



Process-Induced Carbon and Sub-Layer in SiC/BN/SiC Composites: Characterization and Consequences

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PROCESS-INDUCED CARBON SUB-LAYER IN SiC/BN/SiC COMPOSITES: CHARACTERIZATION AND CONSEQUENCES

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ABSTRACT

Following our detection of films of elemental carbon in the Hi-NicalonTM/BN/SiC composite and its deleterious effect on oxidative durability, we have examined other SiC/BN/SiC systems. The problem is pervasive, and significant residues of free carbon are confirmed in SylramicTM/BN/SiC materials. Effective techniques for routine detection and characterization of adventitious carbon in SiC/BN/SiC composites are discussed.

INTRODUCTION

SiC/BN/SiC composites can be undermined by a layer of free carbon underlying the BN interphase, leading to severe impairment of composite oxidative durability at intermediate temperatures [1,2]. In Hi-NicalonTM/BN/SiC the deleterious layer originates from excess carbon content of the non-stoichiometric fiber [1-4]. Close examination of some SylramicTM/BN/SiC composites have revealed similar layers of elemental carbon on the fiber, resulting in severe burner rig degradation as was exhibited by Hi-NicalonTM composites [1,2]. In SylramicTM/BN/SiC the carbon may have come from inadequate removal of the fiber sizing during processing [5]. In either case the carbon source is intrinsic to the system itself, whether it comes from the fiber or a processing step. Thus, the possibility of SiC/SiC contamination by deleterious free carbon is strong, and its consequences must be considered.

High-resolution TEM offers an excellent means of resolving the thin carbon layer in question (≤ 150 nm thick by most estimates [1,5]), but we have achieved better results with surface-sensitive techniques [6,7]. Other workers have used TEM to examine SiC_f/SiC_m composites for adventitious carbon: Giannuzzi and Lewinsohn [8,9] reported that, in a composite reinforced with NicalonTM fibers coated with a 150nm layer of carbon, the carbon coating was found to thicken about an order of magnitude as a result of infiltrating the SiC matrix. That lends strong support to

our suggestion regarding the origin of free carbon layers in NicalonTM/BN/SiC systems [1]. Now that interphase integrity is an issue for SiC/BN/SiC composites, it seems prudent to examine each variety of SiC/BN/SiC for free carbon that can compromise composite durability. Hence, it is useful to establish simple, reliable techniques for its detection. This paper addresses that issue and gives a summary of our results for SylramicTM/BN/SiC. Our findings for Hi-NicalonTM/BN/SiC composites have been described elsewhere [1,2,6,7].

PROCEDURE

The composites in this study were comprised of SylramicTM (stoichiometric SiC) fibers coated with ~0.5 μ m interphase layer of BN, in a dense melt-infiltration (MI) SiC matrix. They were in two groups. One group consisted of samples made with fibers that had been protected with polyvinyl alcohol (PVA) sizing prior to composite processing, the second group with polyethylene oxide (PEO) sizing. They are hereafter referred to as “PVA” and “PEO” materials. There were two PVA materials and seven PEO materials, in the form of standard tensile bars, 6” x 0.5” x 0.08” (152 x 12.7 x 2 mm).

They were exposed in a 0.3 Mach atmospheric-pressure burner rig for 100 hours at 800°C and broken in tension, which we have found a reliable screening test for the weakening and embrittlement indicative of interphase degradation in SiC//SiC composites. Coupons were machined for scanning electron microscopy (SEM) from the ends (which were unaffected by the burner rig flame) mounted, polished, and studied with a high-resolution *Hitachi S4700*, operated at 2-6 kV. For Auger Electron Spectrometry (AES), thin and flat strips (~25 mm x 2 mm x 0.5 mm) were cut from the shoulders of the bars (also far from the flame-affected zone), using only water lubrication to avoid contamination by carbon in resin lubricants. They were cleaned by sonication in alcohol and examined with *Fisons Instrument Microlab* (Model 310-F) spectrometer, operating at 2.0 kV, the samples having been broken *in-situ* in the AES chamber to minimize adventitious carbon. Other tools explored in this study included laser raman spectrometry.

RESULTS AND DISCUSSION

Tensile Tests

All seven PEO materials exhibited drastic drops of strength and strain to failure following exposure in the burner rig. The as-received material exhibited a tensile strength of ~410 MPa and failure strain of 0.3%; after burner rig exposure these values were down to 175-226 MPa and 0.09-0.16%, respectively. The 50-60% decrease in strength and strain to fracture were very similar to the severity of degradation seen in Hi-NicalonTM/BN/SiC composites following the same burner rig exposure [1,2,6,7]. In contrast, none of the PVA materials showed significant

weakening or embrittlement following exposure. This was the first indication of an important difference between the PVA and PEO sizing in the durability of SiC/BN/SiC composites.

Scanning Electron Microscopy

Three PEO materials and one PVA material are used to illustrate some features of interest in the microstructures. Fig. 1 is an SEM image of the fracture surface of a PEO material. The EDS spectra show that the patch labeled A is bare fiber (Si/C peak ratio of ~ 5.0 being characteristic of SiC), and patch B has an overwhelming carbon content. Fig. 2 shows a polished surface from another PEO material. In the image on the left, two interphase layers are discernible between the fiber and CVI-SiC cladding; and the corresponding EDS spectra confirm that feature B is boron nitride (with some carbon), while layer C is almost entirely carbon. Where BN is absent (see spectrum D and its corresponding image on the right side), the gap between fibers is occupied by carbon. Optical fluorescence tests showed the carbon patches (B & D) were not from the epoxy mount. In contrast, no carbon layer was observed by SEM/EDS in the PVA materials.

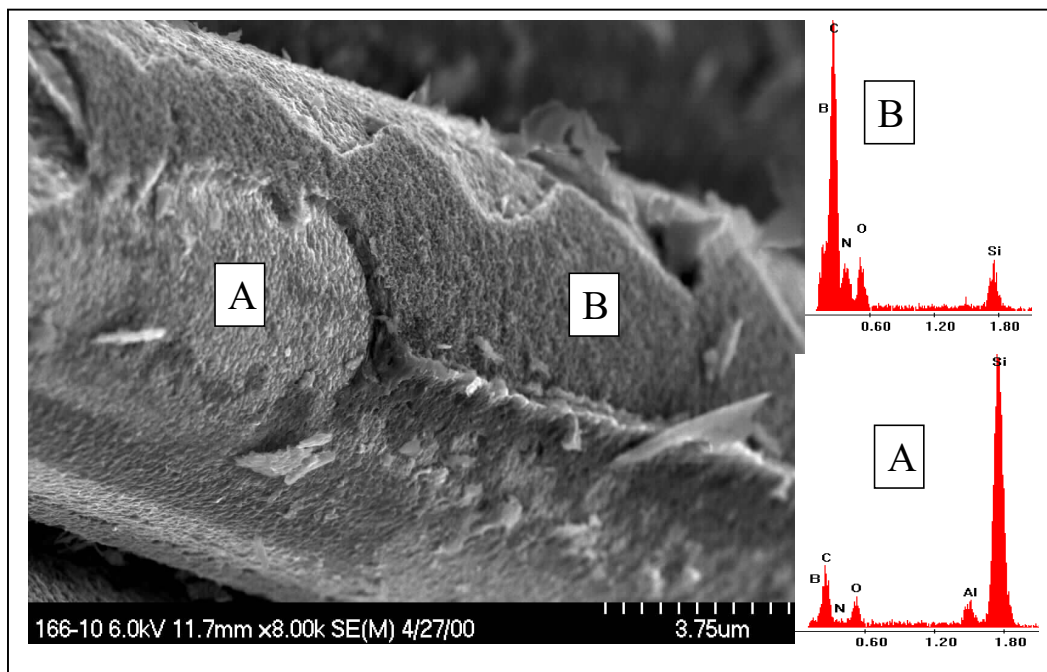


Fig. 1, SEM image and spectra from Sylramic/BN/SiC composite with a high excess of carbon in the interphase.

Auger Electron Spectrometry

Ceramic-matrix composites are designed for preferential fracture through the interphase. That behavior was exploited to advantage in this study: any carbon layers present were preferentially exposed on a fracture surface and its signal thereby enhanced for detection by surface-sensitive techniques. Hence, detection of interfacial carbon in SiC/BN/SiC composites by AES is highly reliable even when it is too thin to resolve in cross section.

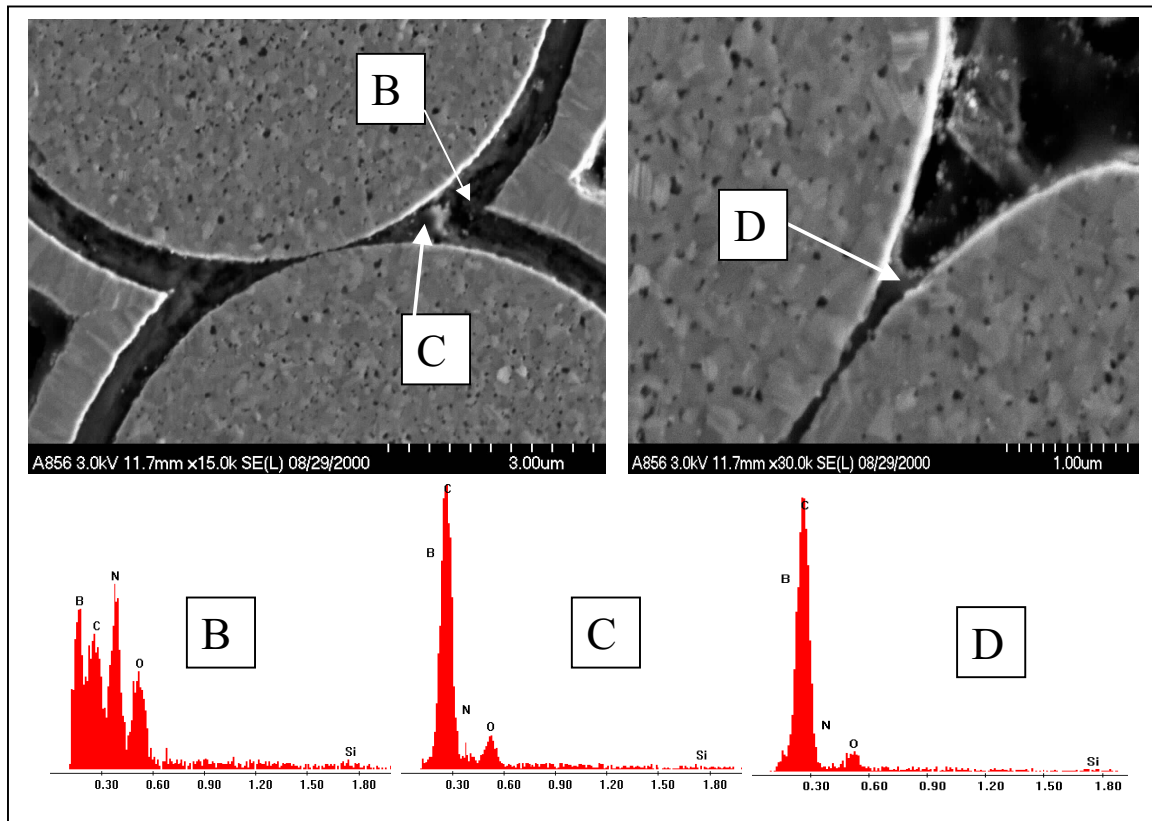


Fig. 2, SEM images and EDS spectra from polished sections of a PEO composite

AES offers the advantage of revealing the chemical state of the carbon detected, so that free carbon is distinguishable from Si-bonded carbon in SiC [7]. This point is illustrated in Fig. 3, which compares AES survey spectra taken from fracture surfaces in four SylramicTM/BN/SiC samples: three PEO materials (**a-c**) and one PVA material (**d**). In sample **d** the silicon signal is of comparable intensity to that of carbon, whereas in samples **a-c** the silicon seems to be absent. This indicates that samples A-C have high amounts of elemental carbon, while sample **d** is free

of elemental carbon, being essentially the SiC fiber surface. Further confirmation comes from fine-structure details indicated with arrows in the spectra: a shoulder or kink in a spectrum at ~260 eV is the hallmark of elemental carbon, and its absence a clear indication that the carbon is bonded (in this case to Si) [7,10].

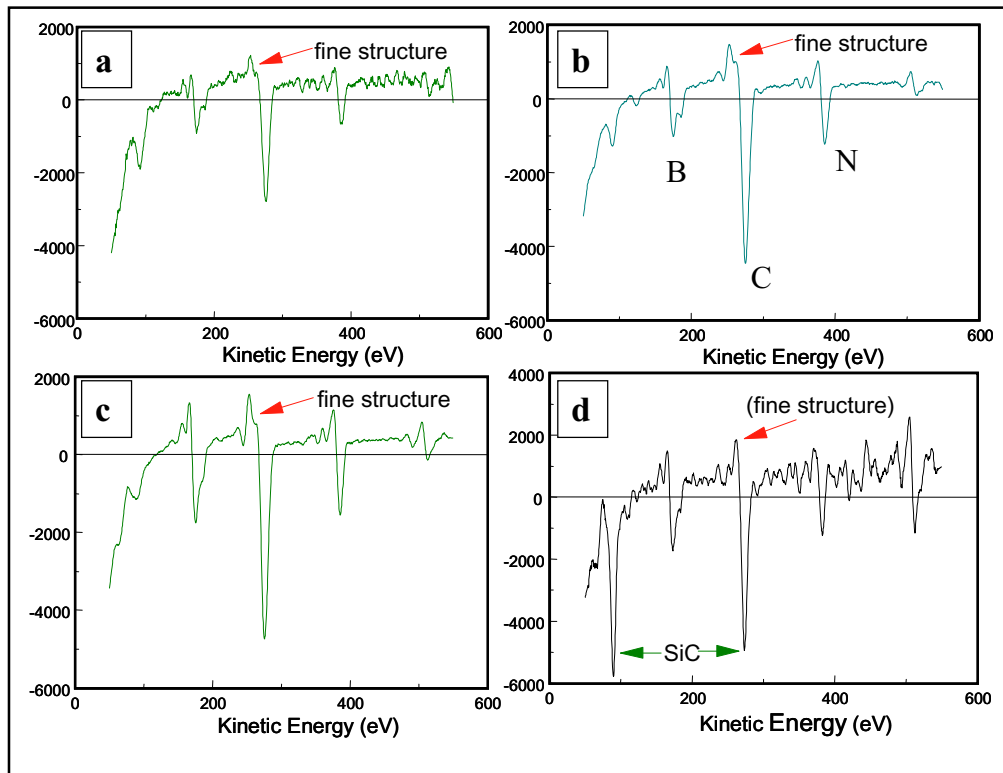


Fig. 3, AES survey spectra from four different SylramicTM/BN/SiC composites showing that free carbon is associated with those materials made with PEO-sized fibers (a-c), but not those with PVA-sized fibers (d).

This result suggests that PEO sizing is more likely than PVA to leave substantial residues of deleterious carbon on fibers. This may reflect an intrinsic difference between PEO and PVA (such as different char yields upon de-sizing), or merely differing amounts of sizing used: Manufacturers' data show that PEO-sized fibers had ~2 wt. % sizing, whereas PVA-sized fibers had only ~0.2 wt. % of sizing.

The amount of residual free carbon observed in the PEO materials varied greatly: from very little in some to substantially thick layers in others. Fig. 4 is an AES depth-profile of the fiber coating from the PEO material in Fig 1. The silicon and carbon profiles are shown accentuated for comparison. (Profiles of all the other constituents lie at the bottom of the chart, close to the detection threshold.) The evident 160-nm layer of free carbon is the thickest observed: depth-profiling of the other PEO materials indicated the carbon layers to be 15-80 nm deep.

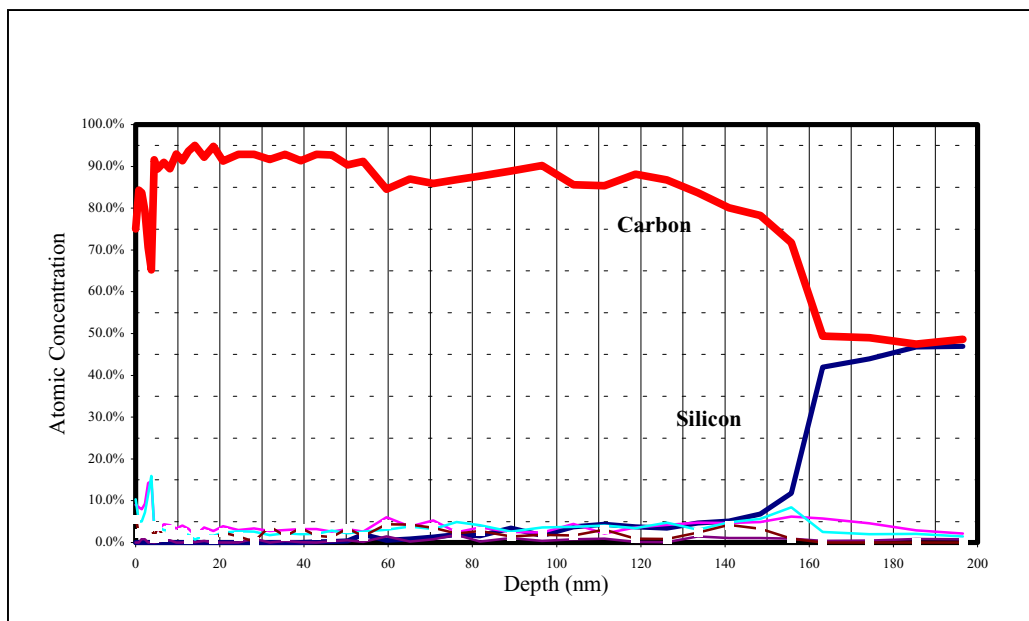


Fig. 4, AES depth profile from a SylramicTM/BN/SiC composite made with PEO-sized fibers, showing a layer of free carbon ~160 nm thick on the fiber.

It was mentioned in Section 3.1 that all seven PEO materials examined exhibited severe degradation in the burner rig, while the two PVA materials did not. It should be noted that free carbon was detected in all the PEO samples but not in the PVA samples. The correlation seems clear: free carbon at the interphase leads to severe degradation in the burner rig. The degradation of SylramicTM/BN/SiC is similar to what was observed in Hi-NicalonTM/BN/SiC composites.

An important difference between the two systems is the origin of the offending carbon. In Hi-NicalonTM composites it comes from excess carbon in the fiber, while in SylramicTM materials the residue of improperly removed (or unsuitable) sizing appears to be the source of carbon. In Hi-NicalonTM systems the carbon diffuses from the fiber during matrix infiltration and hence appears uniform and

continuous on the fibers. In contrast, the free carbon on PEO-sized SylramicTM fibers were quasi-continuous, appearing somewhat like spiral ribbons around the fibers. That difference is depicted schematically in Fig. 5 for NicalonTM fibers (a), and SylramicTM fibers (b).

Raman Spectroscopy

Raman spectrometry was also used on polished cross-sections, without success. Results indicated that graphitic carbon was present in the samples but resolution was inadequate to distinguish between carbon signals from the matrix, fiber, and interphase. Thus Raman spectrometry proved unsuitable for the detection of interfacial carbon in these materials.

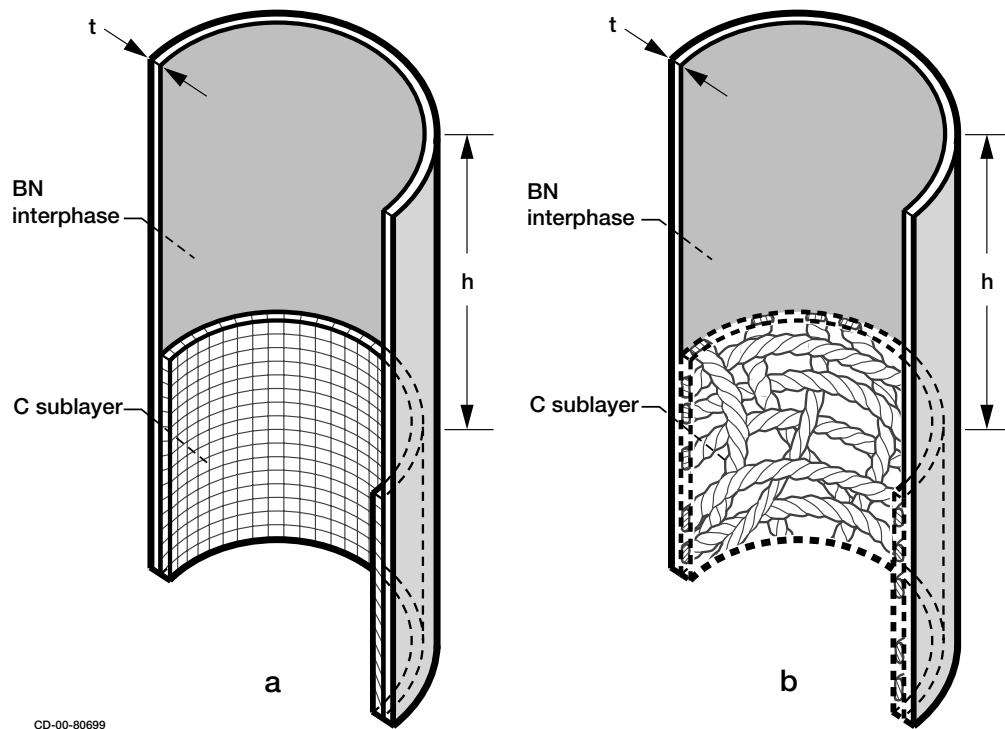


Fig. 5, Schematic illustration of carbon layers on SiC fibers: they are thought to be uniform on NicalonTM (a), but ribbon-like on PEO-sized SylramicTM fibers (b)

SUMMARY AND CONCLUSION

Elemental carbon was observed in SylramicTM/BN/SiC composites made with PEO-fibers, as a (quasi)continuous layer on the fiber analogous to the layer of free carbon found on Hi-NicalonTM fibers. As with Hi-NicalonTM/BN/SiC composites, the presence of free carbon correlated with degradation of composite behavior in these materials. This study has shown that SEM and AES, used in combination, are effective techniques for detecting deleterious carbon layers in SiC/BN/SiC composites.

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