EVOLUTION OF INTERFACE MICROSTRUCTURE IN A DUAL-COATED SILICON CARBIDE FIBER-REINFORCED BMAS GLASS-CERAMIC COMPOSITE

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ABSTRACT

Glass-ceramic composites with promising mechanical properties were produced by incorporating Nicalon fibers with a dual layer coating of CVD SiC/BN into barium magnesium aluminosilicate (BMAS) matrices. Interfaces in this composite were characterized using HRTEM, EDS and scanning Auger microscopy (SAM). Materials with different thermal histories were studied. On occasion, the BN/fiber interface exhibited silica-rich and carbon-rich interlayers. In some cases, the SiC overcoating debonded from the BN layer, and the BMAS matrix glass infiltrated between the two layers. The structure and chemistry of these interphases are presented and explained in terms of the corresponding fabrication and aging conditions.

1. INTRODUCTION

Fiber reinforced glass-ceramic composites are prospective materials for high-temperature, lightweight, structural applications.[1] Polymer derived Si-C-O or Si-C-N-O fibers that contain excess carbon and oxygen over stoichiometric SiC reportedly form a carbon-rich fiber/matrix interfacial layer when incorporated into glass-ceramic matrices at elevated temperatures.[2] This interfacial zone is weak and is responsible for the high toughness observed. Unfortunately, these weakly bonded, tough, and strong glass-ceramic matrix composites undergo embrittlement and concurrent strength and toughness degradation during long-term exposure in oxidative environments at high temperature. During the past few years, attempts have been made to find a replacement coating for the carbon-rich zone that would debond similarly but have improved oxidative stability.[3] In recent work,

CVD coatings of BN with a SiC overlayer, were deposited on small-diameter fibers such as the SiC-based Nicalon fiber and HPZ fiber. The thin SiC overcoat was applied to the BN coating as a diffusion barrier. Incorporating these coated fibers into glass-ceramic matrices such as lithium aluminosilicate (LAS) and barium-magnesium aluminosilicate (BMAS), resulted in composites with superior properties at elevated temperature.[4]

In this paper, we describe the results of a comprehensive study of the interfacial microstructure in BMAS matrix/SiC/BN coated Nicalon fiber composites. The changes in interface structure and chemistry as a function of composite processing and thermal history are investigated. The objective of this study is to arrive at a better fundamental understanding of interface phenomena controlling mechanical behavior and to provide a basis for microstructural design of composite interfaces that result in improved mechanical properties.

2. EXPERIMENTAL PROCEDURE

The material studied was barium-magnesium aluminosilicate (BMAS) reinforced with SiC/BN dual coated Nicalon fiber. The fibers were arranged in a 0/90° ply layup. The BN coatings were close to 1:1 (B:N) with ~15at% carbon. Composites were hot-pressed at 1450°C for 5 min. under 6.9 MPa pressure, then ceramed in argon to 1200°C for 24 hours. The composite materials investigated were in the following four conditions: as-pressed, ceramed, tensile stress-ruptured (1100°C, 344 hrs, stressed to 165 MPa maximum, air), and thermally aged (1200°C, 500 hrs, air).

The mechanical properties of the composite were evaluated by flexural testing (3pt) at both room temperature and elevated temperature. The sample size is ~5.1×2.5×100 mm. The interfacial microstructure was studied using HRTEM, and composition analysis of microstructural features was performed with EDS and SAM. TEM thin foils were prepared in a conventional manner. Specimens were examined using a JEOL 2010 microscope fitted with a Noran x-ray spectrometer capable of light element detection.

3. RESULTS AND DISCUSSION

3.1 Mechanical Properties

The flexural strength of the composite is excellent from RT to 1200°C, but declines after thermal aging for 500 hrs at 1200°C in air, as listed in Table 1 (the numbers in the table represent averages of 10 or more experiments, with the exception of the thermally-aged material). This decline in strength may be related to phenomena occurring in near-surface regions of the composite and/or the formation of very thin interlayers at the BN/fiber interface after this heat treatment, as shown later.

Table 1. Flexural strength (MPa) of BMAS matrix/SiC/BN coated Nicalon fiber composites (0/90°)

as-pressed (RT)	ceramed (RT)	1100°C	1200°C	thermally aged (1200°C, 500 h, air) (RT)
655	675	648	565	510

3.2 TEM Observations

(1) As-Pressed Composite

The microstructures of the Nicalon fibers, the BN and SiC coatings, and the associated interface region were investigated for the as-pressed composite. Fig. 1 shows the general features of the interfacial regions. From left to right in the figure are the Nicalon fiber, the BN coating, and the SiC coating, together with the corresponding SAD patterns. As reported previously,[5] the fibers are nanocrystalline and consist of randomly oriented β-SiC crystallites a few nanometers in size, with a small amount of amorphous phase. The SAD pattern of the Nicalon fibers shows continuous and diffuse rings, which is consistent with the extremely fine grain size and random orientation. The fine BN layer is comprised of nano-scale crystallites with a turbostratic structure. The structure has been
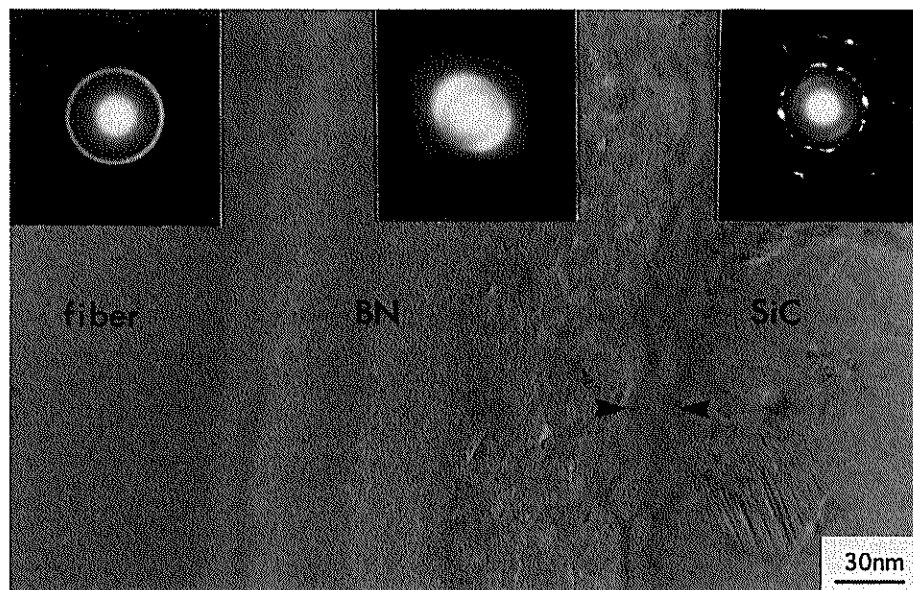

Fig. 1 Interfacial microstructure in as-pressed composite

suggested to be single-phase BN with a large degree of substitution of carbon for nitrogen in the hexagonal BN structure.[6] The BN coating is often composed of multiple sublayers, caused by the multiple passes through the reactor during chemical vapor deposition. The SiC coating deposited onto the BN layer consists of randomly oriented β-SiC crystallites that are several hundred nanometers in diameter. Twins are visible inside the grains, which is typical for CVD SiC. As shown in the SAD pattern, the SiC coating gives a pattern with strong diffraction spots on discontinuous rings. This indicates a polycrystalline structure with distinct grains.

Partial coarsening of the BN coating was often observed in the composite. It can be seen in Fig. 1 that the BN nearest the SiC layer is coarsened compared to the BN nearest the Nicalon fiber. The coarsening or crystallization of the turbostratic BN layer in this composite is associated with cracking of the SiC layer and detachment from the BN layer. This allows matrix elements to penetrate and form a thin amorphous layer between the SiC and BN layer, as indicated by arrows in Fig. 1. This can also be inferred from the SAM depth profile in Fig. 2, (taken from another sample and at a point where the SiC layer debonded,) which shows matrix elements, primarily Si, Ba and Al, have diffused into the BN layer. Some Ba has also diffused into the Nicalon fiber. A high-resolution image of the BN/SiC interfacial region is shown in Fig. 3. The amorphous glassy phase is evident in this image, as are the wavy fringes from the basal planes of hexagonal BN which tend to lie parallel to the fiber axis. The composition of the glassy phase, determined by EDS, was similar to that of the BMAS matrix, which contains BaO, MgO and Al_2O_3. Despite being detached from the BN, the SiC still apparently continued to act as a diffusion barrier for boron. The SAM depth profile (Fig. 2) showed no boron or nitrogen in the matrix near the SiC overlayer.
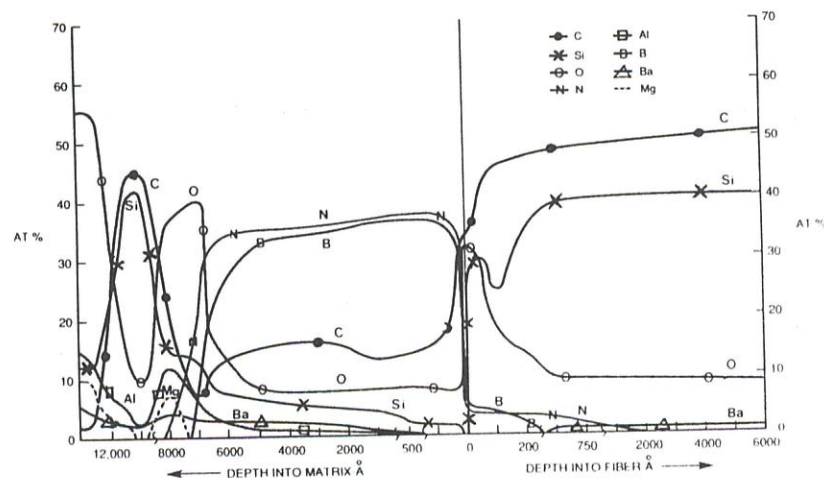

Fig. 2 SAM depth profile of interfacial chemistry in as-pressed composite
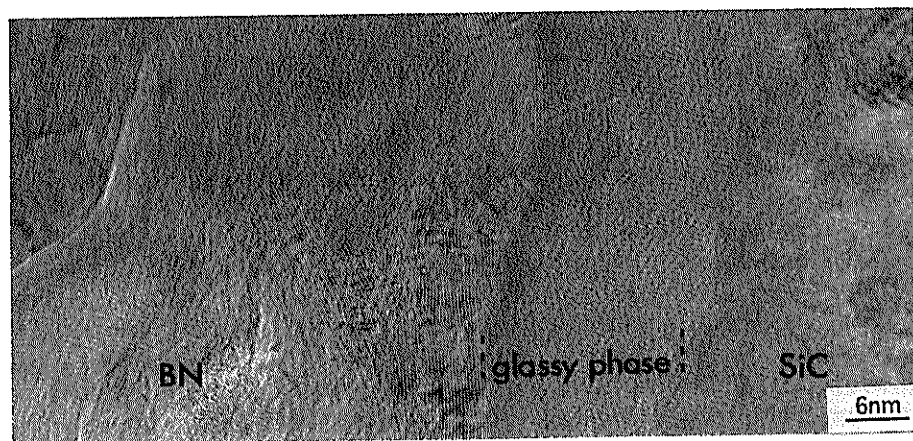
Advances in Ceramic-Matrix Composites

Fig. 3 Amorphous interphase between SiC and BN layers

A subtle amorphous interphase is present at the interface between the turbostratic BN layer and the nanocrystalline Nicalon fiber (Figs. 1 & 4). Fig. 4 shows a phase-contrast image of the BN/Nicalon fiber interface in this composite. EDS measurements of local composition of this interface were inconclusive because of the extremely small scale (5 to 10 nm). A layer rich in silica just to the right (fiber side) of the debond location is indicated by the SAM analysis in Fig. 2. The formation of such an interlayer during composite fabrication could occur as a result of the reaction: $SiC_{(s)} + O_{2(g)} \Rightarrow SiO_{2(s)} + C_{(s)}$, as discussed in section 3.3.
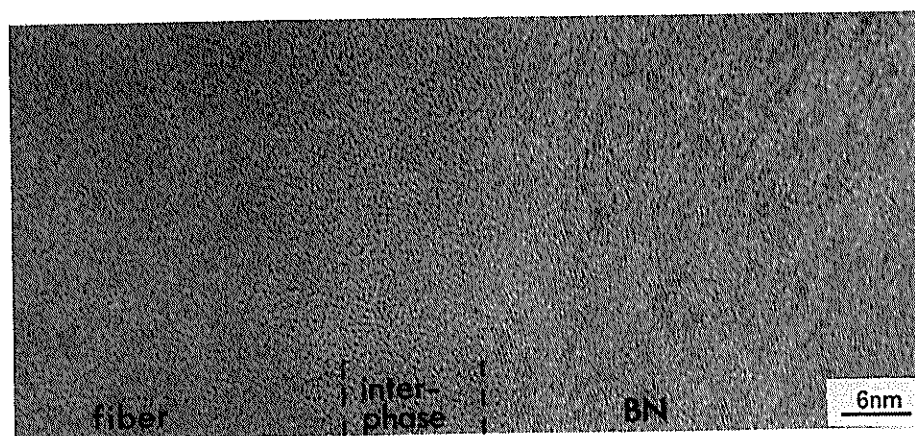

Fig. 4 Interphase region at the BN/Nicalon fiber interface

(2) Ceramed Composite

The microstructure of the composite was examined after the ceraming process (~1200°C, 24 hrs, Ar) to determine the effect of this processing on the interfaces. No distinct interphase was observed at either the SiC/BN interface or the BN/Nicalon fiber interface. A small amount of residual matrix glassy phase was observed after ceraming, particularly at the interface between the SiC coating and the matrix, as shown in Fig. 5. During ceraming, the matrix grains of barium osumilite appear to grow along preferred crystallographic directions in lath-like configurations. Ultimately, the grains impinge on obstacles, such as other grains or, in this case, the Nicalon fibers. Fig. 5 shows three such grains occluded by a Nicalon fiber. Because of local compositional variations, residual glassy phase may remain at sites where the coarse barium osumilite grains terminate. The EDS data shows that the glassy phase is enriched in barium and aluminum and possibly depleted in magnesium compared with the crystalline barium osumilite grains.
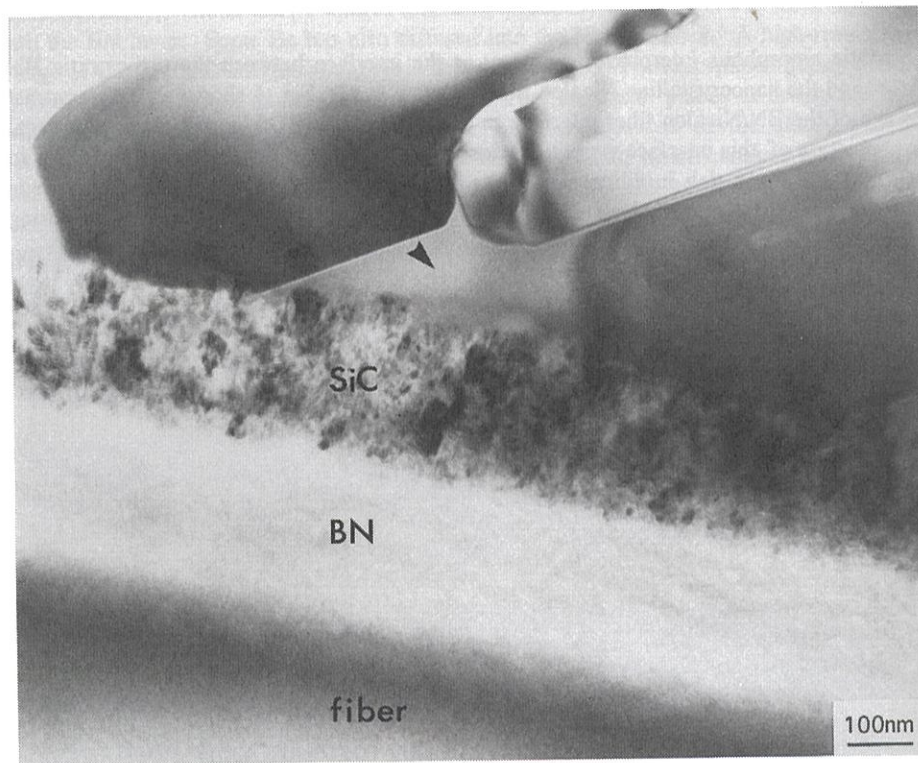

Fig. 5 Residual glassy phase at matrix/SiC coating interface after ceraming

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The SAM depth profile for this composite was taken at a point where the SiC layer remained bonded to the BN layer, with no matrix glass penetrating underneath it. Nevertheless, barium from the matrix diffused through the SiC layer, the BN layer, and into the Nicalon fiber. Barium, despite being a large atom, has been found in this and previous studies, to diffuse rapidly through the SiC and BN layers and deeply into Nicalon fibers. No evidence of carbon or silica film formation at the Nicalon fiber/BN interface was found, which is consistent with HRTEM observations.

(3) Tensile Stress-Ruptured Composite

Crack propagation paths for the 1100°C, 165 MPa stress-ruptured composite were revealed through microscopic observations. Crack propagation occurred through the matrix to the fiber/matrix interface and appeared only in the 90° layers of the 0/90° ply layup composite. The fact that cracks only appeared in the 90° layers, and not in the load-carrying 0° layers, indicates the remarkable structural integrity of this type of composite. The TEM micrograph in Fig. 6 shows that the crack follows the matrix glassy phase that has penetrated between the SiC and BN layers, deflects upwards across a barium osumilite matrix grain and then continues along the matrix/SiC layer interface of another fiber. The matrix grain between the two fibers appears to have sheared where the crack occurred, and dislocations are visible within the grain. This implies that during the test, matrix cracking started at a critical flaw in the matrix, and propagated to the matrix/fiber interface. Interfacial debonding occurred when the stress at the interface exceeded the interfacial strength, allowing the crack to propagate along the interface.

Cracks most frequently propagated in the BN layer, as shown in Fig. 7. In this case, the crack is between the fine and coarsened BN layer (arrow). However, crack propagation was not necessarily confined between the fine and coarsened BN sublayer. Cracking in the fine BN layer and near the BN/Nicalon fiber interface was also observed. Occasionally, debonding occurred in matrix near the matrix/SiC interface, usually in a layer of residual glass between the SiC layer and a barium osumilite grain.

Two distinct nano-scale sublayers were often observed at the BN/Nicalon fiber interface in the 90° plies of this composite, as shown in Fig. 7. The sublayer on the fiber side is light, while the one on the BN side is dark. Both sublayers were continuous and noncrystalline. The thickness of each sublayer is about 15 nm. The chemistry of the sublayers was determined from EDS composition profiles acquired by stepping the probe across the BN/Nicalon fiber interface (see Table 2). The light sublayer next to the Nicalon fiber was carbon-rich, while the dark sublayer next to the BN was silica-rich. The results are consistent with previous studies, reported by Bonney and Cooper on Nicalon fiber reinforced CAS composite,[7] and by Naslain *et al* on chemical vapor infiltrated 2D SiC/BN/SiC-fiber composite.[8] No distinct interphase was observed in the 0° plies, which were parallel to the tensile stress axis in this composite.
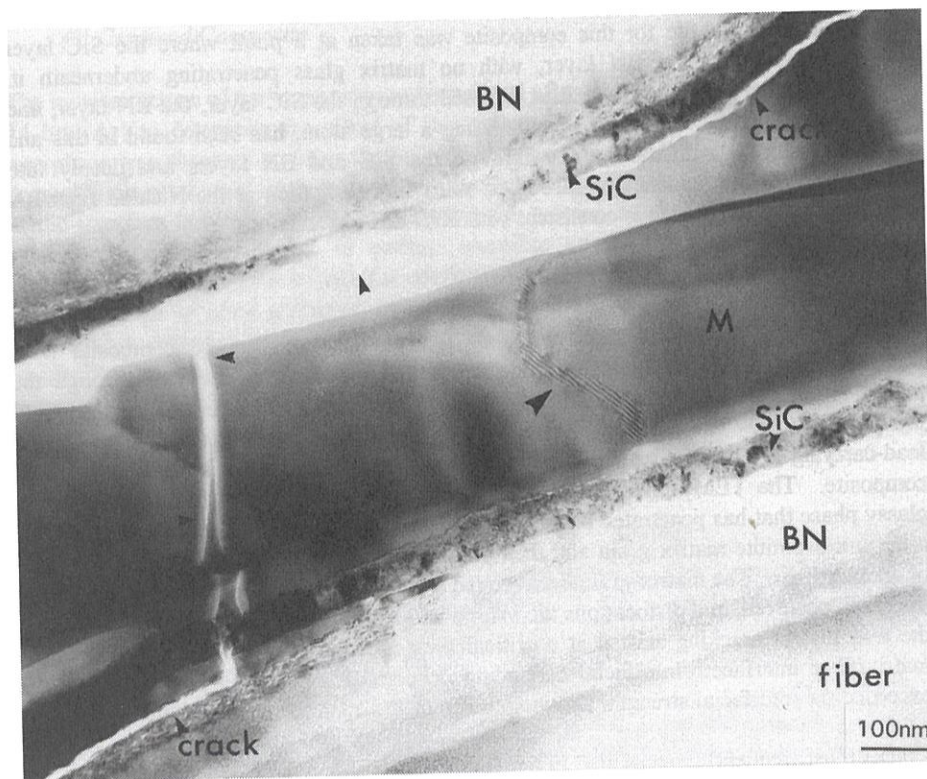
Fig. 6 Cracking in the 90° layers of the tensile stress-ruptured composite

(4) Thermally Aged Composite

After thermal aging at 1200°C in air for 500 hrs, (compared with the ceramed composite,) no significant changes were observed in the Nicalon fibers, the SiC and BN coating, or the BMAS matrix, at least away from the near-surface regions of the composite. Crystallization of the Nicalon fiber was not observed, indicating that the coated fiber is microstructurally stable in the BMAS matrix for long times at 1200°C in air. The SiC and BN coating remained stable and resistant to both oxidation and gross chemical reaction with the matrix. The BMAS matrix did not change in composition or microstructure after thermal aging.

The distinct dual nano-scale sublayers were also observed at the BN/fiber interface, as shown in Fig. 8. The SiC coating appears to be well bonded to the BN layer and no BN coarsening is observed, indicating that matrix material hasn't penetrated the SiC overlayer
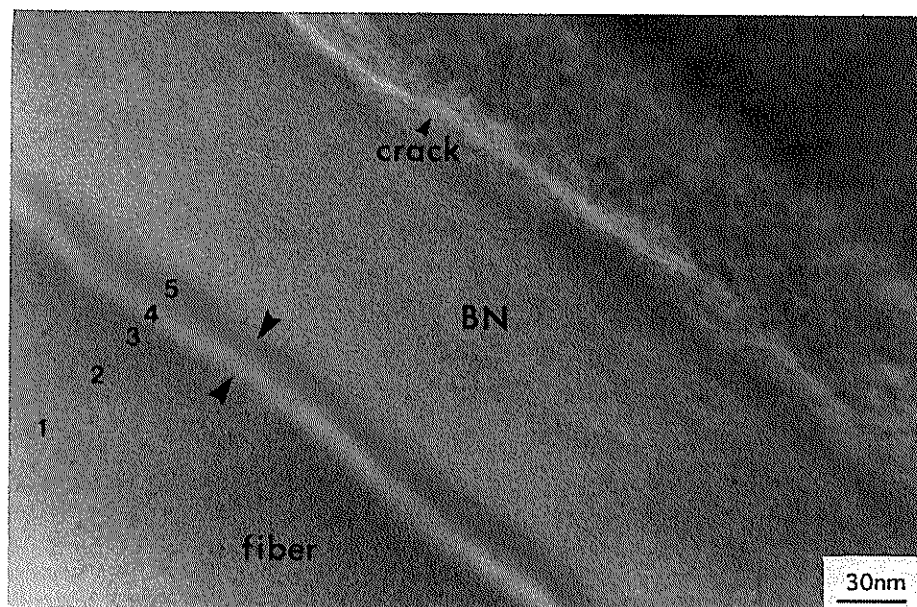
Fig. 7 Interfacial region of a 90° fiber in tensile stress-ruptured composite

Table 2(a). Composition (at %) profile (EDS Data) across the BN/Nicalon fiber interface shown in Fig. 7

Point	C	O	Si	N
1	43	19	37	---
2	43	21	36	---
3	41	22	35	---
4	39	34	26	---
5	---	48	24	28

Table 2(b). Calculated composition (mol%) profile (from data in table 2(a)) across the BN/fiber interface

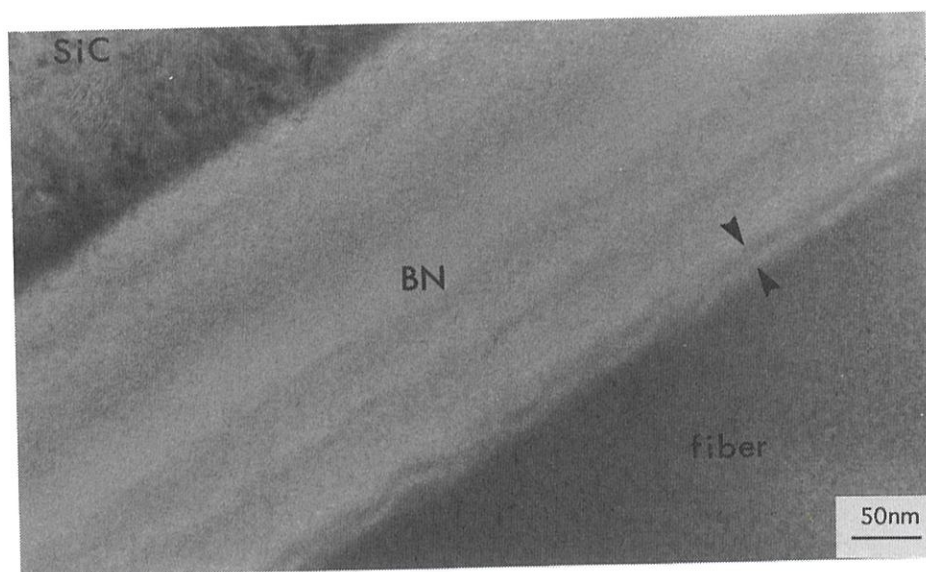| Point	Free C	SiC	SiO$_2$	BN
1	10	59	31	---
2	11	55	34	---
3	11	53	36	---
4	21	21	58	---
5	---	---	58	42

Fig. 8 Interfacial microstructure of the thermally aged composite

and that the formation of the dual sublayers is not necessarily linked to SiC debonding. While the fiber is microstructurally stable under these conditions, the nano-scale structure of the interface changes as a result of the thermal aging.

3.3 Formation of the Dual Sublayer Interface Phase

The formation of the dual sublayers is related to diffusion of oxygen and occurs as a result of the displacement reaction: $SiC_{(s)} + O_2 {}_{(g)} \Rightarrow SiO_{2(s)} + C_{(s)}$. This reaction was proposed by Cooper and Chyung to explain the formation of the carbon interlayer during processing of Nicalon fiber reinforced glass and glass-ceramic matrix composites.[9] The oxygen activity in this case is high enough for the displacement reaction to occur and low enough to prevent the volatilization of the carbon-rich layer. The morphological aspects of this solid-state displacement reaction were studied in detail by Bonney and Cooper.[7] They found that in order to form the dual sublayers in a sequence such that the carbon-rich layer is next to the fiber and the silica-rich layer separates the carbon-rich layer from the matrix, the reaction had to be rate-limited by oxygen diffusion. For composites with uncoated fibers, sources of oxygen are restricted to molecular oxygen dissolved in the glass matrix plus oxygen supplied by heterovalent oxides in the glass that reduced during consolidation of the composite. However, for coated fibers, there is no direct contact between the matrix and the fibers because the

CVD coatings act as a diffusion barrier. Much less oxygen is available to the interface during composite processing. Thus the reaction is limited and only a small amount of silica/carbon is produced. As mentioned before, for the as-pressed composite, the sublayer is less than 10 nm thick and carbon was not detected by SAM. During the ceraming process, (24 hours at 1200°C in argon,) oxidation was suppressed because of the anaerobic environment. The interfacial layer observed after hot-pressing was not observed in the ceramed composite, possibly because of dissolution of silica by the matrix.[10] Thus, in this particular composite system, a distinct interfacial layer did not form at the BN/fiber interface during composite processing.

However, during long-term exposure at high temperatures in an oxidizing environment, oxygen ingress to the BN/fiber interface can occur by diffusion. During thermal aging, the dominant oxygen diffusion mechanism is pipeline diffusion. Oxidation occurs along the interfacial layer that initiates from cut ends of fibers exposed at the composite surface. On the other hand, in stressed material, oxygen diffuses along crack openings. In the stress-ruptured composite, the microcracking is perpendicular to the stress axis, i.e., parallel to the 90° fibers, and usually in the BN layer, as mentioned before. Thus, more oxygen is likely to reach the interface of a 90° fiber if there is a microcrack in the adjacent BN layer. Consequently, the sublayers are thick (~15 nm each) and uniform, as shown in Fig. 7. As expected, no distinct interphase was observed in the 0° layers, because of the absence of microcracking in these plies. The oxygen diffusion mechanism for the 0° fibers is presumably the same as that during thermal aging. Dual sublayers were observed in the thermally aged composite which was treated at 1200°C in air, but not for the 0° fibers in the tensile stress-ruptured composite, which was tested at 1100°C in air. This implies that there may be a critical temperature for the formation of the interphase between 1100°C and 1200°C.

4. Summary

The coated-fiber composite exhibits promising properties up to 1100°C. The CVD SiC/BN coatings function very well as a reaction barrier and result in composites with a stable microstructure that is resistant to gross chemical reaction at 1100°C. Interfacial reaction in this composite is suppressed during composite fabrication because of the coatings. The BN layer also behaves as a weak interfacial zone because of its turbostratic structure, allowing both crack deflection and load transfer to occur. Debonding of the SiC overlayer from the BN underlayer occurs occasionally, allowing residual glass from the matrix to penetrate and come into contact with the BN layer, causing BN coarsening. Nano-scale silica/carbon sublayers are formed at the BN/Nicalon fiber interface by oxidation of the Nicalon fiber surface when it is exposed to oxygen at high temperature for long times. The sublayers were observed in thermally aged composites and in 90° fibers (perpendicular to the axis of tensile stress) after tensile stress-rupture testing, indicating there may be a critical temperature between 1100°C and

1200°C for the formation of the interphase. These sublayers may contribute to the degradation of mechanical properties after thermal aging.

Acknowledgment

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