphase between the fibers and matrix is needed to decouple the fracture processes in the matrix and fibers.[18] The condition for initial debonding is well-defined in terms of a critical interfacial fracture energy.[19] The condition for continued debonding and sliding is less well-defined. When the interface is not perfectly smooth (usually the case), a means of accommodating the asperity contact during constrained sliding is needed, either by elastic strains or by a secondary damage mechanism.

Evidence for such damage mechanisms in $LaPO_4$ interphases has been found from fiber push-out tests in dense composites. The debonding and sliding of four La-monazite coated fibers (alumina and mullite single crystal, YAG/Al_2O_3 and Al_2O_3/ZrO_2 eutectic) have been investigated. The coated fibers were hot-pressed with a matrix of polycrystalline Al_2O_3. Debonding and sliding were assessed using indentation fracture and push-out techniques. Deformation in the La-monazite coating by wear and abrasion during push-out was observed by scanning electron microscopy.

2. POROUS MATRIX COMPOSITES

Monazite coatings improve the high temperature capability of porous matrix composites. However, the effectiveness is very sensitive to processing conditions; some coating processes can lead to degraded fiber properties. Many precursor chemistries and infiltration techniques for fiber coatings have been investigated in our laboratory and elsewhere.[6, 20, 21] Tensile strength measurements of coated, heat-treated single-filaments or fiber tows have been used as screening tests to evaluate the effect of each coating composition on the properties of fibers. In general, the loss of fiber strength during processing has been a major impediment to the use of liquid precursor routes for monazite coatings with the extent of fiber strength loss dependent on the fiber composition for identical coating formulations. Studies to correlate the coating microstructure and stoichiometry to retained fiber strength have identified several potential causes for the degradation, although no conclusive results exist. However, the strength loss appears to be associated with the precursor chemistry in combination with polycrystalline fibers: it does not occur for solution precursors with single crystal fibers or for polycrystalline fibers coated with monazite powder slurries.[17, 21]

Although the cause of fiber degradation by monazite solution precursors is not fully understood, we have discovered that the strength loss for Nextel 610 fibers (3M Company) is significantly reduced with alumina powder additions to the precursor solutions.[6] Adding buffering powders to other precursor chemistries and oxide fibers has also met with some success.[20] The addition of the powder fillers help to distribute the monazite at fiber surfaces, essentially forming the interphase *in situ*.

Composites have also been produced by laminating fabrics infiltrated with powder-filled (Sumitomo AKP50) solution precursors (produced from La-nitrate and phytic acid). The laminated composite consisted of 2-D fabrics (8-harness satin weave) of Nextel 610 (10 plies, each 15 cm X 15 cm) which were dip-coated with slurry and stacked together while wet. The assembly was subsequently placed in a vacuum bag and dried at low temperature (60°C) in an hydraulic press under a slight pressure (~0.2 MPa). The dry composites were then removed from the vacuum bags and sintered, without pressure, at 1100°C for one hour in air. The composites contained ~40% Nextel 610 fiber by volume with half oriented parallel to the loading direction during tensile testing. Composites were not re-infiltrated after sintering and typically contained ~20-25% porosity.

After sintering, the composites were cut into tensile test specimens with fibers oriented 0/90° to the tensile test direction by diamond sawing. Double-edge notched specimens were evaluated as well as straight-sided specimens. Tests were conducted at room temperature for specimens in the as-processed condition (1100°C; 1h) as well as for specimens subjected to high temperature aging heat treatments (1100°C; 24h). Additional tensile tests to temperatures of 1025°C were conducted using quartz lamp arrays to heat the specimen.

Stress-strain traces obtained from monotonic tensile loading of 0/90° laminates showed an initial linear regime (E~ 90 GPa) to stress levels of approximately 150 MPa followed by considerable nonlinearity prior to the peak stress (220-250 MPa). Similar curves were obtained for notched composites tested in the as-sintered and thermally-aged condition tested at room temperature and for notched composites tested at 1025°C. The stress values were determined from the measured loads divided by the composite net-section area between the notches. Strengths for specimens with no notches at both room and elevated temperatures were essentially the same as the notched specimen values. In fact, all net-section strengths were approximately equivalent regardless of notch dimensions and test conditions (Fig.1). Normalizing the peak load value by the total aligned fiber cross-sectional area indicated fiber strength values of ~1.1-1.3 GPa.

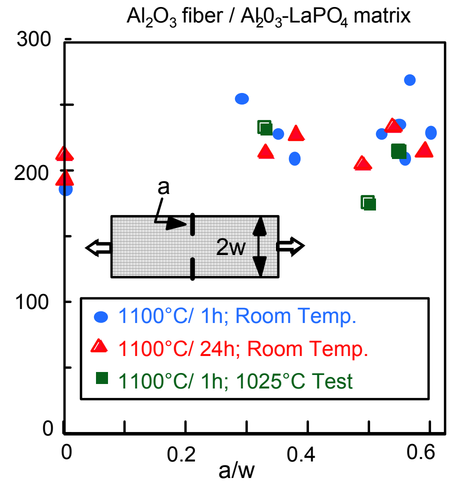

Figure 1. Net-section strength values of porous matrix composite containing monazite.

Coatings produced from monazite powders provide the best fiber strength retention during fiber tests as previously mentioned.[21] Furthermore, fiber coatings of this type have been used successfully to improve the properties of porous alumina matrix composites containing various types of oxide fibers (Nextel 610, 650 and 720).[15] In all cases, unidirectional composites containing coated fibers and heated to temperatures of 1200°C exhibited higher strengths than control specimens containing uncoated fibers. The strength improvement was most significant for the Nextel 610 and 650 fibers.

Monazite powder slurries have also been used to produce oxide composites for durable thermal protection systems (TPS). Thermal protection blankets, consisting of refractory fiber batting sandwiched between two sheets of woven ceramic fabric, are of interest as a lower cost alternative to rigid tiles for protection of re-entry vehicles. These blankets require an outer woven sheet coating that infiltrates and stiffens the fabric to provide an aerodynamic surface. The coating must act as a “high temperature starch” without embrittling the fabric. Since the coated fabric layer is essentially a thin ceramic matrix composite (the infiltrated coating being the matrix), the requirements for blanket durability are the same as those for damage tolerance in structural CMCs: a weak bond is needed between the matrix and the fibers to prevent embrittlement. The upper surface of the orbiter is protected by blankets that consist of silica-based fabric, insulation and coating. At temperatures above ~700-800°C, the silica-based coating bonds strongly to the fibers, embrittling the outer fabric and limiting its lifetime. Development of more refractory blanket fabrics and compatible coatings such as monazite with temperature capability to the range of 1000-1200°C would allow use of blankets over a larger fraction of the vehicle surface.

Comparisons of retained strengths for fiber tows and fabrics (Nextel 440 and 610) coated with monazite powder slurry and the baseline silica system indicated that, for high temperature applications (up to 1300°C), the preferred material system is Nextel 610 fabric infiltrated with monazite.[17] To assess the performance of these materials under relevant thermal and acoustic load conditions, small blanket test specimens were fabricated with Nextel 440 and 610 facesheets coated with monazite powder slurry, and exposed to various tests.

A modulated wind tunnel was used to expose the coated, radiantly heated (1100°C/30 min.) blankets to aerodynamic flow and a fluctuating pressure that simulates the acoustic loading of reentry. Tests were conducted for 600 seconds. The stiffened outer blanket surface performed well under acoustic loading during the wind tunnel testing. In no case was any evidence of coating degradation detected by visual inspection during or after the tests. Out-of-plane displacements (“pillowing”) of the fabric during the tests were minimal.

Exposures to higher surface temperatures in flowing gas were conducted on the Nextel 610 fabric/monazite coating system using the Panel Test Arc Jet Facility at NASA Ames. A test panel with a surface area of approximately 30 cm x 30 cm was infiltrated with monazite powder slurry and subsequently exposed to two heating cycles, giving surface temperatures of 1200°C for 10 min and 1300°C for three minutes.

Post-test evaluations included x-ray diffraction analysis, which indicated that no reaction phases had formed during exposure, and measurement of the retained mechanical performance of the coated fabric facesheet. Impact resistance measurements were conducted using a drop-weight impact tester with a hemispherical projectile tip of radius 0.64 cm. An impact energy of 1.4 J was used and data was obtained from five measurements. Limited coating damage and no fabric penetration were observed for the monazite-coated Nextel 610 surface. This represents a significant improvement over Nextel 440 fabrics coated with a silica-based composition and exposed to 1200°C in the arc jet. Optical micrographs shown in Figure 2 depict the difference in the level of impact damage incurred by both systems after impact under identical conditions.

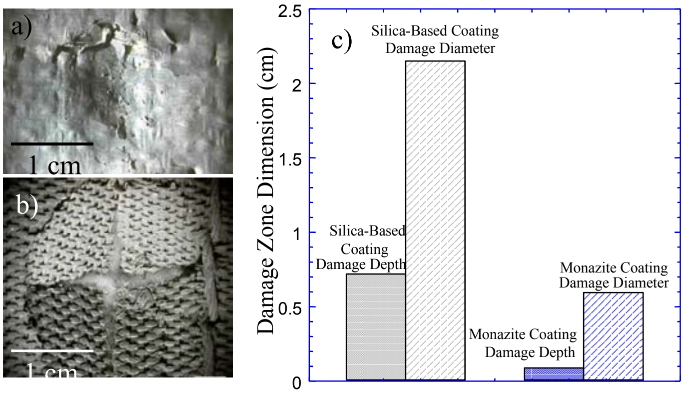

Figure 2. Showing impact damage to arc jet tested blankets with facesheets of a) Nextel 610 fabric/ monazite coating b) Nextel 440/ silica-based coating and c) impact test results.

3. DENSE MATRIX COMPOSITES

The debonding and sliding of four types of La-monazite coated fibers, chosen to provide different residual stress states and interface morphology and embedded in a dense alumina matrix have been investigated and provide evidence for the utility of monazite interphases in dense composites.

Four different single crystal or eutectic oxide fibers (alumina and mullite single crystal, YAG/Al_2O_3 and Al_2O_3/ZrO_2 eutectic, grown at NASA-Glenn by a laser float-zone technique [22, 23]), were coated with $LaPO_4$ by dip coating in a rhabdophane (hydrated $LaPO_4$) slurry. The coating thicknesses were nonuniform (between ~ 1 μm and 5 μm) and largest along fiber surfaces parallel to the hot-pressing direction. The coated fibers were embedded in α-alumina powder (Sumitomo AKP50) and hot-pressed in graphite dies for 1 h at 1400°C. Uncoated fibers were included in the same specimen as controls. No reactions were observed between $LaPO_4$ and the fibers. The fibers had different surface morphology and thermal expansion coefficients, thus allowing some assessment of the effects of interface morphology and residual stress on debonding and sliding (Table I).

The $LaPO_4$ coatings protected all fibers from penetration of matrix indentation cracks whereas uncoated fibers were always penetrated by the indentation cracks. The cracks generally penetrated through the $LaPO_4$ coating and arrested at the coating/fiber interface, causing debonding (Fig 3a). In a few cases ZrO_2/Al_2O_3 fibers debonded at both interfaces (matrix/coating and coating /fiber). The former response was observed previously with coated sapphire fibers[1] and was consistent with the debond criterion of He and Hutchinson[19] and the measured fracture toughnesses of the fibers, coating, and interface. Although the fracture toughnesses of the YAG/$LaPO_4$ and mullite/$LaPO_4$ interfaces have not been measured, the present observations suggest that they are similar to those of the alumina/$LaPO_4$ interface (~4.5 J/m^2).

All of the fibers debonded during fiber push-out experiments. Sliding occurred unstably over ~5 to 10 μm at a critical load between 10 and 20 N. The average shear stress (load divided by fiber surface area) at the critical load was 130 ± 10 MPa for the sapphire fiber; 200 ± 20 MPa for the mullite fiber; 190 ± 20 MPa for the YAG/Al_2O_3 fiber; and 255 ±30 MPa for the Al_2O_3/ZrO_2 fiber.

TABLE I Representative* residual stresses (MPa) for monazite-coated fibers in a dense polycrystalline Al_2O_3 matrix.

Stress component	Fiber			
	Sapphire	Mullite	YAG/Al_2O_3	Al_2O_3/ZrO_2
Radial (coating/fiber)	15	-720	130	240
Radial (matrix/coating)	25	-630	140	240
Hoop (coating)	300	420	290	280
Axial (fiber)	7	-1160	240	420

*These values are intended only as rough guide for stresses. They were calculated using a coaxial cylinder analysis,[24, 25] assuming a temperature change of ΔT = 1000°C, coating thickness 2 μm, zero volume fraction of fibers, and the following Young's moduli and thermal expansion coefficients (nominal isotropic, temperature-independent values): polycrystalline Al_2O_3 (400 GPa, 8×10^{-6} °C^{-1}); sapphire (400 GPa, 8×10^{-6} °C^{-1}); mullite (200 GPa, 4×10^{-6} °C^{-1}); Al_2O_3/ZrO_2 (300 GPa, 9×10^{-6} °C^{-1}); and YAG/Al_2O_3 (350 GPa, 8.5×10^{-6} °C^{-1}).[26, 27]

Extensive wear tracks observed in the $LaPO_4$ coating for both eutectic fibers indicate that sliding involved plastic deformation (Fig. 3b). The plane of sliding was mostly adjacent to the fiber-coating interface, although smeared $LaPO_4$ coating fragments remained on the fiber surface. In some regions sliding occurred near the matrix-coating interface. Transmission electron microscopy observations have shown the presence of extreme deformation by dislocation generation, cleavage and twinning.[28]

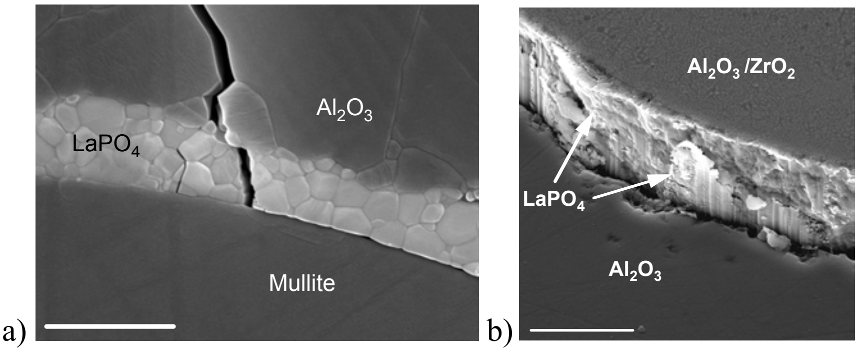

Fig. 3. a) Debonding at $LaPO_4$/mullite interface. B) Deformed $LaPO_4$ coating on a eutectic fiber pushed through a dense alumina matrix.

4. DISCUSSION AND CONCLUSIONS

Monazite fiber coatings and interphases have been demonstrated to improve the properties of some porous matrix oxide composites. However, control of the chemistry, processing and morphology of the coatings are needed to avoid degrading the fiber strength during the processing or during subsequent thermal exposure.

Monazite interphases exhibit characteristics necessary to allow damage tolerance in dense matrix composites. La-monazite is compatible with potential advanced fiber materials such as mullite, YAG, ZrO_2 and Al_2O_3. The interfaces between La-monazite and these materials debond when a crack approaches the interface from monazite. This occurs even when there is significant compressive stress normal to these interfaces, as in the case of mullite fibers in an alumina matrix. The ability of La-monazite to deform plastically relatively easily at low temperatures during fiber push-out may be critical for its use as a composite interface.

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