NASA/CR—2002-211687

Recent Developments in the Environmental Durability of SiC/SiC Composites

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July 2002

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Prepared for the
CIMTEC 2002, International Conferences on Modern Materials and Technologies
cosponsored by the Academy of Ceramics, the International Ceramic Federation, and
the International Union of Materials Research Societies
Florence, Italy, July 14–19, 2002

Prepared under Contract NAS3–98008

National Aeronautics and
Space Administration

Glenn Research Center

July 2002

Acknowledgments

This work was funded by the UEET program of NASA under the GESS contract NAS3–98008.

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RECENT DEVELOPMENTS IN THE ENVIRONMENTAL DURABILITY OF SIC/SIC COMPOSITES

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Abstract
Two types of pest behavior in SiC/BN/SiC composites are distinguished and illustrated: one intrinsic and progressive, the other extrinsic and catastrophic. Their similarities and differences are presented. Some recent remedies for SiC/BN/SiC pest are discussed.

Introduction: Types of Pest in SiC/SiC Composites
The oxidative degradation of ceramic-matrix composites (CMCs) in service environment at intermediate temperatures, known as pest or pesting, is a major limiter of performance and service lifetimes in SiC/SiC composites. It is caused by selective attack of the fiber coatings/"interphase" by ambient oxidants,[1,2] manifested in loss of composite behavior. It is an intermediate-temperature problem in SiC/SiC composites. At lower temperatures oxidation is too slow to be a problem; at higher temperatures fast oxidation of the matrix protects the composite with a cover of silica. Elimination or suppression of pest is an important goal in the development of CMCs for turbine engine and other applications. An effective screening test and a few remedies for SiC/SiC pest are discussed in this paper.

In order to control SiC/SiC pest, we must first understand the nature of it. It has become necessary to distinguish between two types of CMC pest, because each type calls for a different remedy. So far, CMC pest has been portrayed as a progressive phenomenon, with material degradation starting at the surface and advancing inward.[3] Recent work has revealed a more serious kind of pest, which is specific to SiC/SiC composites. This pest mode is peculiar to SiC/BN/SiC composites in which a carbon film underlies the BN interphase; and it has been demonstrated in the burner rig—a proxy ambient for the turbine engine combustor, with its moisture-laden, high-velocity hydrocarbon flame.[1,4] In this type of pest, damage is not progressive but rather catastrophic, causing rapid and pervasive damage. Progressive and catastrophic pest may be designated Types I and II, respectively, to distinguish them.

Both types of pest proceed by destroying the interphase, which plays two crucial roles in the mechanical response of a CMC. One role of the interphase is to deflect matrix cracks along the fiber sides, thus preventing catastrophic crack propagation across fibers; the other is to effect, by its compliance, transfer of load from matrix to fiber and the sharing of load between fibers. These two roles add up to what is called "composite behavior," which culminates in "graceful failure" of the composite: i.e., fracture that is characterized by copious pull-out of fibers. Pest (of both types) degrades composite behavior in two ways: (1) It replaces the compliant BN interphase with non-compliant borosilicate/silica which prevents the deflection of matrix cracks; (2) it bonds the fibers together or to the matrix, preventing broken fibers from sliding and pulling out

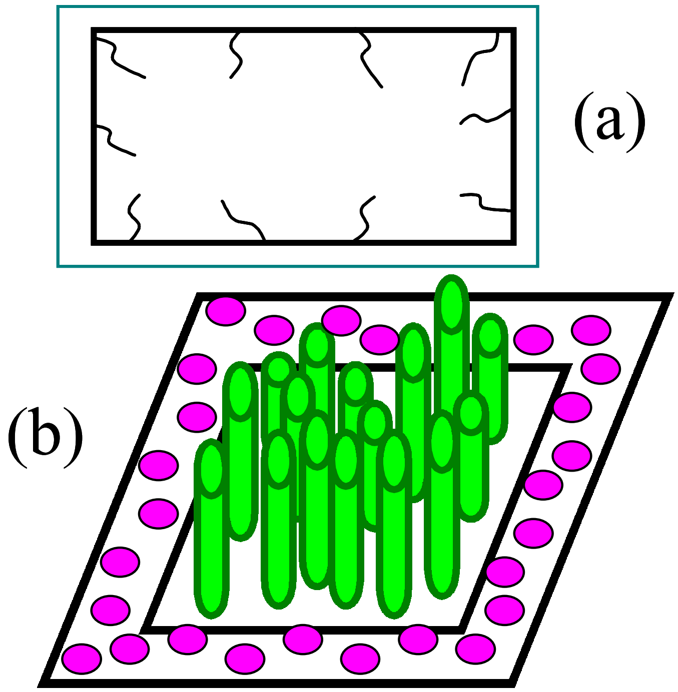

Fig. 1.—Schematic illustration of the origin and fracture features in Type I pest.

Figure 1 illustrates Type I pest. Surface-intersecting cracks facilitate ingress of oxidants to the sample interior and thus promote pest. In SiC/BN/SiC the interphase BN coating on the fibers can itself constitute a pathway for oxidant ingress when fiber ends become exposed. Type I pest in SiC/BN/SiC is caused by permeation of oxidation along those routes. The fracture surface has a "picture frame" appearance,[5] which is illustrated in Fig. 1(b). The "picture" is a core of undamaged material characterized by pull-out of fibers , and the surrounding "frame" is a brittle-fracture zone of damaged material. In SiC/BN/SiC, advance of the damage front correlates with recession of the interphase as it is attacked by ambient oxidants.[6] Hence, Type I pest degradation is time-dependent, like fatigue or creep, and should be amenable to modeling for lifetime prediction. The residual strength of a SiC/SiC tensile bar undergoing a Type I pest is proportional to the cross-sectional area of undamaged material at the core.[3,5] Type I pest is relatively slow, being controlled by the consumption of BN interphase. A primary cause of Type I pest is the intrinsically inadequate oxidation resistance of the BN interphase.

Type II pest occurs when the BN interphase is effectively undermined by a continuous or skeletal film of carbon that is sometimes found on the fibers, and which constitutes an even more effective conduit for oxidant ingress. The mechanistic difference between

Types I and II pest is best understood with reference to Fig. 2(a). A fiber (omitted for clarity) is separated from its BN interphase coating by a film of carbon. Upon exposure to the ambient, the BN presents a cross-sectional area $\pi \mathbf{r}^2 \mathbf{t}_B$ to the flame (where **r** is radius of the coated fiber and **t** thickness of the BN layer). Oxidation causes the BN to recede to a depth h_B; in the absence of the carbon layer this amounts to Type I pest. When the carbon film is present it recedes to a greater depth, $\mathbf{h}_C$, thus exposing the BN to additional oxidation on its inner wall facing the fiber. This additional attack on the BN wall, area $2\pi r(\mathbf{h}_C - \mathbf{h}_B)$, is the hallmark of Type II pest: it does not occur in Type I pest.

Since **r** and **t** are measured in micrometers while $\mathbf{h}_C$ is measured in centimeters (being typically the sample width[1,7]), the area of BN attack in Type II pest is vastly larger than in Type I. Consequently, degradation of Type II pest reaches deep into the material interior very quickly. A big difference between the two types, then, is the speed of attack: Type I correlates with the linear recession of the BN interphase (which is slowed down by the borosilicate from BN oxidation[5]), while Type II follows a short-circuit path of adventitious carbon and destroys the material very quickly.[1] Also, a tensile specimen under Type II pest fails like a monolithic ceramic, with fracture occurring all in one crack plane, as illustrated in Fig. 2(b).

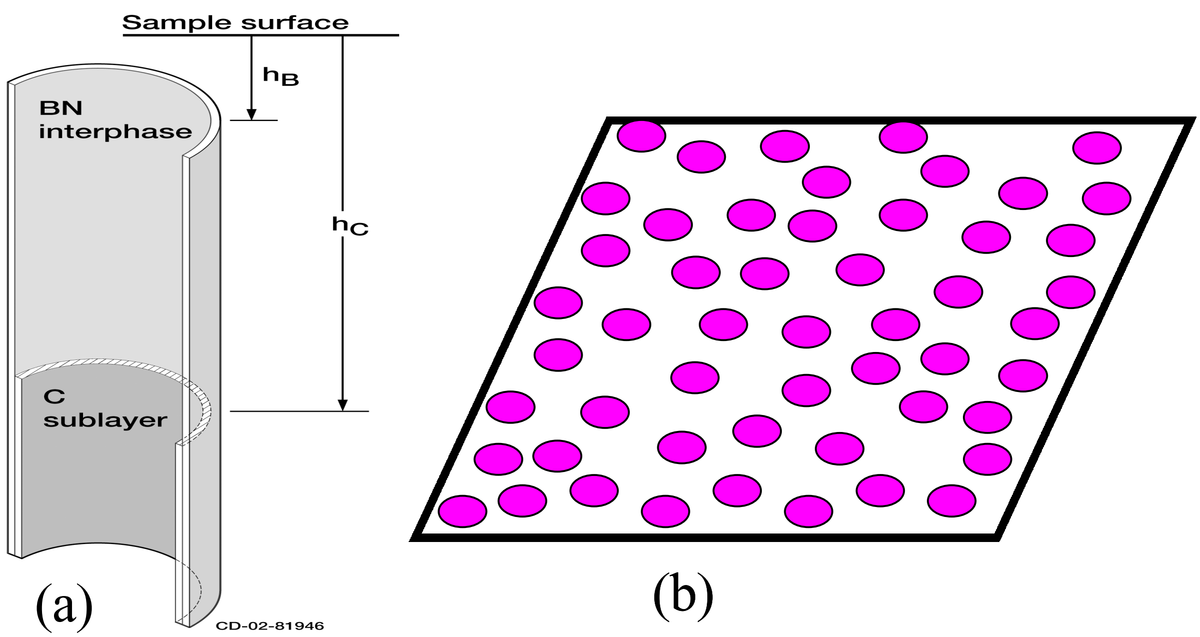

Fig. 2.—Schematics of Type II pest in SiC/BN/SiC: (a) its origin in an interphase sub-layer of carbon; (b) its manifestation in flat and brittle tensile fracture across the sample.

There are other differences between the types of pest. Type I pest occurs in all oxidizing media, but Type II has only been observed in the high-velocity flame of a burner rig.[1,2,6,8] A likely reason for this is that diffusion of CO/CO_2 from the oxidation of carbon, through the resulting boundary layer, is enhanced by increasing ambient velocity (an effect that has been observed in the hydrolytic recession in H_2O of SiC[9] and Si3N4[10] substrates). Also, Type I pest is intrinsic to the system, being tied to the BN oxidation resistance; in contrast, Type II is driven by adventitious carbon, an extrinsic factor. The last distinction is important to the respective remedies for pest.

A high fiber volume fraction is desirable for load carrying strength in SiC/SiC composites; but it also hinders matrix processing, leaving little gap between fibers for infiltration of the SiC matrix. Hence, there is extensive contact between the coatings on adjacent and crossing fibers, and consumption of the coatings can spread rapidly from fiber to fiber. This is especially so when the coating includes a carbon film beneath the BN. All these factors make Type II degradation orders of magnitude faster than Type I. Free carbon, which is responsible for Type II pest, is often present in SiC/BN/SiC composites because their various constituents rely heavily on organo-metallic ingredients.

Experimental: Screening Test For SiC/SiC Pesting

Our test for SiC/SiC pest susceptibility is to expose a sample in an atmospheric-pressure burner rig (APBR) flame, and then measure its residual tensile response. The material is a tensile bar, with fiber ends and their associated coatings exposed along the machined edge. The picture shows a sample in the APBR flame, while the schematics illustrate relevant details of its architecture. The fibers on whose ends the flame impinges are designated [0°] fibers, for distinction from the [90°] fibers, which lie in the longitudinal direction of the sample. In the absence of open matrix cracks, flame gases have no direct access to the [90°] fibers and the interphase coatings around them. Since only the [90°] fiber tows bear load in the subsequent tensile test, a severe reduction in fracture strength or strain implies that interphase degradation has spread quickly from the [0°] to the [90°] fiber tows; this is a good indicator of Type II pest.

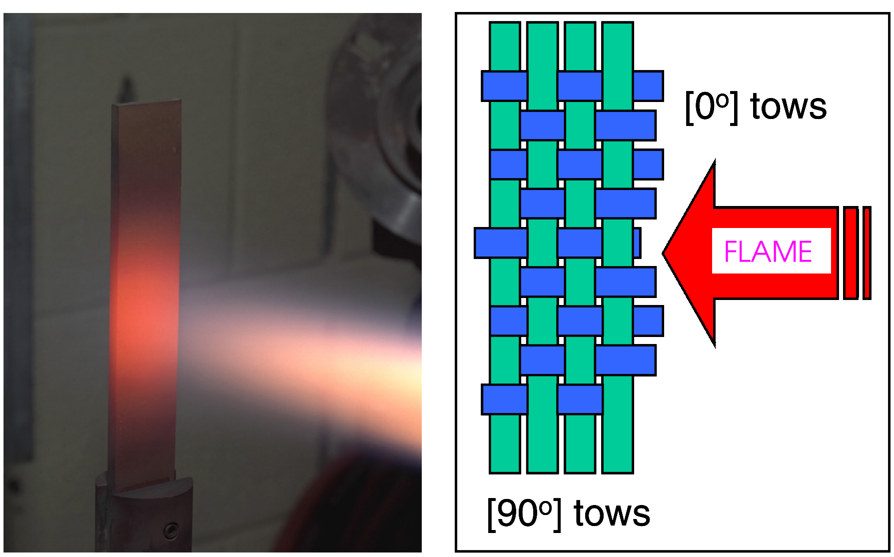

Fig. 3.—Testing for Pest in SiC/SiC: Left, a sample in the APBR flame; Right, the Schematic details of sample architecture.

Following exposure and tensile test the sample is examined by imaging and analytical techniques to determine: (a) appearance of the fracture surface (fibrous or flat/brittle); (b) evidence of glass formation and other interphase degradation products around fibers in the fracture plane; (c) interphase integrity in the flame zone of the sample; (d) presence of a carbon layer between BN interphase and SiC fiber in a pristine area of the sample (such as under the tensile-test grips); etc.

<u>Results and Discussion</u>

Figure 4 illustrates the dramatic effect of Type II pest on the mechanical properties of Hi-Nicalon™/BN/SiC materials, in which excess carbon in the fiber "sweats" out during melt-infiltration of the matrix to form a compact layer of carbon beneath the BN interphase. The residual strength and fracture strain of the three samples exposed in the burner rig are drastically diminished from those of the as-received (AR) sample. In effect, pested material fails at or just above the elastic regime, indicating that the material is behaving as a monolith rather than a composite.

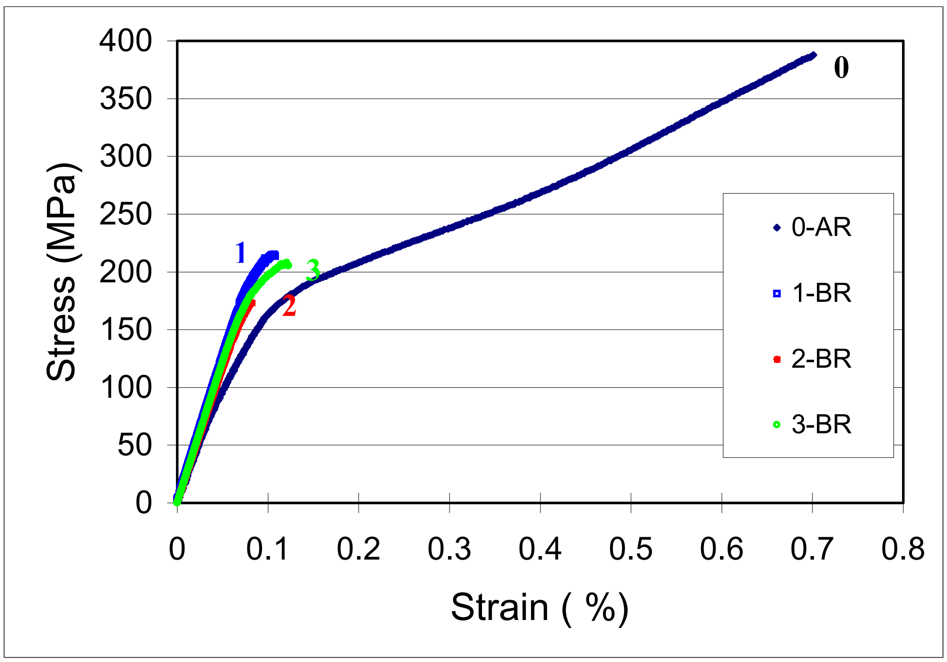

Fig. 4.—The stress-strain behavior of as-received Hi-Nicalon/BN/SiC (#0), and three samples (1–3) of the same material that underwent Type II pest in the burner rig (BR).

Figure 5 shows features of Type I pest: brittle fracture along the edge and fibrous fracture in the interior. When Hi-Nicalon™/BN/SiC bars were exposed to quasi-static room air in a box furnace (containing ~2.5% H_2O), pest started at the cut edges and stepped inward, tow by tow: after 500 hours at 800 °C damage had reached the 3rd tows from each end (consuming ~15% of the cross-section). In contrast, Fig. 6 shows the more pervasive degradation that result from Type II pest. The characteristic features

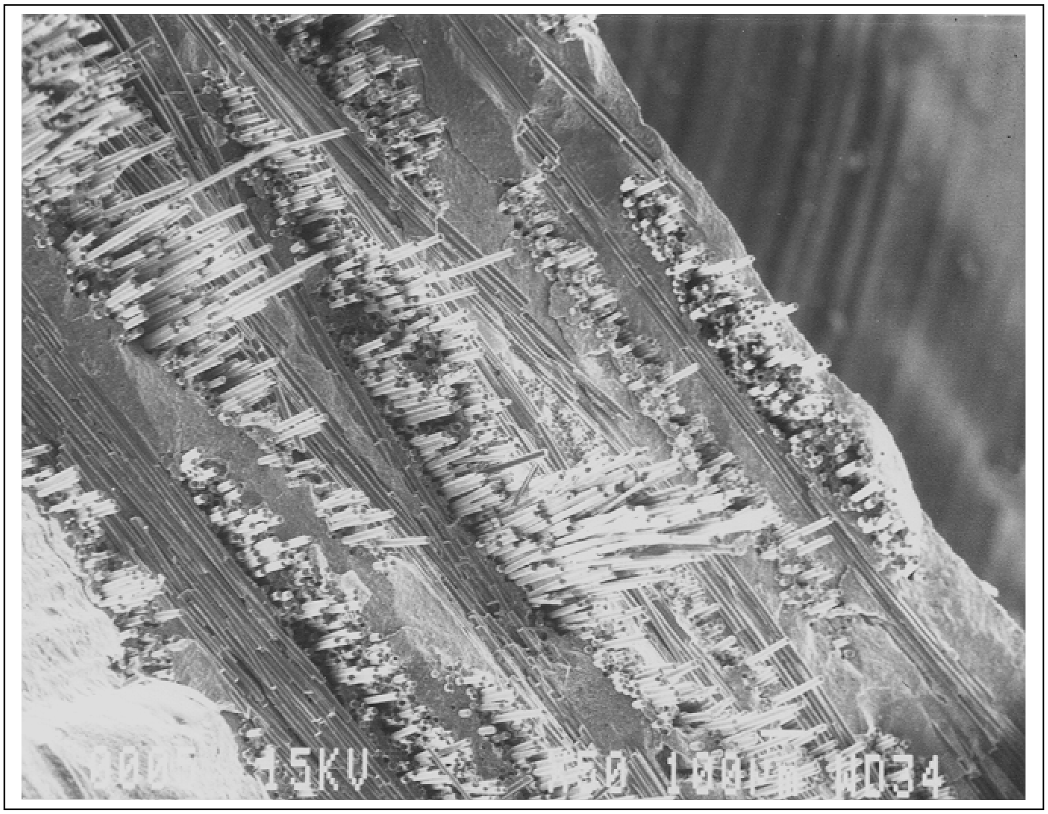

Fig. 5.—"Picture Frame" fracture surface in Hi-Nicalon™/BN/SiC exposed for 200 hours in a box furnace (room air); Type I pest is evident in brittle fracture of fibers at the edges, while the center exhibits millimeters-long fiber pull-out like the as-received material.

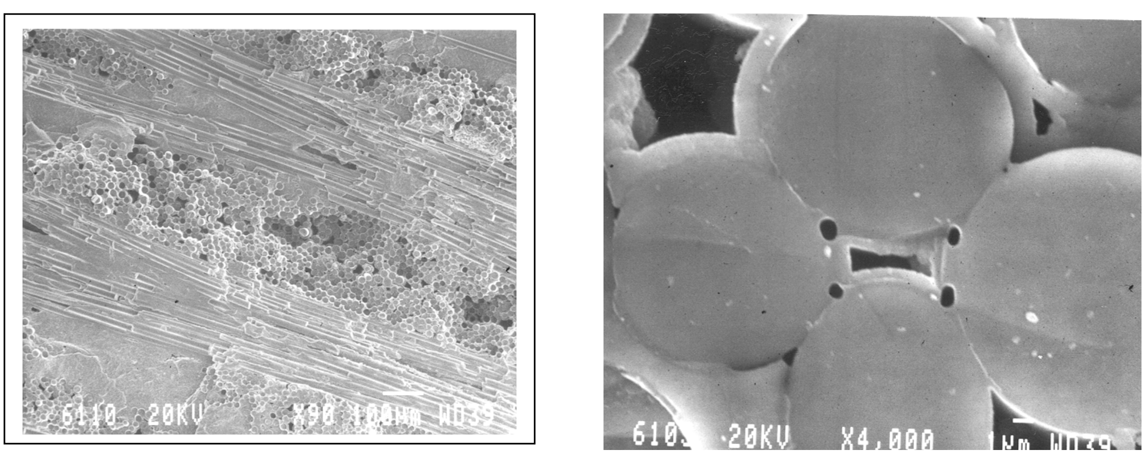

Fig. 6.—SEM micrographs of fracture surface from Hi-Nicalon™/BN/SiC exposed 150 hours in a burner rig, showing Type II pest features: (a) flat/brittle fracture throughout the sample; (b) fibers bonded together by glass, with holes between them for venting gaseous products, and fiber fracture that was typically initiated at bonding spots.

include flat fracture from edge to edge. At higher magnification, Fig. 6(b), it is evident that the fibers have become bonded together or to the matrix by silica, with prominent holes from venting the $B(OH)_x$ volatiles from hydrolysis of borosilicates. In Hi-Nicalon™/ BN/SiC, the offending free carbon came from stoichiometric excess in the fiber.

Figure 7 shows a variety of Sylramic™/BN/SiC that exhibited Type II pest, and flat fracture very similar to that in Fig. 6. The difference is that in this material (Sylramic™/BN/SiC) the offending carbon film came from substantial char residue left by the removal of fiber sizing, rather than from the fiber itself.

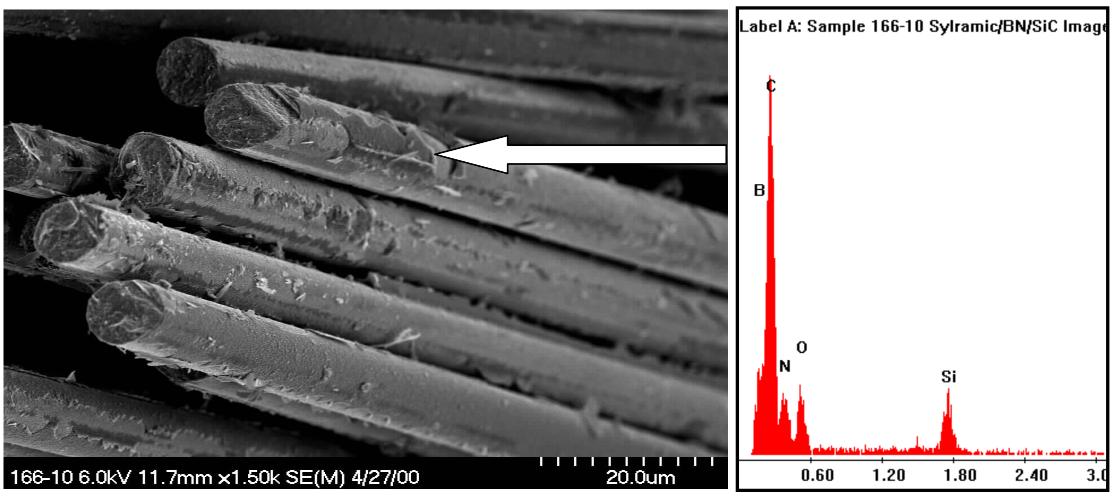

Fig. 7.—SEM micrograph of the fracture surface from as-received Sylramic™/BN/SiC showing a compact "coating" layer on the fibers; the EDS spectrum on the right identifies this layer as almost entirely carbon (from incomplete removal of sizing).

Figure 8 shows the results of studies aimed at reducing or counteracting the presence of graphitic carbon in SiC/BN/SiC composites. Each histogram pair shows the strength of a specific SiC/BN/SiC vintage before and after exposure in our burner rig. Hi-Nicalon™fiber (pair #6) contains ~40% excess carbon, which causes Type II pest. Its successor, Hi-Nicalon-S (#1), has <5% excess carbon, but our burner rig tests showed that this level of carbon was still high enough to cause Type II pest. Histogram pairs #2 and #3 illustrate the effects of further reductions in free carbon, made by the manufacturer in the case of Hi-Nicalon-S (II), or through special heat treatment in our labs (III).[11] Histogram #4 shows the high resistance to pest achieved in Sylramic™/BN/SiC composites by inducing *in-situ* growth of an additional BN layer through special heat treatment,[12] while #5 shows that such resistance is again lost when a carbon layer exists beside the *in-situ* BN.

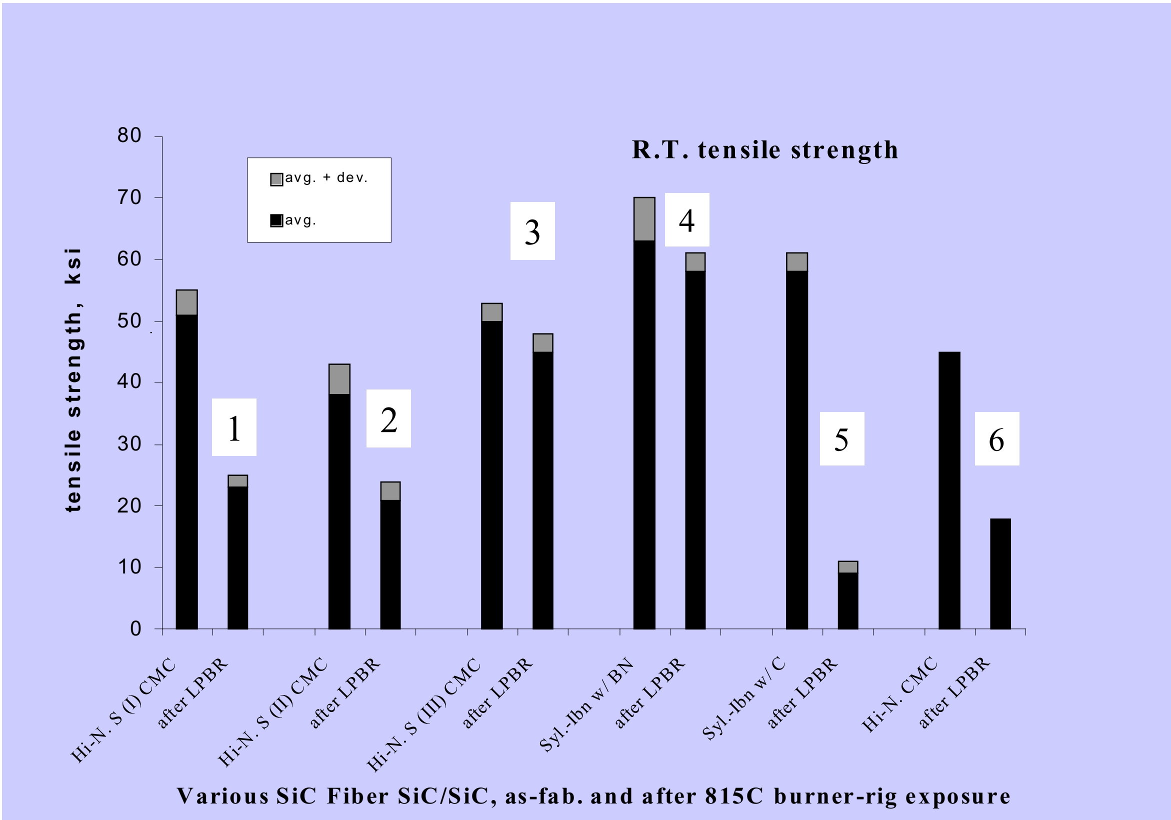

Fig. 8.—Tensile strength of various SiC/BN/SiC materials with different carbon contents, before and after exposure in the burner rig, illustrating some remedies for Type II pest ("APBR" and "LPBR" in this paper refer to the same rig: Our atmospheric-pressure burner rig is sometimes referred to as a "low-pressure burner rig", or "LPBR.").

It is clear from Fig. 8 that the most effective remedy for Type II pest is to exclude free carbon that may arise from handling or treating the constituents. In contrast, Type I pest is intrinsic, and its suppression/reduction calls for remedies that increase oxidation resistance of the interphase. These include the use of high-purity and high-temperature BN for improved crystallinity,[11] doping the BN with Si,[6] and inducing an auxiliary BN layer through in-situ treatment of the composite.[13]

Summary and Conclusion

Two types of pest occur in SiC/BN/SiC composites. Type I corresponds to the linear recession of BN under oxidative attack by the ambient; Type II (the more severe type) arises when the BN layer is undermined by a film of adventitious carbon. Remedies for Type I involve improvements in the intrinsic oxidation resistance of the BN, while Type II may be prevented by the strict exclusion of free carbon from the system.

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (*Leave blank*)

2. REPORT DATE
July 2002

3. REPORT TYPE AND DATES COVERED
Final Contractor Report

4. TITLE AND SUBTITLE
Recent Developments in the Environmental Durability of SiC/SiC Composites

5. FUNDING NUMBERS
WU–714–04–30–00
NAS3–98008

6. AUTHOR(S)
Linus U.J.T. Ogbuji

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
QSS Group, Inc.
21000 Brookpark Road
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8. PERFORMING ORGANIZATION REPORT NUMBER
E–13416

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 CR—2002-211687

11. SUPPLEMENTARY NOTES
Prepared for the CIMTEC 2002, International Conferences on Modern Materials and Technologies cosponsored by the Academy of Ceramics, the International Ceramic Federation, and the International Union of Materials Research Societies Florence, Italy, July 14–19, 2002. Project Manager, L.A. Greenbauer-Seng, Materials Division, NASA Glenn Research Center, organization code 5160, 216–433–6781.

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Subject Category: 24 Distribution: Nonstandard

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14. SUBJECT TERMS
Ceramic-matrix composites; Pesting modes; Oxidation

15. NUMBER OF PAGES
15

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	