

# INFLUENCE OF BORON ON STRUCTURE AND OXIDATION BEHAVIOR OF GRAPHITE FIBER, P120

Jane Y. Howe and Linda E. Jones  
School of Ceramic Engineering and Materials Science,  
Alfred University, Alfred, NY 14802

## Introduction

One limitation in the application of carbon fiber reinforced carbon composites is the preferential attack of the fiber. Carbon matrices of either coal tar pitch or resin are inherently less susceptible to oxidation and can be protected readily via the addition of glass forming particulates such as  $ZrB_2$  or  $B_4C$ . Fiber reactivity is strongly dependent upon development of structure and the location of active surface sites which tend to be concentrated on the fiber ends. The purpose of this study is to examine a graphite fiber (P120) and investigate the influence of boron on its structure and oxidation behavior.

## Experimental

As-received P120 fiber, manufactured by Amoco Performance Products, Inc., is a graphite fiber having an elastic modulus of 820 GPa and a tensile strength of 2.2 GPa. Fiber samples were doped with boron at 2000°C and 200 kPa UHP Ar for 30 min. The reference fiber (HT) was heat treated under the same conditions in the absence of boron. The boron concentrations of as-received fiber (AR), heat treated (HT), and boron doped fibers (BP1 through BP4) are listed in Table 1 along with their interlayer spacing and FWHM. Crystallographic measurements were undertaken using a Siemens Kristalloflex 810 X-ray diffractometer. Powdered fiber specimens were prepared by using silicon internal standard and a zero background sample holder. Monochromatic  $Cu K\alpha$  (40 kV, 30 mA) with a scan step of  $0.02^\circ 2\theta$  and a count time of 10 seconds was used. Boron concentrations were analyzed by ICP-AES. Oxidation runs were conducted in the temperature ranged from 700°C to 800°C in air flowing at 20 cc (STP)/min in a Setaram TAG24 thermal gravimetric analyzer. Fiber images were taken by using Amary 1810 SEM under 15-23kV accelerate voltage.

## Results and Discussion

Heat treating carbon materials at temperatures in excess of 2000°C in boron rich atmospheres positions boron substitutionally[1]. This process is often associated with a corresponding decrease in interlayer spacing,  $d_{002}$  and a lowering of the graphite Fermi level[2]. Graphitization and electron transfer associated with boron

doping are argued to be two possible inhibition mechanisms[3]. However, it seems quite likely as predicted using molecular orbital theory that the B-C bond is partially ionic in nature and B transfers electrons to carbon, thereby, catalyzing oxidation. These are competing mechanisms and the observed reaction behavior is dependent upon the structure of the host material and ultimately the location of boron within that structure.

Although P120 is highly graphitized and has an elastic modulus approaching that of theoretical 1000GPa, P120 is composed of regions of highly ordered graphite structure along with much smaller microporous regions. These fine grains are generally organized having carbon bonds oriented along the fiber axis with crystallite dimensions on the average of 100 $\mu$ m [4]. However, organization of structure in the transverse direction (through the fiber thickness) is much more difficult to describe. Figure 1a is an SEM image of the as-received P120 with a diameter of 10 $\mu$ m prior to oxidation. P120 has previously been described as having a radial orientation of layer planes from the center or core of the fiber[4]. The graphite sheets actually have folded structure with an average dimension of 100 nm between two folds. The center(core) and surface (edge or skin) of these fibers are less ordered. Doping preferentially places boron in these disordered regions[1], yet, there are actually three possible positions for boron within this P120 structure; *i.e.*, at edge sites on the lattice, in interstitial positions and at trigonal positions as a substitutional impurity.

It is shown in Table 1, that there is only a slight difference in the  $d_{002}$ -spacing and FWHM of these P120 fiber samples. There is no significant change in lattice parameters via heat treatment or boron doping. The  $d_{002}$ -spacing is 0.3374 and 0.3375 nm for as-received and HT fiber, respectively; and the standard deviations are  $1 \times 10^{-5}$  nm or less which are much smaller than those of boron doped fibers. From these data it can be argued that heat treatment relaxes the fiber structure hence a subtle increase in  $d_{002}$ -spacing occurs. Compared with the as-received fiber, the  $d_{002}$ -spacing of doped fiber remains almost unchanged at boron concentrations of several hundred ppm level, that is 0.3374 nm for BP1 P120 (200ppm B) and 0.3375nm for BP2 (700ppm B), respectively. The boron atoms preferentially dope

disordered regions (core and skin) instead of positioning in lattice sites. The role of boron in these regions is to catalyze the ordering; however, at low boron concentrations (200 ppm level or so), very little organization of structure has taken place. There is relatively little influence of boron on lattice size at low concentrations. While at a higher concentration of several thousand ppm, most of the edge sites are saturated with boron and the remaining boron atoms migrate into the trigonal lattice sites and thus the  $d_{002}$  decreases to 0.3372 nm.

Boron doping does inhibit the oxidation of P120 fiber. Fiber burn-off in wt% is plotted as a function of time in Figure 2 for doped, heat treated, and as-received specimens. Oxidation preferentially occurs at less ordered region of the as-received fiber which is the less ordered skin and core (Figure 1b). As a result, the fiber diameter decreases quickly and tapers at the fiber end. Figure 1c is a micrograph of the BP4 P120 also oxidized to 25% burn-off, the skin and core of doped fiber are preserved due to the presence of boron in these regions (figure 1c). The preservation of structure may be more strongly linked to the formation of oxides of boron on edges, hence, a mass transport limitation.

### Conclusions

1. There is no significant change in crystallite parameters by heat treatment or boron doping. Heat treatment leads to an ordered structure. Boron preferentially enters the less ordered region.

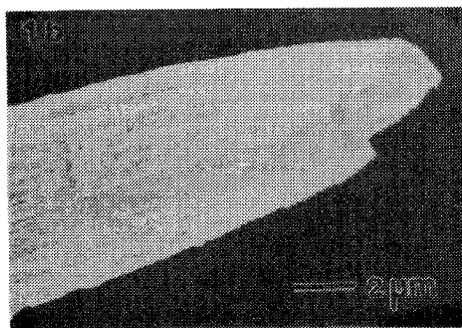
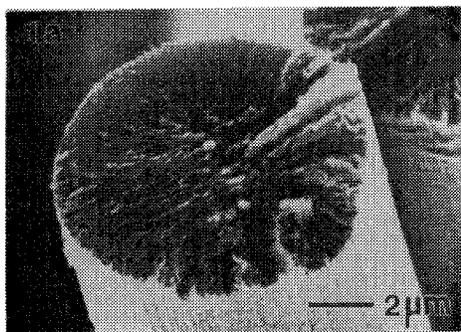
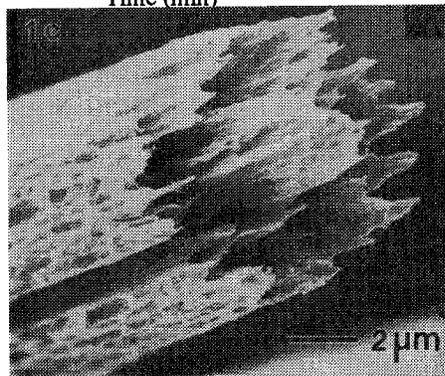


Figure 1. SEM images (SE mode) of P120 fibers. (a) As-received P120 fiber prior to oxidation; (b) As-received P120 fiber oxidized in air at 25% burn-off; and (c) Boron doped P120 fiber oxidized in air at 25% burn-off (boron concentration: 4600ppm).



2. Boron doping inhibits the oxidation of fiber and the oxidation mode has been dramatically altered due to the enriching of boron in less ordered region.

### Acknowledgment

This work is sponsored by Center for Advanced Ceramic Technology at Alfred University.

### References

1. C.E. Lowell, *J. Am. Ceram. Soc.*, (50), 142, 1967.
2. A. Marchand, in *Chemistry and Physics of Carbon*, 7, Ed. by P.L. Walker, Jr., 176-187, Dekker, 1971.
3. L.E. Jones and P.A. Thrower, *Carbon* (29) 251, 1991.
4. I.Mochida, S.-H. Yoon, N.Takano, *et al*, *Carbon* (34), 941, 1996.

Table 1 The  $d_{002}$ -spacing and boron concentrations of as-received and boron doped P120 fibers

P120 Fibers	$d_{002}$ -spacing (nm)	FWHM of $d_{002}$ (degree)	Boron concentration (ppm)
ARP120	0.33741±0.00001	0.25	30
HT	0.33746±0.00000	0.27	34
BP1	0.33742±0.00006	0.26	200
BP2	0.33745±0.00005	0.26	700
BP3	0.33722±0.00004	0.27	3300
BP4	0.33721±0.00006	0.27	4600

Figure 2. The oxidation of the P120 fibers in air at 800°C

