

Precipitation Coating of Rare-Earth Orthophosphates on Woven Ceramic Fibers—Effect of Rare-Earth Cation on Coating Morphology and Coated Fiber Strength

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Monazite (La, Ce, Nd, and GdPO₄) and xenotime (Tb, Dy, and YPO₄) coatings were deposited on woven Nextel[™] 610 and 720 fibers by heterogeneous precipitation from a rare-earth citrate/ phosphoric acid precursor. Coating phases and microstructure were characterized by SEM and TEM, and coated fiber strength was measured after heat treatment at 1200°C for 2 h. Coated fiber strength increased with decreasing ionic radius of the rare-earth cation in the monazite and xenotime coatings, and correlates with the high-temperature weight loss and the densification rate of the coatings. Dense coatings with trapped porosity and high weight loss at a high temperature degrade fiber strength the most. The degradation is consistent with stress corrosion driven by thermal residual stress from coating precursor decomposition products trapped in the coating at a high temperature.

I. Introduction

RARE-EARTH orthophosphates (REPO₄) form two polymorphs: monoclinic monazite for lanthanides from La to Gd and tetragonal xenotime for lanthanides from Tb to Lu, and also Y.^{1,2} Orthophosphates exhibit a number of interesting properties, and have been studied extensively as hosts for actinide waste disposal due to their stability in water,^{3,4} and as constituents of ceramic composites (CMCs).^{5–11} La-monazite, LaPO₄, is used as an oxidation-resistant fiber-matrix interface material for CMCs due to its low hardness and weak bonding to alumina and other structural ceramics; it also has a good CTE match with Nextel[™] 610 and 650 fibers.^{5–7,10,11} Coatings of xenotime (REPO₄ where RE = Tb-Lu and Y) and mixed-phase monazite-xenotime solid solutions have been proposed for Nextel[™] 720 fibers due to a better CTE match with this fiber (~6 ppm/°K) and lower hardness.^{12–15} DyPO₄- and LaPO₄-coated single-crystal alumina fibers have similar sliding stresses in fiber push-out experiments.¹⁶

During the past decade, methods to apply La-monazite coatings to fibers tows using a sol and solution-based continuous dip-coating process were developed.^{17–21} These coated fibers often have to be woven into fiber preforms,²² and the coating may debond during weaving. Recently, methods to coat woven ceramic fibers with La-monazite using heterogeneous precipitation from solution precursors have been developed.^{23–25} One method uses the temperature dependence of the reaction between Lacitrate and phosphoric acid to coat woven fibers by first saturating the woven fibers with the solution precursors and then submerging the saturated fibers in warm water to cause rapid precipitation of rhabdophane, LaPO₄ · xH_2O .²⁵ This method was used to coat NextelTM 610 and 720 fibers with La, Ce, Nd, and GdPO₄ monazite and Tb, Dy, and YPO₄ xenotime to compare coating weight loss, microstructure, morphology, and coated fiber strength following a high-temperature heat treatment. Various factors that may affect coated fiber strength are discussed. As CMC strength is proportional to fiber strength (for in-plane on-axis loading), coated fibers with minimal strength degradation following exposure to composite processing temperatures are desirable.

II. Experimental Procedure

(1) Materials Preparation

NextelTM 610 and 720 oxide fiber 8 harness satin weave cloths (1500 denier, 3M Co., St. Paul, MN) were used for all coating experiments and were desized at 900°C for 5 min in air using a tube furnace. Precursor solutions of phosphoric acid and REcitrate were prepared by dissolving concentrated phosphoric acid (Fisher Scientific Co., Pittsburgh, PA) or a combination of RE nitrate (RE = La, Ce, Nd, Gd, Tb, Dy, or Y, Aldrich Chemical Co., Milwaukee, WI) and citric acid (Fisher Scientific Co.) in deionized water. The precursor solutions were prepared to yield 100 g REPO₄/L on mixing equal volumes of each solution. The RE:citrate:P ratio of the solutions were chilled to $\sim 5^{\circ}$ C before mixing during the coating procedure.

(2) Coating Oxide Fiber Cloths

Coating was performed by submerging a cloth previously saturated with the chilled, mixed precursor solutions into warm water to precipitate the coating onto the fibers. Five milliliter portions of both chilled precursor solutions (RE-citrate and phosphoric acid) prepared to yield 100 g REPO₄/L were mixed in a large beaker, to which a 7.6 cm \times 7.6 cm piece of cloth was added. The beaker containing the mixed solutions and cloth was placed in an ultrasonic bath for 15 s. The beaker was removed from the bath and the cloth was removed from the solution. Excess solution was drained from the cloth against the side of the beaker. The cloth, saturated with the precursor solution, was submerged in a vessel containing deionized water at 90°C to precipitate hydrated REPO₄ rapidly. After 5 min in the warm water bath, the cloth was removed and rinsed for 20 s in 400 mL of deionized water to rinse away any remaining dissolved chemicals and loosely bound solids. The cloth was subsequently dried in air at 120°C for 15 min and finally placed in a tube furnace for 5 min in air; furnace temperatures of 600° and 900°C were used for this intercoat firing. The cloth was quickly moved into and out of the tube furnace, which was equilibrated at the desired temperature. The coating process (saturate, submerge, dry, fire)

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was repeated to build up thicker coatings comprised of either five or 10 coats.

(3) Powder Preparation for Densification Studies

Rhabdophane and churchite^{26,27} (hydrated xenotime, RE- $PO_4 \times H_2O$, RE = Tb-Lu and Y) powders for densification studies were prepared by mixing 10 mL portions of chilled precursor solutions (RE-citrate and phosphoric acid) in a small beaker and pouring the liquid into ~ 600 mL of stirring deionized water at 90°C, resulting in rapid precipitation. The powder was stirred in hot water for 5 min. The vessel containing the powder and hot water was then removed from the hot plate and cooled to near room temperature before being evenly divided into centrifuge jars. The slurry was then centrifuged (Sorvall Super T21, Kendro Laboratory Products, Newton, CT) at 13000 rpm for 25 min to collect the precipitated solids. After centrifugation, the clear supernatant was poured off and 100 mL deionized water was added to each jar. The settled solids were redispersed into the liquid by scraping and stirring with a spatula. The redispersed slurries were then centrifuged as before and the supernatant was poured off. The solids were allowed to dry in laboratory air and then ground with a mortar and pestle to a fine powder. To prepare pellets for densification studies, powders were mixed with ethanol and 4 wt% (based on powder weight) PEG-8000 (Carbowax Sentry, Dow Chemical Co., Midland, MI) was added. The mixture was then ground in a mortar and pestle and the ethanol was allowed to evaporate. Dried powder mixtures were then pressed in a 12.7 mm die at 200 MPa for 5 min. The resulting pellets were then fired at 900°C for 30 min to provide mechanical integrity for density measurements. Both Archimedes and geometrical densities of the pellets were measured following heat treatment at 1200°C for 2 h.

(4) Characterization and Testing

Coatings were characterized using both polished cross sections of coated cloth and fiber tows extracted from the coated cloth.^{28,29} Cross sections and surfaces of extracted tows were examined using a scanning electron microscope (SEM) (Leica 360 FE, Ernst Leitz, Westler, Germany). Transmission electron microscopy (TEM) (Phillips CM200FEG, Eindhoven, the Netherlands) was performed to characterize the coating microstructure and identify any intergranular phases. Thermogravimetric analysis of powders was performed using a combined DSC/TGA instrument (SDT Q600, TA Instruments, New Castle, DE); experiments were performed at a fixed heating rate of 10°C/min to a final temperature of 1400°C with the sample held in a small alumina crucible.

Tensile strengths of coated fibers were measured on an MTS machine (Synergie 400, MTS Systems Corp., Eden Prairie, MN). Tows were extracted from the coated cloth and 20-50 filaments from each coating condition were tested using a 25.4 mm gauge length^{30,31}; fewer fibers were tested if the strengths were very low. Fibers were tested following a 2-h exposure at 1200°C in air within a box furnace with MoSi₂ elements. This heat treatment was chosen to simulate matrix processing temperatures for an alumina matrix that would likely be used with these fibers. For control experiments, the strength of uncoated Nextel[™] 610 and 720 fibers was measured following exposure to the same 2-h 1200°C heat treatment performed an coated fibers. The results of this testing appear in a companion paper.³² The lot-to-lot variation in the average single filament strength of Nextel[™] 610 and 720 is estimated by the manufacturer to vary by as much as +7%. In our work, the average single filament strengths for Nextel[™] 610 fibers extracted from woven cloths and heat treated for 2 h at 1200°C ranged from 2.3 to 2.8 GPa with an average of 2.6 GPa. For uncoated Nextel[™] 720, heattreated strengths ranged from 2.0 to 2.2 GPa, with an average of 2.1 GPa.³² This is consistent with the variations reported by the manufacturer. The results of single-filament testing of heattreated monazite-coated fibers were compared with these values



Fig. 1. Normalized heat-treated strength as a function of rare-earth cation.

to assess the level of strength degradation by fiber coatings for the given processing conditions.

III. Results and Discussion

Figure 1 shows the heat-treated strengths of Nextel[™] 610 and 720 fibers coated with different rare-earth orthophosphates under fixed processing conditions (five coats, 900°C intercoat firing temperature). The strengths are normalized by the heat-treated strengths of uncoated fibers. The heat-treated strengths of both fibers increase with decreasing ionic radius of the rare-earth cation in REPO₄ across the lanthanide series of the periodic table. The strengths of coated Nextel[™] 720 fibers are lower than those of Nextel[™] 610. This is consistent with a strength degradation mechanism driven by residual stress.¹⁹⁻²¹ Higher residual stresses are present in Nextel[™] 720 due to the CTE mismatch between the alumina and mullite phases and the CTE anisotropy of these phases. In Nextel[™] 610, the residual stresses are due solely to CTE anisotropy of the alumina grains. The difference in average polycrystalline CTE between mullite and alumina is ~4 ppm/°K, whereas the difference in CTE along the *a*- and *c*axis of alumina is $\sim 1 \text{ ppm/}^{\circ}\text{K}$. In polycrystalline alumina, residual stresses on the order of several hundred megapascals are obtained on cooling from a high temperature;^{33,34} these stresses relax with increasing temperature but are nonzero at the temperatures where high-temperature outgassing of the coatings occurs, i.e., 900°-1200°C. The large CTE mismatch in Nextel™ 720, coupled with the elastic modulii reported for the fibers (380 GPa for Nextel[™] 610 vs 260 GPa for Nextel[™] 720), leads to residual stresses that are more than twice as large as those in polycrystalline alumina (Nextel[™] 610) cooled from a high temperature.



Fig. 2. Effect of intercoat firing temperature and number of coats on the normalized heat-treated strength of NextelTM 610 and 720 fibers with LaPO₄ and DyPO₄ coatings.



Fig. 3. Coating evolution during first two coats of LaPO₄ and DyPO₄ coatings on Nextel[™] 720 fibers using an intercoat firing temperature of 900°C.

Figure 2 shows the variation in heat-treated strength with increasing number of coats and different intercoat firing temperatures for NextelTM 610 and 720 fibers coated with LaPO₄ and DyPO₄. As observed in previous work,³² the heat-treated strengths decrease with increasing number of coats, and for a fixed number of coats, coated fibers with a lower intercoat firing temperature have higher strength. The heat-treated strengths of DyPO₄-coated NextelTM 610 and NextelTM 720 fibers are much higher than those of the same fibers coated with LaPO₄ under the same conditions.

Figure 3 shows the evolution of LaPO₄ and DyPO₄ coatings on Nextel^M 720 fibers. In the first coat, nuclei ~200 nm in diameter are deposited on the fiber surface. In the case of LaPO₄, these nuclei appear as barrel-shaped polycrystalline aggregates. The nuclei exhibit stepped and nodular surfaces that are aligned along the long axis of the particle. In the case of DyPO₄, the nuclei are round and have a surface texture that suggests a polycrystalline aggregate. After the second coat, the nuclei in both cases grow while simultaneously a new generation of particles nucleate. This new generation of particles has an appearance similar to the first generation but a smaller size, ~100 nm. Figure 4 shows the nuclei morphology on NextelTM 720 fibers for different rare-earth orthophosphates after one coat. The difference in nuclei morphology may be due to differences in the solubility product constant for rhapdophane (La–Gd) and churchite (Tb–Lu) and variation in growth rate along different crystallographic axes under the conditions of precipitation.^{35,36} Additional studies are necessary to understand the effect of a rare-earth cation on nuclei morphology. Similar coating deposition behavior was observed for all rare-earth orthophosphates:



Fig. 4. Effect of rear earth cation on the nuclei morphology after one coat using and intercoat firing temperature at 900°C.



Fig. 5. Proposed mechanism by which coatings are deposited on fibers using the coating procedure described herein.

the initial nuclei grow during the second coat and a new generation of smaller nuclei appears. Based on these observations, it is proposed that the mechanism by which uniform coatings form is through simultaneous nucleation on bare fiber surfaces and on existing rare-earth orthophosphate particles during each sequential coating, as shown schematically in Fig. 5. Figure 6 shows representative TEM micrographs of heattreated LaPO₄- and DyPO₄-coated NextelTM 720 fibers applied using an intercoat firing temperature of 600°C; samples coated five times with DyPO₄ and 10 times with LaPO₄ are shown. Despite the differing number of coats applied to the samples, the differences in coating microstructure are clear. The DyPO₄



Fig. 6. Representative transmission electron spectroscopy micrographs of LaPO₄ and DyPO₄ coatings on Nextel[™] 720 fibers.



Fig. 7. Representative scanning electron microscopy micrographs of LaPO₄, DyPO₄, and YPO₄ coatings on Nextel^M 610 fibers. (a) LaPO₄, (b) DyPO₄, (c) and (d) YPO₄.

coatings are porous with both inter- and intragranular pores. In contrast, the LaPO₄ coatings are hermetic and almost fully dense, with occasional intergranular pores. In both cases, the coating fiber interface is free of second phases, indicative of coating nonstoichiometry such as AlPO₄. Figure 7 shows SEM micrographs of the coated fiber surfaces following heat treatment. For LaPO₄, the coating is dense with very few intergranular pores. For DyPO₄, many intergranular pores are visible and the grains on the surface of the coating are rounded. YPO₄ coatings had an appearance similar to DyPO₄ coatings, but some parts of the fiber surface were uncoated, which may contribute to the high strengths of these coated fibers.

The coating microstructure observations suggest that coated fiber strength following heat treatment may correlate with densification of the coating. To investigate this correlation, the weight loss and densification of citrate-derived REPO₄ powders was studied. Figure 8 shows TGA data for citrate-derived REPO₄ powders where RE = La, Gd, Tb, Dy, and Y³⁷; the powders were precipitated by warming precursors to 30°C using



Fig. 8. Thermogravimetric analysis curves illustrating the effect of rare earth cation on outgassing behavior of citrate-derived REPO₄ powders.

an RE:citrate:P ratio of the solutions set at 1:5:5. The hydrated REPO₄ powders were collected by centrifugation and washed once with deionized water before drying and TGA analysis. High-temperature weight loss, i.e., above 900°C, was observed for all powders; the amount decreases as follows: La> Dy > Y > Gd > Tb.

The densification behavior of citrate-derived REPO₄ powders has been studied previously for pellets of REPO₄ powders sintered for 2–3 h at different temperatures.^{38,39} The data at 1200°C appear in Fig. 9. It shows the percentage of theoretical density for different REPO₄ powders and is compared with our measurements for a 2-h heat treatment at 1200°C. The results are consistent with previous work and show a pronounced decrease in sintered density for xenotimes near the middle of the lanthanide series in comparison with monazite. The xenotime coatings studied here are more porous than monazite coatings due to intrinsically slower densification rates. The increased porosity may contribute to higher coated fiber strengths by allowing high-temperature precursor decomposition products that cause



Fig. 9. Measured density following 1200° C heat treatment for citratederived REPO₄ powders. Blue bars = data from Hikichi *et al.*,^{34,35} red bars = measured in this study.

stress corrosion to escape without being trapped near the fiber surface.

The collective observations suggest that coated fiber strength depends on both the high-temperature weight loss from the coatings¹⁹⁻²¹ and the tendency of the coating to form closed pores near the fiber surface, which is related to densification rates. More high-temperature weight loss and faster densification (e.g., LaPO₄) lead to severely degraded fiber strength after heat treatment at matrix processing temperatures. Less hightemperature weight loss, coupled with poor densification, yields a more porous coating (e.g., DyPO₄ and YPO₄) and higher coated fiber strengths; here, the precursor decomposition products that do remain at a high temperature can escape and are not trapped near the fiber surface. GdPO₄ and TbPO₄ powders showed the smallest high-temperature weight loss, but these powders densified faster than DyPO₄ and YPO₄. Despite a higher weight loss than GdPO4 and TbPO4, DyPO4- and YPO₄-coated fibers are suggested to have higher coated fiber strength because their poor densification allows surface-active species that cause stress corrosion to escape. GdPO₄ showed densification behavior similar to LaPO₄, but has less hightemperature weight loss, and so GdPO₄-coated fibers were stronger than LaPO₄-coated fibers. Similar results were found in a recent work by Boakye *et al.*⁴⁰, which showed inhibition of densification in mixed (Y,La)PO₄ coatings on Nextel[™] 720 and correspondingly higher coated fiber strengths following heat treatment despite having a high-temperature weight loss comparable to LaPO₄ coatings.

The results in this work are consistent with high-temperature stress corrosion as a degradation mechanism-surface-active decomposition products from the coating precursor attack strength-limiting flaws along grain boundaries under a high residual stress. The mechanism requires (1) residual stresses in the fiber, (2) high-temperature weight loss from the coating, and (3) trapped porosity next to the fiber surface. Operation of this strength degradation mechanism implies: (1) improved strength with a lower residual stresses in the fiber (higher strengths with Nextel[™] 610 vs Nextel[™] 720), (2) improved strength with less high-temperature weight loss (GdPO₄ vs LaPO₄), and 3) improved strength in coatings with continuous porosity (DyPO₄ vs LaPO₄). Future work should concentrate on defining the surfaceactive chemical species responsible for high-temperature stress corrosion. With this knowledge, it may be possible to develop coating precursors that do not degrade coated fiber strength.

IV. Conclusions

Various rare-earth orthophosphates, both monazite and xenotime, were applied as coatings to Nextel[™] 610 and 720 fibers by heterogeneous precipitation. The extent of strength degradation during fiber coating was assessed following a high-temperature heat treatment. Higher coated fiber strengths were obtained for Nextel[™] 610 fibers due to lower thermal residual stresses. Higher coated fiber strengths were obtained for both types of fibers when coatings had lower high-temperature weight loss and slower densification rates. These results are consistent with a stress corrosion mechanism for strength degradation, where the surface-active species responsible for stress corrosion arises from high-temperature decomposition products of the coating precursor, which are trapped at the fiber-coating interface in coatings that densify rapidly.

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