ISSN 0020-1685, Inorganic Materials, 2011, Vol. 47, No. 10, pp. 1066–1071. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © A.V. Utkin, A.A. Matvienko, A.T. Titov, N.I. Baklanova, 2011, published in Neorganicheskie Materialy, 2011, Vol. 47, No. 10, pp. 1176–1181.

Preparation and Characterization of Multilayered ZrO_2 Coatings on Silicon Carbide Fibers for SiC/SiC Composites

A. V. Utkin[a], A. A. Matvienko[a], A. T. Titov[b], and N. I. Baklanova[a]

[a] *Institute of Solid-State Chemistry and Mechanochemistry, Siberian Branch, Russian Academy of Sciences, ul. Kutateladze 18, Novosibirsk, 630128 Russia*

[b] *Joint Institute of Geology, Geophysics, and Mineralogy, Siberian Branch, Russian Academy of Sciences, pr. Akademika Koptyuga 3, Novosibirsk, 630090 Russia*

e-mail: utkinalex@hotmail.com

Received January 21, 2011

Abstract—We have studied the surface morphology, phase composition, and oxidation resistance of multilayered tetragonal zirconia coatings produced on silicon carbide fibers by a sol–gel process and measured the tensile strength of individual fibers as a function of the number of layers in the coating. SiC-fiber-reinforced silicon carbide minicomposites have been prepared through pyrolysis of an organosilicon polymer, and their fracture surfaces have been examined. Using microindentation, we have determined the critical fiber–matrix debonding stress. The results demonstrate that the ZrO_2 coating on the fibers has the form of uniform, weakly bonded layers. The presence of a multilayered ZrO_2 interphase alters the fracture behavior of the SiC/SiC composites. The fiber debond stress in the composites markedly decreases with an increase in the number of layers in the interphase.

DOI: 10.1134/S0020168511090238

INTRODUCTION

Advances in aerospace engineering are highly dependent on the development of novel oxidation-resistant high-temperature ceramic materials possessing high thermomechanical performance. Among such materials are SiC-fiber-reinforced silicon carbide composites. An effective approach for raising the fracture resistance of SiC/SiC composites is to produce an interfacial layer between the fiber and matrix (interphase), which weakens the fiber–matrix bonding, thereby raising the fracture toughness of the material [1].

The best results were obtained with coatings consisting of pyrolytic carbon, hexagonal BN, or alternating C/SiC layers, which markedly improved the mechanical performance of SiC/SiC composites owing to their layered structure and low debond stress [2–4]. At the same time, the low oxidation resistance of such coatings considerably lowers the maximum working temperature of the composites [5].

An alternative approach to producing an appropriate interphase for SiC/SiC composites is to use oxygen-containing compounds (refractory oxides or salts) capable of weakening the fiber–matrix bonding and raising the fracture toughness of the composite owing to some specific features of their structure or the possibility of various stress-induced processes (interlayer shear, twinning, and phase transitions) [6]. A candidate material for this application is zirconia, ZrO_2, which possesses high stability in oxidizing atmospheres at elevated temperatures. Yttria-stabilized tetragonal ZrO_2 offers high fracture toughness owing to the $T\text{-}ZrO_2 \longrightarrow M\text{-}ZrO_2$ phase transition induced by the mechanical stress of a growing crack and accompanied by an increase in volume [7].

In this paper, we report a coating design that combines the advantages of the two approaches above, namely, a multilayered structure made up of poorly bonded, thin layers consisting of one, oxidation-resistant material.

EXPERIMENTAL

Zirconia coatings were produced on Nicalon silicon carbide fibers (13–15 μm in diameter, ceramic grade, Nippon Carbon Vo., Japan). Before the coating process, the sizing was removed by etching for 24 h in a 1 : 1 mixture of ethanol and acetone, followed by room-temperature drying and heat treatment at 450°C for 1 h in air.

Coatings were applied by immersing fiber tows in a film-forming sol, followed by drying at room temperature. Next, the fibers were heated in vacuum to 950°C and held there for 1 h. The sol was prepared by dissolving zirconyl chloride octahydrate, $ZrOCl_2 \cdot 8H_2O$, in an 8 : 1 mixture of ethanol and water with additions of polyethylene glycol and rare-earth nitrates. To pro-

duce multilayered coatings, the procedure was repeated several times.

The surface morphology and microstructure of the coatings were examined by high-resolution scanning electron microscopy (SEM) on an LEO 1430VP (LEO Electron Microscopy Ltd, UK). Raman spectra were taken with a SPEX Triplemate spectrometer (France) equipped with a CCD detector and microscope. The spectra were measured from 40 to 1700 cm^{-1}. As the excitation source, we used a 488-nm laser beam, which was focused by a lens to a 2-μm spot diameter on the fiber surface. Uncoated and coated fibers were tested in tension on an FM-27 tensile testing machine (Hungary) at room temperature.

Uncoated and coated fibers were oxidized in air at 1000°C for 35 h in a KO-14 muffle furnace (Roemhild, Germany). To determine the sample weight, the fibers were withdrawn from the furnace, cooled to room temperature in a desiccator, and weighed on an AX 120 electronic balance (Shimadzu, Japan), having 0.1-mg divisions.

The silicon carbide matrix was prepared through vacuum pyrolysis of polydimethylsilethyne, $(-(CH_3)_2Si-C\equiv C-)_n$, at 950°C. Uncoated and coated fibers were immersed in a polymer suspension in chloroform. The resultant samples were dried at room temperature, and then the polymer was pyrolyzed for 1 h. The procedure was performed twice in order to fill the spaces between the fibers. The volume fraction of the filler in the unidirectional composites was ≈40%.

Vickers microhardness was measured at room temperature using the MPH 100 diamond microindenter of a NEOPHOT-21 optical microscope (Carl Zeiss Jena). The fiber debond stress was measured as described by Marshall [8]. A fiber was indented with a diamond pyramid. Above a critical load, the fiber debonded from the matrix and slid into the composite. From analysis of indents on the fiber and matrix, we evaluated the critical fiber–matrix debonding stress.

Indented minicomposite surfaces were imaged by scanning electron microscopy (TM-1000, Hitachi, Japan and LEO 1430VP, LEO Electron Microscopy Ltd, UK).

RESULTS AND DISCUSSION

SEM examination of the surface morphology and microstructure of the coated fibers showed that the coating had the form of dense, uniform layers ranging in thickness from 50 to 100 nm (Figs. 1a, 1b). No bonding between fibers through the coating was detected, but some of the fibers had elongated ridges on their surface. This was because the sol was retained between the closely spaced fibers, leaving ridges after heat treatment (Fig. 1c). The retained sol volume depended on the viscosity of the sol. In view of this, to reduce the density of flaws the initial total salt concentration in the sol was lowered to 0.1 M, and polyethylene glycol was added to the sol in order to maintain its film-forming properties unchanged.

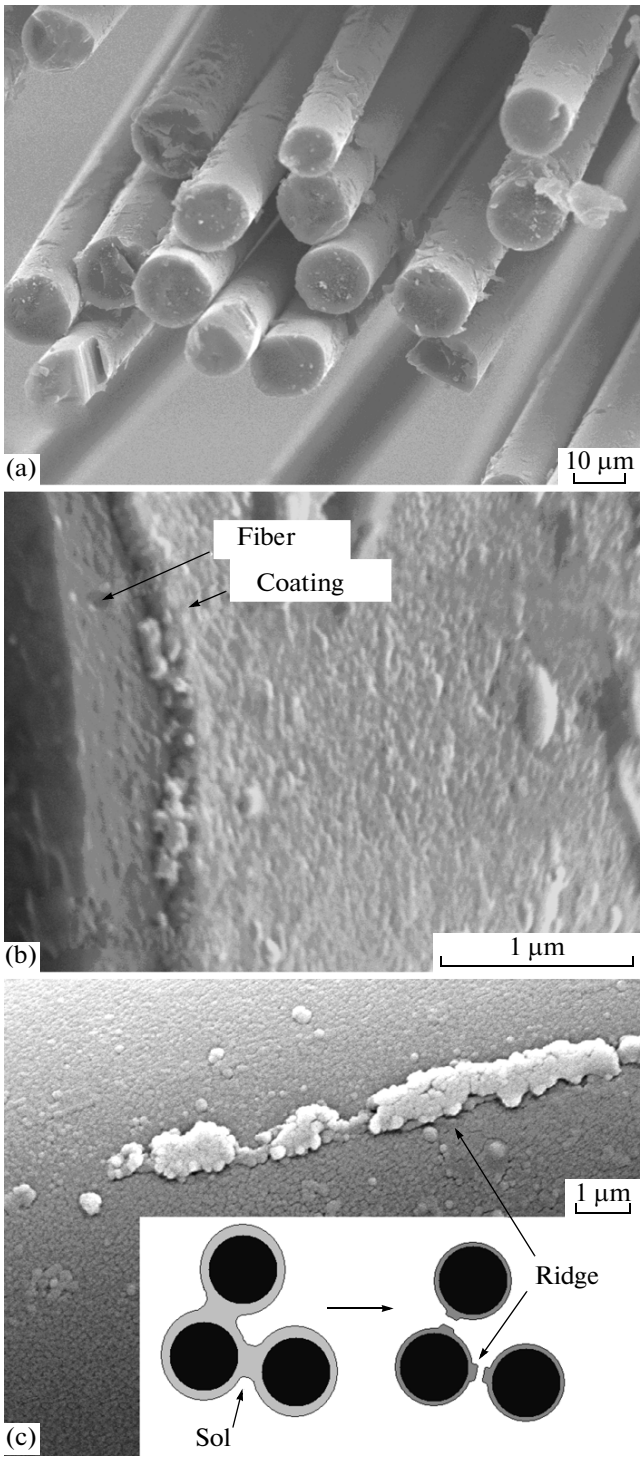

Fig. 1. Coated fibers: (a) general view of a fiber tow, (b) surface of an individual fiber, (c) surface ridge and schematic illustrating ridge formation.

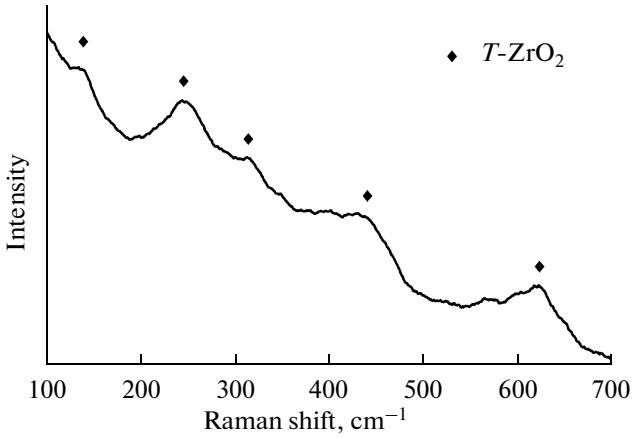

Fig. 2. Raman spectrum of the surface of a coated fiber.

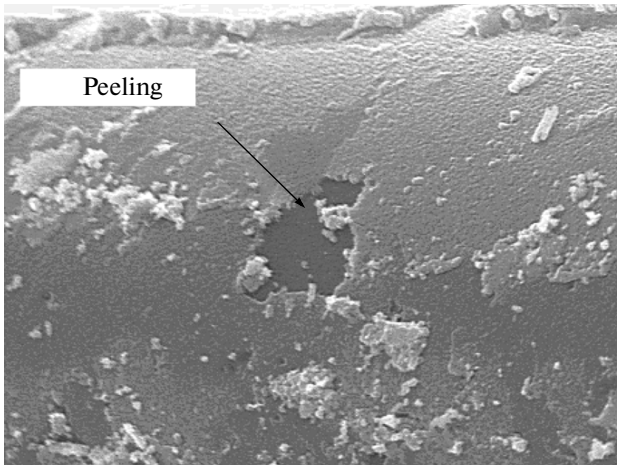

Fig. 3. Peeling of the outermost layer in a multilayered coating.

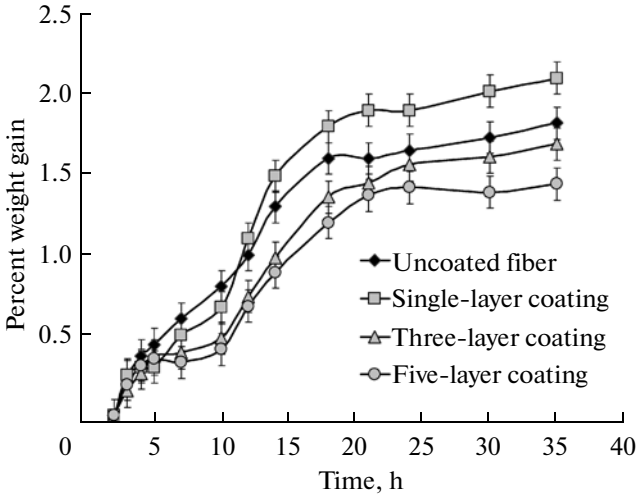

Fig. 4. Weight gain as a function of fiber oxidation time.

Raman spectroscopy data for the surface of the coated fibers demonstrate that the coating consists predominantly of tetragonal zirconia (Fig. 2). SEM images of some fibers having three- to five-layer coatings showed local peeling of the outermost layer (Fig. 3). This was caused by the mechanical stress arising during cooling because of the thermal expansion mismatch between SiC and ZrO_2. The peeling of the outermost layer of the coating from the underlying layers points to poor adhesion between the layers in the multilayered coating.

A similar multistep sol–gel coating process was reported by Fair et al. [9–11], but they obtained monolithic coatings, in contrast to the poorly bonded layers in this study, and the only effect of each processing step was to increase the thickness of the coating. The likely reason for this was that the layers were not sufficiently well crystallized before the next coating cycle and were thus well bonded to one another. In this study, the fibers were heat-treated at high temperature after each coating cycle, so each layer was deposited on the surface of a dense, well-crystallized layer, without firmly adhering to it. Moreover, the loss of water and ethanol molecules during heating reduces the thickness of the growing layer, resulting in spaces between the layers, which further reduce the interlayer bonding.

To assess the coating effect on the mechanical properties of the fibers, we measured the tensile strength of all the types of fibers. The experimental tensile strength data were analyzed in terms of the Weibull statistics. The results were used to determine the average tensile strength for each type of fiber. According to data in the literature, the strengths of the unprocessed and heat-treated fibers are 2.0 and 1.8 GPa, respectively [12]. In our measurements, the tensile strength of all the coated fibers was ≈1.6 GPa. Thus, the first coating layer reduces the mechanical strength of the fiber by ≈10%, which is probably due to the formation of above-mentioned surface ridges on the coated fibers. Analysis of SEM images of the end portions of the coated fibers suggests that surface ridges may initiate fiber fracture. The strength of the fibers coated with two or more layers is also 1.6 GPa, despite the larger number of surface ridges. It seems likely that the strength of the fibers is only influenced by the flaws in the first coating layer, which is well-bonded to the fiber. The ridges in the next layers do not reduce the mechanical strength of the fiber because of the poor bonding between the layers.

Oxidation testing results showed that, in the initial stage of oxidation (less than 10 h), all of the coated fibers had enhanced oxidation stability (Fig. 4). At longer oxidation times, the oxidation rate of the fibers having three- and five-layer coatings was slower. It seems likely that the microstructure of the single-layer coating was not dense enough to prevent atmospheric

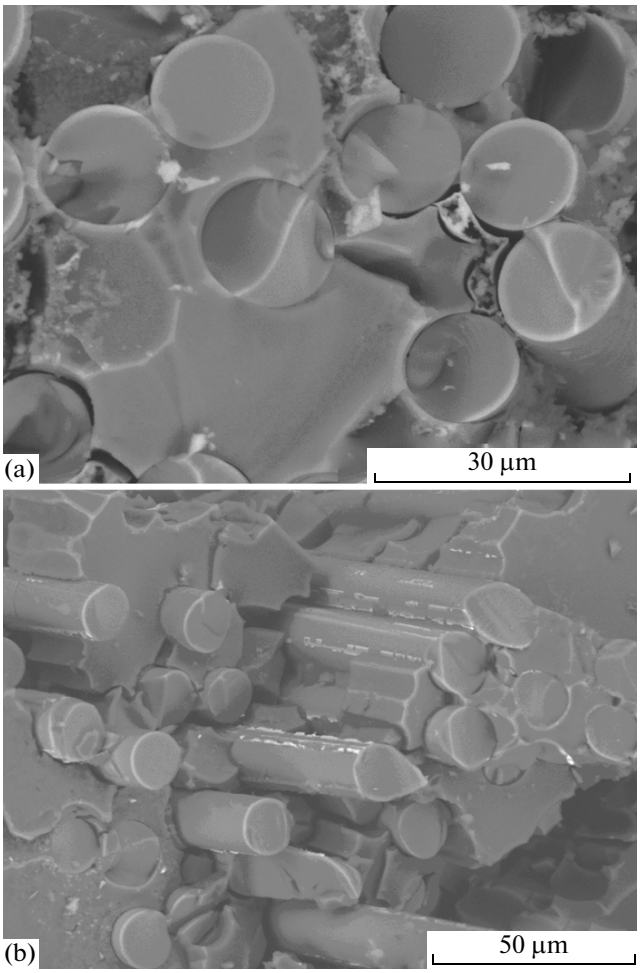

Fig. 5. Fracture surfaces of SiC/SiC composites: (a) no interphase, (b) three-layer interphase.

oxygen from reaching the fiber surface. The next layers closed the pores in the first layer, thereby reducing the oxidation rate of the fiber.

Using SEM, we examined fracture surfaces of minicomposites reinforced with uncoated and coated fibers. Micrographs of the composites reinforced with uncoated fibers point to brittle fracture behavior of the materials: there is no fiber pullout from the matrix, and the surface is weakly branched (Fig. 5a). In the case of the fibers with multilayered coatings, the appearance of fracture surfaces points to ductile fracture: the fibers are pulled out of the matrix, and the fracture surfaces have a complex shape (Fig. 5b). A more detailed examination of fracture surfaces of the composites having a multilayered interphase indicated that the fibers debonded from the matrix along an interface between the layers of the interphase, which remained bonded to both the fiber and matrix (Fig. 6).

To evaluate the fiber–matrix bonding strength in the composites, we measured the critical fiber–matrix

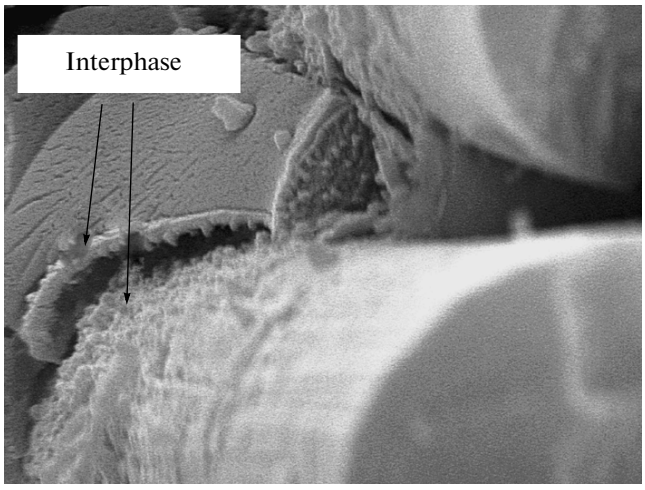

Fig. 6. Interphase delamination upon fracture of the composite.

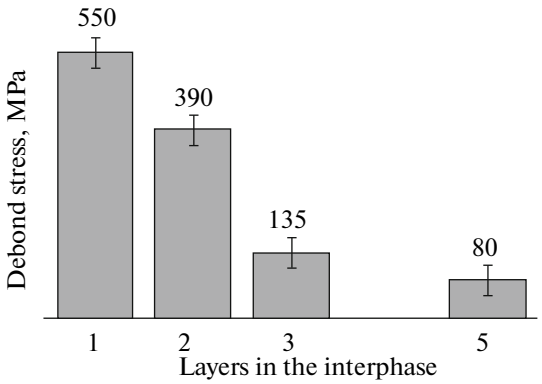

Fig. 7. Fiber debond stress in the composite against the number of ZrO_2 layers in the interphase.

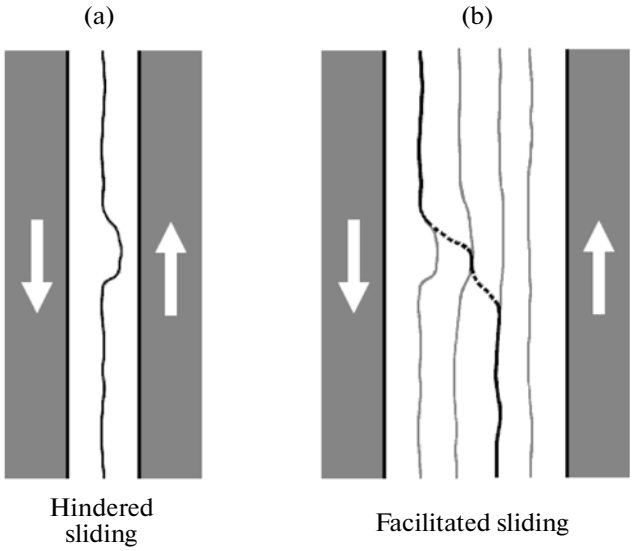

Fig. 8. Schematic illustrating fiber sliding relative to the matrix: (a) sliding hindered by an asperity; (b) a change in sliding plane to obviate an asperity.

debonding stress. The measurement results are presented in Fig. 7. Indentation of the interphase-free composites caused no fiber debonding from the matrix. Instead, the fiber cracked, and the cracks propagated into the matrix. The single-layer coatings failed to ensure the desired weakening of the fiber–matrix bonding. Indentation of such composites caused partial fiber debonding from the matrix and fiber cracking.

In the case of the fibers coated with two or more layers, the composites exhibited a different indentation behavior: the fiber completely debonded from the SiC matrix and slid relative to it. It is worth pointing out that the fiber debond stress in the composites markedly decreases with an increase in the number of layers in the interphase (Fig. 7). The likely reason for this is that the presence of a multilayered interphase with weak interlayer bonding in the composites leads to the development of potential surfaces along which the fiber may slide relative to the matrix. The fiber debond stress then depends on the interlayer bonding strength, the roughness of the sliding surfaces, and the density of flaws that impede sliding (Fig. 8a). When there are flaws or asperities that prevent sliding, an interphase consisting of several layers enables a change in sliding plane to obviate the asperity (Fig. 8b), thereby reducing the fiber debond stress.

Under service conditions, the interlayer boundaries in an interphase may act as facilitated propagation paths for microcracks nucleating in the matrix. Microcrack deflection by the interphase and facilitated fiber sliding in the composite ensure reinforcement integrity during matrix crack propagation and raise the fracture energy of the composite.

CONCLUSIONS

A multilayered interphase design concept was applied to silicon carbide fiber reinforced composites. Using a sol–gel process, we produced multilayered yttria-stabilized zirconia coatings on SiC fibers, with weak interlayer bonding in the coatings. Reinforcing SiC composites with the coated fibers, we obtained composites with ductile fracture behavior. The ductile fracture behavior is assumed to result from the weakening of the fiber–matrix bonding on account of the multilayered ZrO_2 interphase. The proposed interphase design allows one to control the fracture behavior of composites and ensures high thermal stability and oxidation resistance of the fiber, which makes it highly attractive for the fabrication of SiC/SiC composites.

The proposed approach to producing multilayered coatings can be successfully used to apply other oxide coatings to various substrates using film-forming sols.

Therefore, optimizing not only the coating material, possessing appropriate physicochemical properties and microstructure, but also the number of layers in the coating, one can effectively control the processes at the fiber/matrix interface in SiC/SiC composites. This, in turn, offers the possibility of tailoring the thermomechanical properties of the entire composite material.

ACKNOWLEDGMENTS

This work was supported by the Chemistry and Materials Science Division of the Russian Academy of Sciences, grant no. 5.2.1.

REFERENCES

1. Ceramic Fibers and Coatings: Advanced Materials for the Twenty-First Century, *Committee on Advanced Fibers for High-Temperature Ceramic Composites,* Washington, DC: National Academy, 1988.
2. Katoh, Yu., Nozawa, T., and Snead, L.L., Mechanical Properties of Thin Pyrolytic Carbon Interphase SiC-Matrix Composites Reinforced with Near-Stoichiometric SiC Fiber, *J. Am. Ceram. Soc.*, 2005, vol. 88, pp. 3088–3095.
3. Naslain, R., Dugne, O., and Guette, A., Boron Nitride Interphase in Ceramic-Matrix Composites, *J. Am. Ceram. Soc.*, 1991, vol. 74, pp. 2482–2488.
4. Bertrand, S., Lamon, J.L., and Naslain, R.R., $(PyC–SiC)_n$ and $(BN–SiC)_n$ Nano-Scale Multilayered Interphases by Pressure Pulsed-CVI, *Key Eng. Mater.*, 2002, pp. 2189–2192.
5. Naslain, R., Pailler, R., and Lamon, J., Single- and Multilayered Interphases in SiC/SiC Composites Exposed to Severe Environmental Conditions: An Overview, *Int. J. Appl. Ceram. Technol.*, 2010, vol. 7, no. 3, pp. 263–275.
6. Kerans, R.J., Hay, R.S., Parthasarathy, T.A., and Cinibulk, M.K., Interface Design for Oxidation-Resistant Ceramic Composites, *J. Am. Ceram. Soc.*, 2002, vol. 85, pp. 2599–2632.
7. Bocanegra-Bernal, M.H. and De La Torre, S.D., Review: Phase Transitions in Zirconium Dioxide and Related Materials for High Performance Engineering Ceramics, *J. Mater. Sci.*, 2002, vol. 37, no. 23, pp. 4947–4971.
8. Marshall, D.B., An Indentation Method for Measuring Matrix–Fiber Frictional Stresses in Ceramic Composites, *J. Am. Ceram. Soc.*, 1984, vol. 67, pp. 259–260.
9. Fair, G.E., Hay, R.S., and Boakye, E.E., Precipitation Coating of Monazite on Woven Ceramic Fibers: I. Feasibility, *J. Am. Ceram. Soc.*, 2007, vol. 90, pp. 448–455.
10. Fair, G.E., Hay, R.S., and Boakye, E.E., Precipitation Coating of Monazite on Woven Ceramic Fibers: II. Effect of Processing Conditions on Coating Morphology and Strength Retention of Nextel™ 610 and 720 Fibers, *J. Am. Ceram. Soc.*, 2008, vol. 91, pp. 1508–1516.
11. Fair, G.E., Hay, R.S., and Boakye, E.E., Precipitation Coating of Monazite on Woven Ceramic Fibers: III—Coating without Strength Degradation Using a Phytic Acid Precursor, *J. Am. Ceram. Soc.*, 2009, vol. 92, pp. 420–428.
12. Simon, G. and Bunsell, A.R., Creep Behavior and Structural Characterization at High Temperatures of Nicalon SiC Fibres, *J. Mater. Sci.*, 1984, vol. 19, pp. 3658–3670.