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Monazite-containing oxide/oxide composites

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Abstract

An extremely simple processing route has been used to produce $LaPO_4$ (La-monazite)/alumina continuous fiber-reinforced ceramic composites. In this paper, the processing, microstructure and tensile properties are reviewed. In particular, the damage tolerance and notch insensitivity of this system, which contains monazite-coated fibers, will be compared to the properties reported for other oxide composites.

Keywords: Al_2O_3; Aluminosilicate fibres; Composites; Laminates; $LaPO_4$; Mechanical properties

1. Introduction

The development of tough ceramic matrix composites capable of operating for thousands of hours at high temperatures in oxidizing environments is a long-standing goal for turbine engine development programs. This goal is driven by potential cost savings, performance benefits resulting from small increases in material operating temperatures, and reduced NO_x emissions. The preferred composite system would consist of thermodynamically stable oxide fiber and matrix materials. Historically, the use temperature of such systems has been limited by the lack of a suitable fiber and fiber/matrix interphase.

The requirements for fiber–matrix interphases in oxide/oxide composites depend, to a large extent, upon the relative density of the matrix. Provided the matrix remains sufficiently porous and does not degrade the fiber strength, no fiber coating is needed to achieve some degree of damage tolerance. The matrix typically fails at lower strain levels than the fibers and cracks forming in the matrix do not readily propagate into the fibers.[1–3]

Dense matrix composites, however, need a suitable interphase for fiber debonding. Several oxide systems have satisfied, to varying degrees, the properties required for composite interphases.[4–10] Mixed rare-earth and alkaline earth phosphates, tungstates and vanadates, bond weakly to oxide fibers and are a likely approach for a successful weak interface composite.[11,12] The most refractory, and the most thoroughly investigated, of these is $LaPO_4$ (La-monazite). The melting point of $LaPO_4$ is over 2000°C and it is stable in air and water-containing environments. Our studies with single crystal and eutectic fibers have demonstrated that La-monazite is phase-compatible with alumina, mullite, YAG, and zirconia at temperatures to at least 1600°C in air, well above the temperature limitation of any existing or prospective polycrystalline oxide fibers. Moreover, these model studies showed that fiber debonding and sliding occurs in composites with fully dense alumina matrices and fully dense coatings.[13]

Even in the light of such encouraging results, producing dense matrix composites remains a challenge owing to restrictions on processing temperatures imposed by commercially available polycrystalline oxide fibers. To date, no dense refractory oxide composites have been produced with reinforcements consisting of small diameter fibers woven into useful fabric architectures.

Difficulties associated with coating production methods have also had limited progress. Several research groups, motivated by the need to produce inexpensive fiber coatings, have developed solution precursors and slurry coatings of monazite.[14–16] Although many precursor chemistries and infiltration techniques have been investigated, two fundamental problems remain: all of the monazite precursors investigated degrade Nextel 610 and 720 fibers during heat treatment; and coating uniformity is difficult to control. Typical coating morphologies for solution infiltrated ceramic fabrics are shown

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in Fig. 1. The two most common morphological defects are illustrated: fiber bridging and incomplete fiber coverage. The former limits infiltration of the matrix into fiber bundles, whereas the latter leads to fiber/matrix bonding and embrittlement of the composite.

The loss of fiber strength during processing is presently the major impediment to the use of liquid precursor routes for monazite coatings. Although extensive studies to correlate the precursor chemical constituents, coating microstructure and stoichiometry to retained fiber strength have identified several potential causes for the degradation, no conclusive results or critical experiments to confirm these hypotheses have been reported.

In this paper, we describe a simple composite processing approach that has been used to circumvent many of the problems associated with typical fiber coating methods. The matrix was formed by infiltrating woven preforms with a slurry consisting of alumina powder in a monazite precursor solution, which produced a monazite coating on the fibers. Furthermore, by selecting appropriate slurry compositions, the fiber strength was retained in the composites after sintering. While the composites have porous matrices, direct benefit of the $LaPO_4$ interphase was obtained. These materials exhibit better damage tolerance and notch insensitivity than other porous matrix composites.

2. Experimental procedure

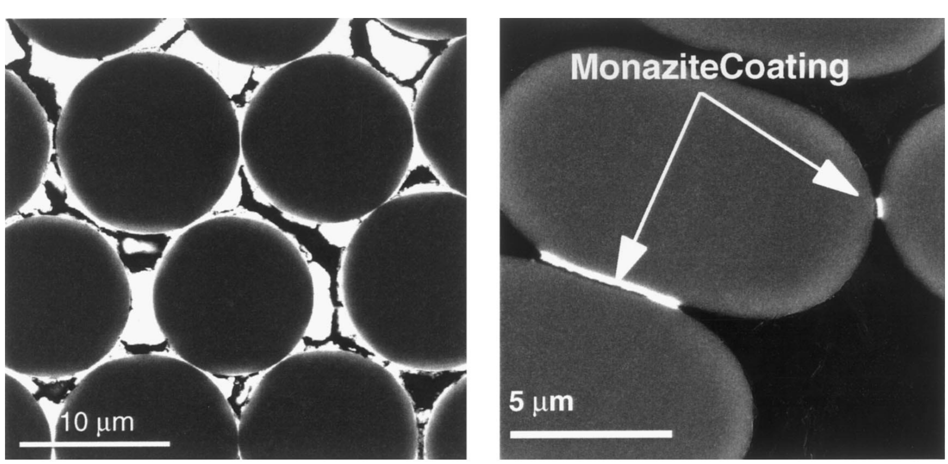
2.1. Fiber strength

Several different aqueous monazite precursor solutions with La-nitrate were synthesized. Various sources of phosphorus were investigated including phosphorous acid, phytic acid and methylphosphonic acid. The useful concentration of each composition, in the range 1–2.5 M, was determined by its stability against precipitation. The composition of each precursor batch was adjusted to yield a product with a La:P ratio of 1:1. The procedures developed to achieve this are described elsewhere.[17]

In addition to adjusting the stoichiometry, screening tests were conducted to evaluate the effect of each precursor composition on the properties of fibers. Tensile testing of coated, heat-treated Nextel™ 610 alumina fiber tows was used to evaluate the retained strengths, with uncoated fiber tows from the same spool, subjected to identical handling and heat treatments, being used as a reference. Heat treatment was performed in an air furnace and testing was conducted at room temperature. Tow strengths were obtained using one inch gauge lengths from the peak load normalized by the total cross-sectional area of fiber within each tow, assuming 420 filaments of 12 μm diameter; average strengths for each condition were determined from 15 to 30 separate tow measurements.

2.2. Composite processing and evaluation

Composites were produced using a slurry infiltration approach. The slurry comprised high purity alumina powder (Sumitomo Chemical Co., AKP-50) mixed with monazite precursor solution. The low pH of the solutions facilitated this process and the alumina powder was well dispersed after ball milling for short times (30 min). The laminated composite consisted of 2-D fabrics (8-harness satin weave) of Nextel 610 (10 plies, each 15×15 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 a hydraulic press under pressure (~0.2 MPa). The dry composites were then removed from the vacuum bags and sintered, without pressure, at 1100°C for 1 h in air.



(a) (b)

Fig. 1. (a) Fiber bridging produced by concentrated monazite solution precursor coating. (b) Poor fiber coverage produced by dilute monazite solution precursor coating.

After sintering, the composites were cut by diamond sawing into tensile test specimens (1cm wide×15 cm long) 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. The notches were produced with a thin diamond wafering blade (150μm) and notch depths ranged from 1.7–2.5 mm. Tensile tests were conducted under constant displacement rate conditions (0.02 mm/s) and specimen response was monitored with a clip gauge extensometer (1.27 cm gauge length) that spanned the notch as shown (Fig. 2).

3. Results and discussion

3.1. Fiber strength

The measured coated fiber tow strengths for each of the precursor compositions as well as the uncoated reference fibers after heat treatment at 1100°C for 1 h are summarized in Fig. 3. The results indicate that solution precursors caused up to 50% strength loss, whereas the retained strengths were improved significantly when alumina powder was mixed with the precursors prior to coating the fiber tows. In the case of the phosphorous acid/La-nitrate precursor with alumina powder, the retained strength was as high as the uncoated reference fibers. A possible explanation is that the fine alumina powder may buffer the solution, making the fibers less susceptible to deleterious reaction with the precursors. However, further experiments are needed to confirm this.

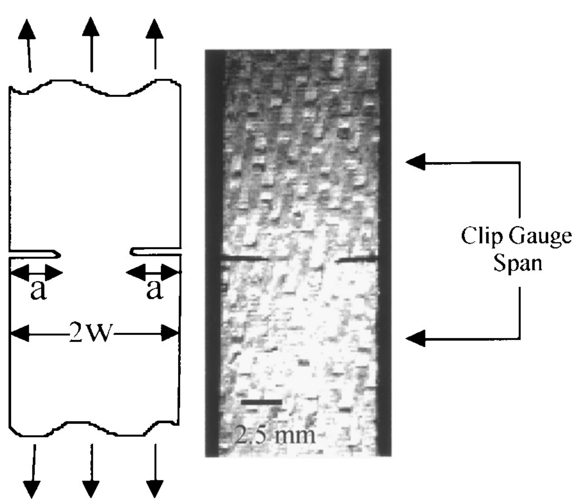


Fig. 2. Notch geometry used for tensile testing.

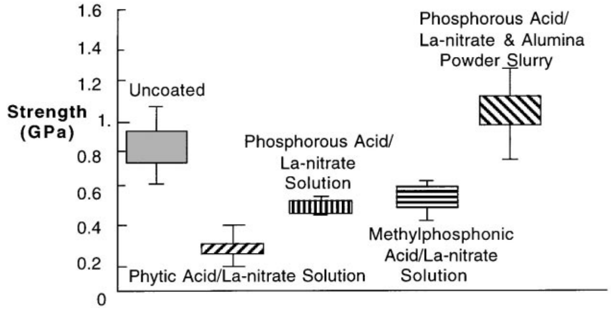


Fig. 3. Room temperature strengths of monazite-coated, Nextel 610 fiber tows after heat treatment at 1100°C for 1 h.

3.2. Composite evaluation

Adding alumina powders to the monazite precursor solutions not only improved the retained strength of Nextel 610 fibers but also produced a more uniform coverage of monazite on the fiber surfaces. This is usually difficult to accomplish with solution coatings as previously discussed (Fig. 1). The powder fillers, however, provide a network of particle–fiber contacts around the filaments, and capillary forces evidently draw the liquid to the fiber surface as the solution dries. Therefore, during slurry coating of fabric preforms, the monazite precursor is deposited on the fibers in situ which eliminates the need for a separate fiber coating step and greatly simplifies composite processing. The fiber surfaces are covered with monazite after heat treatment, and the remainder of the matrix is a refractory two-phase mixture of alumina and monazite as shown in the polished cross-section of infiltrated fabric (Fig. 4.). Typical slurry compositions yielded a sintered matrix with ~10–20% (by volume) of monazite and matrix porosity levels of ~30–35%. The composites contained ~40% fiber by volume with half oriented parallel to the loading direction during tensile testing.

Significant non-linearity in the stress–strain behavior was observed under monotonic tensile loading with and without edge notches. The stresses plotted for notched composites in Fig. 5 represent the measured load normalized by the composite net-section area, and the "strain" values correspond to the clip gauge extension normalized by the initial gauge length. The peak strengths (~230 MPa) and the stress–strain traces for both specimens are similar, even though the ratios of notch depth to specimen width differed (0.35 and 0.52). Furthermore, strengths obtained for unnotched specimens were similar to these values, indicating that the net-section stress for these composites was insensitive to the presence of such notches. In all composites tested, extensive fiber pull-out was observed from each side of the notch (over distances of ~1 cm). Individual fibers, rather than bonded fiber tows, were clearly discernable and the fracture surface appeared quite "brushy". Fibers which had pulled out appeared relatively smooth with monazite coatings that exhibited evidence of wear [Fig. 5(b)]. The behavior of these oxide composites that contain weakly-bonded monazite contrasts to reported observations for strongly-bonded porous matrix

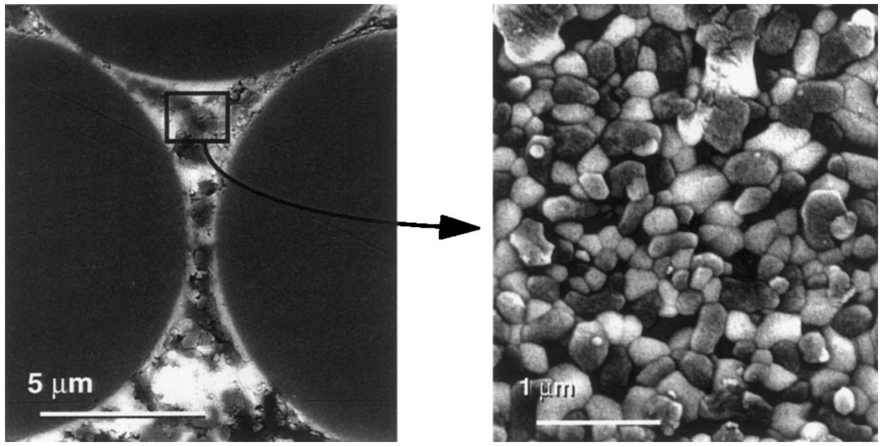


Fig. 4. Monazite/alumina matrix with N610 alumina fibers. The light phase in both micrographs is monazite.

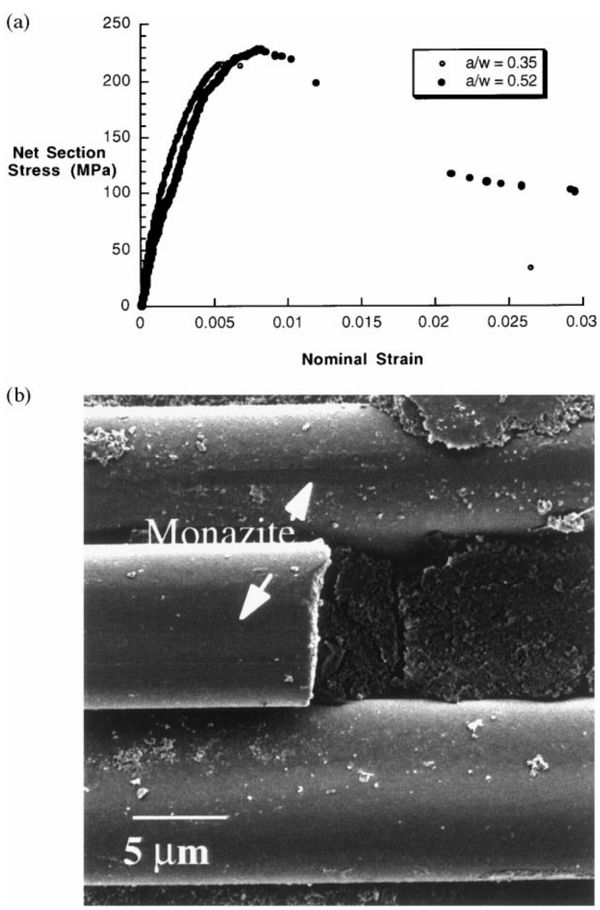


Fig. 5. (a) Stress–strain behavior of notched monazite/alumina matrix composites. (b) Fiber surfaces were smooth after pullout with adhering monazite, shown.

composites.[3] The non-linear deformation is enhanced significantly by the presence of monazite and the gradual load decrease during fiber pullout is not observed for the strongly bonded systems. Furthermore, the composites are less sensitive to the presence of sharp notches and fiber pullout is greatly enhanced.[3]

4. Conclusions

In summary, we have demonstrated that by mixing monazite solution precursors with Al_2O_3 powders and infiltrating ceramic fiber preforms, we can produce oxide/oxide composites with monazite coated fibers using a single processing cycle (similar to methods for polymer matrix composite consolidation). These composites contain porous matrices which contribute to the mechanical response. They show damage-tolerance and notch-insensitivity that surpass strongly bonded porous matrix composites, indicating that the monazite interphase enhances performance.

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