Improvement of Oxidation Resistance by Coating on C/BN Composites

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Borosilicate, B_2O_3 and BN derived from liquid precursors have been tested as shielding materials for the long period of oxidation resistance of C/BN composites at 650°C. Borosilicate coating displayed excellent oxidation resistance and low moisture absorbance, while B_2O_3 and BN were less effective in elevating the oxidation resistance. The enhancement of the oxidation resistance was explained as self-healing effect by viscous flow of the borosilicate glass over T_g, resulting in the reduction of the exposed carbon fibers in a BN matrix.

Key words : Oxidation resistance, C/BN composite, Coating, Borosilicate, Boron nitride

I. Introduction

C arbon 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 improvement of oxidation resistance, primarily by chemical vapor deposition (CVD) methods. However, the cost and difficulties in controlling the CVD process limit the potential applications.[2]

In recent work, we reported the first successful preparation of carbon fiber/boron nitride matrix (C/BN) using low viscosity oligomers of borazine that facilitated impregnation of the carbon fiber lay-up.[3] Very high yields of up to 90% BN from these oligomers reduced processing time for such composite fabrication from months to days with concomitant cost savings. Another important advantage of these composites is to improve resistance to oxidation up to 850°C, possibly replacing the uses of C/C composites. But microcracks may develope with volume shrinkage due to conversion of the polymeric precursor into dense BN on pyrolysis, as well as the surface damaged with machining the composites. These defects can lead to critical failure for long period of use since penetration of oxygen through the surface defects will result in rapid oxidation of the carbon fiber to CO_2 and the BN matrix to B_2O_3, NO_2.[4]

One might be expected that the use of liquid precursors, which in turn acts as an anti-oxidation shielding, is appropriate in coating and sealing such surface defects. In this paper we report the BN, B_2O_3-SiO_2(borosilicate) and B_2O_3 glass coatings improve oxidation resistance of the C/BN composite which was cut to expose the carbon fibers.

II. Experimental Procedure

The C/BN composites used in this study were prepared as reported in a previous paper.[3] The composite of 60% fibers and 40% matrix by weight was cut with a diamond saw into small pieces of 5 mm×5 mm×1.5 mm, resulting in the severly damaged surface. Carbon fibers in a BN matrix were exposed to air at the four out of six faces of the composite pieces.

Sol-gel B_2O_3-SiO_2 (borosilicate) coatable solution was prepared with a little modification compared to the method in literature.[5] Tetraethoxysilane (Si(OEt)$_4$, TEOS) was mixed with ethanol (EtOH), the mole ratio EtOH/TEOS being 5. Then H_2O containing 6.1 wt% HNO_3 was added to the solution, the mole ratio H_2O/TEOS being 6. The solution obtained was refluxed at 70°C for 4 h for partial hydrolysis of TEOS. An appropriate amount of boron tributoxide (B(OBu)$_3$) was then poured into the solution and the reflux was continued at the same temperature for an additional 4 h The clear solution obtained was diluted with EtOH and served as a coating solution.

To coat B_2O_3 and BN on the composite, two kinds of liquid precursors were also used; 25% solution of boric acid (B(OH)$_3$) in H_2O and viscous borazine polymer. Reaction of borazine (B$_3$N$_3$H$_6$) with itself was carried out as described in the literatures.[3,6] In a typical reaction, 10 g of borazine was heated with stirring under N_2 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.

The C/BN samples were immersed into three kinds of liquid precursors for 30 min. The coated pieces were kept for one day in a desiccator to let the solvents slowly evaporate and then heat-treated in air or N_2 atmosphere. In

the sol-gel coated samples, they were slowly heat-treated to 600°C under flowing air in rate of 3-20°C/min, and some samples were further annealed at 800°C, 1100°C under Ar. The other two types of coated samples were also dried, then heated in different processes: for B_2O_3 coated sample up to 500°C in flowing air and for BN coated sample up to 1200°C after crosslinking step at 40-100°C for 10 h under N_2 atmosphere.

On the other hand, some of the green C/BN composites were slightly oxidized at 350-400°C in air to form a thin B_2O_3 layer, prior to pyrolysis. The oxidized composites were treated with silylating agents such as $SiCl_4$ (at room temperature), $Si(CH_3)Cl_3$ (at 57°C) and TEOS (at 60°C) at the indicated temperatures. After vacuum drying the samples were heated in oxygen at 400°C and then in Ar at 800°C.

The thickness of the coatings was measured by a Hitachi S-800 scanning electron microscopy (SEM), depending on the viscosity of the precursors in a range of about 1-10 μm. Differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) were done on du Pont thermal analysis systems at a heating rate of 20°C/min. The effect of the coatings was evaluated in two conditions; one is isothermal oxidation for 10 h at various temperatures, the other is heat scanning of 20°C/min up to 1000°C in flowing air. The structural development of the precursors was characterized by X-ray diffraction (Rigaku D/Max2) and infrared spectroscopy (Perkin Elmer Model 1605).

III. Results and Discussion

1. Characterization of the precursors

In Fig. 1, thermal properties of borosilicate gel, obtained by keeping the solution at 50°C, were characterized using DTA and TGA. The bulk gel shows an endothermic peak at 100°C, due to removal of residual solvents, and an exothermic peak at around 350°C, due to burning of unreacted organics. The glass transition temperature (T_g) is observable at 700°C, which is approximately equal to T_g of a melt quenched $20B_2O_3$-$80SiO_2$ glass.[5,7]

Figure 2 shows the IR absorption spectra of borosilicate as a function of heat-treatment temperatures. The peaks at 1380 and 670 cm^{-1} originate from B-O bonds and Si-O-B bonds, respectively.[7] As the temperature of heat treatment is increased, the absorption peak due to Si-OH bonds (960 cm^{-1}) becomes weak and finally disappears at 600°C, indicating that residual Si-OH bonds polymerize above this temperature. In contrast to this, a new peak becomes appreciable at around 920 cm^{-1} over 600°C, which is also ascribed to Si-O-B bonds. In addition, the thin borosilicate layer could be formed by reaction of silylating agents and B_2O_3 layer produced by oxidation of green C/BN composite. IR spectra show the most significant peaks of 920 and 670 cm^{-1}
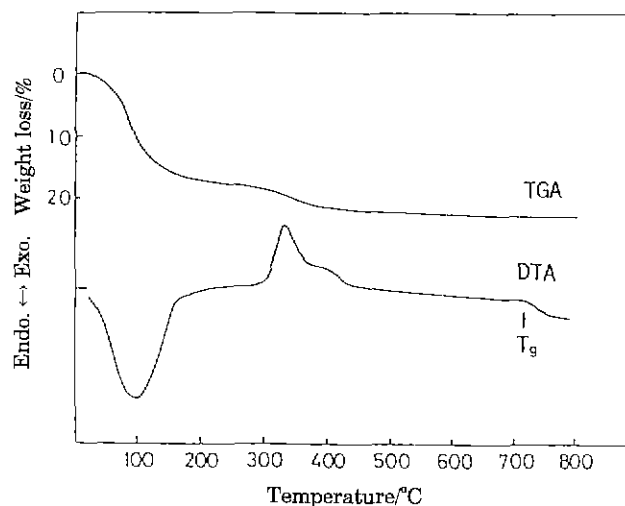

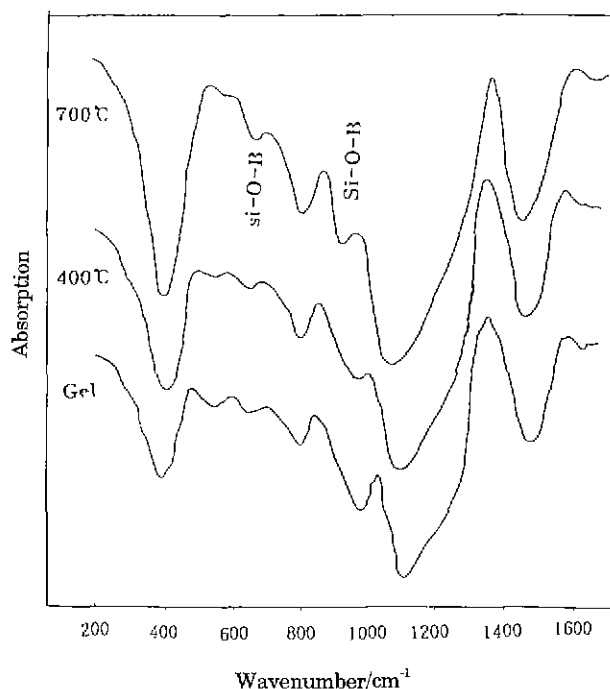**Fig. 1.** Thermal properties of a borosilicate gel.

Fig. 2. Infrared spectra of borosilicate gel treated at various temperatures.

for the borosilicate formed from $SiCl_4$. It might involve strong adhesion of the borosilicate on the surface.[2]

Figures 3 and 4 show the changes in structure in converting borazine polymer to BN. In Fig. 3, the absorptions assigned to N-H and B-H groups, 3440 and 2490 cm^{-1} respectively, decrease in intensity with increasing heat treatment temperature because of dehydrogenation accompanying polymerization and condensation of the rings. As a result of these reactions the sharp B-N absorption of borazine at 1430 cm^{-1} changes to a broad absorption. The spectrum of the product formed at 1200°C is similar to that of crystalline BN.[6]

Figure 4 shows the powder X-ray diffraction patterns

for the conversion of borazine polymer to stable BN. Interestingly, the solid borazine polymer already displays the diffuse diffractions corresponding to the (002) and (10) lines, but with high interlayer spacing of 3.7Å. As the structure is heated to higher temperatures, the (002) peak shifts to a higher diffraction angle with narrower width, indicating a smaller interlayer spacing and larger crystallites. The samples annealed at 1200°C display a turbostratic BN structure with (100), (101) doublet or the less intense (004) peak compared to those of the commercial hexagonal BN.[6]
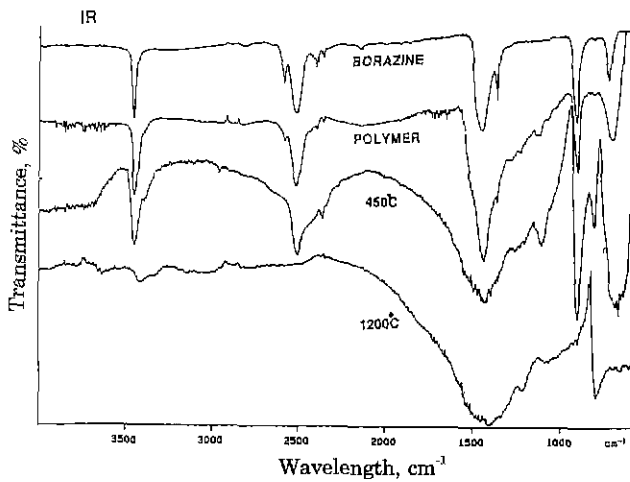
2. Oxidation resistance

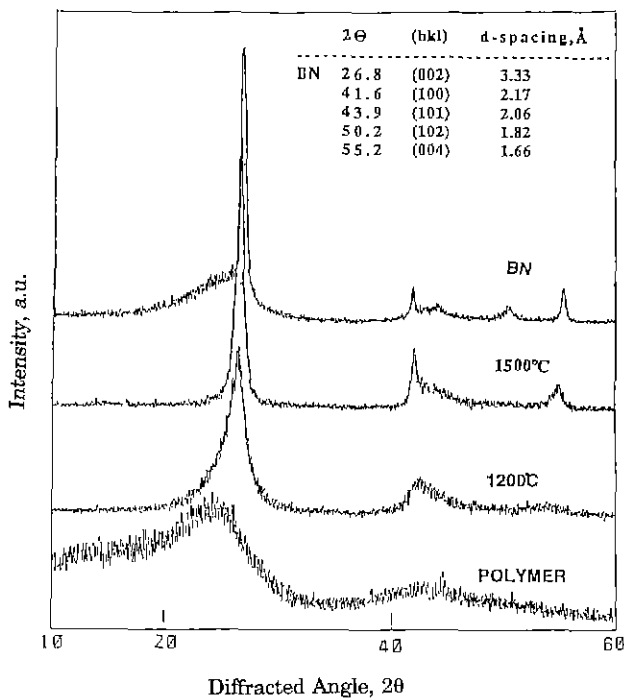**Fig. 3.** Infrared spectra of BN precursor treated at various temperatures.

Fig. 4. X-ray powder diffraction patterns for BN samples treated at various temperatures.

It is well known that BN shows outstanding resistance to oxidation compared to graphite. As shown in Fig. 5, C/C composites begin to oxidize at 425°C while the C/BN composite begins to oxidize at 850°C. It indicates that BN provides oxidative protection for the carbon fibers. However, when surface of the composite is damaged by machining as shown in Fig. 6, the exposed carbon fibers begin to readily burn away, and an weight increase above 900°C is consistent with rapid conversion of BN to B_2O_3.

Figure 7 shows the isothermal oxidation behavior of the composites exposed at 500°C, 650°C for 10 hours to flowing air. The as-cut composite shows significant weight loss on oxidizing at 650°C due to oxidation of the
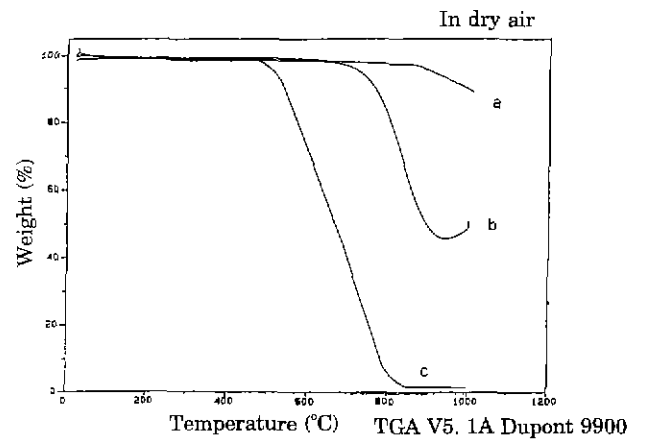

Fig. 5. Comparison of oxidation resistance among (a) C/BN composite, (b) as-cut C/BN composite, (c) C/C composite, at a heating rate of 20°C/min.

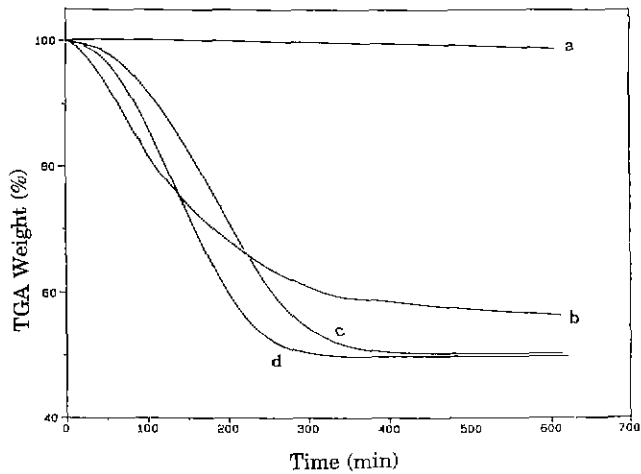

Fig. 6. As-cut surface of a C/BN composite.

Fig. 7. Long period of oxidation resistance for BN and B_2O_3 coated composites; (a) as-cut, measured at 500°C, (b) B_2O_3 coating, at 650°C, (c) BN coating, at 650°C, (d) as-cut, at 650°C.
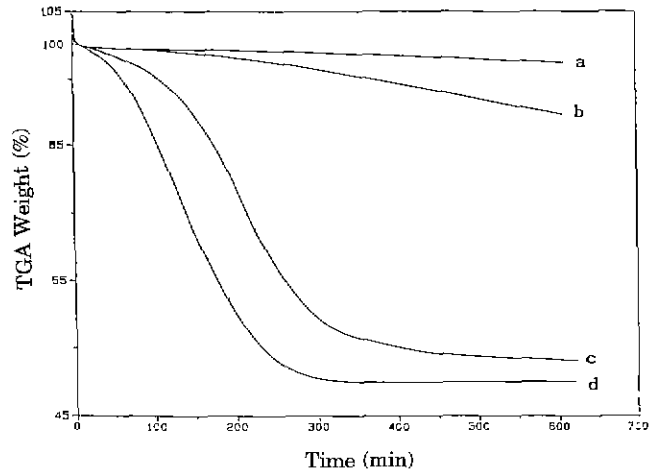

Fig. 9. Long period of oxidation resistance for borosilicate coated composites, measured at 650°C; (a) annealed at 800°C, (b) at 1100°C, (c) at 600°C, (d) as-cut.

Fig. 8. Cracks of BN coating on C/BN composite.

Fig. 10. Surface of borosilicate coated composite annealed at 1100°C.

exposed carbon fibers. But only little weight loss at 500°C may indicate that the protecting role of BN matrix is still effective even to the exposed carbon fiber. In case of BN coating, inhomogeneity of coating thickness usually develops the cracks due to volume shrinkage on pyrolysis (Fig. 8). Particularly coatings over 5 μm thick limit the significant improvement of oxidation resistance because the cracks play the role as a diffusion path for air/oxygen. In this context, crack-free coating process requires further study especially to optimize the various parameters such as viscosity, curing and pyrolytic con-
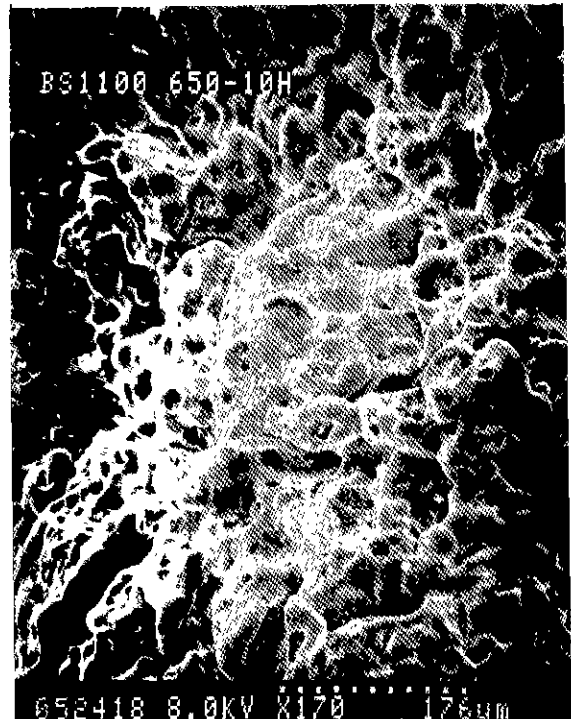
ditions.

In a comparison of B_2O_3 and BN coatings at 650°C, the earlier weight loss of B_2O_3 coated specimen presumably is caused by the dehydration of hydrolyzed glass.[9] It is reasonable that oxidation resistance may be rather improved by the sealing effect of low melt B_2O_3 glass, compared to BN coating. However, thin B_2O_3 coating derived from $B(OH)_3$ solution is not so effective in retarding oxidation.

Figure 9 presents the various oxidation behavior of borosilicate coated specimens, a significantly different

resistance to oxidation depends on annealing temperatures. Annealing process over T_g of borosilicate greatly enhances the oxidation resistance of the composites while annealing below T_g little improves, because the melt glass must be flow to cure the cracks formed on coating over 1 μm thick, that is, a healing effect. However, on annealing at 1100°C, the oxidation protection of borosilicate coating becomes less effective because oxygen may permeate through the pinholes produced by volatilization of the glass (See Fig. 10).

In addition, borosilicate coated composite showed low moisture absorbance. It resulted in only less than 1.0% increase of weight on exposure the composites to air for one week while the B_2O_3 coated composites absorbed more than 5% of moisture in the same conditions. It is known that high moisture absorbance of B_2O_3 due to gradual hydrolysis results in swelling and crumbling of the composites.[10]

IV. Conclusion

In this study, the effectiveness of BN, B_2O_3 and borosilicate coatings on C/BN composites is evaluated by long period of oxidation resistance. Borosilicate coating displays only 5% weight loss for 10 hours at 650°C while both of B_2O_3 and BN coatings lose about 50 weight % at 650°C. Sol-gel borosilicate acts as the best anti-oxidative coating due to self-healing effect over T_g and also significantly reduces the ambient moisture sensitivity while B_2O_3 and BN coatings are less effective to protect oxidation. It suggests that the borosilicate coating on the composites might provide a fail-safe mechanism against catastrophic failure in high temperature use.

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