Fiber Coatings for Sic-Fiber-Reinforced BMAS Glass-Ceramic Composites

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Interfaces in SK-fiber-reinforced glass-ceramic matrix composites were modified by applying different coatings to the fibers and varying the coating thickness. Coatings of SiC/BN, Si_3N_4/BN, and BN were applied to the fibers by CVD prior to composite fabrication. Interfacial microstructures were characterized using high-resolution and analytical transmission electron microscopy. Oxidation of the SiC fibers during composite fabrication was suppressed by the fiber coatings, provided that the coatings were sufficiently thick to prevent oxygen diffusion from the matrix. The SiC/BN and BN coatings were stable during high-temperature exposures, while the Si_3N_4/BN coating underwent chemical reactions.

I. Introduction

FIBER coatings have emerged as one of the most viable approaches to design and control interfaces in fiber-reinforced ceramic-matrix composites.'[-4] For example, recent efforts to incorporate SiC/BN dual-coated fibers into lithium aluminosilicate and barium-magnesium aluminosilicate (BMAS) glass-ceramic matrices resulted in composites with superior properties at elevated temperatures.'[-6] However, despite the initial success of the dual coating approach, the SiC overlayer often tended to detach from the BN layer during composite fabrication, allowing matrix species to diffuse into the fiber.[4,5] The debonding of the SiC layer was attributed to thermally induced stresses arising from expansion mismatch between the two coatings during composite fabrication." To reduce the effect of thermal expansion (CTE) mismatch, composites were fabricated with different coating thickness as well as different coatings. Specifically, thinner SiC/BN coatings and Si_3N_4/BN coatings were investigated. Si_3N_4 was selected because of the smaller CTE mismatch with BN compared with SiC and BN. In addition, composites with BN-coated fibers were also fabricated to evaluate the effectiveness of the SiC overlayer as a diffusion and reaction barrier in a BMAS matrix. In this paper,

we present the results of microstructural analyses on BMAS glass-ceramic matrix composites with the aforementioned interfacial designs. The changes in the interfacial structure and chemistry resulting from composite fabrication were investigated for each of the coating systems. The objective of the study was to address the debonding problem of the SiC overlayer and to better understand the role of fiber coatings and the interfacial diffusion-reaction mechanisms in coated fiber-reinforced glass-ceramic matrix composites.

II. Experimental Procedure

The composite systems investigated consisted of a BMAS glass-ceramic reinforced with coated SiC (Nicalon) fibers. Details of composite fabrication can be found in Ref. 7. Three different CVD coating systems were investigated, including BN, SiC/BN, and Si_3N_4/BN, and the thickness of the SiC/BN coatings was systematically varied. Coating conditions are listed in Table I. Interfacial microstructures were characterized using analytical and high-resolution transmission electron microscopy (HRTEM). TEM thin foils were prepared in a conventional manner by mechanical polishing, dimpling, and ion milling. Specimens were examined using a 200 kV microscope (JEOL 2010), and composition analyses of microstructural features were performed with energy dispersive spectroscopy (EDS) and parallel electron energy loss spectroscopy (PEELS).

III. Results

(1) SiC/BN Fiber Coating

The microstructures at the BN/fiber interface were similar in composite A1 and composite A2, where the RN layers were both 350 nm, but the SiC overlayers were of different thickness. In these two composites, when the SiC coating layer adhered well to the BN coating layer, the BN layer exhibited a turbostratic structure and was comprised of nanoscale ordered domains. HRTEM studies showed that there was no interfacial reaction at

Table I.   Coating Conditions in the Composites Investigated

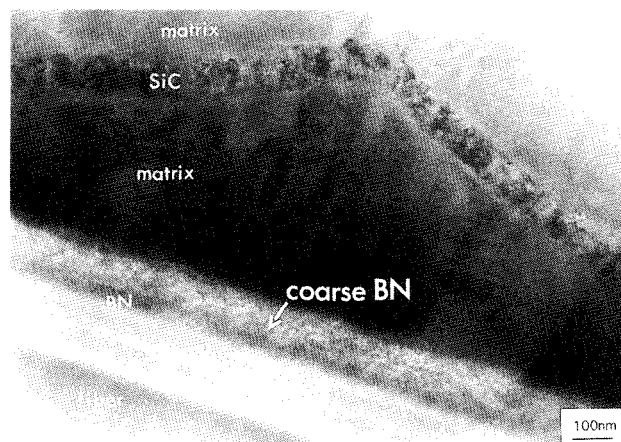| Composites	Fiber coatings	
	Underlayer	Overlayer
A1	BN (350 nm)	SiC (250 nm)
A2	BN (350 nm)	SiC (150 nm)
A3	RN (250 nm)	sic (I so nm)
B	BN (350 nm)	Si_3N_4
c	BN (350 nm)	

Fig. 1. Interfacial region in composite A2 where the SiC overlayer debonded from the BN layer. Coarsening of the BN occurred through one-third of the layer thickness.

Fig. 2. Interfacial region in composite A3 where the SiC overlayer debonded from the BN layer. Crystallization of BN occurred through the layer thickness and dual sublayers formed at the BN/fiber interface.

either the SiC/BN or the BN/fiber interface. However, detachment of the SiC coating layer occurred much more frequently in composite A2 with thinner SiC coatings (150 nm) than in composite A1 with thicker SiC coatings (250 nm). A typical interfacial region in composite A2 where the SiC overlayer debonded from the BN layer is shown in Fig. 1. When the SiC overlayer debonded from the BN layer (during matrix infiltration), the matrix glass penetrated through the cracks in the SiC layer and formed an amorphous layer between the SiC and the BN in both composites. The glass penetration led to coarsening of the BN layer and the formation of subtle dual silica/carbon interlayers at the BN/Nicalon fiber interface. Coarsening of the BN occurred through one-third of the layer thickness in both composites A1 and A2 (Fig. 1). The subtle silica/carbon dual layer at the BN/fiber interface was discontinuous, noncrystalline, and extremely fine (about 5–10 nm thick), consistent with previous studies.⁵

Significant differences in the interfacial microstructures were observed in composite A3 compared to composites A1 and A2. Similar to composite A2, detachment of the SiC coating was frequently observed in composite A3. In many of the fibers, the SiC overlayer cracked and debonded from the BN layer. However, because of the thinner BN coating (250 nm in composite A3 vs 350 nm in composites A1 and A2), crystallization of BN occurred through the thickness of the BN coating in composite A3 (Fig. 2) instead of only one-third (Fig. 1). In addition, the silica and carbon sublayers at the BN/fiber interface were more pronounced. Both sublayers were continuous and about 20 nm thick, as shown in Fig. 2.

(2) Si₃N₄/BN Fiber Coating and BN Coating Only

Microstructural analysis indicated that the Si_3N_4 layer dissolved in the BMAS glass-ceramic matrix during composite fabrication. The Si_3N_4 layer was not present in the as-pressed composite, although the BN layer was largely intact. As with composites A1 and A2, the 350 nm thick BN layer was partially coarsened and subtle dual layers were occasionally evident at the BN/fiber interface. However, during the ceraming process in which the glass-ceramic matrix crystallized into the barium–osumilite phase, a chemical reaction occurred in the material. Gaseous products were evolved and the matrix became porous. Although the reaction that occurred is not understood, Si_3N_4 may not be suitable as a fiber coating in BMAS glass-ceramic matrix composites.

Interfacial microstructures in composite C (350 nm thick BN coating, no SiC overlayer) exhibited two thick sublayers at the BN/fiber interface (Fig. 3). Coarsening of the BN coating through half of its thickness occurred during fabrication of composite C. The two sublayers at the BN/fiber interface were similar to those observed in composite A3, although both layers
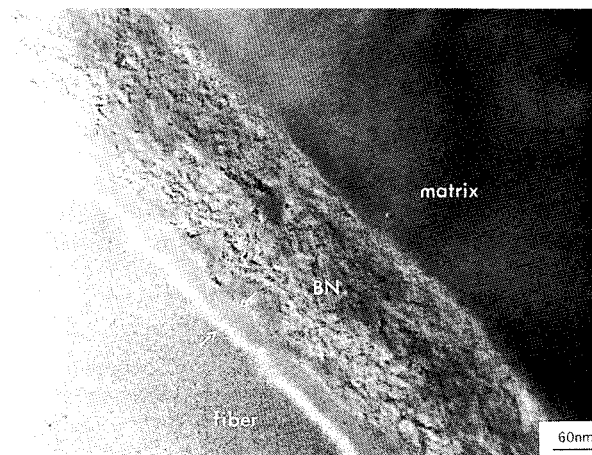
(especially the light layer) were substantially thicker (~40 nm) and more uniform. The PEELS analyses indicated that the dual layers were of the same composition as thinner dual layers observed in the other composites; i.e., the light layer was carbon-rich, while the dark layer consisted primarily of silica.

IV. Discussion

(1) Fiber-Coatings Function as a Diffusion-Reaction Barrier

The results presented above indicate that turbostratic BN limits interfacial reactions during composite fabrication. As shown in composites A1 and A2, no interfacial layers were formed during hot-pressing and ceraming as long as the SiC overlayer remained well-bonded. Even when the SiC layer detached, only subtle interfacial layers (~5 nm thick) were formed (during fabrication). However, to function effectively as a diffusion barrier, the BN coating apparently must be of sufficient thickness. For this particular composite system and the fabrication conditions employed, the required thickness is greater than 250 nm. If the BN layer is 250 nm or thinner, as in composite A3, crystallization occurs through the thickness of the layer and interfacial layers form at the BN/fiber interface.

The overlayer (SiC or Si_3N_4) was originally applied to the BN-coated fibers to prevent boron diffusion, because it was found in LAS glass-ceramic matrix composites that outward diffusion of boron could prevent complete crystallization of the
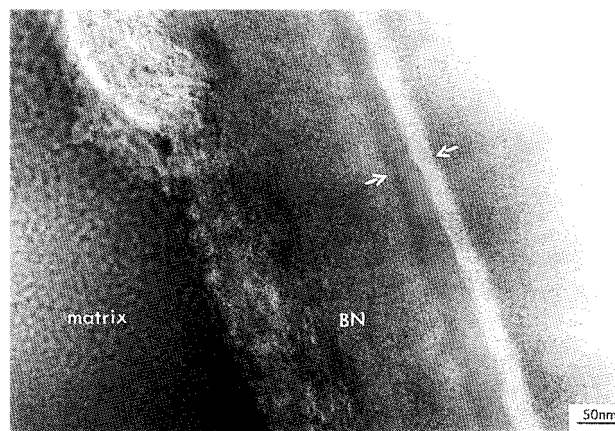

Fig. 3. Interfacial region in ceramed composite C, in which the fibers were coated only with BN. Two thick sublayers formed at the BN/fiber interface.

glass-ceramic matrix.' However. the present study revealed that SiC layer also limited the amount of oxygen diffusing to the fiber surface. In composites without the overlayer (composite C), surface oxidation of the tibers was much more severe than in composites A and B. although the BN layer was of the same thickness as in composites A 1, A2, and B. In composite B, the Si_3N_4 overlayer dissolved into the matrix during hot-pressing. It is possible that a thicker and more crystalline Si_3N_4 layer would be more stable. Nevertheless. the oxygen diffusion from the matrix to the fiber surface was apparently limited and slowed in this composite compared to composite C.

(2) *Detachment of the SiC Overlayer*

Detachment of the SiC overlayer occurred frequently in all of the composites investigated. This phenomenon was attributed to the thermal mismatch stress induced during composite fabrication. The coating layers were deposited at about 1100°C. and the composites were ho-pressed at 1450°C. Because the thermal expansion coefficient of BN (along the c-axis) was larger than that of SiC. tensile stress was induced in the SiC overlayer during heating. When the stress level exceeded the strength of the SiC overlayer. the overlayer cracked and debonded from the BN layer. The circumferential or "hoop" stress in the SiC coating layer is inversely proportional to the coating thickness." Thinner SiC overlayers increase the likelihood of cracking. as revealed by the TEM observations. In addition to thermal expansion mismatch. the detachment problem is also related to the deposition parameters. For example. the SiC overlayer on a smooth BN coating layer tended to debond frequently, while debonding usually did not occur on tibers with rough BN coatings in which soot asperities were incorporated.' The effect of surface roughness on coating adhesion appears to be a fertile area for future work.

V. Conclusion

Coatings were applied to SiC fibers to control the matrix/fiber interface in glass-ceramic composites. The dual SiC/BN coatings effectively prevented diffusion and reaction at the interface during composite fabrication. provided that the BN layer was sufficiently thick. For this particular composite system and the conditions employed, the critical thickness for BN was apparently greater than 250 nm. Si_3N_4 was not suitable as a fiber-coating material because it dissolved in the BMAS matrix during composite fabrication. A BN coating alone was permeable to oxygen diffusion from the matrix, although a SiC overlayer effectively inhibited oxygen diffusion from the matrix and boron diffusion into the matrix. One problem that awaits further

study is the debonding of the SiC overlayer from the BN layer that often occurs during matrix infiltration, which was not solved by reducing the thickness of the coatings. Further improvements in the performance of the SiC/BN coating may be possible through increasing the thickness of the SiC coating while maintaining a BN thickness of 350 nm. Alternatively. greater adhesion of the SiC overlayer might be achieved by introducing roughness in the BN underlayers.

The results confirm that the primary source of oxygen involved in interface reactions during composite fabrication was the matrix, as proposed in early studies." Some coatings did not prevent oxygen diffusion from the matrix. resulting in oxidation of the near-surface region of the fibers. In such cases. heat treatment of composites even in inert atmospheres should cause oxidation of the fiber, leading to fiber degradation and diminution of composite mechanical properties. In this respect. fiber coatings are of great importance in controlling interfacial microstructures in fiber-reinforced ceramic-matrix composites. However. the dual coating approach. in which each layer has a different function. is technically viable for the design and control of interfaces for high-temperature continuous-fiber-reinforced composites.

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