

# Phase Changes in Polymeric Precursor Oxidation Protection Coatings for Carbon-Carbon

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## INTRODUCTION

The development of coating systems for carbon-carbon composites poses a significant challenge due to the low thermal expansion of carbon-carbon and the extreme application environments for which it is designed. Both factors cause cracking and spallation of external coatings from thermal shock and thermal expansion mismatch which promotes rapid oxidation of the underlying substrate. A new family of coatings has been developed based on preceramic polymer technology [1-9] which are more tolerant to exposure conditions than the industry standard CVD coatings. A significant advantage of these coatings systems is the ability to tailor the composition through the use of solid additives to provide additional oxidation protection. The additives perform several functions including:

- (1) increasing the refractory nature of the coating,
- (2) providing a physical barrier to oxygen ingress,
- (3) forming crack-sealing glasses upon oxidation, and
- (4) toughening the coating by creating a more tortuous crack path.

In this study, the effects of thermo-oxidative exposure on several coatings systems were examined to determine the effectiveness of the additives in providing oxidation protection. X-ray diffraction was employed to analyze the phases present in the "as produced" coatings and after oxidation.

## EXPERIMENTAL

**Materials** - Coatings were prepared in bulk form by first dissolving the preceramic polymers in xylene and/or diglyme and mixing overnight with magnetic stirrers in glass jars. The solids were then added with SiC milling balls and the mixtures milled 16 hr. The compositions were transferred to alumina crucibles, ramped to 200°C in a drying oven in air, then pyrolyzed to 1240°C under flowing nitrogen. For protection of carbon-carbon materials, these compositions would be applied to the composite surface by spraying or dipping. Until the drying

step, the polymers were never exposed to air to prevent degradation and contamination.

Table 1. Preceramic polymeric coatings' added constituents.

<u>Coating</u>	<u>Added Constituents</u>
A	Si, B <sub>4</sub> Si, B <sub>6</sub> Si, Al-Si, AlN, BaF <sub>2</sub>
B	Si, B <sub>4</sub> Si, AlB <sub>12</sub>
C	HfB <sub>2</sub> , Si <sub>3</sub> N <sub>4</sub> , Si, B <sub>4</sub> Si, SiB <sub>6</sub>
D	HfB <sub>2</sub> , Si <sub>3</sub> N <sub>4</sub> , Si
E	HfB <sub>2</sub> , Si <sub>3</sub> N <sub>4</sub> , SiC

**Oxidation exposure** - Table 2 lists the exposure conditions for the coatings. Each sample was oxidized in the alumina crucible used for pyrolysis. The furnace itself was maintained at a constant temperature which was PID controlled. The samples were held at constant temperature in static air by a pneumatically operated servo-controlled ram which continuously locates the programmed test temperature in the furnace. A multi-channel chart recorder was used to monitor the furnace and sample temperatures.

Table 2. Oxidation exposure times and temperatures.

<u>Designation</u>	<u>Time</u>	<u>Temperature</u>
0	Unexposed	
1	16 hrs	650°C (1200°F)
2	392 hrs	650°C (1200°F)
3	4 hrs	815°C (1500°F)
4	98 hrs	815°C (1500°F)
5	20 min	1425°C (2600°F)
6	10 hrs	1425°C (2600°F)

**X-ray diffraction** - The exposed coatings were ground in a ball mill and the powders placed in a Rigaku DMAX-B diffractometer in the symmetric reflection geometry. The x-ray source was an RU-200 Rotating anode generator using a copper target operating at 40 kV and 150 mA and a diffracted beam crystal monochromator. The data was collected by computer over a range from 10 to 140° 2θ in 0.05° increments. The data was analyzed using a

combination of manual and automated (JADE by Materials Data, Inc.) searching of the JCPDS powder diffraction files.

## RESULTS AND DISCUSSION

The crystalline phases present in the ceramic oxidation protection coatings were identified before exposure to oxidation. The phases observed are given in Table 3. In several cases, some of the added constituents were not observed as phases in the coatings.

Table 3. Unoxidized phases in ceramic coatings.

Coating	Major phase(s)	Minor phase(s)
A	Si	B <sub>4</sub> Si, β-Al <sub>4</sub> SiC <sub>4</sub>
B	Si	B <sub>4</sub> Si
C	Si, HfB <sub>2</sub>	B <sub>4</sub> Si, α-Si <sub>3</sub> N <sub>4</sub>
D	Si, HfB <sub>2</sub>	α-Si <sub>3</sub> N <sub>4</sub>
E	HfB <sub>2</sub>	α-Si <sub>3</sub> N <sub>4</sub> , SiC

On exposure to even mild oxidation, the B<sub>4</sub>Si containing samples (A-C) all showed the formation of a mixture of H<sub>3</sub>B<sub>3</sub>O<sub>3</sub> and B<sub>2</sub>O<sub>3</sub>. This was determined by the emergence of peaks at 27.8, 14.6, and ~40° 2θ. In the same fashion other phases and changes were cataloged for the coatings under the various oxidation conditions.

Based on the phases observed after oxidation of the ceramics coatings, the results can be summarized as:

- (1) Boron containing species oxidize to form boric acid and boria.
- (2) Silicon oxidizes to silica, gradually depleting the silicon.
- (3) Hafnium diboride oxidizes at relatively low temperatures to form hafnium oxide and most likely contributes to the boric acid/boria content.
- (4) Silicon nitride oxidizes with severe loss of the material at 1425°C.
- (5) Silicon carbide remains relatively stable throughout the oxidation process.

The oxidation of the constituents to form mixed oxide glasses is the basis for the specific additions to the polymers. The XRD results demonstrate the effectiveness of the particulates as inhibitors or glass formers. The oxide formation results in a volumetric increase which seals cracks and prevents further ingress of oxygen. However, some unexpected findings include the degradation of silicon nitride and rapid oxidation of hafnium diboride. These materials are added to improve the refractory nature of the coating, yet are oxidizing and depleting quickly. One possible explanation for these phenomena is the fluxing of the particulates by boria or borosilicate glasses

formed at low temperatures. Normally, phases such as α-Si<sub>3</sub>N<sub>4</sub> are stable to high temperatures because of the formation of a protective silica glass layer or scale. Boria and silica can have complete solid solution formation, thus leading to dissolution of the protective scale into the surrounding glass.

The onset of oxidation of hafnium diboride has been reported to be as low as 700°C which partially explains its poor oxidation performance here. Surrounding the particulate hafnium diboride with low melting point borosilicate glasses may cause the same types of effects as seen with silicon nitride. To improve the capability of these additives, the layers in which they are contained should be isolated from the boron containing layers.

## CONCLUSIONS

The effectiveness of the additives in preceramic polymeric coatings was demonstrated by analysis of the XRD peaks after oxidation. The formation of boria (and boric acid) and silica promotes crack sealing and improves the oxidation protection of the coatings. Some detrimental effects of the glass formation were also observed as some of the refractory constituents were oxidized more rapidly than expected. These results will be used to further improve the compositions by isolating refractory additives from highly reactive glasses.

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## REFERENCES

1. P. Lu and D. Bauer, *Polymeric Precursor Coating for Oxidation Protection of Carbon-Carbon Composites*, presented at the 16th Ann Conf. on Composites, Materials, and Structures, Cocoa Beach, FL (Jan. 1992).
2. NASA Contract No. NAS1-19199, "Adherent Coating Development for Carbon-Carbon Materials".
3. Air Force Contract No. F33657-86-C-0061, "NASP Path D Coating Repair Program".
4. A. S. Gurney and K. M. Kliner, *Low Cost Coatings for Carbon-Carbon Composites*, to be presented at the 40th Int'l SAMPE Conf. (May 1995).
5. L. M. Niebyiski, U. S. Patent #4,910,173 (1990).
6. L. M. Niebyiski, U. S. Patent #5,009,961 (1991).
7. G. A. Zank, U. S. Patent # 5,164,344 (1992).
8. L. M. Niebyiski, U. S. Patent #5,196,059 (1993).
9. L. M. Niebyiski, U. S. Patent #5,198,488 (1993).