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THE EFFECT OF FIBER COATINGS ON INTERFACIAL SHEAR STRENGTH AND THE MECHANICAL BEHAVIOR OF CERAMIC COMPOSITES

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ABSTRACT

Thin coatings deposited on ceramic fibers prior to densification employing chemical vapor infiltration techniques have been used to limit fiber-matrix bonding. This has resulted in improvements in strength and toughness at room and elevated temperatures in Nicalon® fiber-reinforced/SiC matrix composites. The properties of the fiber-matrix interface in fiber-reinforced ceramic composites have been examined utilizing an indentation method in which a standard microhardness indentor is used to push on fibers embedded in the ceramic matrix. Compositions and microstructures at the interface have been characterized employing analytical electron microscopy. Correlations between interfacial phenomena and observed mechanical behavior have been made.

INTRODUCTION

In evaluating the mechanical behavior of Nicalon/SiC composites fabricated during the development of the forced-flow, temperature-gradient chemical vapor infiltration process (FCVI), both brittle failure and ductile composite fracture were observed in specimens produced under similar conditions. A thorough analysis of the fracture surfaces of the composite specimens employing scanning and transmission electron microscopy revealed a thin film at the fiber-matrix interface of specimens that exhibited fiber pull-out. No film could be detected in the specimens that failed in a brittle manner.[1]

Auger electron spectroscopic (AES) analysis of the fracture surfaces of the composites exhibiting fiber pull-out, showed the fiber pull-out grooves to be oxygen rich and the fiber surfaces to be coated with a thin carbon film.[2] In comparison, it has been shown that a carbon-rich layer forms on the fiber surface in Nicalon-reinforced lithium aluminosilicate (LAS) glass-ceramic composites during processing.[3-5] The carbon-rich layer weakens bonding at the fiber-matrix interface resulting in a composite with high toughness. The layer could not be detected in samples with low strength and low toughness.[5]

To improve the reproducibility of the properties of Nicalon/SiC composites, a thin pyrolytic carbon layer was deposited on fibrous preforms prior to densification to provide a uniform interface. The carbon deposition conditions were chosen to produce a graphitic coating with a laminar structure that lies parallel to the fibers.[6,7] (Fig. 1) The coatings were found to prevent chemical damage of the fibers during processing, as well as weaken the fiber-matrix interface, enhancing fiber pull-out and slip.[2,8] The coating of the fibers with carbon resulted in an increase in the toughness and the ultimate strength of the composite materials; however, the usefulness of pyrolytic carbon is limited by its low resistance to oxidation. Therefore, other fiber coatings with similar mechanical properties but improved oxidation resistance were examined.

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Boron nitride has been employed as a modifying interlayer in various composite systems.[9,10] Submicrometer boron nitride coatings have proved to be valuable in controlling fiber-matrix bonding and interaction in zircon and zirconium titanate composites, as well as in other glass matrix systems. Boron nitride is relatively inert and has a greater resistance to oxidation than carbon.[11] These properties combined with its graphite-like structure make it a potentially excellent alternative to carbon as an interlayer in ceramic composite materials for service at elevated temperatures.

This report describes a study of fiber coatings used to alter the fiber-matrix bond and change the mechanical behavior of a ceramic fiber-reinforced ceramic matrix composite. The strength of the fiber-matrix bond was determined using established indentation methods[12]. Room and elevated temperature flexure strengths and resulting fracture behavior were used to qualitatively compare the effects of the various fiber pretreatments. Scanning and transmission electron microscopy have been used to characterize the structure and composition of the interface coatings.

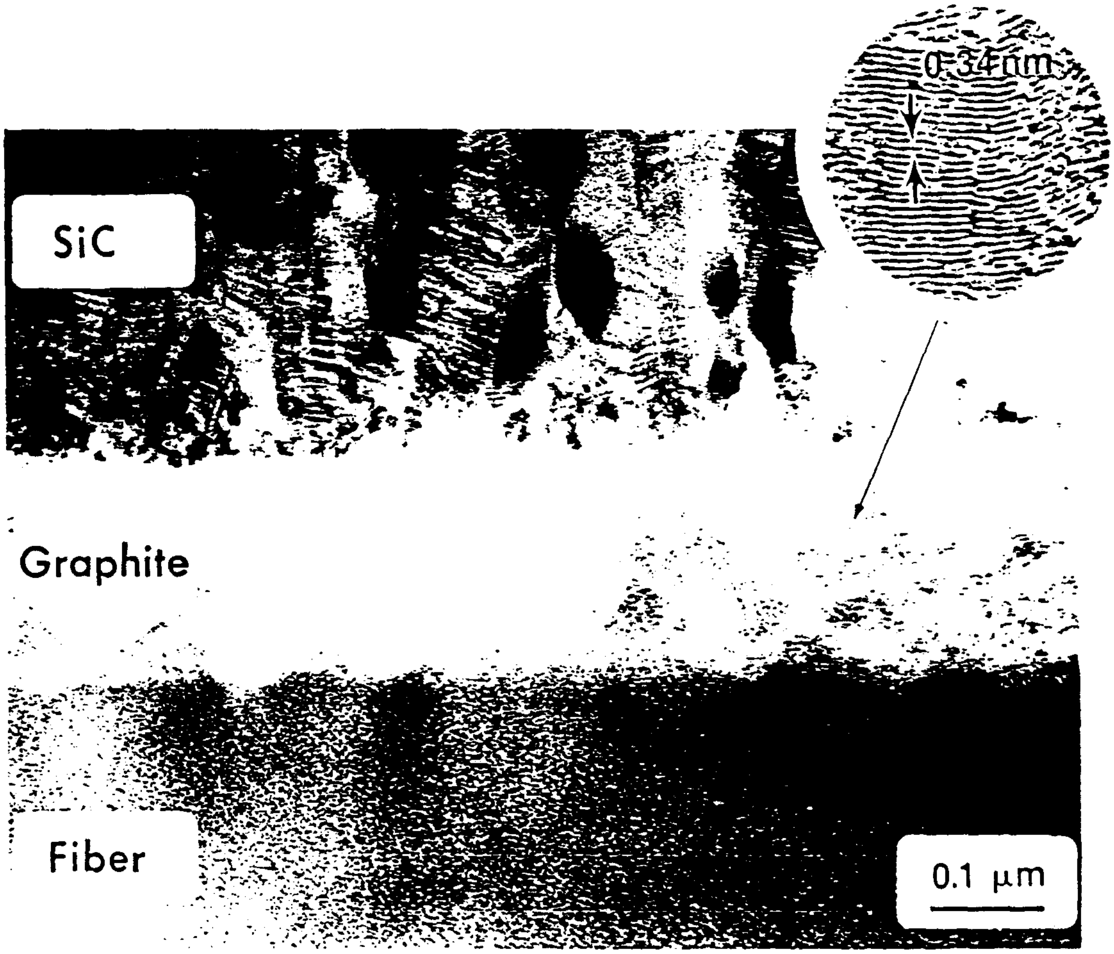

Fig. 1. TEM micrograph of the graphitic carbon layer at the interface of a Nicalon/SiC composite.

EXPERIMENTAL PROCEDURES

Composite Fabrication

Fibrous preforms were fabricated by stacking multiple layers of Nicalon plain-weave fabric rotated in a 0°± 30° sequence within the cavity of a graphite holder. The layers were hand compressed to produce a preform with a nominal loading of 40 vol. % fiber and were held in place by a perforated graphite lid pinned to the holder. The cloth sizing was removed through multiple washings with acetone. Two sizes of fibrous preforms were constructed, small disks, 45 mm in diameter and 12.5 mm thick, and larger disks, 75 mm diameter by 16 mm thick.

Selected preforms were next precoated with thin layers of carbon. The coatings were deposited from an argon/propylene mixture at 1375 K and 3 KPa pressure. The thickness of the carbon layer was varied by changing the concentration of the propylene and was measured using polarized-light optical microscopy of cross-sections. All coating times were two hours. Control samples of uncoated fibers were prepared for comparison.

The boron nitride coatings were applied to fabric samples prior to preform fabrication. The coated fabric was prepared by the CVD Department of Comhurex, Pierrelatte, France. BN layers were deposited on plain weave cloth from a mixture of boron trichloride, ammonia, and hydrogen utilizing proprietary processing conditions. Fibrous preforms were produced from the cloth as previously described.

The preforms were densified using the FCVI process developed at ORNL.[13,14] The composites were infiltrated with SiC produced by the decomposition of methyltrichlorosilane (MTS) in hydrogen at a hot-surface temperature of 1473 K and atmospheric pressure.

Flexure Testing

Bars were cut from the samples parallel to the 0°-90° orientation of the top layer of cloth using a diamond saw, and tensile and compression surfaces were ground parallel to the long axis of the specimen. The average dimensions of the test bars from the composite samples were 2.5 × 3.3 × 40 mm for the small samples and 3 × 4 × 55 mm for the larger composites. All specimens were measured and weighed to determine densities.

Room temperature flexural strengths were measured using four-point bending methods, with a support span of 25.4 mm, a loading span of 6.4 mm, and a crosshead speed of 0.051 cm/min. The larger bend bars were used for elevated temperature flexure testing. The specimens were first coated with a 35 μm SiC layer prior to testing. The elevated temperature flexure strengths were measured in four-point bending, with a support span of 40 mm, a loading span of 20 mm, and a loading rate of 1.0 kg/sec. The tests were performed using alumina fixtures at 298, 773, 1023, 1273, and 1473 K. All specimens were loaded perpendicular to the layers of cloth. The fracture surfaces of the specimens were examined using a Hitachi S-800 scanning electron microscope. Specimens that did not completely separate during flexure testing were broken by hand so that the fracture surfaces could be examined.

Fiber-Matrix Bond Measurements

Several methods have been developed to quantify the strength of interfacial bonding in fiber-reinforced composites.[12,15,16] Such tests permit a semiquantitative determination of interfacial stresses derived from relatively simple load and displacement relationships. A common technique is the indentation method, which has been thoroughly examined.[12,15] This technique involves using a microhardness indentor to apply a force to the end of a fiber embedded in a matrix. Interfacial shear stresses can be evaluated from the applied load and the displacement of the fiber.

A 6.0-mm thick cross-sectional specimen was cut from each completed composite sample to be used for indentation testing. The specimens were cut along the 0-90° orientation of the top layer of cloth to ensure that a portion of the exposed fibers would be oriented perpendicular to the cut surface. This alignment is essential for proper implementation of the indentation mechanics. The specimens were mounted and polished using standard metallographic techniques. Loads were applied to fiber ends using a Vickers diamond indentor and a Shimadzu Type M instrument. Loading to the fiber ends was progressively increased until debonding was observed and continued until contact of the indentor with the edge of the fiber cavity was evident. Loads of up to 3.0 N were required to displace the fibers. Indents were also placed in longitudinally polished fibers to determine fiber hardness values.

RESULTS

Interfacial Stresses and Mechanical Behavior

Room temperature flexure strengths, densities, and interfacial frictional stress measurements are summarized in Table 1. The difficulties in interpreting flexure test results for continuous fiber-reinforced composites are recognized and the results are reported only for intercomparison. Load-crosshead displacement curves were recorded and were used to characterize fracture phenomena.

Table 1. The influence of fiber coatings on the properties of Nicalon/SiC composites.

Precoat	Thickness* (microns)	Frictional Stress (MPa)	Matrix Fracture Stress (MPa)	Ultimate Flexure Strength (MPa)	Observed Behavior
Uncoated	—	49 ± 15	82 ± 10	82 ± 10	Low strength, brittle
Carbon	0.07	11 ± 5	257 ± 29	344 ± 20	Moderate strength, low pull-out
Carbon	0.17	4.3 ± 1.2	193 ± 28	420 ± 36	High strength, improved pull-out
Carbon	0.28	0.6 ± 0.4	160 ± 16	390 ± 13	Moderate strength, pull-out
Carbon	>0.5	—	—	352 ± 33	Lower strength, high pull-out
Boron Nitride	0.15	6.6 ± 1.7	—	350 ± 40	Moderate strength, pull-out

*Calculated from weight gain.

The composites prepared from uncoated fibers exhibited low flexure strength and displayed brittle failure, with no signs of toughening (Table 1). The lack of fiber pull-out and the flat, smooth fracture surfaces of test specimens suggest a high degree of bonding between fiber and matrix and/or complete failure of the reinforcement. Indentation measurements confirmed the high interfacial frictional stresses and in some cases the loads were enough to cause splitting of the fiber and extensive cracking of the surrounding matrix (Fig. 2).

The influence of the thickness of the carbon layer on the mechanical behavior of the composites was investigated. The concentration of reactant propylene was varied to produce films that ranged in thickness from 0.10 to > 0.5 μm. The thickness of the interfacial film had a significant effect on the matrix fracture stress, ultimate strength, and toughness of the specimens. (Table 1) The influence of carbon interlayer thickness on the fracture of the composites is shown in the load-displacement curves in Figure 3. A single matrix crack was observed in all tests and can be seen as the sudden drop in the curve and subsequent deviation from linearity. Matrix cracking stress and interfacial frictional stress decreased with increasing interlayer thickness. The decrease in frictional stress was also accompanied by an increase in the degree of fiber pull-out.

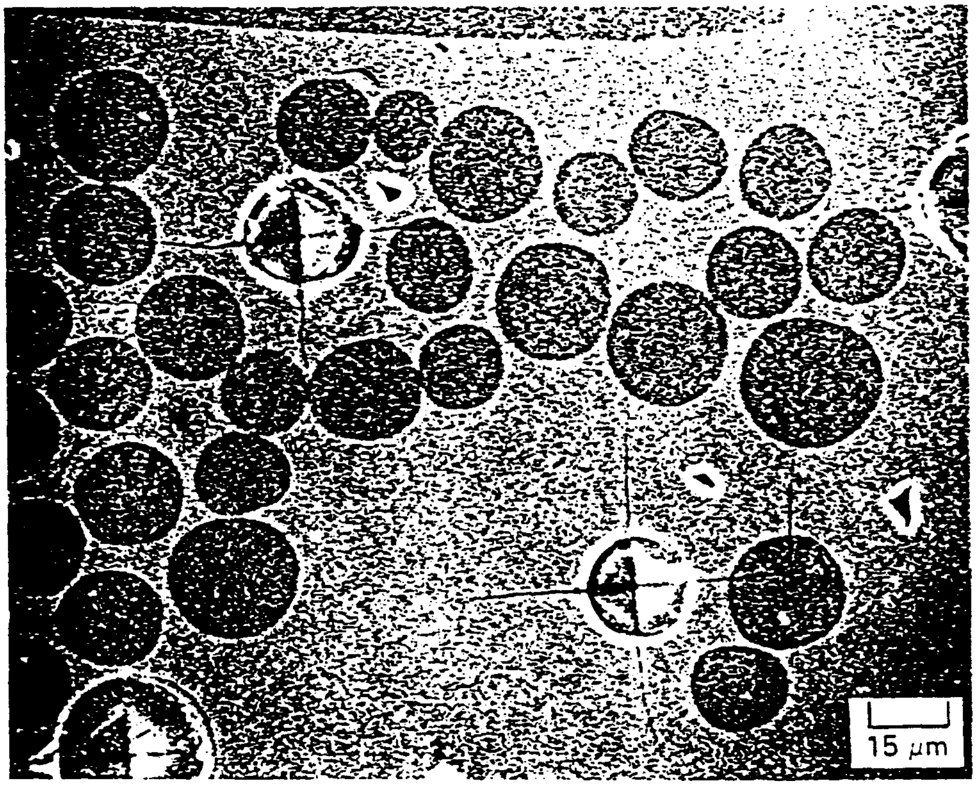

Fig. 2. Indent impressions on uncoated Nicalon fibers in a SiC matrix. (interfacial frictional stress, $\tau_i = 49 \pm 15$ MPa).

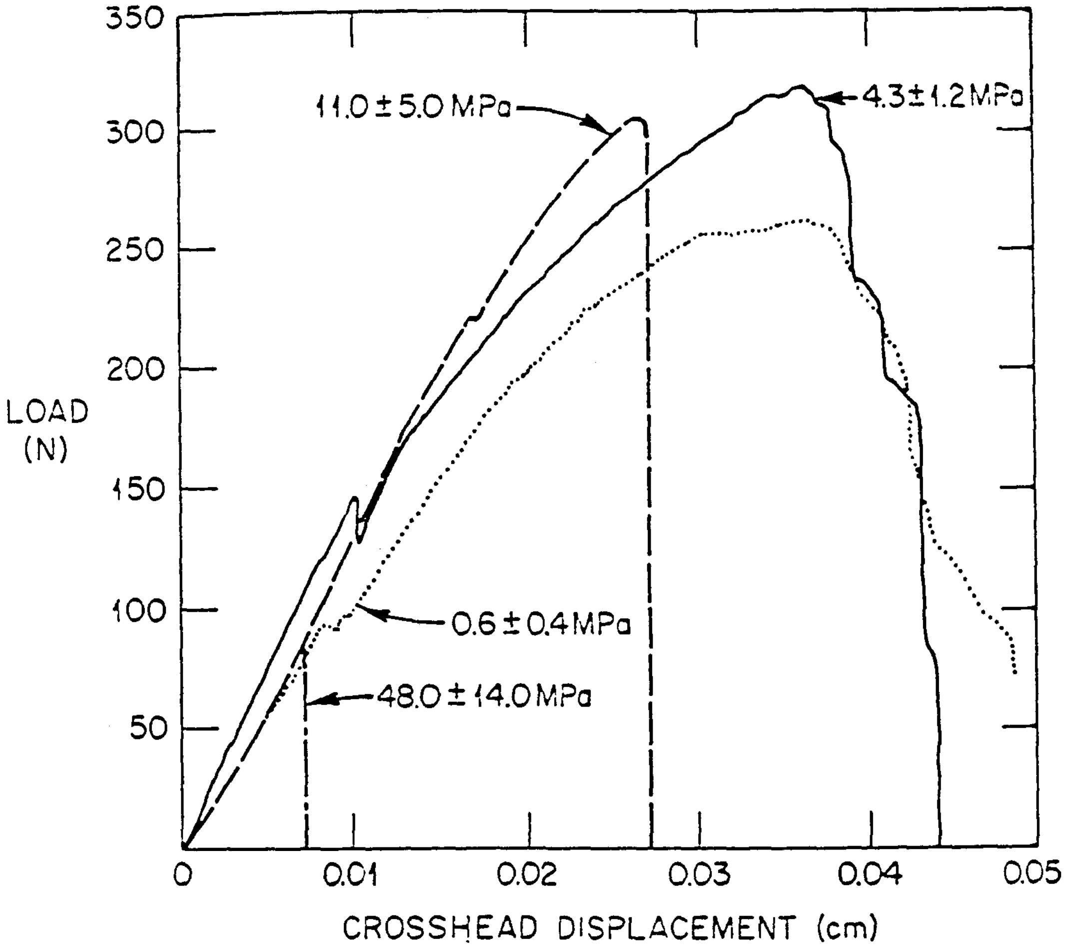

Fig. 3. The effect of carbon interface coating thickness on the flexure behavior of Nicalon/SiC composites. Indentation frictional stresses for the curves are indicated.

Composites produced with boron nitride-coated fibers exhibited strength values and fracture behavior comparable to composites with carbon interfacial layers. Transmission electron microscopic analysis of the interface in the composites found the BN coatings to be ~0.2 μm thick and composed of extremely fine grains of hexagonal BN. The graphitic structure of the hexagonal, BN grains was evident in high resolution TEM micrographs of the interface layer. (Fig. 4)

The ultimate strength of the composites increased slightly with temperature up to 1273 K where degradation of fiber properties results in a reduction in composite strength. (Fig. 5) The composites exhibited good strengths and gradual failure in all tests. No differences in the performance of specimens containing fibers with similar thicknesses of carbon and boron nitride (~0.2 μm) were observed.

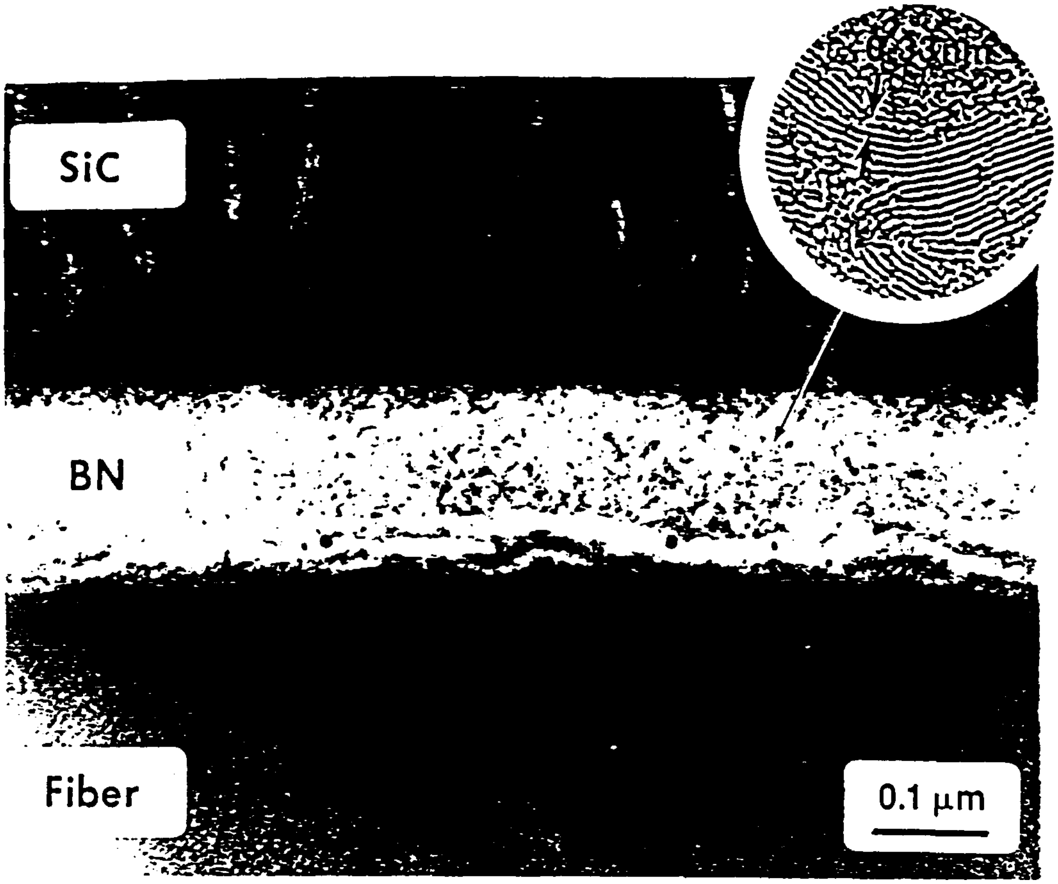

Fig. 4. TEM micrograph of the polycrystalline BN interlayer in a Nicalon/SiC composite. Inserted high resolution TEM micrograph shows graphitic structure of the coating.

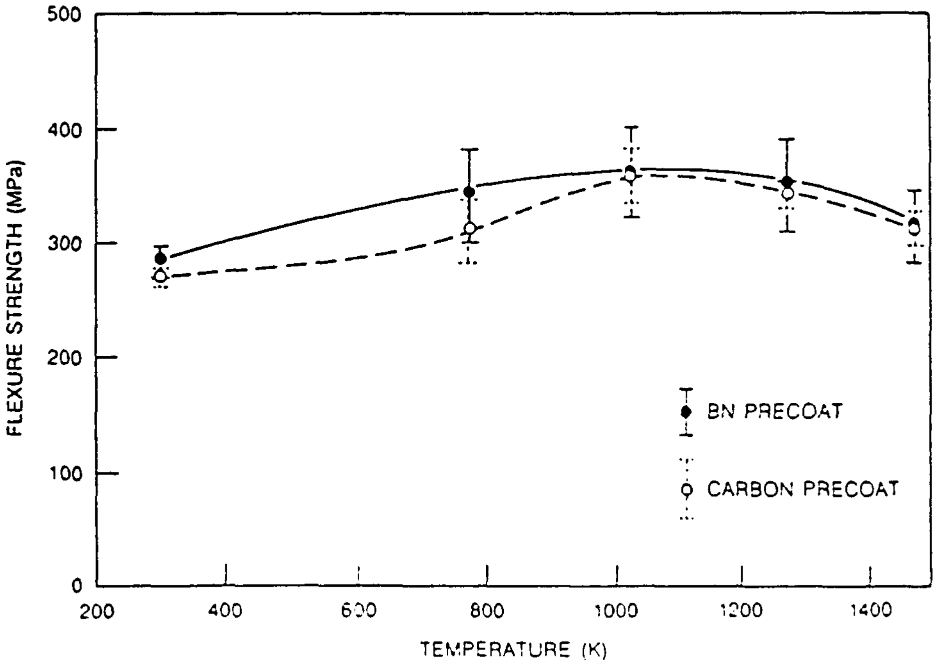

Fig. 5. High temperature flexure strengths for Nicalon/SiC composites with ~ 0.2 μm carbon and BN interface coating.

DISCUSSION

Precoating and Fracture Behavior

Pyrolytic carbon and boron nitride layers deposited on fibrous preforms prior to densification improved the mechanical properties of Nicalon/SiC composites fabricated using FCVI techniques. Precoating fibers prior to matrix deposition not only reduced interfacial stresses, but may have also provided protection from chemical attack during processing. The values for interfacial frictional stress for the samples containing uncoated fibers were relatively high; 49 ± 15 MPa as calculated from indent measurements. In comparison, reported shear numbers for Nicalon/glass composites are ~ 2.0 MPa.[12] The high values for Nicalon/SiC composites fabricated from uncoated fibers are consistent with observed behavior, for these composites exhibited brittle, catastrophic failure. Carbon coatings at the fiber-matrix interface significantly reduced interfacial frictional stresses in the Nicalon/SiC composites. Composites with carbon interlayers had measured interfacial stresses of <1 to ~10 MPa. Specimens with thicker carbon layers, thus lower interfacial stresses, exhibited a high degree of pull-out, comparable to the degree observed in the aforementioned glass matrix composites.

Polycrystalline hexagonal BN possesses structure and properties very similar to those of graphite and a coating of this material deposited on the fibers produced results comparable to those of carbon interfacial coatings. The room and elevated temperature mechanical properties and fracture behavior of the Nicalon/SiC composites with graphitic carbon and polycrystalline boron nitride coatings of the same thickness were identical. Interfacial frictional stress measurements were virtually the same for the carbon and BN interlayers, 4.3 ± 1.2 and 6.6 ± 1.7 MPa, respectively. Thus it is indicated that BN can be used as an alternative to carbon in this system for applications in oxidizing environments and at elevated temperatures.

CONCLUSIONS

The fiber-matrix interface in fiber-reinforced ceramic composites controls the mechanical behavior of these materials. An extremely strong bond does not allow for crack deflection or debonding at the fiber-matrix interface. A crack propagating in the matrix simply passes through the fibers undisturbed resulting in brittle fracture. Conversely, an extremely weakened interface leads to a low matrix fracture stress and low ultimate strength, for as the composite is stressed, load is not transferred efficiently from the matrix to the fibers, thus the properties of the reinforcement are not utilized. Interfacial forces must be controlled to produce a composite material with good matrix failure stress and ultimate strength that also exhibits gradual composite failure through effective fiber pull-out.

Carbon has been shown to be an effective interfacial coating for the Nicalon/SiC system. The deposition of a graphitic carbon coating on the fibers prior to infiltration improved the ultimate strength and toughness of the material. The thickness of the coating affects the properties of the interface and thus can be varied to produce material with different mechanical properties. Boron nitride, which possesses properties similar to carbon, produced room and high temperature strengths identical to those of the carbon layers. BN coatings may provide improved elevated temperature stability through improved oxidation resistance.

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