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**CRADA Final Report
for
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**Final Report for the ORNL/3M CRADA
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ABSTRACT

Oxide fiber-reinforced silicon carbide matrix composites were fabricated employing the forced-flow, thermal gradient chemical vapor infiltration (FCVI) process. Composites using NextelTM fibers of varying composition were prepared to investigate the effectiveness of each NextelTM fiber as a reinforcement for the given matrix. A carbon interface coating was used for the baseline materials, however, alternate interlayers with improved oxidation resistance were also explored. Room-temperature flexure strengths of as-fabricated composites and specimens heated in air at 1273 K were measured and compared to results for other SiC-matrix composites.

INTRODUCTION

Continuous fiber, SiC matrix composites are being developed for use in high temperature environments.¹ The forced flow, thermal gradient chemical vapor infiltration process has been used to fabricate oxide fiber/SiC composites before.² The work reported here was intended to provide an understanding of how the various compositions of these oxide fibers, and to some extent the fiber architecture, would effect the processing and final performance of a composite specimen. Composites were made using the different compositions of NextelTM fiber. These compositions are marketed as NextelTM 312, NextelTM 440, and NextelTM 550. The composition and mechanical properties of these fibers are presented in Table 1. As can be seen in the table these fibers present a range of tensile strength and modulus values.

NextelTM is a trademark of 3M Company, St. Paul, MN
Nicalon[®] is a trade designation of Nippon Carbon of Japan

It is well known that although the fibers and matrix play major roles in determining the final properties of a composite, the fiber-matrix interface has a significant influence on the fracture behavior and mechanical properties of reinforced ceramics. Typically, coatings are used to protect ceramic fibers from chemical attack during processing and to modify interfacial forces. The effects of an interlayer at the fiber-matrix interface in whisker- and fiber- reinforced ceramic composites have been examined.³ The coefficient of thermal expansion (CTE) mismatch between the matrix and reinforcement results in a residual stress at the interface. Calculations of this stress for uncoated fibers indicate that for NextelTM 312 this would be ~ 430 MPa (compressive), for NextelTM 440 ~ 100 MPa (compressive), and for NextelTM 550 ~40 MPa (tensile). A coating can modify the forces acting at the interface, influencing fiber debonding and sliding. Carbon, whether intentionally deposited on the fibers prior to consolidation⁴ or formed serendipitously during processing,⁵ is the most commonly used interlayer in ceramic composites today.

The poor oxidation resistance of carbon however, has lead to the examination of alternate coating materials or concepts for controlling the force at the fiber-matrix interface.^{6,7} It has been shown that the oxidation of Nicalon[®]/SiC composites begins by attack of the carbon interlayer coating at exposed fiber ends.^{8,9} Once the carbon is removed along the entire fiber length, the matrix and fiber oxidize and can bond together. A strong bond at the fiber-matrix interface does not permit easy debonding and sliding, and results in brittle behavior. The oxidation of the interlayer is likely to occur in any composite that uses carbon as an interface. However, the interaction of the fiber and the matrix will be determined by the composition of those materials.

Boron has been a key ingredient in oxidation resistant graphite and carbon-carbon composites. Boron oxidizes to form B₂O₃ which melts at 725 K, allowing the glass to flow and protect the carbon at temperatures relevant to many applications for ceramic composites. Boron doped carbon was thus chosen for investigation as an interlayer material.

Hexagonal boron nitride possesses a structure and mechanical properties similar to those of graphitic carbon, however, BN offers a distinct improvement in oxidation resistance.^{10,11} Due to these attributes, it is expected BN could be used as a direct replacement for carbon. Boron nitride interface coatings have already proven to be useful in controlling chemical and mechanical interaction between fibers and matrices.¹² Composites with good strength and toughness have been fabricated using BN-coated fibers and filaments. Composites were thus fabricated in this study using BN as an interlayer with both NextelTM 312 and NextelTM 440 fibers.

1. EXPERIMENTAL PROCEDURE

1.1 Composite Fabrication

Fibrous preforms were fabricated by stacking multiple layers of NextelTM fabric rotated in a $0 \pm 30^\circ$ sequence within the cavity of a graphite holder. The layers were hand compressed to produce a preform with a nominal fiber loading of 40 vol.% and were held in place by a perforated graphite lid pinned to the holder. The organic cloth sizing

was pyrolyzed, in argon, by exposing the cloth and the holder to 1373 K heat for 1 hour. This left a thin (~10 nm) layer of carbon on the surface of each fiber. The nominal size of the fibrous preforms was 75 mm in diameter and 15 mm thick.

Preforms were next coated with the various interface layers. The coatings were deposited using forced-flow, isothermal chemical vapor infiltration. A gas mixture containing argon and C_3H_6 was used to deposit carbon at 1373 K, and ~5 kPa. A gas mixture of argon, BCl_3 , and C_3H_6 or CH_4 , was used to deposit a boron containing carbon interface at 1373 K, and ~5 kPa. The ratio of boron to carbon in the gas mixture was varied from 1:6 to 1:18. A gas mixture containing BCl_3 , NH_3 , and hydrogen was used to deposit hexagonal BN as an interlayer, at 1373 K, and ~5 kPa. The ratio of boron to nitrogen in the reactant gas mixture was held constant at unity. Reactant flows and concentrations were chosen to produce: (i) deposition rates similar to those for the standard graphitic carbon layer (~1 nm/min.), (ii) microstructures comparable to those of graphitic carbon, and (iii) a uniform layer throughout the preform. Deposition times were then varied to control coating thickness. The final thicknesses of the interface layers were calculated from preform weight gains. In both cases where boron trichloride is used as a precursor gas a thin (40 nm) layer of carbon was deposited first to protect the oxide fiber from SiC precursor chloride attack.

The preforms were densified with SiC using the forced-flow, thermal-gradient chemical vapor infiltration (FCVI) process. The densification of porous structures using the FCVI process has been previously described in detail.^{1,13} The SiC matrix was produced by the decomposition of methyltrichlorosilane (CH_3SiCl_3 or MTS) in hydrogen at a hot-surface temperature of 1473 K and atmospheric pressure. The preforms were infiltrated with SiC to a maximum of 85 to 90% of theoretical density in ~28-35 hr.

1.2 Characterization and Testing

Test bars were cut from the composite samples parallel to the 0° 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 specimens were 2.5 x 3 x 40 mm and all specimens were measured and weighed to determine densities.

A portion of the specimens were tested in the as-fabricated state. Another portion of the specimens were oxidized in flowing air at 1273 K for 100 hours. Flexure bars were placed on an alumina plate in the cavity of a quartz tube furnace. Air was flowed through the furnace at 1 l/min, during heat up and soak. Once the furnace achieved equilibrium, the final temperature was measured and then maintained using a thermocouple-controlled programmer. At the specified time, the furnace was turned off and allowed to cool unassisted. The remaining specimens were treated in flowing argon (1 l/min) at 1273 K for 100 hours. Furnace controls and part placement were equivalent to the above conditions.

Room-temperature flexure strengths for as-fabricated and heat-treated composites were measured in four-point bending. A support span of 25 mm and a loading span of 6 mm were used with a crosshead speed of 0.50 mm/min. The load was applied perpendicular

to the layers of cloth. Load-displacement curves were recorded to examine the fracture process and determine the loads for ultimate strength calculations. The fracture surfaces of the specimens were examined using scanning electron microscopy (SEM).

2. RESULTS AND DISCUSSION

2.1 Mechanical Properties - As Fabricated

Typical flexure load-displacement curves for the Nextel™/SiC composites with pyrolytic carbon interfaces are shown in Figure 1. The composites exhibited good strength and composite behavior, i.e. failed with fiber pullout. The three fibers that were used to fabricate the composites are chemically very similar, and in mechanical properties are also quite similar. The flexure curves in Figure 1 illustrate that composites fabricated from these fibers with a carbon interlayer also exhibit similar mechanical properties

Typical flexure curves for the Nextel™ 312/SiC composites with pyrolytic carbon and BN fiber coatings are shown in Figure 2. The strength of the composites were influenced by the interlayer composition. Composites fabricated with a carbon interlayer had an ultimate strength of 220 ± 22 MPa. The samples fabricated with a BN interlayer had an ultimate strength of 300 ± 28 MPa.

Presented in Figure 3 are typical flexure curves for the Nextel™ 440/SiC composites with pyrolytic carbon, boron doped carbon, and BN interlayers. Again, the strength of the composites are influenced by the interlayer composition. Carbon interlayer samples had an ultimate strength of 220 ± 21 MPa, boron doped carbon interlayer samples had an ultimate strength of 250 ± 44 MPa, and BN interlayer samples had an ultimate strength of 340 ± 55 MPa.

2.2 Mechanical Properties - After Oxidation and Heat Treatment

Exposure to 1273 K in dry flowing air for 100 hours produced a slight discoloration of all specimens suggesting some degree of surface oxidation. As shown in Table 2 all composites with a carbon interlayer (CVI639, CVI623, and CVI644) exhibited reduced flexure strength after the exposure. However, samples of similar composition demonstrated little change in mechanical behavior when heat treated for 100 hr. at 1273 K, in argon.

Samples CVI620 and CVI650 have BN as an interlayer, and demonstrated higher flexure strength as compared to samples prepared with carbon coated fibers. These samples also exhibited little change in flexure strength after oxidation or heat treatment in argon.

The sample fabricated using the boron doped carbon as an interlayer demonstrated reduced resistance to oxidation as compared to a carbon interlayer. However, the boron doped carbon sample was inadvertently fabricated with an extremely thin interlayer (0.05 μm). It is hypothesized that an interlayer this thin would be ineffective in preventing fiber-matrix interactions. The properties of this sample were unaffected by heat treatment in argon.

2.3 Microstructural Characterization

The composite fracture surfaces were examined using scanning electron microscopy. All as-fabricated specimens demonstrated good fiber pull-out. The level of pull-out depended on the type and thickness of the interface material. For those composites with carbon as an interlayer, debonding appeared to occur largely at the NextelTM fiber-carbon interlayer interface. Some debonding also occurred at the carbon SiC matrix interface.

After oxidation the NextelTM 312 fiber materials with carbon as an interlayer exhibited brittle failure. SEM examination of these surfaces revealed no fiber pullout and a smooth fracture surface. The NextelTM 440 based composites did not exhibit brittle failure, and the fracture surface revealed some fiber pull-out. No evidence of the carbon interlayer could be found. The NextelTM 550 based composite also had good fiber pull-out in the oxidized specimens. Again, no evidence of the carbon interlayer could be found using SEM and optical microscopy. SEM examination of those samples that had undergone the argon heat treatment found complex fracture surfaces that had good fiber pull out and the interlayers were found intact.

3. CONCLUSIONS

A boron nitride interlayer proved to be an effective method to improve the oxidation resistance of the NextelTM/SiC composites. The strength and toughness of these composites were improved relative to those fabricated with carbon or boron doped carbon interfaces. Strength loss after exposure to air was minimal, and toughness remained comparable to as-fabricated carbon interlayer composites.

The flexure strengths of the NextelTM/SiC composites with the BN interlayer exhibited higher flexure strengths than comparable samples prepared with a graphitic carbon interlayer. This indicates that the BN coating was performing better than the graphite layer in accommodating the residual stresses in the composites. Oxidation did not alter these properties significantly.

Oxide fibers with the proper infiltration technique and interface layers can be used to fabricate composite materials that have useful flexure strengths. The long term oxidation stability, and lower cost of an oxide fiber can make them an attractive alternative to other fiber compositions.

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REFERENCES

- ¹T. M. Besmann, B. W. Sheldon, R. A. Lowden, and D. P. Stinton, "Chemical Vapor Infiltration", *Science* 253, pp. 1104-1109, September 6, 1991.
- ²R. A. Lowden, D. P. Stinton, and T. M. Besmann, "Characterization of Fiber-Matrix Interfaces in Ceramic Composites", pp. 253-264 in *Whisker- and Fiber- Toughened Ceramics*, Proceedings of an International Conference, ed. by R. A. Bradley, et al., ASM International, Oak Ridge, Tennessee (1988).
- ³C.-H. Hsueh, P. F. Becher, and P. Angelini, "Effects of Interfacial Films on Thermal Stresses in Whisker-Reinforced Ceramics", *J. Am. Ceram. Soc.* 71(11), 929-933 (1988).
- ⁴R. A. Lowden, "Fiber Coatings and the Mechanical Properties of a Fiber-Reinforced Ceramic Composite", pp. 619-630 in *Ceramic Transactions*, Vol. 19, Advanced Composite Materials, ed. by Michael D. Sacks, The American Ceramic Society, Westerville, Ohio (1991).
- ⁵J. J. Brennan, "Interfacial Characterization of Glass and Glass-Ceramic Matrix/Nicalon SiC Fiber Composites", pp. 549-560 in *MRS Proceedings*, Vol. 20, Tailoring Multiphase and Composite Ceramics, ed. by R. E. Tressler et al., Plenum Publishing Corporation (1986).
- ⁶M. A. Kmetz, J. M. Laliberte, and S. L. Suib, "Synthesis, Characterization, and Tensile Strength of CVI C/SiC, SiC/B₄C, and C/B₄C Composites", *Ceramic Eng. Sci. Proc.* 13[9-10], 743-751 (1992).
- ⁷R. A. Lowden, *Characterization and Control of the Fiber-Matrix Interface in Ceramic Matrix Composites*, ORNL/TM-11039, March 1989.
- ⁸R. A. Lowden and R. D. James, *High Temperature Corrosion of Nicalon[®]/SiC Composites*, ORNL/TM-11893, August 1991.
- ⁹R. D. James, R. A. Lowden, and K. L. More, "The Effects of Oxidation on the Properties of Nicalon[®]/SiC Composites", pp. 925-935 in *Ceramic Transactions*, Vol. 19, Advanced Composite Material, ed. by Michael D. Sacks, The American Ceramic Society, Westerville, Ohio (1991).
- ¹⁰N. J. Archer, "The Preparation and Properties of Pyrolytic Boron Nitride", pp. 167-181 in *High Temperature Chemistry of Inorganic and Ceramic Materials*, Special Publication No. 30, Edited by F. P. Glasser and P. E. Potter, The Chemical Society, London (1976).
- ¹¹T. Matsuda, "Stability to Moisture for Chemically Vapour-Deposited Boron Nitride", *J. Mater. Sci.* 24, 2353-2358 (1989).
- ¹²R. N. Singh and M. K. Brun, "Effect of Boron Nitride Coatings on Fiber-Matrix Interactions", *Adv. Ceram. Mater.* 3[3], 235-237 (1988).
- ¹³T. M. Besmann, R. A. Lowden, D. P. Stinton, and T. L. Starr, "A Method for the Rapid Chemical Vapor Infiltration of Ceramic Composites", *J. de Physique* 5(50), Colloque C5, 229-239 (1989).

Figure 1. Flexure Curves for NEXTEL 312, NEXTEL 440, and NEXTEL 550 with carbon interfaces.

Figure 2. Flexure Curves for NEXTEL 312 with carbon and BN interfaces.

Figure 3. Flexure curves for Nextel™ 440 with carbon, carbon plus boron, and BN interfaces.

Table 1. Fiber Properties

Fiber Type	Composition	Density (g/cm ³)	Tensile Strength (MPa)	Tensile Modulus (GPa)	CTE (10 ⁻⁶ /K)	Fiber (μm)
NEXTEL 312	Alumina-boria-silica	2.70	1,724	138.5	3.00	10
NEXTEL 440	Alumina-boria-silica	3.05	2,069	186.3	4.99	10
NEXTEL 550	Alumina-silica	3.03	2,000	193.2	5.70	11

Table 2. Flexure Strengths

Sample Number	Fiber Type	Interlayer Composition	Interlayer Thickness (μm)	As * Fabricated (MPa)	Oxidized ** (MPa)	Argon + (MPa)
CVI639	NEXTEL 312	CVD Carbon	0.12	222 ± 21	56 ± 5	185 ± 25
CVI620	NEXTEL 312	CVD BN	0.25	300 ± 18	285 ± 24	NA
CVI623	NEXTEL 440	CVD Carbon	0.22	220 ± 21	173 ± 28	251 ± 39
CVI647	NEXTEL 440	CVD C + Boron	0.05	250 ± 44	114 ± 30	221 ± 24
CVI650	NEXTEL 440	CVD BN	0.28	340 ± 55	300 ± 58	300 ± 72
CVI644	NEXTEL 550	CVD Carbon	0.31	192 ± 55	145 ± 8	181 ± 56

* As-Fabricated = No heat treatment.

** Oxidized = 100 hours at 1273 K in flowing air heat treatment.

+ Argon = 100 hours at 1273 K in flowing argon heat treatment.