X-RAY PHOTOELECTRON SPECTROSCOPY OF BORON-DOPED CARBON

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INTRODUCTION

A number of studies have been conducted on the effects of various boron-based oxidation inhibitors, protective coatings and sealants for carbon and carbon/carbon composites [1-5]. The results available from these studies are somewhat inconsistent in nature. McKee *et al.* [3] studied the oxidation behavior of graphite impregnated with aqueous solutions of boric oxide and organo-borates and reported a marked reduction in the rate of oxidation of the graphite in dry or moist air between 600 and 1000°C. Allardice and Walker [4] reported that interstitially doped boron in graphite decreased the oxidation rate in either moist or dry oxygen at 600°C. Jones and Thrower [5] studied the inhibiting effect of substitutional boron on carbon fibers. They found that the degree of inhibition was directly proportional to the amount of boron in the fibers. On the other hand, a study by Thomas and Roscoe [6] showed that boron oxide deposited on graphite catalyzed the oxidation reaction of carbon in moist oxygen around 800°C. The reasons for this uncertainty are the plethora of methods that have been employed to introduce boron into carbon [4,7-10],the wide range of carbons used for the evaluations, and the lack of quantitative characterization of where and how the boron is located in the carbon structure.

The proposed mechanisms for boron inhibition of carbon oxidation involve situating boron into the graphite lattice, either randomly or ordered, as in the proposed BC_3 structure (Fig. 1). It is evident that boron can be located in many different sites–especially in the presence of oxygen at the surface. X-ray photoelectron spectroscopy (XPS) is one of the few techniques which can be used to identify the local chemical environment of boron in carbon. A complete description of the local environment of boron in the bulk and at the surface would give insight as to the role it plays during oxidation. However, there have been few attempts to characterize the local bonding states of boron in carbon via this technique.

Kowbel *et al.* [9] used XPS to determine the chemical state of boron in an implanted C/C composite, but, it was difficult to extract information because of the many types of carbon present in the composite. In one of the only attempts to examine the B1s chemical shift for BC_3, Kaner *et al.* [10] reported a binding energy of 188.5eV for the $\begin{smallmatrix} C \\ | \\ C^{\diagup B \diagdown} C \end{smallmatrix}$ site in a graphite structure. However, his assignment was based

upon the assumption that CVD deposited $B_xC_yN_x$ contained these structural units. Unfortunately, there are no well-characterized standard materials which can be used to provide a definitive assignment of substitutional boron-in-graphite.

It is clear that a fundamental understanding of the role of boron in carbon oxidation still does not exist. This is due, in part, to a lack of direct information about the structural role of boron in the bulk and at the surface of carbon/graphite. Therefore, the objective of this work is to analyze the local bonding environment of boron in many different pristine, boron-containing compounds that can be used as standard materials for future XPS studies of boron-doped carbon and C/C composites.

EXPERIMENT

The B1s binding energy was obtained and compared for seven different boron-containing carbon standards. Since XPS is a surface sensitive technique, special precautions were taken to ensure that the chemical state of the boron atom represents that of the bulk. Analysis of the monolithic standards took place on a clean fracture surface to expose sites that are typical of the bulk. The powder samples were prepared and handled in an inert atmosphere to ensure that the sample would not be contaminated.

Boron oxide (B_2O_3) was fractured under vacuum within the XPS chamber because it is extremely reactive with water. This clean surface was then analyzed. The boron carbide (B_4C) was also fractured and immediately analyzed to prevent contamination. Triphenylboron ($B(C_6H_5)_3$) and triphenylboroxine ($B_3O_3(C_6H_5)_3$) (Johnson Matthey Alfa Aesar) was received packed under nitrogen and subsequently opened under nitrogen within a glove bag attached to the XPS sample chamber to guarantee a pristine sample.

The other three "standards" were carbons that had been doped with boron at high temperatures. It is known that a graphite/boron solid solution containing 2.3^a/$_o$ boron can be produced via a solid state diffusion process [11]. Consequently, any boron-doped carbon, processed in this fashion, should contain boron bonded to carbon in the graphite structure (up to 2.3^a/$_o$). A slab of HOPG was placed in a graphite crucible and surrounded with an ultrapure flake graphite (SP-1) and glassy B_2O_3 and subsequently heated to 2,773K [12]. Another graphite

crucible was similarly prepared, however, elemental boron was used as the dopant. A third graphite standard was obtained by graphitization of a boron-doped carbon pitch at 2,773K.

The XPS analyses were carried out with a Kratos XSAM 800 using 1253.6eV MgKα radiation. The binding energy scale was calibrated by assigning the C1s peak at 284.6eV. The peaks were deconvoluted by constraining the peak positions and FWHM's to ± 0.1eV and 1.8 to 2.2eV, respectively, assuming a Gaussian-Lorentzian distribution

RESULTS AND DISCUSSION

The boron oxide exhibited the highest B1s binding energy component while the boron carbide and the boron-doped graphites showed the lowest energy components. This is qualitatively consistent with the charged shell potential model for photoelectron emission. The electron charge density near the boron atom is decreased due to the electronegativity of the bonding environment (carbon or oxygen). Therefore, the B1s peak will shift to higher binding energies with oxygen neighbors and lower binding energies with carbon neighbors. Beyond this general trend, the XPS high-resolution spectra are more difficult to interpret. In the case of B_4C, the rhombohedral unit cell consists of six coordinated boron in two dissimilar sites. In one site the neighboring atoms are all boron while in the other site there is one carbon atom combined with five boron atoms [13]. However, the high resolution XPS spectra did not resolve distinct components for each of these sites.

The local environments around boron in triphenylboron and triphenylboroxine (Fig. 2 and 3, respectively) are more similar to those expected in graphite (see Figures 1-3). The B1s binding energy for the oxygen-containing compound is slightly higher than for the polymer with only carbon, and they both are observed to be lower than in boron oxide and higher than in the carbide or carbons.Unfortunately, there is an uncertainty involved in the effect of next nearest neighbors in XPS spectra; hence, a direct correlation between the polymers and graphitic materials would be premature.
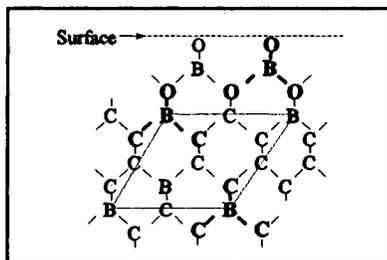
The high temperature doped graphites showed a broader distribution of boron chemical states. There were basically three components ranging from ~192eV to ~186eV. It is interesting to note that the ~186eV component is the lowest energy B1s line ever reported. The ~188eV line could correspond to boron carbide or B_4C-like precipitates (since ~188eV is the main line in B_4C) while the high energy component (~192eV) probably represents oxide or oxycarbide sites. While it is tempting to assign the 186eV component to the substitutional-boron which exists in these graphites, further studies will be required to make the definitive assignment.

CONCLUSIONS

Several standard materials were analyzed with XPS in order to determine the sensitivity of the B1s binding energy to the local environment around the boron atom. It is clear that XPS will be a crucial tool for identifying the mechanism by which boron inhibits the oxidation of carbon. Thus, the effort required to obtain and further interpret the XPS spectra for boron in carbon is warranted.

REFERENCES

1.J.R.Strife, J.E.Sheehan, *Am Ceram Soc Bull*,67,364 (1988)
2.D.W. McKee, *Carbon*, 25, 551 (1987).
3.D.W. McKee, *et al.*, *Carbon*, 22, 285 (1984).
4.D.J. Allardice, P.L. Walker,Jr., *Carbon*, 8,375, 773(1970).
5.L.E.Jones,P.A.Thrower,*J de Chim Physiq*,84 1431 (1987)
6.J.M. Thomas, C. Roscoe, *Proc 2nd conf Industrial Carbon and Graphite*, London, 249 (1965).
7.D.W. McKee, *Carbon*, 24, 737 (1986).
8.N.M.Rodriguez,R.T.K.Baker, *J. Mater. Res*,8, 1886(1993).
9.W. Kowbel, *et al.*, *Carbon*, 31, [2] 355 (1993).
10.R.B.Kaner, *et al.*, *Mat. Res. Bull.*, 22, 399 (1987).
11.C.E. Lowell, *J. Amer. Cer. Soc.*, 50 [3] 142 (1967).
12.C.E. Crossland, B.S.Thesis, Penn State University(1991).
13.A. Lipp, *Technische Rundschau*, 14,28,33 (1965) and 7 (1966).

Figure 1. Proposed BC_3 structure[10] and schematic of relevant surface sites[5].
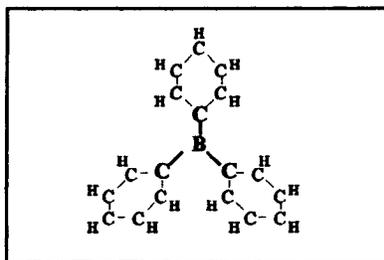

Figure 2. Structure of $(B(C_6H_5)_3)$ triphenylboron.

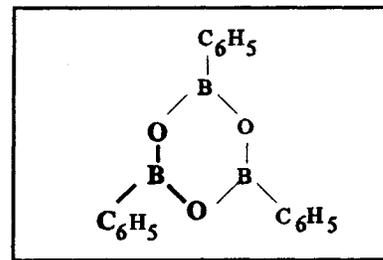Figure 3. Structure of $(B_3O_3(C_6H_5)_3)$ triphenylboroxine.