NASA/TM—2001-211069

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

L.U.J.T. Ogbuji
QSS Group, Inc., Brook Park, Ohio

D.R. Wheeler
Glenn Research Center, Cleveland, Ohio

T.R. McCue
QSS Group, Inc., Brook Park, Ohio

Prepared for the
25th Annual International Conference on Advanced Ceramics and Composites
sponsored by the American Ceramic Society
Cocoa Beach, Florida, January 21–26, 2001

National Aeronautics and
Space Administration

Glenn Research Center

July 2001

Acknowledgments

The assistance of Mike Cuy with burner rig exposures of our samples at NASA Glenn Research Center is gratefully acknowledged.

Available from

NASA Center for Aerospace Information
7121 Standard Drive
Hanover, MD 21076

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22100

Available electronically at http://gltrs.grc.nasa.gov/GLTRS

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

L.U.J.T. Ogbuji
QSS Group, Inc.
Brook Park, Ohio 44142

D.R. Wheeler
National Aeronautics and Space Administration
Glenn Research Center
Cleveland, Ohio 44135

T.R. McCue
QSS Group, Inc.
Brook Park, Ohio 44142

ABSTRACT
Following our detection of films of elemental carbon in the Hi-Nicalon™/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 Sylramic™/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-Nicalon™/BN/SiC the deleterious layer originates from excess carbon content of the non-stoichiometric fiber [1-4]. Close examination of some Sylramic™/BN/SiC composites have revealed similar layers of elemental carbon on the fiber, resulting in severe burner rig degradation as was exhibited by Hi-Nicalon™ composites [1,2]. In Sylramic™/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 Nicalon™ 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 Nicalon™/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 Sylramic™/BN/SiC. Our findings for Hi-Nicalon™/BN/SiC composites have been described elsewhere [1,2,6,7].

PROCEDURE

The composites in this study were comprised of Sylramic™ (stoichiometric SiC) fibers coated with ~0.5μm 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-Nicalon™/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.

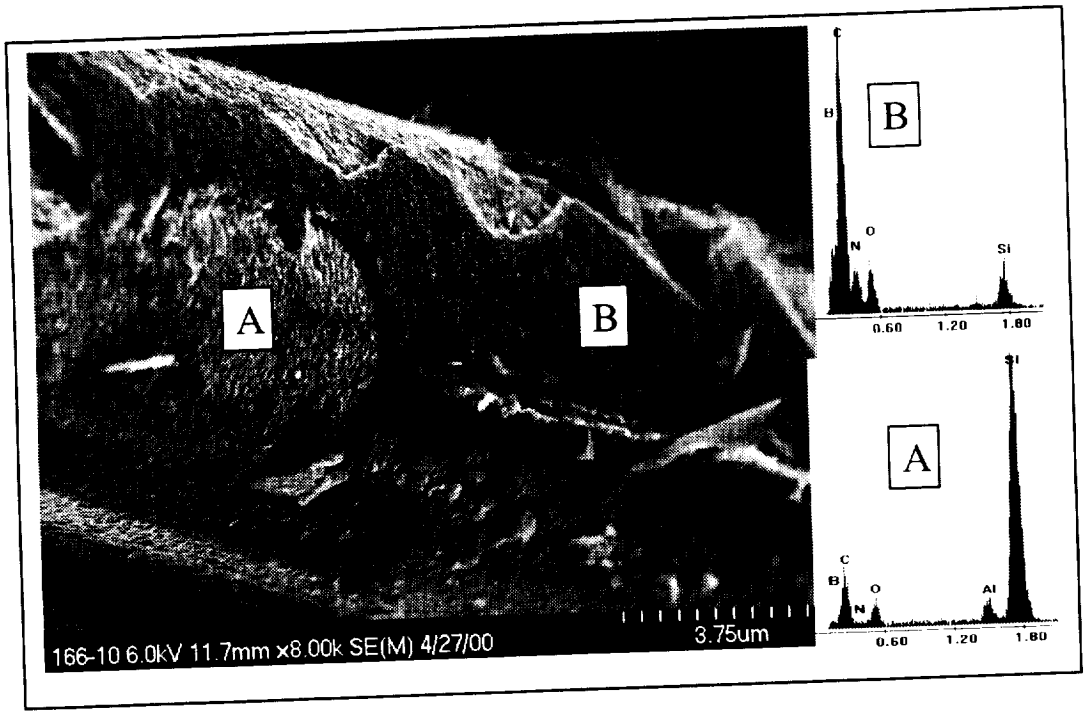

Fig. 1, SEM image and spectra from Sylramic/BN/SiC composite with a high excess of carbon in the interphase.

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.

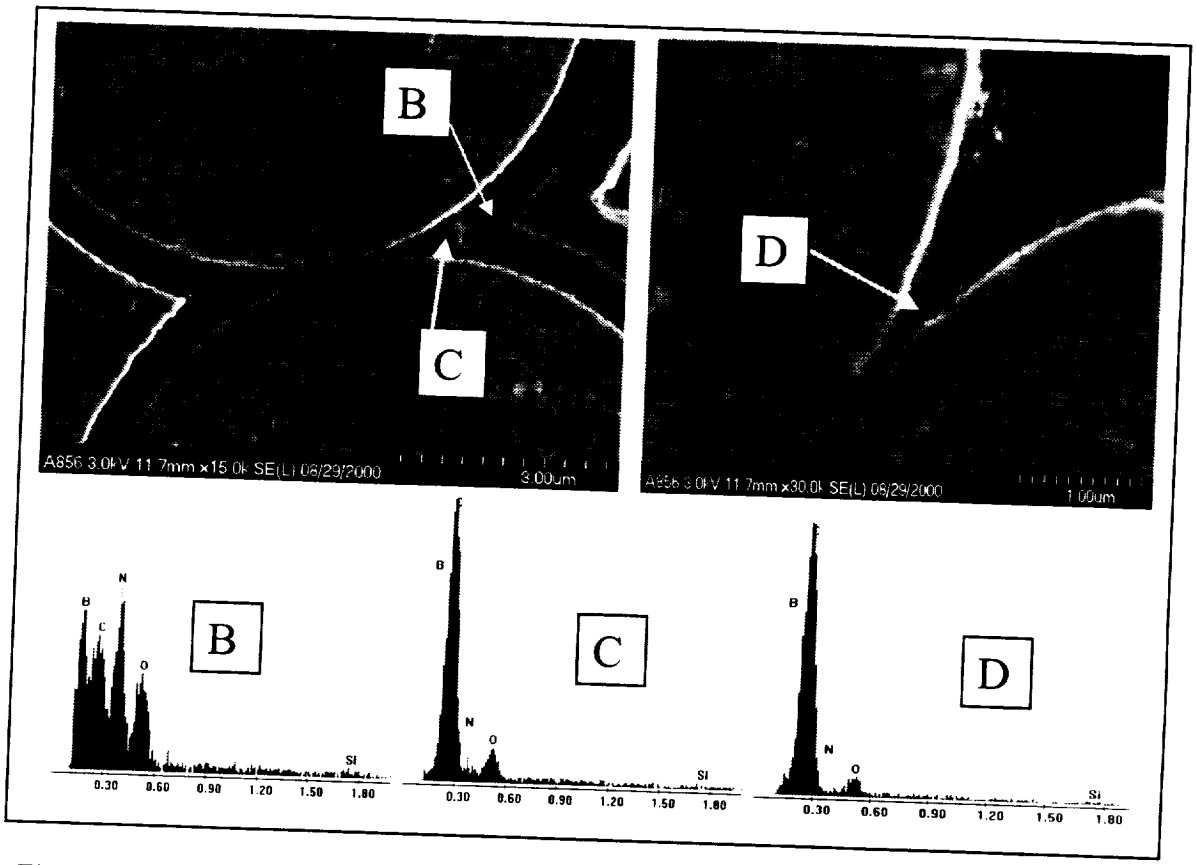

Fig. 2, SEM images and EDS spectra from polished sections of a PEO composite

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 Sylramic™/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].

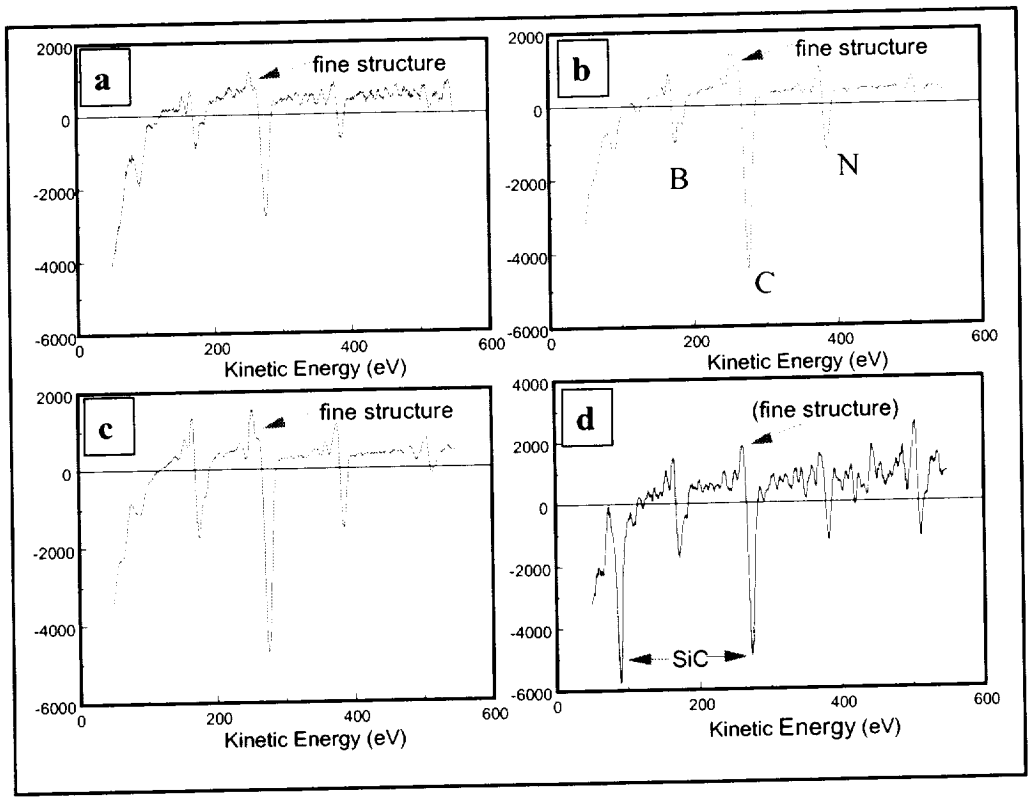

Fig. 3, AES survey spectra from four different Sylramic^{TM}/BN/SiC composites showing that free carbon is associated with those materials made with PEO-sized fibers (a-c), but not those with PVA-sized fibers (d).

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.

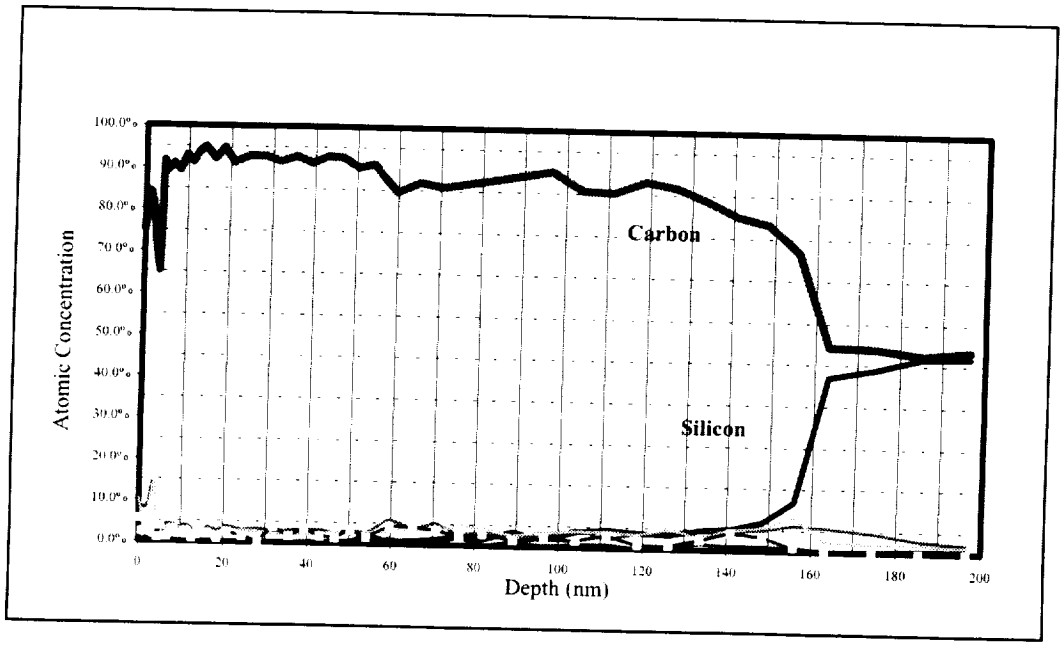

Fig. 4, AES depth profile from a Sylramic^{TM}/BN/SiC composite made with PEO-sized fibers, showing a layer of free carbon ~160 nm thick on the fiber.

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 Sylramic^{TM}/BN/SiC is similar to what was observed in Hi-Nicalon^{TM}/BN/SiC composites.

An important difference between the two systems is the origin of the offending carbon. In Hi-Nicalon^{TM} composites it comes from excess carbon in the fiber, while in Sylramic^{TM} materials the residue of improperly removed (or unsuitable) sizing appears to be the source of carbon. In Hi-Nicalon^{TM} 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 Sylramic™ fibers were quasi-continuous, appearing somewhat like spiral ribbons around the fibers. That difference is depicted schematically in Fig. 5 for Nicalon™ fibers (a), and Sylramic™ 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.

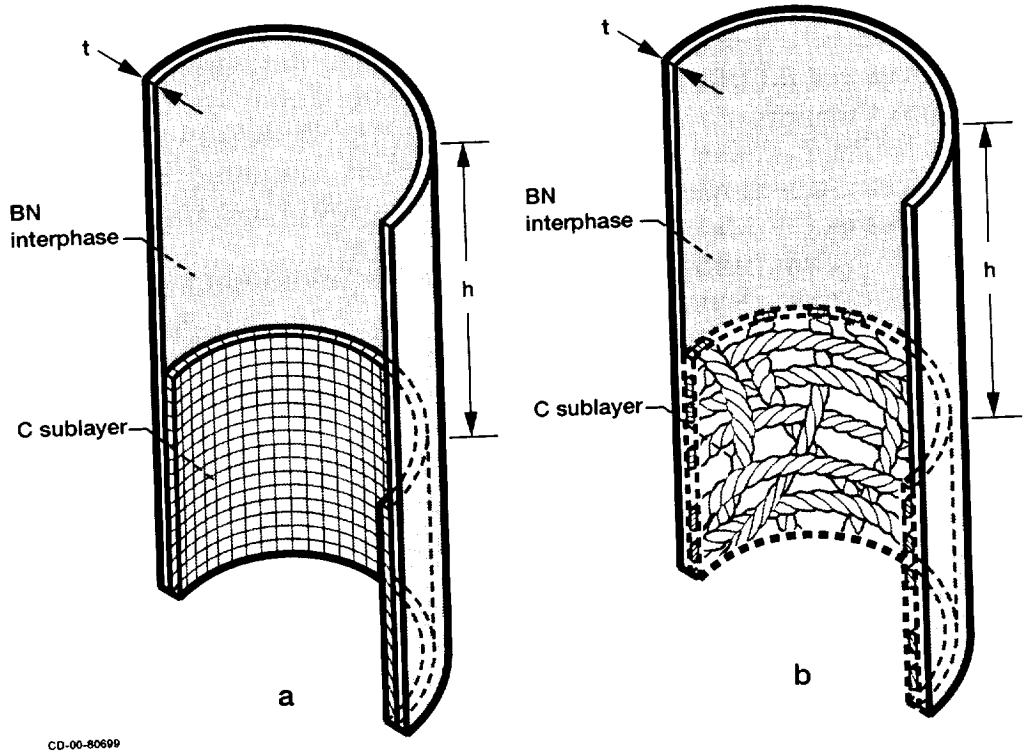

Fig. 5, Schematic illustration of carbon layers on SiC fibers: they are thought to be uniform on Nicalon™ (a), but ribbon-like on PEO-sized Sylramic™ fibers (b)

SUMMARY AND CONCLUSION

Elemental carbon was observed in Sylramic™/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-Nicalon™ fibers. As with Hi-Nicalon™/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.

REFERENCES

1. L.U.J.T. Ogbuji, "Degradation of SiC/BN/SiC Composite in the Burner Rig", p. 257 in Ceram. Eng. & Sci. Proc., vol. **19**, issue 4 (1998)
2. L.U.J.T. Ogbuji, "A Pervasive Mode of Oxidative Degradation in a SiC-SiC Composite", J. Am. Ceram. Soc., **81** [11] 2777 (1998)
3. E.Y. Sun, S.R. Nutt, and J.J. Brennan, "Interfacial Microstructure and Chemistry of SiC/BN Dual-Coated Nicalon-Fiber-Reinforced Glass-Ceramic-Matrix Composites", J. Am. Cer. Soc., **77** [5] (1994) 1329-39
4. G. Chollon, R. Pailler, R. Naslain, F. Laanani, M. Monthioux, and P. Olry, "Thermal Stability of a PCS-Derived SiC Fibre with a Low Oxygen Content (Hi-Nicalon)", J. Mater. Sci., **32** [2] (1997) 327-47
5. L.U.J.T. Ogbuji, Silicon-Based Ceramic-Matrix Composites for Advanced Turbine Engines: Some Degradation Issues", p. 767 in Proc. *Parsons 2000:* Fifth International Charles Parsons Turbine Conf. (A. Strang et al. eds.),Cambridge University, 3-7 July 2000; Cambridge University Press, UK, 2000
6. L.U.J.T. Ogbuji, "Degradation of SiC/SiC Composite in the Burner Rig: Investigation by Fractography", p. 369 in Materials at High Temperatures, Proc. 4th International Conf. on the Microscopy of Oxidation (G. Tatlock, ed.), Cambrian Printers, UK, 2000
7. L.U.J.T. Ogbuji, "Identification of Carbon Sublayer in a Hi-Nicalon/BN/SiC Composite", J. Mat. Sci. Let. **18** (1999) 1825
8. L.A. Giannuzzi and C.A. Lewinsohn, "Interphase Oxidation in SiC/SiC Composites at Varying Partial Pressures of Oxygen", p. 115 in Ceram. Eng. & Sci. Proc., vol. **20**, issue 4 (E. Ustundag and G. Fischman eds.), Am. Ceram. Soc., Westerville OH, 1999
9. L.A. Giannuzzi and C.A. Lewinsohn, "Interphase Oxidation in SiC/SiC Composites", p. 469 in Ceram. Eng. & Sci. Proc., vol. **21**, issue 3 (T. Jessen and E. Ustundag, eds.), Am. Ceram. Soc., Westerville OH, 2000
10. D. Briggs and J.C. Riviere, Ch. 3 ("Spectra Interpretation") in Practical Surface Analysis, 2nd Edition, vol. 1: Auger and X-ray Photoelectron Spectroscopy, D. Briggs and M.P. Seah (eds), John Wiley & Sons, NY 1990

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (*Leave blank*)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	July 2001	Technical Memorandum

4. TITLE AND SUBTITLE

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

5. FUNDING NUMBERS

WU-714-04-30-00

6. AUTHOR(S)

L.U.J.T. Ogbuji, D.R. Wheeler, and T.R. McCue

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
John H. Glenn Research Center at Lewis Field
Cleveland, Ohio 44135-3191

8. PERFORMING ORGANIZATION REPORT NUMBER

E-12905

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
Washington, DC 20546-0001

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

NASA TM—2001-211069

11. SUPPLEMENTARY NOTES

Prepared for the 25th Annual International Conference on Advanced Ceramics and Composites sponsored by the American Ceramic Society, Cocoa Beach, Florida, January 21–26, 2001. L.U.J.T. Ogbuji and T.R. McCue, QSS Group, Inc., 2000 Aerospace Parkway, Brook Park, Ohio 44142 (work funded under NASA Contract NAS3-00145); D.R. Wheeler, NASA Glenn Research Center. Responsible person, D.R. Wheeler, organization code 5140, 216–433–5837.

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Unclassified - Unlimited
Subject Category: 24 Distribution: Nonstandard

Available electronically at http://gltrs.grc.nasa.gov/GLTRS

This publication is available from the NASA Center for AeroSpace Information, 301–621–0390.

12b. DISTRIBUTION CODE

13. ABSTRACT ***(Maximum 200 words)***

Following our detection of films of elemental carbon in the Hi-Nicalon™/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 Sylramic™/BN/SiC materials. Effective techniques for routine detection and characterization of adventitious carbon in SiC/BN/SiC composites are discussed.

14. SUBJECT TERMS

Composites; Fiber sizing; Interphase degradation; Carbon

15. NUMBER OF PAGES

14

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	