

THE ROLE OF SUBSTITUTIONAL BORON IN THE OXIDATION OF CARBON FIBER REINFORCED CARBON (CFRC) COMPOSITES

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Introduction

Despite their excellent mechanical and chemical properties [1,2], carbon fiber reinforced carbon (CFRC) composites have found use in only a limited number of applications due to poor oxidation stability in air. Reaction with oxygen is well known to result in catastrophic failure of the material. A great deal of research has thus been devoted to improve and understand their oxidation resistance.

Most such studies are about coatings and/or sealants. However, these are not very suitable to prevent carbon oxidation due to the coefficient of thermal expansion (CTE) mismatch between the carbon and the coating materials. Boron is one of the few remaining candidates for effective oxidation inhibition. However, it is now known to have an intriguing and multifaceted role, not only as a surface coating, but also as a unique element that can be located at substitutional positions in the graphite lattice.

Substitutional boron often inhibits carbon oxidation, but the mechanism of inhibition is not clear. Perhaps the only well established effect of substitutional boron is the increasing degree of graphitization that would be beneficial for increasing oxidation resistance. Meanwhile, the formation of a boron oxide coating on the carbon surface also occurs during carbon oxidation. Therefore, it is often difficult to discern whether the inhibiting effect by substitutional boron is from a decrease in active site concentration due to surface coating or to intrinsic inhibition.

In this study, elemental boron is doped separately into the carbon matrix and the carbon fibers, as well as into the CFRC composites made from these two components. Some previous work exists on this issue, where B has been incorporated into either the fibers or the composites and the role of boron in oxidation remained unclear [3-5]. Our objective is to attempt to clarify the role of boron in the oxidation of each one of these carbon materials.

Experimental

Four-dimensional CFRC composites were made from PAN-based carbon fibers and coal-tar pitch matrix. The densification process -- carbonization, pressure impregnation and carbonization (PIC) and graphitization -- was repeated until the density of the composites became 1.8 g/cm^3 .

In order to characterize each component of CFRC composites as well as the composites themselves, they were heat-treated with or without elemental B at different initial B levels. Carbon fibers and the composites had already been treated at high temperature. In contrast, coal-tar pitch was graphitized after doping with boron.

The carbon fibers, carbon matrix and their composites were mixed in a crucible with elemental B at 0, 1, 2 and 5 wt.%. The crucibles were placed in a graphitization furnace and evacuated. Argon was introduced to raise the pressure to 0.1 MPa. The furnace was then heated to 2300 °C. The samples were held for 30 minutes at the final temperature to enhance boron diffusion into the graphite lattice.

The concentration of boron in the samples after heat treatment was determined by inductively coupled plasma (ICP) emission spectroscopy. X-ray diffraction (XRD) was used to obtain the interlayer spacings and average crystallite widths and heights. The oxidation resistance was determined by thermogravimetric analysis (TGA).

Results and Discussion

The boron content of the various samples is reported in Table 1. The results highlight the difference between initial and final boron concentrations in these materials. The discrepancy is due to varying boron retention in the samples and to losses in the crucibles and the furnace.

Some interesting trends also need to be noted. First, at nominal 0% initial B level, the resulting carbon fibers and composites have ca. 0.2% B after heat treatment. This could be due to sample contamination in the furnace. Comparison between carbon fibers and carbon matrix is also noteworthy. At low boron concentration, carbon fibers have higher boron content than the matrix, while the results are reversed at high boron concentration (5%). Preferential boron doping of a less ordered structure [3,4] is a factor to consider; this issue deserves more attention. The differences observed here could simply be due to the fact that the carbon matrix material is initially a fine powder with a higher surface area than the carbon fibers. Finally, boron loading in the composites is seen to be very low. The samples are cubes, $2 \times 2 \times 2 \text{ mm}^3$, so the same surface area argument is applicable; in addition, boron concentration is expected to have a gradient from the surface inward, as reported by Kowbel et al. [5].

The x-ray diffraction patterns were also examined for samples with different boron contents. The boron-doped samples showed a peak shift to higher angles, which is evidence of enhanced ordering of the carbon structure. Even though the carbon matrix is already quite graphitic, the incorporation of substitutional boron was beneficial: the 2% B sample had the lowest d-spacing value, which is very close to that of perfect graphite. At high B concentration (5%), the d-spacing increased again; it is assumed that this is evidence for the presence of interstitial boron which causes a distortion of the lattice. The results of crystallite height variations confirm these interpretations.

The splitting of the {10} peak into {100} and {101} peaks is evidence of three-dimensional ordering, and this is the case for all carbon matrix samples. The same trend was observed here with increasing B content as for the d-spacings and L_c values: the sample with 2% B had higher L_a than the 5% B sample. Interestingly, the increase in L_a (in Å) was consistently larger than that of L_c , $421/290 = 145\%$ vs. $191/163 = 117\%$; furthermore it is also larger than the decrease in d-spacing.

Figure 1 shows the isothermal TGA data for the carbon matrix. The oxidation resistance of the samples increased as boron content increased. Analogous data were obtained for the fibers.

A complicated and interesting trend is revealed by isothermal TGA of the composites. After 2 hours, all results follow the same trend seen in the other experiments, which is that oxidation resistance increases as boron content increases. Even the 0% B sample was completely consumed before 2 hours of reaction at 800 °C. However, the initial stage of the reaction is very interesting. Figure 2 shows these results. The inhibiting effect of boron is not seen until after 40% burn-off. Instead, a catalytic effect is evident at low burn-offs. As boron concentration increases, the extent of burn-off increases at the beginning of the reaction. These results are consistent with our previous reports [6,7]. Eventually, the rate of oxidation of the 0% B sample increases substantially, while that of the 5% B sample decreases. In all cases, 40% burn-off is achieved within an hour and the 5% B sample reaches this burn-off level first.

Conclusions

Substitutional boron acts as an oxidation catalyst at low doping levels. It is an inhibitor at higher levels, presumably after boron oxide has formed on the carbon surface during oxidation. The predominance of the inhibiting effect over the intrinsic catalytic effect [7] appears to depend on the ability of boron oxide to form an oxygen diffusion barrier on the entire surface of the carbon sample.

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Table 1
Final boron concentration of matrix, fibers and composites (wt.%)

Initial Conc.	0%	1%	2%	5%
Matrix	<100ppm	0.40%	1.45%	4.04%
Fibers	0.20%	1.06%	1.56%	2.00%
Composites	0.24%	0.14%	0.33%	0.41%

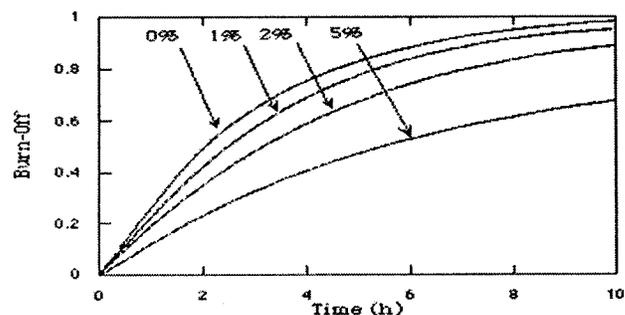


Figure 1. Isothermal TGA of carbon matrix.

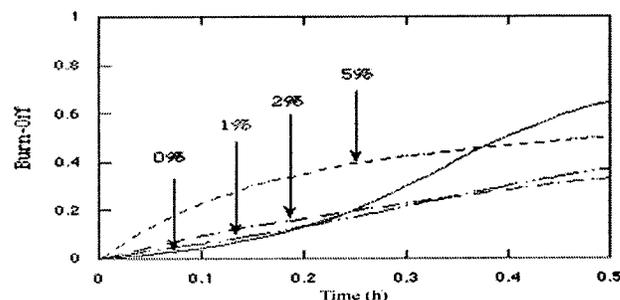


Figure 2. Isothermal TGA of CFRC composites.