PROGRESS ON BN AND DOPED-BN COATINGS ON WOVEN FABRICS

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ABSTRACT

A novel, multistep process for applying interface coatings to woven structures using a pulsed CVD process is being evaluated. Borazine ($B_3N_3H_6$), a neat liquid, and several Si precursors are used in the process to produce BN and SiBN coatings on Hi- Nicalon fabrics and preforms. A three variable, two level, full factorial matrix is proposed to define the influence of processing parameters. Coating morphology, uniformity and chemistry are characterized by field emission scanning electron microscopy (FESEM), energy dispersive (EDS) and Auger spectroscopies.

INTRODUCTION

Boron nitride has been shown to provide a mechanically weak interphase in non-oxide ceramic matrix composites (CMCs), to yield tough composite behavior. BN, however, is susceptible to oxidation from environmental oxygen and moisture,[1-3] particularly at intermediate temperatures (600-1000°C),[4,5] limiting material lifetimes. Such exposure of the interphase can occur either by oxygen diffusion along the interphase from exposed fiber ends, or through matrix cracks.

Susceptibility of BN to oxidation and moisture has been shown to be a function of BN morphology. High temperature deposited, turbostratic BN is more resistant to oxidation than are less crystalline, lower temperature coatings.

Oxygen diffusion is high in B_2O_3, the liquid reaction product of BN oxidation, but is much lower in SiO_2. Therefore, doping of the BN interphase with Si, which has a higher affinity for oxygen than B, should provide a "gettering" effect, to form a high viscosity glass through which further oxygen ingress is substantially slowed, and which in effect acts as a sealant.[6] Si-doped fiber coatings with good debonding characteristics have been demonstrated by Moore, Morscher and coworkers.[7,8] These doped coatings, deposited at 1400°C, were characterized as "glassy", and, when exposed to water vapor, showed

resistance to recession along the interphase equal to that of a higher temperature (1800°C deposited pyrolytic BN), and substantially greater than that of a low temperature deposited, undoped BN.

Improved moisture resistance relative to BN also has been demonstrated for SiBN ternary films deposited at low temperatures (300-500°C).[9,10] This work has been focused in the electronics industry, rather than applied to structural composites.

Current commercially produced interphase coatings for structural composites are available for infiltration into 3D preforms. These coatings achieve very low levels of silicon dopant (3-5 atomic percent). Higher levels have been attained for deposition on cloth, but have failed to provide uniform coatings in preforms. The present work focuses on the development of a CVD reactor suitable for pulsed flow infiltration of 3D preforms, although the initial establishment of coating parameters will be carried out using 2D satin weave Hi-Nicalon™ cloth.

COATING DEPOSITION
Borazine ($B_3N_3H_6$, b.p. 55°C), a neat liquid with a high (40 wt. %) boron yield, was used as the BN precursor.[11-13] The precursor was synthesized by Boron Biologicals (Fancy Gap, VA), using a process patented by the Sneddon and Wideman.[14,15] A refrigerated liquid delivery system developed by ATMI, Inc., (Danbury, CT) was used to introduce the borazine to the CVD reactor. Dichlorosilane served as the Si source.

A new batch process reactor was developed which utilizes a pulsed flow technique. Initial deposition runs to establish coating parameters are being carried out using 2D 5HS cloth woven at 17 ends per inch (276 g/m^2).

The pulsed flow process is essentially isothermal, and is expected to provide good infiltration of preforms.[16,17] A series of specific steps, including variation in the gaseous species present in the reactor and the timing and duration of each processing step, control deposition rate and coating quality. The reactor design allows for overcoating the BN with SiC to protect the coating from moisture pick-up subsequent to BN coating deposition. Initial runs produced deposition rates of 200nm/h. The system design is expected to provide improved infiltration of preforms so that any coating thickness gradient is minimized. It offers the potential to eliminate gas phase nucleation, to enable lower deposition temperatures, and to permit admixture of the dopant on a molecular level.

The precursor is maintained in a refrigerated reservoir at -10°C to improve the stability of borazine. Multiple precursors can be used during a single run. The system has the capability to introduce four process and dopant gases in any desired sequence at specified rates, using a power and computer control system designed by Refractory Composites, Inc. (Glen Burnie, MD).

The reactor has a working zone diameter of 20 cm, and a length which can be varied from 30-60 cm. for more efficient use of the precursor. Operating pressures are from 10 to several hundred torr. Maximum temperature capability is 1400°C. The delivery system and reactor are shown in Figure 1.
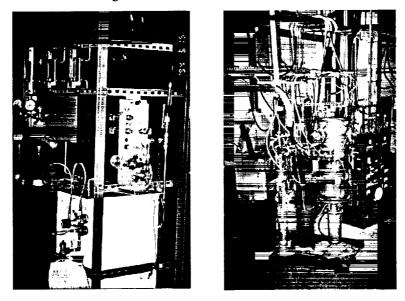

Figure 1. Precursor delivery system (left) and CVD reactor.

Possible processing variables include precursor delivery rate (ml/sec), duration of borazine delivery (sec), deposition temperature, reactor pressure, H_2 and NH_3 input timing, number of cycles and annealing temperature. To simplify an initial screening of parameters, a two level, three parameter, full factorial design was selected, in which the variables were pressure, temperature and number of cycles, as shown in Table I. All other processing variables were fixed, including the level of silicon dopant, which was targeted at 15 atomic percent Si relative to B. All samples were heat treated for one hour at 1000°C following coating deposition, so as to encourage stabilization of the BN or SiBN.

Table I. Initial test matrix.

Exp. No.	Reactor P. (torr)	Reactor temp. (C)	Interact (AxB)	No. Cycles temp. (C)	Interact (AxC)	Interact (BxC)	Interact (AxBxC)
1	1 (50)	1 (350)	1	1 (50)	1	1	1
2	1 (50)	1 (350)	1	2 (100)	2	2	2
3	1 (50)	2 (600)	2	1 (50)	1	2	2
4	1 (50)	2 (600)	2	2 (100)	2	1	1
5	2 (100)	1 (350)	2	1 (50)	2	1	2
6	2 (100)	1 (350)	2	2 (100)	1	2	1
7	2 (100)	2 (600)	1	1 (50)	2	2	1
8	2 (100)	2 (600)	1	2 (100)	1	1	2

RESULTS AND DISCUSSION

Initial FESEM and EDS characterization of the coated fabric samples revealed a wide variety of microstructures. EDS and initial Auger profiles also indicated the incorporation of substantial levels of oxygen in the BN coating. Such internal sources of oxygen can lead to the formation of a "layered" interphase structure, with formation of SiO_2 and $Si_xBN_yO_z$ on further exposure to elevated temperatures.[18,19] Internal formation of oxides have been shown to limit composite lifetimes.[19] Several leaks were found in the system, and a number eliminated. However, oxygen incorporation in the coatings has continued to be a problem.

Early runs produced stiff fabrics and embrittled fibers, which broke upon handling the cloth. After elimination of the apparent leaks, coated fabrics were produced that were flexible and there was no evidence of fiber damage, although oxygen incorporation has persisted.
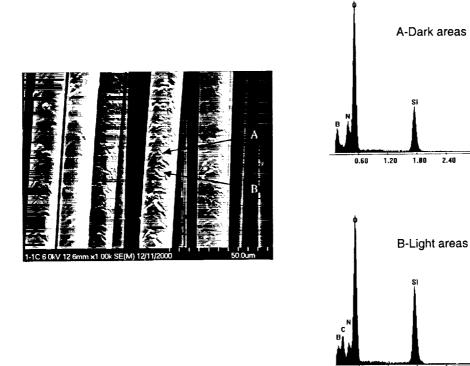

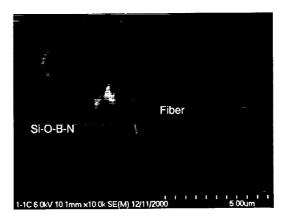Figure 2. SiBN coating deposited at 50 torr, 350°C, 50 cycles.

Figure 3. End-on view of fractured fiber from the same coating run
shown in Figure 2. Note lighter contrast regions are recessed relative
to darker areas. Coating thickness is nominally 0.5μm.

One of the coating morphologies produced at 50 torr, 350°C, 50 cycles (experimental
condition 1), is shown in Figures 2 and 3. The coating in the dark areas, as indicated by
point A, Figure 2, is nominally 0.5 μm in thickness, as seen in end on views of the coated
fiber (Figure 3). The coating appears to have shrunken and/or cracked, with light areas,
indicated by point B, forming a type of "crazing" pattern. The end-on view also shows
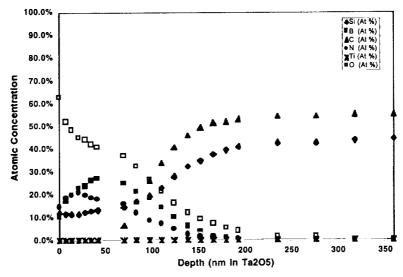the light areas to be recessed relative to the darker regions.

Figure 4. Auger spectra of coating in Figure 2, darker region.

The darker regions of the coating (A) contain B, N, a large O peak, and Si by EDS; the
lighter, more glassy areas contain B, N, a large O peak, Si and some C. Auger spectra of
the darker regions (Fig. 4) is consistent with the EDS findings, showing substantial

oxygen incorporation in the coating, and a Si dopant level of nominally 11-13 atomic percent. (There is a shift in the Si peak for Si bonded to O vs. Si bonded to C.) The B/N ratio is 1 near the surface, but then becomes N deficient. There is no clear boundary
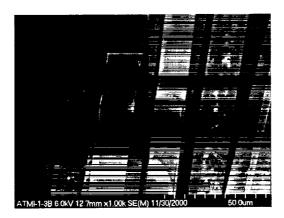

Figure 5. Coating deposited at 600°C, experiment 3.

between the coating and the fiber. Auger of the lighter region (not shown) indicates C incorporation just below the coating surface. Coatings deposited at 600°C (experimental condition 3, Table I) showed similar levels of Si incorporation, and some fibers showed similar coating shrinkage (Figure 5).
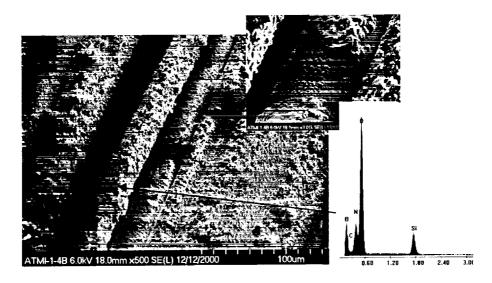

Figure 6. Coating deposited at 600°C, 100 cycles.

A deposition run under experimental condition 4 (600°C, 100 cycles) produced rougher, thicker coatings (1.5-2.0 μm), with periodic gaps, and "bubbles" of Si-O-C on the fiber

surface between those gaps (Figure 6). Substantial oxygen incorporation in the coating is noted by EDS.

Because of the high levels of oxygen incorporation in all the coatings, and a the large variation in coating morphology, a decision was made not to continue with the deposition experiments at higher reactor pressure until the oxygen incorporation could be eliminated. The source of oxygen incorporation has since been identified as impurities in several of the processing gases. Higher purity gases will be used for all subsequent runs.

SUMMARY AND CONCLUSIONS
A pulsed CVD coating reactor which includes a liquid delivery system with low temperature reservoir, a computer controlled gas manifold able to handle four process gases, and a variable volume reaction chamber has been designed and built to produce BN and Si doped BN coatings utilizing a borazine liquid precursor. Coating deposition has been demonstrated on cloth, with Si dopant levels on the order of 10-13 atomic percent. Deposition of the doped BN coatings has been accomplished at 350 and 600°C, with 0.5µm coatings attained at 50 pulsed cycles at 50 torr. In several samples, coating uniformity within tows has been very promising.

All of the coatings contained unacceptably high levels of oxygen. Several leaks have been eliminated from the system, and gettering of process gases and substitution of higher purity gases is underway. Many of the coatings exhibited possible "crazing" or shrinkage cracks after heat treatment for one hour at 1000°C in the same reactor. This may be resolved with elimination of oxygen, or might require deposition at higher temperatures. (The system is capable of operating at temperatures to 1400°C.)

Once the oxygen contamination is eliminated, the originally proposed test matrix will be repeated, initially without Si addition, to characterize a baseline BN coating. Following that, Si dopant level will be varied. Once uniform coatings are attained on 5 HS cloth, infiltration of 3D preforms will be carried out, and these coatings characterized.

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