Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Journal of the European Ceramic Society 23 (2003) 613–617

www.elsevier.com/locate/jeurceramsoc

Pest-resistance in SiC/BN/SiC composites

Linus U.J.T. Ogbuji*

QSS Inc., NASA Glenn Research Center, Cleveland, Ohio, USA

Received 4 October 2001; received in revised form 1 July 2002; accepted 14 July 2002

Abstract

State-of-the-art non-oxide ceramic-matrix composites (consisting of SiC fibers, *cvi*-BN interphase coating, and *mi*-SiC matrix) exhibit excellent mechanical properties at room temperature, as well as above ~1000 °C (where oxidation easily seals flaws with silica); but they are prone to pest degradation at intermediate temperatures in an oxidizing environment, and especially so in the fast, moist flame of a jet engine. Two modes of pest may be distinguished in these composites. The more severe type of pest is promoted by extraneous factors, like a layer of elemental carbon underlying the BN interphase and undermining its intrinsic oxidation resistance. It is shown that, when care is taken to exclude such a carbon layer, SiC/BN/SiC composite can easily survive a 100-h exposure in a burner rig without noticeable loss of strength or strain to fracture.

Keywords: BN interphase; Composites; Oxidation; Pest; SiC/SiC

1. Introduction

The potential of ceramic-matrix composites (CMCs) for service in advanced engines has been known for decades, but realization of that promise has been frustrated by a slow developmental curve. Most designs of advanced turbines for aircraft engines or land-based power generators assume significantly higher operating temperatures than in current engines, both for gains in thermodynamic efficiency and for mandated reductions in exhaust emissions. Hence, it is assumed that hot sections of advanced turbines (especially combustor liners, nozzles, and vanes) will be made of ceramic-matrix composites (CMCs). CMC development has been led by progress in the fiber and matrix constituents. For non-oxide CMCs, reaction-bonded silicon nitride (RBSN) and chemical-vapor-infiltrated silicon carbide (*cvi*-SiC) proved unsuitable as matrix materials and melt-infiltrated silicon carbide (*mi*-SiC) became the matrix of choice; similarly, ‘‘fat’’ fibers (e.g. SCS-0 and SCS-6) have been superseded by thin fibers, with preference shifting successively from Nicalon^{TM} to Hi-Nicalon^{TM} and to Sylramic^{TM} varieties of increasingly refined chemistry and microstructure. The current state-of-the-art non-oxide CMC is a Sylramic^{TM}/BN/mi-SiC composite. The salient points of its development under a succession of NASA programs are highlighted in a companion paper.[1]

While significant progress has been made on the CMC matrix and fibers, development of the CMC interphase (material at the fiber/matrix interface) has been slow, though interphase problems were evident from the start. Initially, carbon was used as an interphase in SiC/SiC composites due to its excellent compliance, but that advantage was offset by its oxidative volatility, which rendered carbon unsuitable at intermediate temperatures. Above 500 °C oxidative loss of interphase carbon becomes catastrophic;[2] only above 1000 °C is protection achieved as SiO_2 from matrix oxidation becomes substantial enough to seal off ingress of oxidants. Boron nitride, the currently preferred interphase, also oxidizes almost as readily as carbon in the same intermediate temperature range, so that SiC/BN/SiC composites can pest as severely as SiC/C/SiC composites.[3] Still, BN remains the interphase material of choice because its shortcomings seem, in principle, remediable. However, the remedies have been slow in coming, and pesting remains a major obstacle to SiC/BN/SiC utilization.

As in a SiC/C/SiC composite, pesting of SiC/BN/SiC also involves selective attack of the interphase by ambient oxidants. However, whereas pesting of SiC/C/SiC

---

* Tel.: +1-216-433-6463; fax: +1-216-433-5544.
E-mail address: thomas-ogbuji@grc.nasa.gov (L.U.J.T. Ogbuji).

0955-2219/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
PII: S0955-2219(02)00268-6

composites involves conversion of the interphase to CO, leaving no solid residue, SiC/BN/SiC pesting is more complex. It seems to involve the synergistic oxidation of all constituents in the interphase area. Whether SiO_2 forms first via SiC oxidation[4] or it is B_2O_3 via BN oxidation[5] (depending on local conditions), the net result is that the compliant BN interphase is removed or replaced by stiff, brittle silica which ''cements'' the fibers down and hence destroys composite behavior. The likely reaction sequence in SiC/BN/SiC pesting is summarized in Table 1. Where the BN interphase is intersected by a crack open to the surface, it is oxidized locally to B_2O_3. The boria may be volatilized by hydrolysis with ambient moisture if the temperature is low, leaving a trench around the fiber;[6] or it may react with the surrounding SiC to form borosilicate. (Compare, for instance, Fig. 7a and b in ref. 6.) Hydrolysis of the borosilicate by ambient moisture results in a cementitious plug of silica in place of the BN interphase.[5–8]

The foregoing describes what we may call the ''normal'' pest mode of SiC/BN/SiC: degradation starts at the surface/edge and proceeds inwards at a rate limited by intrinsic oxidation resistance of the BN. The fracture surface looks like a picture frame, as shown in Fig. 1, with a border of pested material (characterized by brittle/flat fracture) around a shrinking core of undamaged material (characterized by composite behavior and fibrous fracture, with copious fiber pull-out). Evans and co-workers reported that mode of pesting in SiC/SiC and SiC/glass composites,[9] and illustrated the picture-frame effect with a SiC/MAS (magnesium aluminosilicate) minicomposite in which the sample was found to exhibit ''a time-dependent (residual) strength''.[10] Morscher and co-workers have reported the same phenomenon in SiC/BN/SiC composites[6] as well as in SiC/BN/SiC and SiC/C/SiC minicomposites[11] and correlated sample failure to growth of the pested zone at the borders.

From our work on SiC/BN/SiC composites it has become obvious that a second and more pernicious mode of pest occurs in these composites. The details have been presented elsewhere.[5] This mode is driven by extrinsic factors at work in the interphase region as a whole. It occurs in SiC/BN/SiC materials where a continuous or skeletal film of carbon forms under the BN, from a carbon-rich fiber or from sizing char yield. In the fast flame of a burner rig (which simulates a jet engine) the carbon layer rapidly burns off, leaving an annular trench around the BN as a pathway for deep ingress of the ambient. The same reactions occur as before (sequence 0–3 in Fig. 2) but in this case it is exacerbated by the 10% moisture in the combustion product of the hydrocarbon fuel, by the high flame velocity, and by the huge surface area of BN exposed to ambient attack.[5,12,13] The BN surface area is the biggest factor. The interphase may be likened to a thin sheet of paper and the effect of an underlying layer of fugitive carbon

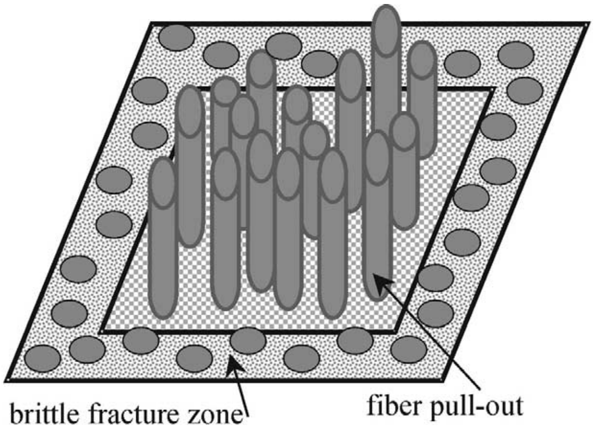

Fig. 1. Normal or intrinsic mode of pest damage in SiC/BN/SiC.

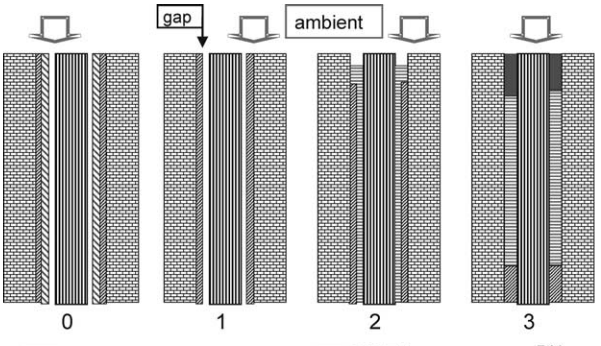

Fig. 2. Severe/extrinsic mode of SiC/BN/SiC pest, which is assisted by free carbon.

Table 1
Oxidative degradation of the SiC/BN/SiC interphase

Step	Process	Comments
1	Oxidation of BN to B_2O_3	This is favored over SiC oxidation except in very low oxygen partial pressures [Ref. 4].
2	B_2O_3 dissolves fiber and *cvi*-SiC to form borosilicate liquid	Borosilicate has a very low-melting eutectic composition (near 400 °C).
3	Borosilicate is hydrolyzed by H_2O, releasing $B(OH)_4$(g) [Ref. 7]	H_2O is from combustion of hydrocarbon. Boron loss increases borosilicate viscosity.
4	The residue is SiO_2(s)	The SiO_2 residue bonds fibers to the *cvi*-SiC. Holes in the SiO_2 indicate emission of gaseous products—i.e. boron hydroxides

is to expose that sheet to extensive attack on its broad surface (instead of its edge as in "normal" pest). That accelerated mode of pest is the main thrust of this paper.

SiC/BN/SiC processing occurs in several steps,[14] some of which can degrade interphase integrity: (a) covering the fibers with protective "sizing"; (b) weaving or braiding the fiber tows into a preform; (c) desizing; (d) coating fibers with chemical-vapor-infiltrated BN (*cvi*-BN) interphase; (e) protecting the BN by chemical-vapor infiltration of SiC cladding (*cvi*-SiC); (f) impregnating the preform with a slurry, including carbon to be converted to SiC; and (g) melt-infiltration of Si to form the SiC matrix (*mi*-SiC). Table 2 outlines the ways in which these steps can influence interphase integrity and hence impact pest behavior. Some recent remedies aim at improving the BN quality: by crystallizing the BN (to densify it),[15] doping it with silicon,[8] or reinforcing the normal BN with an adjoining layer of high-temperature BN generated in-situ.[16] However, it is apparent that control of extrinsic factors is still needed to protect the BN layer whether or not its intrinsic properties are improved.

2. Materials and methods

The four varieties of SiC/BN/SiC studied, which are of the utmost interest in aerospace applications, are described in Table 3, along with their respective severity of pesting as evidenced in strength loss. They include two made with Hi-Nicalon™ and Hi-Nicalon(S)™ fibers that contain ~40 and ~5% excess carbon, respectively, and two varieties made with the stoichiometric Sylramic™ fibers. The Sylramic™/BN/SiC materials include one made with fibers that had been covered with oxide-based sizing and another with alcohol-based sizing. In contrast, all Hi-Nicalon™ fibers had been covered with alcohol-based sizing. Scanning electron microscopy (SEM) and Auger electron spectroscopy (AES) of as-received samples showed substantial carbon between the fiber and its BN coating in composites containing either Hi-Nicalon™ fibers or oxide-sized Sylramic™ fibers. The carbon was in essentially continuous layers in both cases, albeit skeletal on the oxide-sized Sylramic™ fibers.

The samples were made by Honeywell Advanced Composites, Inc., in the approximate processing steps summarized above. Work in our laboratories have shown that a simple and direct way to assess the pest behavior of these materials is to expose tensile bar specimens in the 0.3 Mach flame of an atmospheric-pressure burner rig (APBR) at 800 °C, determining their residual tensile strength and strain-to-fracture after exposure, and analyzing the tensile fracture surfaces by micrography and spectrometry. A 100-h APBR exposure has been found adequate for screening purposes.

3. Results and discussion

The only SiC/BN/SiC varieties that did not undergo severe (extrinsic) pest in the burner rig (Table 3) are those that featured (stoichiometric) Sylramic™ fibers with PVA sizing; all composites made with (carbon-rich) Nicalon fibers (i.e. Hi-Nicalon™ or Hi-Nicalon(S)™) as well as those made with PEO-sized Sylramic™ fibers sizing on the fibers exhibited severe pesting in our tests.

Table 2
Possible interphase effects of composite processing

Step	Process	Possible effects
1	Choice of fiber	Excess carbon in the fiber can migrate to the fiber surface.
2	Choice of sizing	Some sizing materials can char to carbon on the fiber.
3	De-sizing	Sizings can leave significant carbon residue on fiber.
4	Interphase deposition	Deposition conditions will determine interphase quality.
5	*cvi*-SiC deposition	Tecnique can leave residue on interphase.
6	Matrix infiltration	High temperatures can cause carbon precipitation on fibers.

Table 3
SiC/BN/SiC materials tested after 100 h at 800 °C in the burner rig

Fiber/sizing	Carbon under BN	Strength loss in APBR	Comments
Hi-Nicalon/alcohol-based sizing	Continuous	−60% of 380 MPa	After BR exposure adjacent fibers became bonded together by SiO_2.
Hi-Nicalon(S)/alcohol-based sizing	Continuous	−56% of 395 MPa	After BR exposure adjacent fibers became bonded together by SiO_2.
Sylramic/oxide-based sizing	Quasi-continuous	−53% of 405 MPa	After BR exposure adjacent fibers became bonded together by SiO_2.
Sylramic/alcohol-based sizing	None	None of 420 MPa	BN/*cvi*-SiC interface was carbon-rich in some cases (C/Si ratio ~1.4). A SiO_2 layer grew at that interface during BR exposure.

The origin of the carbon depends on the fiber or coating. With carbon-rich fibers the excess carbon builds up between the fiber surface and BN interphase; with oxide-sized fibers it comes from residual char yield upon de-sizing. Alcohol sizing seems to avoid the latter problem, reflecting either an intrinsic superiority or a more negligible char yield, since fiber makers tend to make the sizing considerably thicker when it is oxide-based. Fig. 3 shows that in these composites (which have a high fiber fraction, $\geqslant 40$ vol.% fiber to maximize load bearing) nearly all fibers are in contact with their neighbors, the number of contacts averaging 3.3 instead of the ideal zero. The higher-magnification image inset in this figure reveals a carbon sublayer under the BN interphase—which probably links up with the carbon layers on adjacent fibers. Contact of [0°] and [90°] tows in the third dimension extends the web of carbon throughout the composite and leads to a rigid network of silica following burn-out of carbon. This occurs most easily in the high flame velocity of the burner rig but the effect has been suspected in Hi-Nicalon^{TM}/BN/SiC that pested during stress-rupture tests in air at intermediate temperatures.[11]

In some Sylramic/BN/SiC materials that did not exhibit extrinsic pest, significant carbon enrichment was detected at the BN/*cvi*-SiC interface (see the bottom of Table 3). After burner rig exposure that carbon-rich layer was replaced by silica, as shown in Fig. 4. The silica may afford protection to the BN and so prove beneficial to overall durability. However, its actual effect is yet to be determined.

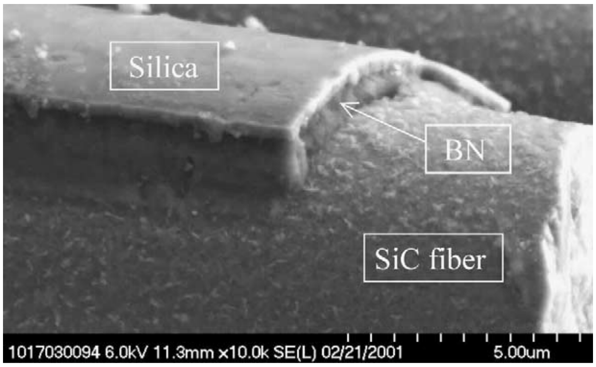

Fig. 4. Following burner rig exposure, a layer of silica covers the BN interphase in a Sylramic^{TM}/BN/SiC material that was carbon rich at the BN/*cvi*-SiC interface.

4. Summary and conclusion

Pest resistance of SiC/BN/SiC composites has been studied by burner-rig exposure at intermediate temperatures, followed by tensile tests and microstructural characterization to determine residual strengths and pest-related features. All samples reinforced with Hi-Nicalon^{TM} and Hi-Nicalon(S)^{TM} fibers exhibited the severe, extrinsic mode of pesting. Those with Sylramic^{TM} fiber reinforcements resisted extrinsic pesting except in cases where the fibers had been sized with oxide-based sizing. The common characteristic in all cases where extrinsic pesting occurred is that a film of carbon was observed between the BN interphase and fiber, originating from excess carbon in the Nicalon-type fibers and

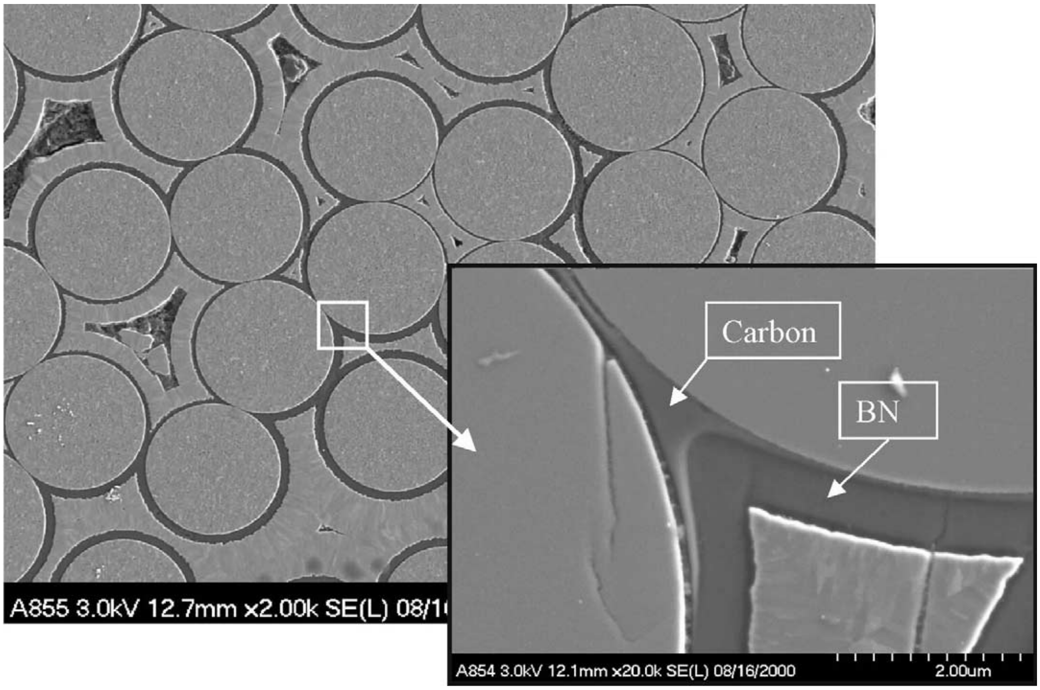

Fig. 3. SEM image showing carbon beneath the BN layer in Hi-Nicalon(S)^{TM}/BN/SiC.

from sizing residue in the case of Sylramic fibers. The carbon caused degradation by providing an easy route for deep penetration of the composite by ambient oxidants. The samples that were free of elemental carbon proved to be resistant to pest degradation.

Therefore, the severest form of pest degradation in SiC/BN/SiC composites can be suppressed by ensuring that they are free of elemental carbon and its precursors in the interphase region.

Acknowledgements

This work was done at NASA GRC under contract # NAS3-98008. The author acknowledges the assistance of M. Cuy (APBR), T. McCue (S-4700 SEM), D. Wheeler (AES); with sample exposure and examination; helpful discussions with G. Morscher on pesting modes are highly appreciated.

References

1. DiCarlo, J., Yun, H.M., Morscher, G.N., and Ogbuji, L.U.J.T., Progress in SiC/SiC composites for engine applications. *Proceedings of Materials Week 2001*, Munich, Germany.
2. Windisch, C. F., Henager, C. H., Springer, G. D. and Jones, R. H., Oxidation of the carbon interface in Nicalon-fiber-reinforced SiC composite. *J. Am. Ceram. Soc.*, 1997, **80**(3), 569–574.
3. Heredia, F. E., McNulty, J. C., Zok, F. W. and Evans, A. G., Oxidation embrittlement probe for ceramic-matrix composites. *J. Am. Ceram. Soc.*, 1995, **78**(8), 2097–2100.
4. Sheldon, B. W., Sun, E. Y., Nutt, S. R. and Brennan, J. J., Oxidation of BN-coated SiC fibers in ceramic-matrix composites. *J. Am. Ceram. Soc.*, 1996, **79**(2), 539–543.
5. Ogbuji, L. U. J. T., A pervasive mode of oxidative degradation in a SiC-SiC composite. *J. Am. Ceram. Soc.*, 1998, **81**(11), 2777–2784.
6. Morscher, G. N., Tensile stress-rupture of SiC/SiC minicomposite with carbon and boron nitride interphases at elevated temperatures in air. *J. Am. Cram. Soc.*, 1997, **80**(8), 2029–2042.
7. Jacobson, N. S., Morscher, G. N., Bryant, D. R. and Tressler, R. E., High-temperature oxidation of boron nitride: II BN layers in composites. *J. Am. Ceram. Soc.*, 1999, **82**(6), 1473–1482.
8. Morscher, G. N., Bryant, D. R. and Tressler, R. E., Environmental durability of BN-based interphases (for SiC/SiC composites) in H_2O-containing atmospheres at intermediate temperatures. *Ceramic Engineering & Science Proceedings*, 1997, **18**(3), 525–533.
9. Evans, A. G., Zok, F. W., McMeeking, R. M. and Du, Z. Z., Models of high-temperature, environmentally assisted embrittlement in ceramic-matrix composites. *J. Am. Ceram. Soc.*, 1996, **79**(9), 2345–2352.
10. Heredia, F. E., McNulty, J. C., Zok, F. W. and Evans, A. G., Oxidation embrittlement probe for ceramic-matrix composites. *J. Am. Ceram. Soc.*, 1995, **78**(8), 2097–2100.
11. Morscher, G. N., Hurst, J. and Brewer, D., Intermediate-temperature stress rupture of a woven Hi-Nicalon, BN-interphase, SiC-matrix composite in air. *J. Am. Ceram. Soc.*, 2000, **83**(6), 1441–1449.
12. Ogbuji, L. U. J. T., Identification of carbon sublayer in a Hi-Nicalon/BN/SiC composite. *J. Mat. Sci. Lett.*, 1999, **18**, 1825–1827.
13. Ogbuji, L. U. J. T., Silicon-based ceramic matrix composites for advanced turbine engines: degradation issues. In *Proc. PARSONS 2000: Advanced Materials for 21st Century Turbines and Power Plants*, ed. A. Strang *et al.* The University Press, Cambridge, 2000, pp. 767–778.
14. Brewer, D., HSR/EPM combustor materials development program. *Mat. Sci. and Eng.*, 1999, **A261**, 284–291.
15. Rebillat, F., Gallet, S.L., Bourrat, X., and Naslain, R., Oxidation resistance of BN coatings with different textures (poster). *Materials Week 2001*, Munich.
16. Yun, H., and DiCarlo, J., unpublished work.