MICROSTRUCTURES OF BN/SiC COATINGS ON NICALON FIBERS

R.M. DICKERSON* AND M. SINGH**
*Case Western Reserve University, 10900 Euclid Ave., Cleveland, OH 44106
**NYMA Inc., Lewis Research Center Group, Cleveland, OH 44135

ABSTRACT

The microstructures of Nicalon silicon carbide (SiC) fibers and layered coatings of boron nitride (BN) followed by chemical vapor infiltrated silicon carbide (CVI-SiC) were characterized using optical and electron microscopy. Two different precursors and reactions were used to produce the BN layers while the deposition of CVI silicon carbide were nearly identical. Coated tows were examined in cross-section to characterize the chemistry and structures of the constituents and the interfaces. One BN precursor yielded three sublayers while the other gave a relatively homogeneous nanocrystalline layer.

INTRODUCTION

In recent years, there has been an increasing demand for high performance and light weight ceramic matrix composites (CMC's) for high temperature aerospace applications. The major requirements for these applications have been high strength and toughness, low density, high thermal conductivity and oxidation resistance. Silicon carbide fiber reinforced SiC matrix composites have attracted a great deal of attention for the above purposes [1-2]. The mechanical behavior of these composites is greatly influenced by the intrinsic properties of the reinforcement and the matrix materials, the fiber-matrix interface, and processing conditions. These interact to determine the fiber-coating-matrix interfacial structures and residual shear stresses, which, in turn, control whether the composites fail 'gracefully' or in a brittle fashion.

One method of manufacturing CMC's is through infiltration of woven fiber mats using gaseous or liquid species which deposit or react to form the matrix material. In order to utilize such processes to their full potential, some interfacial coating is required which protects the fibers from any deleterious effect of this processing. In the present investigation, a BN/SiC dual layer coating has been used. For optimum performance, the BN coating should be sufficiently thick, continuous and free of porosity to forestall any chemical reaction with the fiber. In this investigation, two different BN/SiC coatings have been investigated. These two particular coatings are a subset of an ongoing program exploring the effects of coating type and thickness on the processing and properties of reaction formed silicon carbide (RFSC) matrix composites [6].

EXPERIMENTAL

The fibers used in this study were ceramic grade Nicalon (8-HS weave) cloth supplied by Nippon Carbon Co., Japan. Two types of precursors were used for boron nitride deposition to create two types of interfaces. Details of the experimental set up are described elsewhere [3].

In the first case, β-trichloroborazine[1] was used as precursor. It is a white solid powder that has a high vapor pressure under ambient conditions. It is hygroscopic and needs special handling. At the deposition temperatures (800-1000°C), it decomposes to BN and hydrochloric acid according to following reaction. The BN is deposited as solid and HCl is trapped as a gas phase at the deposition temperatures.

$$\beta\text{-}B_3N_3H_3Cl_3 \rightarrow 3\ BN + 3\ HCl$$

[1] Strem Chemicals, Inc., 7 Mulliken way, Newburyport, MA 01950.

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For the second case, a commercial vendor was utilized. The precursors in this case were boron trichloride and ammonia, with the reaction given below. The deposition temperatures were roughly the same.

$$BCl_3 + NH_3 \rightarrow BN + 3\,HCl$$

SiC was deposited by CVI on both types of BN coating. The SiC coatings were typically between 1.0 and 1.5 μm thick and the BN layers were usually between 120 and 220 nm in thickness.

Sections from each of the coated mats were mounted in epoxy and vacuum degassed to reduce porosity. Cross-sections from the epoxy mounts were polished to a 1μm finish for optical and SEM analysis. SEM was performed on a JEOL JSM6100 primarily using backscattered electron (atomic number) contrast. Cross-sectional TEM thin foils were prepared from both coated mats following techniques typical for ceramics, finishing with Ar ion beam milling. TEM imaging was performed on a Philips EM400T operating at 120 keV and x-ray energy dispersive spectrometric (XEDS) compositional analysis of the cross-sections was done on a VG HB501 operating at 100 keV with a Kevex Delta thin window detector and analyzer.

RESULTS AND DISCUSSION

The optical microstructures of the two coated Nicalon SiC weaves are similar, but not identical (Fig. 1). Some variation in the Nicalon fiber diameter is observed in both samples, when an individual tow is viewed in cross-section. The BN layer in coating A (β-trichloroborazine precursor) is nearly invisible optically, whereas the BN layer in sample B (boron trichloride and ammonia precursors) is very distinct. It is also worth noting that the SiC layer of coating A is somewhat thicker at the outside of the tow (top Figure 1b) whereas the coating of sample B is more uniform in thickness.

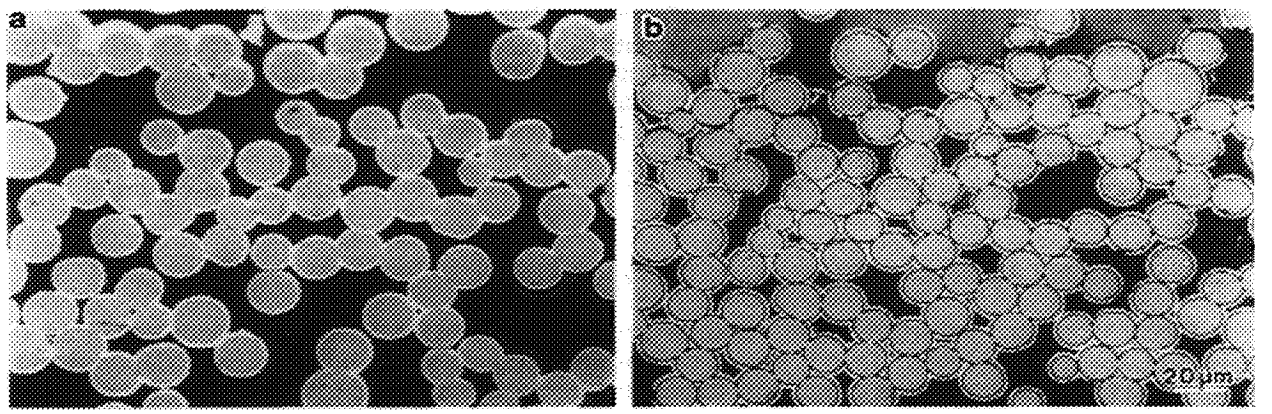

Figure 1. Optical cross-sectional micrographs of tows in the Nicalon weaves at the same magnification showing the BN/CVI-SiC coatings A (a) and B. (b) Notice the greater contrast from the BN layer and the more even SiC coating in coating B.

When viewed using backscattered electron contrast in the SEM, a similar result is obtained. The BN layer of sample B appears to be both thicker and lower in average atomic number in Figure 2. The BN/CVI-SiC interface is rougher, as well.

TEM micrographs of the Nicalon/BN/CVI-SiC interface in cross-section reveal many differences. Three distinct layers are seen in the BN layer of coating A (Fig. 3A). The total width of the BN layer in sample A is between 130 and 150 nm. The inner, middle, and outer

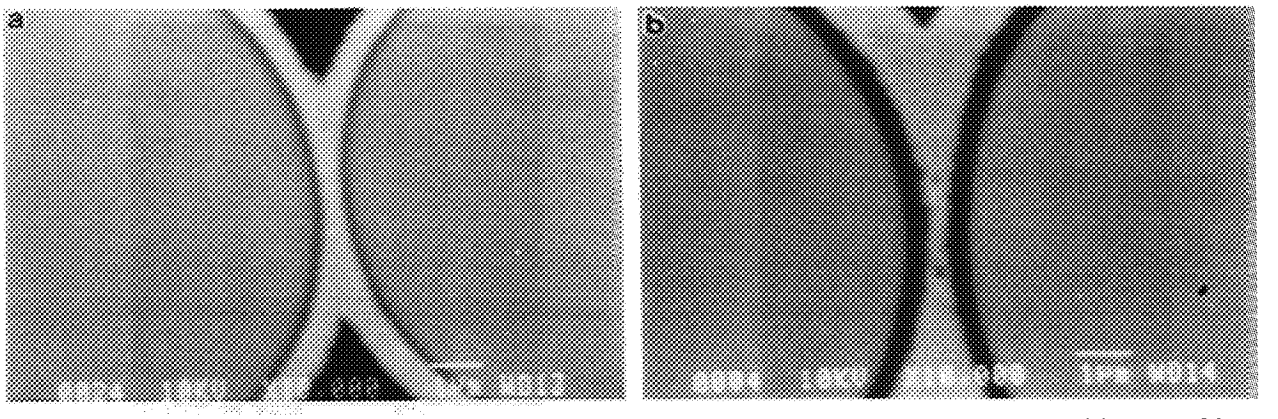

Figure 2. Cross-sectional SEM backscattered electron (BSE) images of two neighboring fibers in samples A (a) and B (b). The BN layer of coating B appears thicker, darker (lower average atomic number), and rougher at the BN/SiC interface.

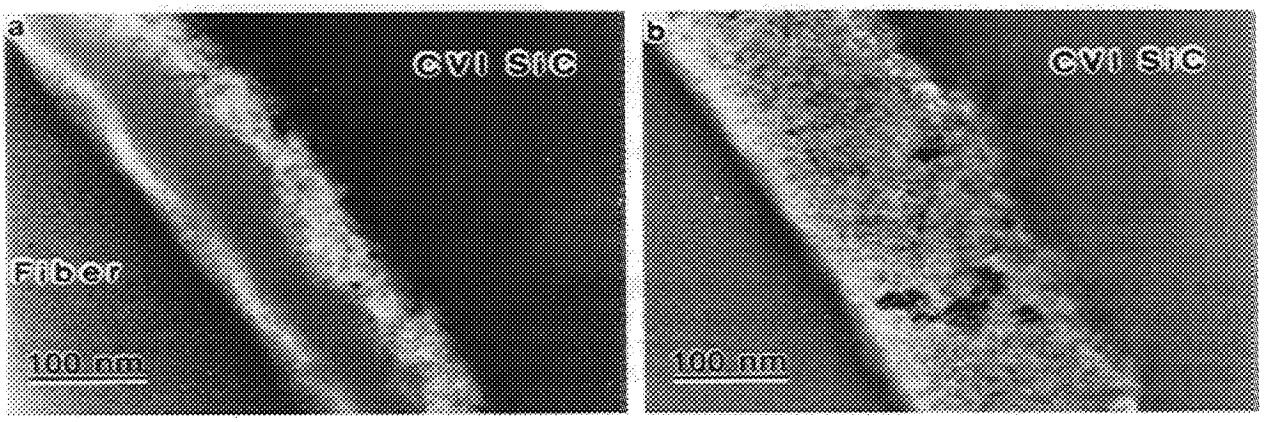

Figure 3. TEM micrographs of the Nicalon/BN/CVI-SiC layers of coatings A (a) and B (b). Three distinct layers are seen in the BN of coating A. The BN of coating B is more homogeneous but contains small, 15-40 nm, particles.

sublayers are approximately 15-35 nm, 9-70 nm, and 40-65 nm thick respectively. The BN coating of sample B is radially more homogeneous but contains small particles. Its width is generally between 160 and 220 nm.

It should be noted that the basic structure of all the BN layers in both samples is close to that of turbostratic BN. The interlayer spacing, as determined from electron microdiffraction patterns, is approximately 0.345 nm in all cases. This is as expected because turbostratic BN is, to a large degree, a disordered version of hexagonal BN which has an inter-layer distance of 0.333 nm [4]. Disorder in the layer stacking increases the inter-layer distance to the 0.345 nm observed. Any fine differences in the interatomic spacing were not analyzed in depth because the microdiffraction patterns were not sharply detailed (Fig. 4).

A microdiffraction pattern from the Nicalon fiber is given as Figure 4a. The continuous but somewhat diffuse ring has a diameter consistent with the 0.251 nm interatomic spacing expected from nanocrystalline β-SiC. An XEDS spectrum from a Nicalon fiber is shown in Figure 5a. The strong silicon peak and relatively weak carbon peak are typical of SiC. The small but significant oxygen content is expected in Nicalon fibers, particularly near the outside surface [5].

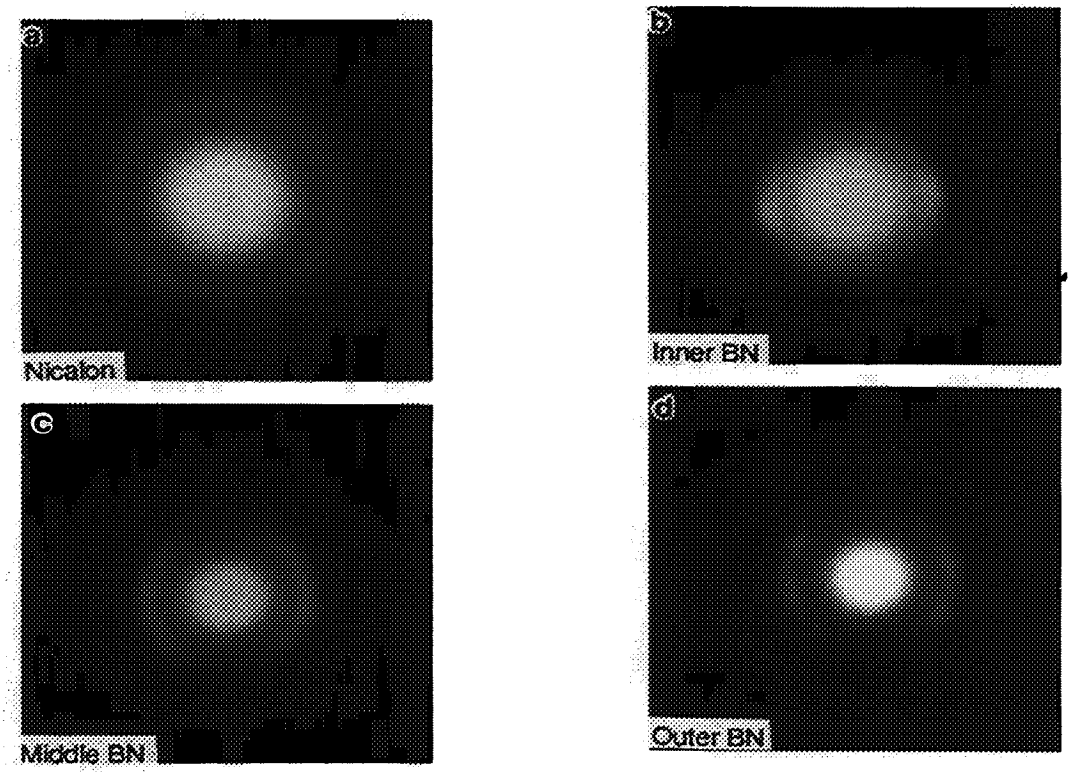

Figure 4. TEM microdiffraction patterns from the Nicalon fiber (a) and the three BN layers of BN/CVI-SiC coating A (b-d). A continuous ring consistent with the 0.251 nm spacing of (111) in β-SiC is seen for the Nicalon fiber. The arcs of intensity from the turbostratic BN give a spacing of approximately 0.345 nm. Note the increasing degree of order (shorter rings indicationg less tilt of the basal planes between structural units) in the outside layers.

Each of the BN sublayers in coating A is slightly different in composition and structure. The innermost layer is rich in silicon, carbon, and oxygen (Fig. 5b) and is the most random in structure, having a nearly continuous diffraction ring (Fig. 4b). Note that boron is not detectable using the present XEDS system. The middle BN layer is still rich in silicon and oxygen but is depleted in carbon (Fig. 5c). The outer BN layer has nitrogen as a major constituent but still yields peaks for Si and O and possibly C (Fig. 5d). The degree of ordering of the turbostratic BN increases through each subsequent layer (Fig 4b-d).

The boron nitride layer in coating B is fairly homogeneous and only moderately turbostratic, having a nearly continuous diffraction ring (Fig. 6a). The small, 15-40 nm particles give sharp diffraction spots (Fig 6b) and have an interlayer spacing 0.338 nm, closer to the value for hexagonal BN than to the 0.345 nm expected for turbostratic BN. The centerline of the 20° angle between the highest intensity spots in Figure 6b corresponds to possibly planar defects that are observed in the particles. The nature of these defects, which typically are radially related to the fiber, has not yet been determined.

The chemistry of the BN layer varies in a continuous fashion from the fiber outward (Fig. 7). Near the Nicalon fiber, the nitrogen-rich layer contains appreciable silicon and some oxygen. As the CVI-SiC layer of the coating is approached, the Si content decreases and the O fraction increases.

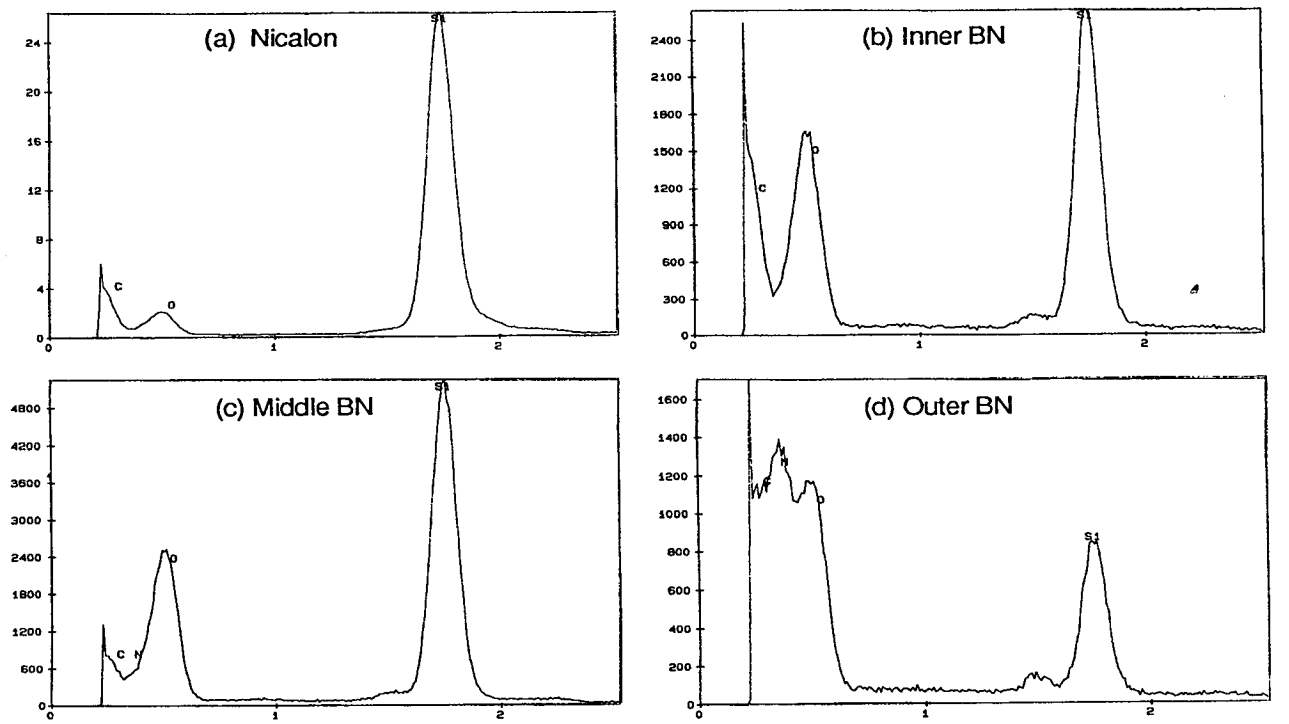

Figure 5. STEM XEDS spectra from the Nicalon fiber (a) and each of the three BN sublayers (b-d) in coating A. The small peak at ~1.5 keV is due to alumina powder used to harden the mounting epoxy.

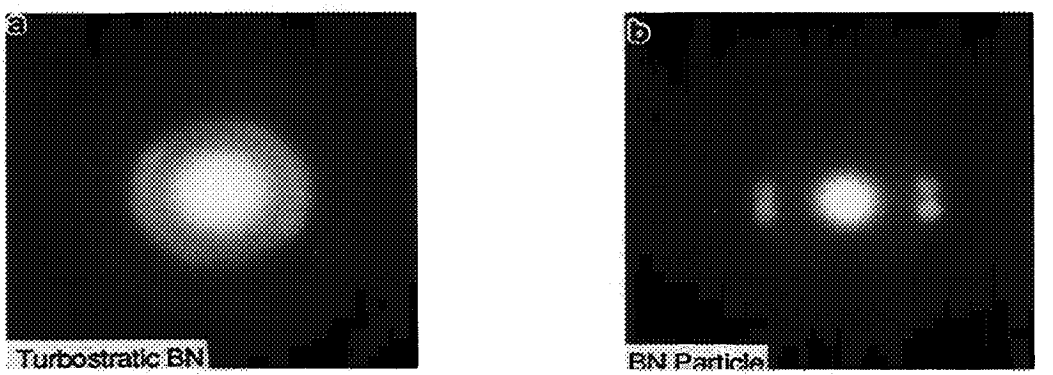

Figure 6. TEM electron microdiffraction patterns from the turbostratic BN (a) and more crystalline particles (b) of the coating B.

SUMMARY AND CONCLUSIONS

Two different BN/SiC protective coatings on Nicalon fibers were characterized using optical and electron microscopy. Both samples' CVI deposited SiC layers are the expected highly faulted β-SiC and, as such, were not examined in detail. The BN coatings A and B (β-trichloroborazine and boron trichloride plus ammonia precursors, respectively) yielded distinctive microstructures, although both provided a continuous coating of the fibers in the

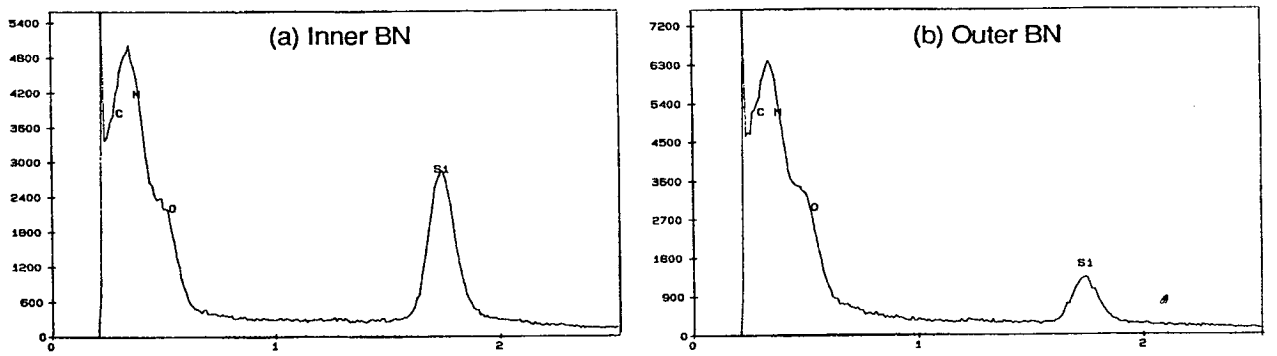

Figure 7. STEM XEDS spectra of the turbostratic BN of coating B near the Nicalon fiber (a) and near the CVI-SiC (b).

weaves, which is important for the formation of composites from these coated samples. Three distinct layers were observed in the BN of coating A. The inner two layers are rich in silicon and oxygen and are separable mainly through their differing carbon content and the degree of ordering of the BN structural units. The outermost BN layer is the most ordered and N-rich of the layers. The boron nitride layer of coating B is homogeneous turbostratic BN throughout but with an enrichment in Si near the fiber and O near the outside CVI-SiC. Small particles observed throughout the layer are structurally more similar to crystalline hexagonal BN than to the surrounding turbostratic material. XEDS spectra from both BN coatings contained appreciable Si. This might be due to sputtering of the surrounding SiC during ion milling, electron beam interactions with the SiC in the thin foil, or deposition of Si with BN; the Si being etched from the Nicalon fiber by the reaction gasses.

Either coating will probably work to protect the Nicalon fibers in the preparation of a ceramic matrix composite based on a silicon carbide matrix as long as the outer SiC coating remains continuous during processing. The technology of the coating based on boron trichloride and ammonia, being a commercially available process, is fairly well developed. The β-trichloroborazine-based processing, being performed under experimental conditions at a lesser vacuum, led to a higher oxygen content. Mechanical characterization of the coated weaves and composites made from the coated weaves will be used to determine the applicability of both of the coating techniques.

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