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Fabrication of Oxidation-Resistant Carbon Fiber/Boron Nitride Matrix Composites

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A low-viscosity borazine oligomer has been prepared which readily wets carbon fiber layups and converts in very high yield to a stable boron nitride (BN) matrix when heated at 1200 °C. Composites could be prepared after only one or two impregnations which displayed excellent oxidation resistance up to 850 °C. In most cases, the composites showed outstanding mechanical properties after heating at 1200–1500 °C with flexural strength and modulus values as high as 130 ksi and 15 Msi, respectively.

Introduction

Carbon fiber/carbon matrix (C/C) composites are attractive materials for use in high-temperature applications requiring strength, light weight, and toughness.[1] However, their high temperature use in air is limited to about 425 °C. Great interest has therefore focused on the development of oxidation protective coatings.[2] Thick CVD coatings of SiC are currently used to protect C/C composites at temperatures up to 1300 °C; however, microcracks in such coatings may develop with thermal cycling due to mismatch in coefficient of thermal expansion. These microcracks can lead to catastrophic failure since penetration of oxygen through the crack will result in rapid oxidation of the C/C composite to CO and CO_2. Development of a BN matrix has to our knowledge never been attempted for use with carbon fibers. The obvious advantage of developing a carbon fiber/BN matrix composite is that oxidation resistance of the composite could be increased from 425 to 850 °C.[3] A CVD coating of SiC in combination with the BN matrix might be expected to also provide a fail-safe mechanism against catastrophic failure as opposed to the C/C composite. For example, if microcracks developed in the SiC coating, the BN matrix would oxidize to B_2O_3 which only begins to evaporate at temperatures above 1500 °C. In the mid-1970s we reported on preparing a BN fiber/BN matrix composite using a partially nitrided B_2O_3 fiber as a precursor to the BN matrix.[4] This was a rather complicated process and depended on disproportionation of partially nitrided fiber to BN, B_2O_3, H_2O, and NH_3. The mechanical properties were low probably because of attack of the BN fiber by the B_2O_3.

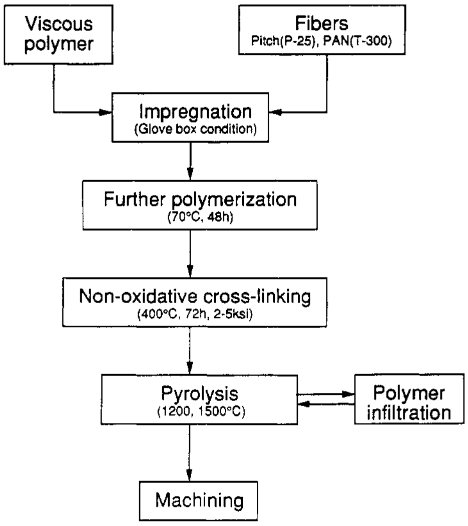

Figure 1. Flow chart of process for making C/BN composite materials.

Recently it came to our attention that several types of borazine oligomers had been prepared and polymerized starting at relatively low temperatures and on further heating to 1200 °C produced a boron nitride-like material.[5] This work suggested that one might be able to develop low viscosity oligomers that would facilitate impregnation of a carbon fiber layup. Also, one might anticipate very high yields of BN from these oligomers which would permit a greatly simplified process for composite fabrication.[6]

In this paper we report the first successful preparation of carbon fiber BN (C/BN) matrix composite using either a one or two step impregnation. From preliminary tests these composites display outstanding mechanical properties and excellent resistance to oxidation up to 850 °C.

Experimental Section

Preparation of BN Oligomer. Reaction of borazine with itself was carried out as described in the literature,[5a] but with the goal of developing an oligomer with a suitable viscosity. In a typical reaction, 10 g of borazine was heated with stirring under

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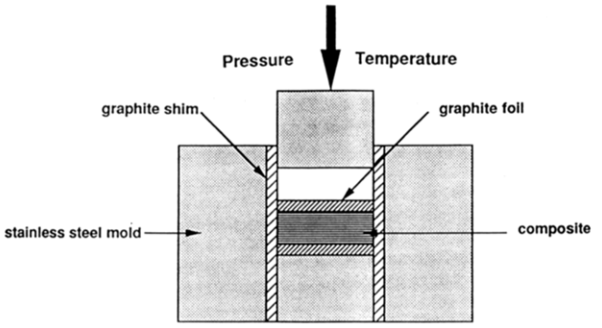

Figure 2. Mold for fabrication of composites.

nitrogen atmosphere at 70 °C in a 3-ounce pressure reaction vessel. The reaction was continued for 40 h, at which point the borazine became viscous.

Fibers. Two kinds of carbon fibers were used, Amoco carbon fiber Thornel P-25 4K (pitch) and Thornel T-300 12K (PAN). Their densities and tensile strengths are 1.90 g/cm^3 and 200 ksi (1.4 GPa), 1.76 g/cm^3 and 530 ksi (3.65 GPa), respectively.[7] Typically, they were treated at 1000 °C in nitrogen for 10 min to remove sizing from the surface.

Composite Preparation. The procedure for composite fabrication is shown in Figure 1. The samples were prepared by placing unidirectionally aligned fibers in a stainless steel mold fitted with graphite shims and graphite foils (Figure 2) as release agents. Working in an inert glovebox the borazine oligomer was gently poured into the mold. The ratio of starting materials was designed to yield a composite of 60% fibers and 40% matrix by weight after pyrolysis. In one case, this ratio was changed to yield a fiber loading of 20 wt % fiber after pyrolysis. It is noteworthy that the viscous borazine oligomers easily wet the carbon fibers. The oligomer was advanced further by heating at 40–70 °C for 2 days under a nitrogen atmosphere. The samples were further stabilized by heating in a Carver press at 30 °C/h to 400 °C under inert conditions. The pressure was increased to 5 ksi, after reaching 200 °C. The total processing time for crosslinking under pressure was 60–65 h. Conversion of the matrix to BN was performed in a furnace which was fitted with quartz or mullite tubes. The samples were placed in a ceramic boat and heated in a nitrogen atmosphere for periods of 30 min to 3 h at temperatures of 1200–1500 °C with no applied pressure. The prepared samples were 25 mm × 45 mm with a thickness in the range 1.3–1.7 mm. The specimens were machined with a diamond saw to beams of 5 mm × 45 mm. Some of the samples were further densified using a second impregnation with the borazine oligomer and then slowly pyrolyzed to the same temperature as described before.

Sample Characterization. Three-point bending tests were carried out on a TMS machine at room temperature and a crosshead speed of 1 mm/min. The span to thickness ratio for most of the samples was in the range 30–25. There is a certain contribution of the interlaminar shear deformation in the flexural data. This effect is neglected. The ultimate flexural strength and the flexural modulus were calculated as recommended.[8] In most cases, five samples of the composite were tested for each variation in the process. In the graphical data described in Figure 7, the spread of values is indicated by vertical error bars. The surfaces of the fractured test samples were examined in a Hitachi S-800 scanning electron microscope (SEM). Prior to viewing, the surfaces were covered with a thin gold–palladium layer in a polaron sputtering chamber.

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were done on du Pont thermal analysis systems 2910 and 2950 at a heating rate of 20 °C/min using N_2 or dry air for high-temperature oxidation. The C/C composite used in the oxidation study was prepared as reported in a previous paper.[9] Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. The boron nitride products with SiC additions as an internal standard were characterized by X-ray diffraction using Rigaku D/Max 2 instrument, with Cu Kα radiation. The apparent density of the composites was calculated from the measured weight and geometric volume. The moisture pickup of the composites was determined by the change of weight in air after 1 week.

Results and Discussion

Preparation of BN Precursor Oligomers. In early 1960, the reaction of borazine with itself to form a borazine-like polymer had been reported by several workers and shown to form a BN-like material.[10] To explain these reactions it is convenient to describe them in terms of

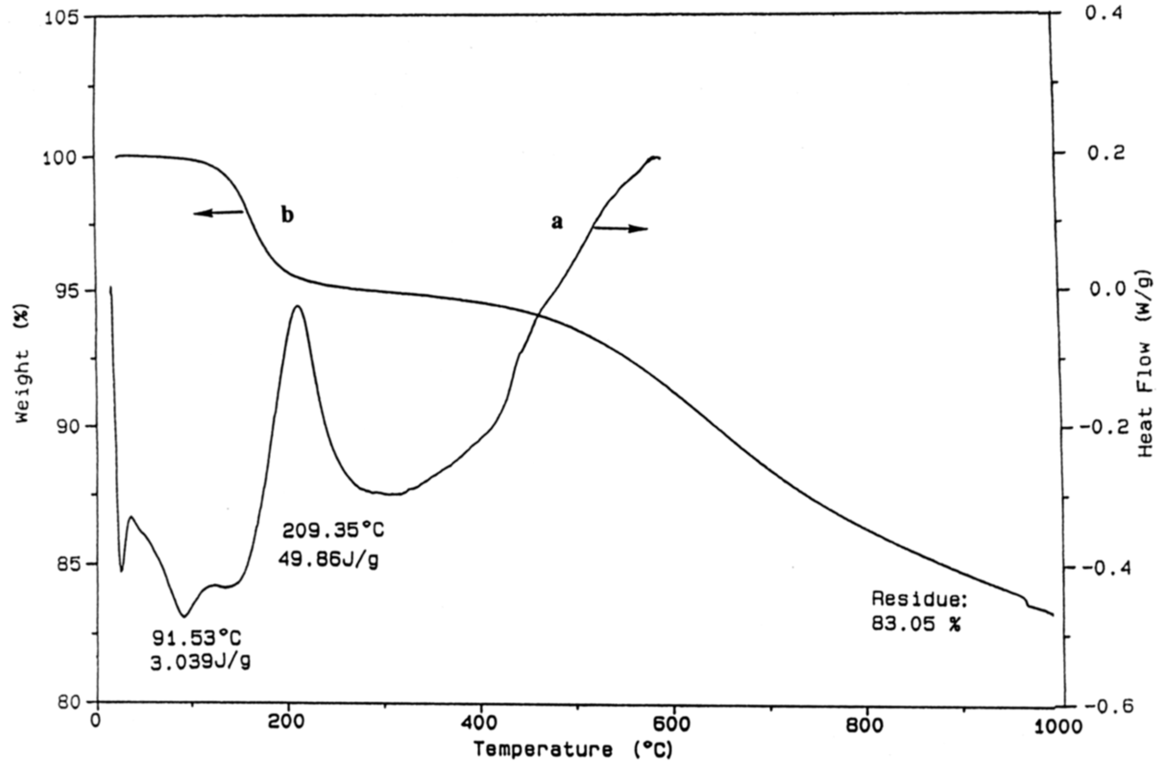

Figure 3. (a) DSC and (b) TGA patterns of borazine polymer.

Table I. Elemental Analyses (percent) of Bulk BN at Different Annealing Temperatures

annealing temp, °C	B	N	H	composition
70	37.2	58.2	4.2	$B_3N_{3.6}H_{3.7}$
300	33.5	54.6	2.9	$B_3N_{3.8}H_{2.8}$
600	39.9	52.5	0.84	$B_3N_{3.1}H_{0.7}$
1200 (30 min)	42.0	50.0	0.34	$B_3N_{2.8}H_{0.3}$
1500 (2 h)	41.8	46.8		$B_3N_{2.7}$
theoretical	43.5	56.5		B_3N_3

Table II. Effect of Heat Treatment on the Structure of Bulk BN and Properties of Composites

heat treatment	interlayer spacing of bulk BN, Å	density of composite, g/cm^3
1200 °C (30 min)	3.5	1.4 (1.5–1.6)[a]
1200 °C (3 h)	3.36	
1500 °C (2 h)	3.34	

[a] The value of densified composites in parentheses.

condensation of six-membered benzene-like rings. Heating of borazine at relatively low reaction temperatures produces intermediates that correspond to biphenyl and naphthalene. On the other hand, the pyrolysis of benzene forms only phenyl intermediates at much higher temperature.[11] The reactions presumably continue on heating to 700–1000 °C to form polynuclear, layered structures which resemble disordered carbon structures. This kind of BN is known to be very sensitive to moisture and is typically characterized by relatively large interlayer spacings of >3.5 Å.[12]

In our study following this procedure developed by Sneddon, we deliberately carried out the reaction of borazine with itself to produce a viscous melt suitable for impregnating the carbon fiber layup. In Figure 3 are shown the DSC and TGA patterns for the conversion of borazine polymer into BN. The broad endothermic peak at 60–120 °C may indicate the evaporation of low molecular weight volatiles. The TGA shows a small weight loss up to the corresponding temperature. The exotherm in the temperature range 160–270 °C is believed to be a cross-linking reaction involving a weight loss of 5%, followed by further condensation above 400 °C.[13] It should be pointed out that the ceramic yield of up to 85% of BN from borazine polymer is very high compared to those of other polymeric precursors used to prepare SiC and carbon. From the elemental analyses in Table I one can infer partially branched-chain and cross-linked structure at reaction temperatures of 70 and 300 °C, respectively.[13b]

Composite Fabrication. C/BN composites were prepared using PAN- or pitch-based carbon fibers. The impregnated prepregs were gently heated at 40–70 °C for 2 days to solidify the matrix through further polymerization. At this point the composite was heated under pressure to 400 °C, after which the specimens displayed very good green strength. Subsequent heating to 1200–

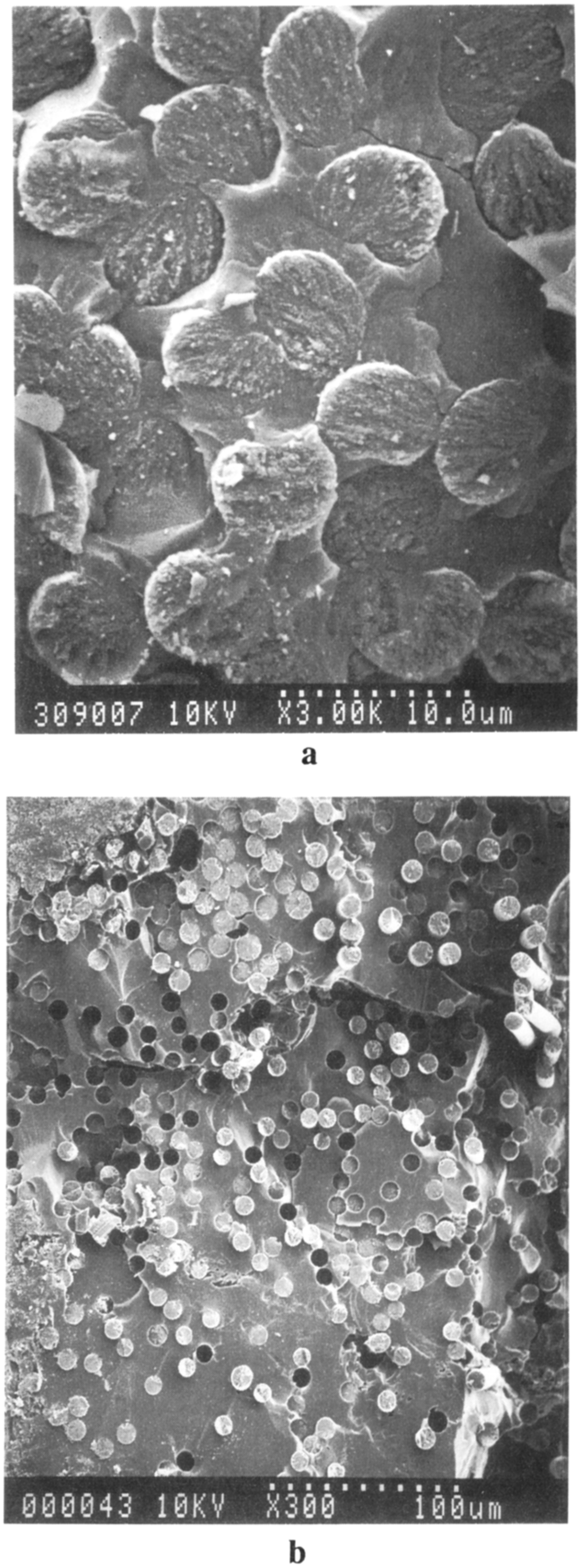

Figure 4. SEM micrographs of a fractured surface. (a) Fracture surface of 60 wt % of PAN/BN annealed at 1200 °C for 3 h. (b) Fracture surface of 20 wt % of pitch/BN annealed at 1200 °C for 30 min.

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Figure 5. SEM image of fracture side view for 60 wt % of pitch/BN composite annealed at 1200 °C for 3 h.

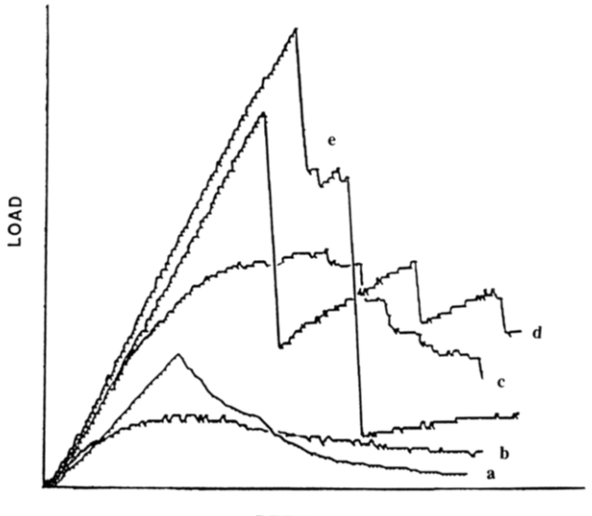

Figure 6. Load–deflection curves from the three-point flexural test. (a) Densified 20 wt % of pitch/BN; (b) 20 wt % of pitch/BN; (c) 60 wt % of pitch/BN; (d) 60 wt % of PAN/BN; (e) densified 60 wt % of PAN/BN. Annealed at 1200 °C for 3 h.

1500 °C produced specimens with outstanding mechanical properties even though the average apparent density of the various specimens was about 1.4 g/cm^3. These composites could be further densified to a density of 1.6 g/cm^3 by a second impregnation. Typically C/C composites require 5–6 cycles of reimpregnation and charring to reach such a density. It should be emphasized that high ceramic yield of the viscous oligomer greatly simplifies the composite processing. As can be seen in Table II the time of heating of 1200 °C is very important to produce a stabilized BN matrix. Thus after 3 h at 1200 °C the interlayer spacing is down to 3.36 Å, which is indicative of a BN structure which is stable against moisture.

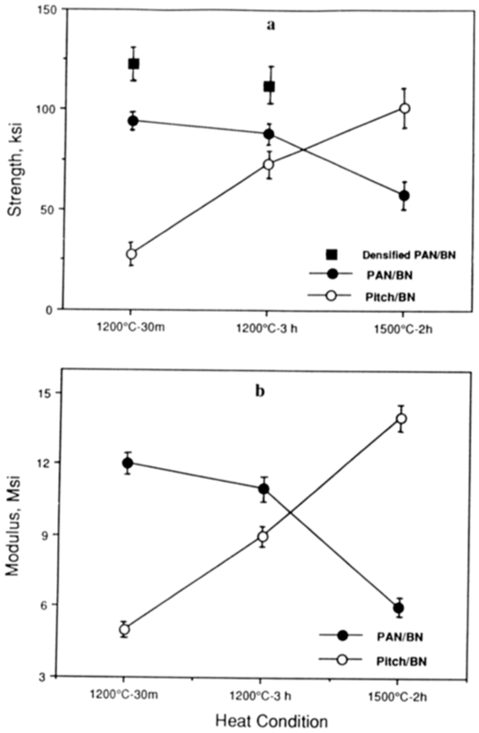

Figure 7. Dependence of (a) flexural strength and (b) modulus of 60 wt % of pitch/BN and PAN/BN composites on heat treatment.

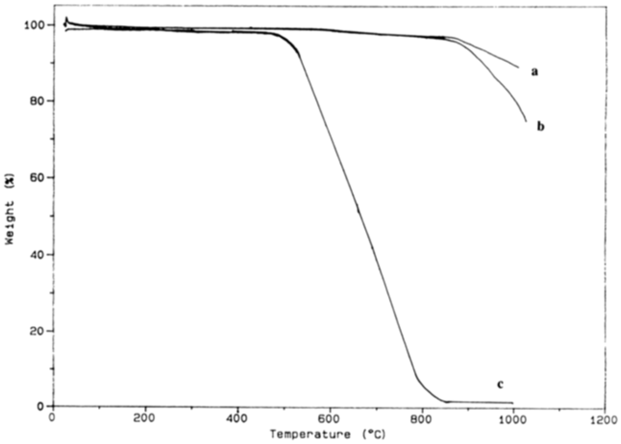

Figure 8. Comparison of oxidation resistance among (a) pitch/BN and (b) PAN/BN composites annealed at 1200 °C for 3 h and (c) C/C composite.

The very high mechanical properties of all of the specimens suggested optimal bonding at interface. This is illustrated in Figure 4, where a fracture surface shows good bonding between the fiber and matrix. The borazine oligomer was found to easily wet the fiber layups permitting excellent infiltration into the interstices between fibers. It has been known that the flexural test is useful in simulating actual behavior during service.[8] In these tests with high ratio of span to thickness, failure involved buckling of the fibers and fragmentation of the matrix on the compressive side of the specimen and cracking along the neutral planes where the shear stresses was highest as seen in Figure 5. The load deflection curves for these tests are shown in Figure 6. Those samples which were tested without a second impregnation displayed a much tougher behavior consistent with porosity in the structure.[14]

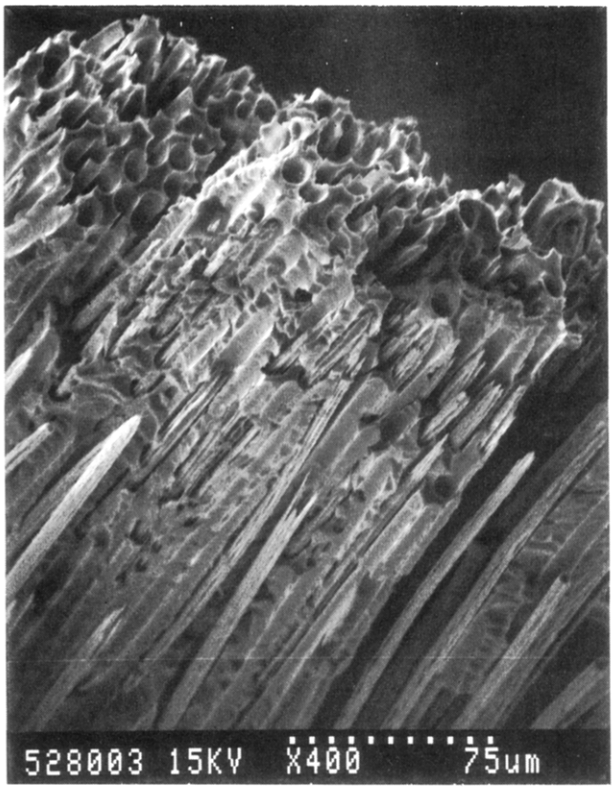

Figure 9. Surface of C/BN composite after isothermal oxidation at 1000 °C for 20 min.

In Figure 7 is shown the dependence of the strength and modulus of these composites on heat treatment. Surprisingly, heating the pitch-based carbon fiber composites to 1500 °C led to a further increase in mechanical properties, while the composites based on PAN-based carbon fiber decreased with higher heat treatment.[15] This decrease with the PAN-based fiber may be caused by the elimination of nitrogen from the fiber. The strength of the composite based on pitch was somewhat higher than predicted from the rule of mixtures suggesting some kind of beneficial role for the BN matrix. This is surprising considering the large mismatch in coefficient of thermal expansion between the anisotropic fiber and the isotropic matrix.[16] We are currently examining the reasons for this behavior and hope to have an interpretation within the near future. On the other hand, samples which were reimpregnated to increase the density showed significantly improved flexural strength with a failure strain of 1%.

One of the most exciting aspects of this study is that the boron nitride matrix does indeed provide oxidative protection for the carbon fibers up to 850 °C. As shown in Figure 8, C/C composites begin to oxidize at 425 °C while the C/BN composite begins to oxidize at 850 °C. C/BN composites were not completely burned away even with isothermal oxidation at 1000 °C for 20 min as shown in Figure 9. It is somewhat surprising that in the C/BN case we do not observe an initial weight increase at 850 °C consistent with conversion of BN to B_2O_3. Rather a rapid weight loss occurs suggesting that at these temperatures oxygen can readily diffuse through the B_2O_3 to react with the carbon fibers. This area requires further study especially to evaluate the effect of SiC coatings.

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