LOW-COST OXIDATION RESISTANT C-C COMPOSITES

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Introduction

Carbon-carbon (C-C) composites exhibit excellent mechanical, thermal and chemical properties. Their commercial applications are limited by high cost and poor oxidation protection. A low cost process was developed to fabricate C-C composites in one manufacturing step, which leads to substantial cost savings over conventional processing methods. This low cost manufacturing process has been combined with novel oxidation inhibition. Low cost boron, and/or silicon and other additives based liquid precursors are used during the prepregg step. A high temperature heat treatment yields C-C composites exhibiting 1.75-1.85 g/cm^3 density. The molecular level inhibition employed in this processing results in excellent oxidation protection, that has demonstrated up to 2000 hours of isothermal oxidation at 600°C with zero mass loss. The inhibition formula applied on the molecular level results in a moisture insensitive oxidation protection scheme. The mechanical properties of inhibited C-C composites are on par with the uninhibited composites. Tensile strengths of 210 MPa and compressive strengths of 150 MPa are typical. Process-structure-property relationships for this low cost inhibited class of C-C composites will be presented.

The susceptibility of C-C composites to air oxidation at temperatures above 480°C represents one of the major technological obstacles preventing a wider commercialization of C-C composite technology [1]. The oxidation of C-C composites can be considered in three regimes.

In the low temperature regime (below 750°C), carbon oxidation is controlled by a chemisorption/desorption reaction, were the activation energy for the surface reaction is the main factor. In this temperature regime, the application of boron-containing inhibitors was found to be effective in reducing the oxidation rate of carbon-carbon composites [2].

In the intermediate temperature range (750 - 1100°C), the oxidation reaction become diffusion controlled. Glassy sealants have been employed to retard the oxidation kinetics in this regime [3]. However, high viscosity of silicon-containing glasses in this temperature regime results in limited oxidation protection. Practically, it is difficult to obtain a glass that will flow at low temperatures to seal the cracks in the external oxidation protection coating and still remain viscous at high temperatures.

At high temperatures (above 1100°C), the oxidation rate is governed by diffusion through a stagnant layer of oxidation products. The very low oxygen permeability of silica provides good oxidation protection. Silicon-based coatings (e.g., SiC and Si_3N_4) are primarily used as the oxidation protection barriers in the high temperature regime [3].

Both SiC and Si_3N_4 ceramic coatings applied to the C-C composite substrate suffer from microcracking due to the CTE mismatch of SiC or Si_3N_4 external coating with the anisotropy of 2-D C-C composites. The application of sealants and inhibitors is necessary to produce advanced C-C composites capable of operating in the temperature regime between 600 - 1400°C. Inherent limitations of both sealants and inhibitors combined with the high cost of the advance coating system (inhibitors + sealants + external coating) greatly hinders commercial applications of C-C composites.

Excellent oxidation protection was achieved using fiber tow composites [4]. Fiber spreading was the key factor enabling the penetration of inhibitors within the fiber bundle. Fiber tow may not be suitable for all applications. Several emerging new applications for C-C composites including aircraft heat exchangers are more easily made with fabric processing. This paper addresses the issues of effective oxidation protection of fabric-based C-C composites.

Experimental

The phenolic/filler/B_4C slurry was used on T-300 1k plain weave (2 layers) and XN-50 (1 layer) composites. Two types of B_4C powders were used: 3 micron size and 100 nm size. In addition, a liquid based boron precursor was used.

The best density obtained in one-step inhibited C-C processing was 1.8 g/cm^3. A high temperature heat treatment (HT) (up to 2500°C) was utilized. In addition to the B$_4$C inhibitor, a SiC-containing polymer was blended with the phenolic/filler/B$_4$C slurry. This blending provides a molecular level inhibition/protection with the B$_4$C/SiC system.

Oxidation testing was performed on 1 cm x 1 cm x 0.1 cm C-C composites at 600°C (1112°F). Initially, isothermal air oxidation in a closed furnace was performed. The composites were placed in a pre-heated oven for over 24 hours and then quickly removed to measure the mass change and replaced back in the 600°C oven. Flexure strength was measured by four point bending.

Thermal conductivity was calculated as the product of density, heat capacity (DSC measurement) and thermal diffusivity (laser flash method).

Results and Discussion

Figure 1-3 show the time dependence of the oxidation rate in dynamic conditions (flowing air). The flowing air condition increases the overall weight gain and decrease the time performance. These results underscore the ultimate limitations of the B$_4$C-based inhibition. The B$_4$C starts to oxidize around 600°C and forms B$_2$O$_3$. Thus, the oxidation rate becomes controlled by the oxygen diffusion through the B$_2$O$_3$ layer, as well as possible volatilization of B$_2$O$_3$.

Luthra [5] performed the oxidation analysis of the C-C composite protected with a B$_2$O$_3$ layer (at 100 μm B$_2$O$_3$ layer thickness and 600°C). The calculated oxidation rate of the C-C composite was 6 x 10^{-3} g/m^2*min. The lower rate exhibited due to the B$_4$C inhibition can be possibly attributed to the oxidation protection of the B$_4$C layer formed during the high temperature heat treatment. However, with increased oxidation time, the B$_4$C layer can be disrupted and the resulting B$_2$O$_3$ thin layer protection becomes insufficient leading to the net composite mass loss. The oxidation performance is further compromised by poor moisture resistance of the B$_2$O$_3$ outer layer. On contact with moisture B$_2$O$_3$ reacts with water and forms H$_3$BO$_3$, which exhibits greatly enhanced vapor pressure, Figure 5, leading to the overall loss of the protective B$_2$O$_3$ layer. In order to alleviate these shortcomings of the B$_4$C/B$_2$O$_3$ oxidation protection, a B$_4$C/SiC inhibition system was developed. This system offers at least two advantages over the B$_4$C-based inhibition. The oxygen diffusion through B$_2$O$_3$ is four orders of magnitude higher than that through SiO$_2$. Thus, a borosilicate glass has decreased

diffusion coefficient over that of B$_2$O$_3$. In addition, borosilicate glass offers significantly improved moisture resistance over boria.

A B$_4$C/SiC inhibition was obtained via B$_4$C inhibition combined with a polymer-derived SiC.

Figure 1 shows the oxidation resistance of C-C composites made with micron size B$_4$C, while Figure 2 shows nanosize B$_4$C inhibited C-C composites. A significant increase in oxidation resistance is observed for the nanosize B$_4$C inhibited composites.

In general B$_4$C powder inhibited C-C composites exhibited significant brittleness. Thus, liquid boron-based technology was employed. Figure 3 shows the oxidation resistance of liquid boron inhibited C-C composites. Good oxidation resistance was achieved combined with non-brittle behavior.

b) Mechanical Testing

Figure 4 shows a general degradation of the mechanical properties of inhibited C-C composites. The best results were obtained with liquid based boron. Both micron size and nanosize B$_4$C degraded the tensile strength of the carbon fibers upon processing. Some degradation of flexure strength in liquid-based boron composites is attributed to the interaction between boron and the carbon fibers during high temperature heat treatment. This high temperature heat treatment is necessary to provide oxidation resistance for the carbon fibers. The difference is attributed to the higher heat treatment in this case.

c) Thermal Conductivity

The importance of the through-the-thickness thermal conductivity for the C-C composite heat exchanger fins underscores its importance. The B$_4$C/SiC inhibited C-C composite exhibited a room temperature (RT) through-the-thickness thermal conductivity of 30 W/mK. The high temperature heat treatment appears to be critical to achieving this high conductivity value. Chung [7] showed that boron greatly promotes carbon matrix graphitization at 2300°C HT, which can increase thermal conductivity.

Conclusions

The best results in terms of oxidation protection of inhibited C-C composites were achieved using a liquid precursor method. In addition, minor degradation of mechanical properties was achieved.

References

1. E. Fitzer, <u>High Temperature High Pressure</u>, 10 (1978), p. 79.
2. D.W. McKee, Carbon 24 (1986), p. 737.
3. R. Naslain, Revue de Chimie Minerale, 18 (1981), p. 544.
4. W. Kowbel et. al, 44th SAMPE, p. 1930 (1999).
5. L. Luthra, Chemistry and Physics of Carbon, Vol. 23, p. 219 (1991).
6. T. Zhang, Carbon, 35, p. 935 (1998)
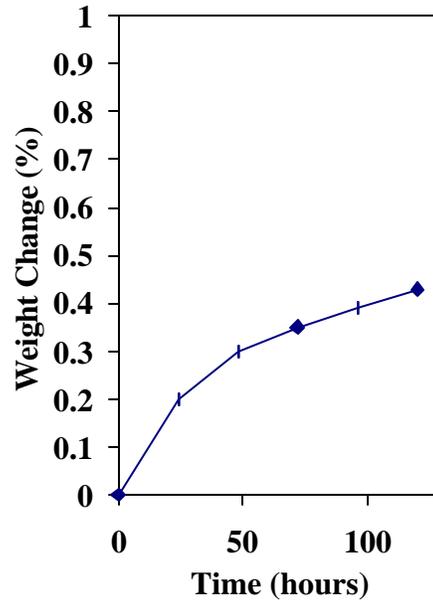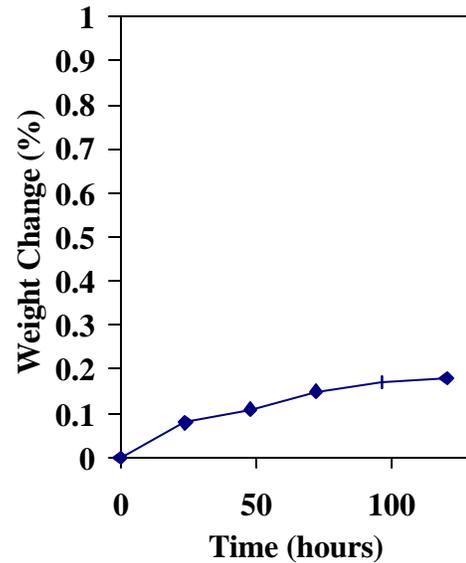7. T.C. Chung, Carbon, Vol. 35, p. 1101 (1997).
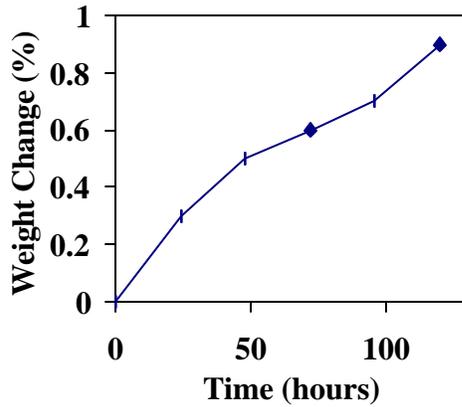
a)   T-300
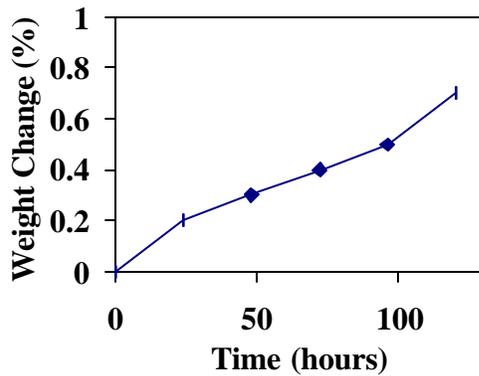
b)   XN-50
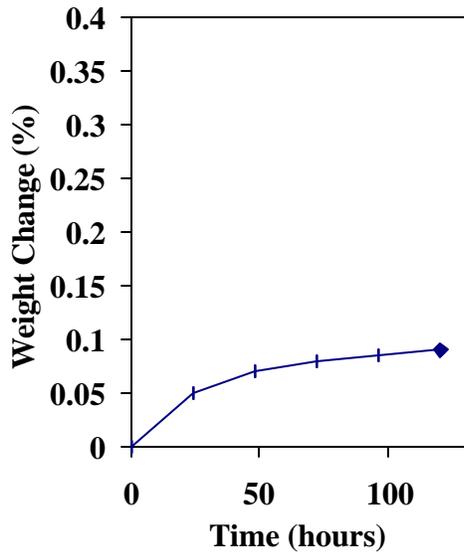
Figure 1. Mass loss of composites made with B₄C powder.

a)XN-50

b) T-300

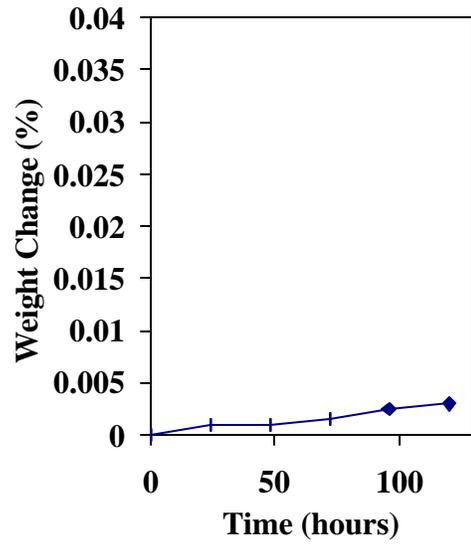**Figure 2. Mass loss of composites made with nanoparticle B₄C powder.**

a) T-300   b)XN-50

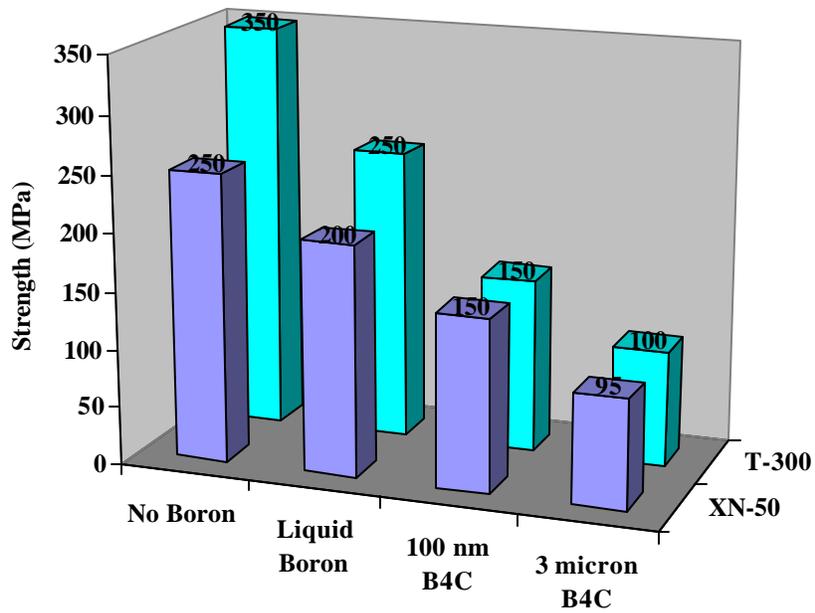**Figure 3. Mass loss of composites made with liquid boron.**

Figure 4. Flexural Strength of C-C Composites.