

ISOTHERMAL OXIDATION RESISTANCE OF VARIOUS COATED C/BN COMPOSITES

*Dong-Pyo Kim, and James Economy**

*Fine Chem. Eng. & Chemistry, Chungnam National Univ., Taejeon 305-764, Korea
Dept. of Mater. Sci. & Eng., Univ. of Illinois at Urbana-Champaign, Urbana, IL61801

Introduction

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[1]. But microcracks within matrix may develop either by volume shrinkage during conversion of the polymeric precursor into BN, or by surface damage on machining the composites. These defects can lead to critical failure for during long periods of use since penetration of oxygen through the surface defects will result in rapid oxidation of the carbon fiber to CO₂ and the BN matrix to B₂O₃, NO₂. In this paper we report the BN, B₂O₃-SiO₂(borosilicate) and B₂O₃ glass coatings improve isothermal oxidation resistance of the C/BN composite.

Experimental

The C/BN composites used in this study were prepared as reported in a previous paper[1]. The composite of 60% fibers and 40% matrix by weight was cut with a diamond saw into small pieces of 5mm x 5mm x 1.5mm, resulting in severe damaged surfaces. Sol-gel B₂O₃-SiO₂(borosilicate) coatable solution was prepared by a slight modification to the method in the literature[2]. To coat B₂O₃ on the composite, 25% solution of boric acid(B(OH)₃) in H₂O was used. A BN coating was prepared using a viscous borazine oligomer which was synthesized as described in the literatures[1]. 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 N₂ atmosphere. In the sol-gel coated samples, they were slowly heat-treated to 600°C under flowing air at a 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, and then heated as followings: for B₂O₃ 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 10h under N₂ atmosphere. The effect of the coatings was evaluated under two conditions; one under isothermal oxidation for 10 h at various temperatures, the other using a rising temperature of 20°C/min up to 1000°C in flowing air.

Results and Discussion

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 70 0°C, which is approximately equal to T_g of a melt quenched 20B₂O₃-80SiO₂ glass[2].

As shown in Figure 1, C/C composites begin to oxidize at 425°C while the C/BN composite begins to oxidize at 850°C under non-isothermal condition. It indicates that BN provides oxidative protection for the carbon fibers. However, when a surface of the composite is damaged by machining, the exposed carbon fibers begin to readily burn away, and the weight increase above 900°C is consistent with rapid conversion of BN to B₂O₃.

Figure 2 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 exposed carbon fibers. In case of BN coating, inhomogeneity of coating thickness develops the cracks due to volume shrinkage on pyrolysis. Coatings over 5 µm thick limit displayed significant improvement in oxidation resistance because the cracks play the role as a diffusion path for air/oxygen[3]. It is noteworthy that, in previous

work, the C/BN composite prepared by cross-linking step under pressure showed excellent mechanical strength due to no severe cracks[1]. In a comparison of B_2O_3 and BN coatings at $650^\circ C$, the earlier weight loss of B_2O_3 coated specimen presumably is caused by the dehydration of hydrolyzed glass. 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 3 presents the oxidation behavior of various 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 flow to cure the cracks formed on coating over $1\ \mu m$ thick, that is, a healing effect. However, on annealing at $1100^\circ C$, the oxidation protection of borosilicate coating becomes less effective because oxygen may permeate through the pinholes produced by volatilization of the glass.

Conclusions

Sol-gel borosilicate acts as the best anti-oxidative coating due to a self-healing effect over T_g and also significantly reduces the ambient moisture sensitivity while B_2O_3 and BN coatings are less effective against protect oxidation.

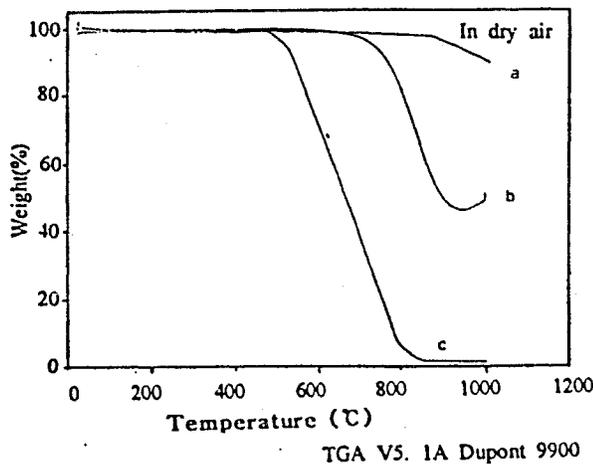


Fig. 1. Comparison of oxidation resistance among (a) C/BN composite, (b) as-cut C/BN composite, (c) C/C composite, at a heating rate of $20^\circ C/min$

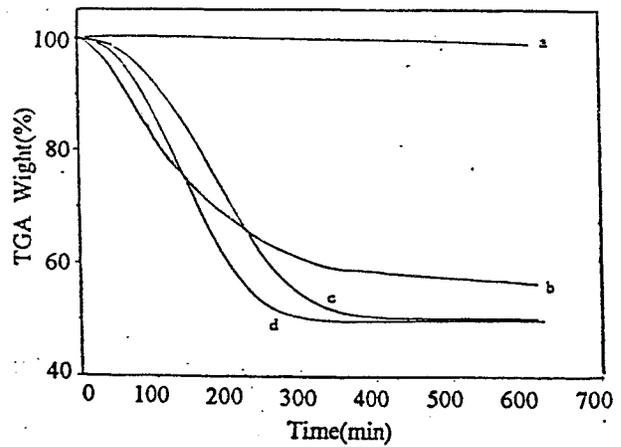


Fig. 2. Long period of oxidation resistance for BN and B_2O_3 coated composites; (a) as-cut, measured at $500^\circ C$, (b) B_2O_3 coating, at $650^\circ C$, (c) BN coating, at $650^\circ C$, (d) as-cut, at $650^\circ C$.

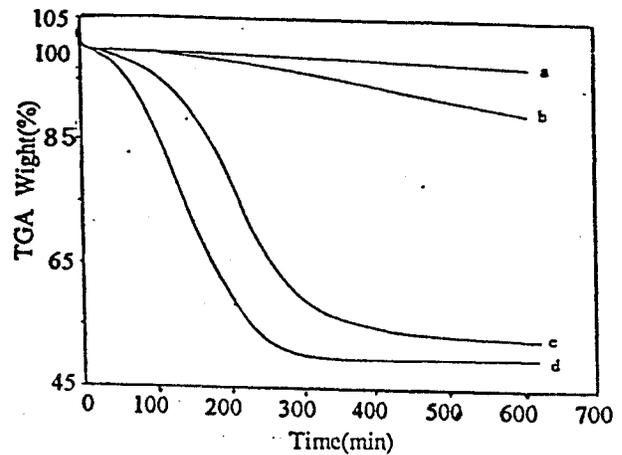


Fig. 3. Long period of oxidation resistance for borosilicate coated composites, measured at $650^\circ C$; (a) annealed at $800^\circ C$, (b) at $1100^\circ C$, (c) at $600^\circ C$, (d) as-cut.

References

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