SURFACE OXIDATION OF BORON-DOPED CARBONS

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Introduction

It has been known for a long time that boron additions enhance the oxidation resistance of carbon and carbon/carbon composites.[1-5] But the mechansism is still a matter of debate.[6] Some of the reasons for this apparent confusion are the multitude of doping-methods and carbons used to study the effects, and the lack of quantitative characterization of where and how the boron is located in the carbon structure before and after oxidation. In this study, attention was focused on the use of a high-temperature reaction to introduce the boron, and the application of x-ray photoelectron spectroscopy (XPS) and high-resolution microscopy to determine the chemical and physical characteristics of boron in the carbon surface. A wide variety of bron sources and carbon substrates were employed throughout, but due to space limitations, the results for the HOPG substrates are emphasized here.

Experimental

Small monolithic plates of HOPG, LOPG and vitreous carbon were placed in graphite crucibles and surrounded with a mixture of ultrapure flake graphite (SP-1) and either boron-oxide, elemental boron, or boron carbide and subsequently heated to 2450°C for 40 minutes in argon using a carbon furnace. The XPS peak positions for boron-oxide, substitutional boron and the two forms of boron oxycarbide were determined in an earlier study.[7] The oxidations were performed in UHP O_2 in a tube furnace or in a TGA. The TGA experiments provided confirmation of the boron-doping effect upon oxidation inhibition, and yielded samples for the surface analyses whose degree of burn-off was known.

Results

HOPG doped with boron-oxide was oxidized at 400°C for 1 hour, 500°C for 1 hour and 600°C for 3 hours under flowing UHP O_2. The resultant B1s spectra of the basal plane surfaces are shown in Figure 1. In the as-doped basal plane surface, the boron atoms (~ .7 atomic percent) are present almost exclusively in substitutional sites as indicated by the peak at 186.5 eV. After oxidation at temperatures between 600°C and 800°C, a boron-oxide phase formed on the surface, as revealed by the peak at 193.2 eV. There were also minor concentrations of boron-oxycarbide formed on this surface as revealed by the background betweeen 188 and 190 eV. But it is more significant to point-out that oxidation of the HOPG did not deplete the basal plane surface of the substitutional boron.

Figure 1. As-prepared; 400°C 1hr; 500°C 1hr; 600°C 3hr. B_2O_3, B-in-C. Binding Energy (eV)
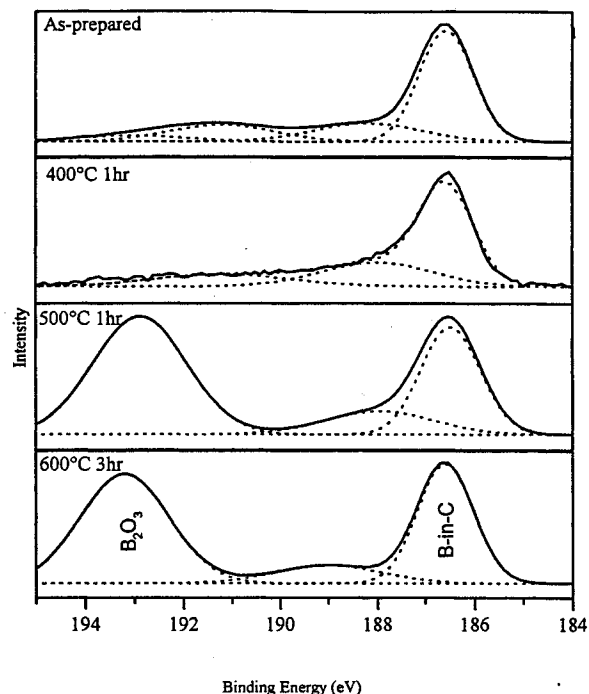
A field emission scanning electron microscope (FESEM) was used to examine the oxidized surfaces of undoped and boron-doped HOPG. There was a significant difference in the density, size, shape and orientation of the etch pits in the doped and undoped HOPG surfaces. The etch pits were randomly distributed over the surface of the undoped HOPG and the sizes ranged between 1 and 100 microns in diameter. Moreover, the majority of the hexagonal pits on the surface were found parallel to the observed twin bands in the HOPG. This suggests that the oxidation pits in the undoped HOPG have primarily armchair sites on the surfaces of pit the walls. Conversely the oxidation pits on the doped HOPG were less distinct; they were shallow and much smaller (10nm to 1μm). And in those cases where well-developed pits could be found, they were oriented perpendicular to the observed twin bands. If true, this suggests that the surfaces of these pit walls are made up primarily of zig-zag edge sites.

AFM revealed some unique features associated with the oxidized surfaces of the boron-doped HOPG. Figure 2 shows the phase contrast image obtained on the

basal surface of boron-doped HOPG after 2 hours oxidation at 700°C. The brightness in the phase-contrast image corresponds to the relative hardness of the material under the AFM-tip. Thus, it seems likely that the particulate phase in the base of some etch pits corresponds to the boron-oxide detected by XPS. The droplet shape of the particles indicates that they are most likely glassy. This conclusion was further verified by washing the oxidized boron-doped HOPG surfaces in water, and then re-analyzing their surfaces with XPS and AFM. The particulate phase was eliminated in the AFM image due to the washing, while the boron-oxide concentration determined with XPS was reduced by 75%. It is important to emphasize, though, that the substitutional boron concentration was not reduced by the washing.

0   4.00 μm

The AFM images in Figure 2 show some other noteworthy features. Many of the pits do not contain any observable boron-oxide phase; in fact, some regions of the surface were not visibly oxidized in any way. It can also be seen that the size of the boron-oxide droplets increases towards the center/bottom of each pit. The droplets are considerably smaller on the sidewalls of the pit. Finally, the AFM analysis of the washed (oxidized) surfaces revealed that the pits which contained boron-oxide (before washing) had distinctly flat-bottomed pits while many of the other pits were rounded on the bottom. In general, the pits ranged in depth between 70 to 250 nm.

Discussion

XPS showed that a boron-oxide phase builds-up during oxidation of the carbon surface, while there was little or no change in the substitutional boron surface concentration. There are very few glassy particles located on the bottom surface of the pits in the samples oxidized for short times, but the samples that were oxidized for longer times contained large irregularly shaped boron-oxide droplets on the bottom of some of the etch-pits; smaller more uniform clusters appeared at the upper ridge of the pore walls. Since the bottom of the pit is exposed to oxygen for shorter times than the upper ridges of the pore walls, it can be concluded that the boron-oxide builds up along the edge sites on the pit walls, and after it agglomerates into a droplet of critical mass, it falls into the bottom of the pit. This is consistent with the AFM data which showed that the pits which contained the boron-oxide phase were much flatter and shallower than the pits without the oxide phase. It suggests that a boron-oxide liquid-phase gathers on the bottom surface of the pit during oxidation and physically blocks any active sites or defects where further pit growth may proceed. In this sense, boron inhibition of carbon oxidation occurs because a boron-oxide reaction product forms a physical barrier to the oxygen atoms, and in turn, prevents the increase in surface area that accelerates the oxidation process.

The fact that the etch-pit diameters are comparable, even though some contain the boron-oxide reaction product while others do not, may be the most important observation. Consequently, oxidation along the graphite planes must be prevented by some means other that the build-up of a liquid oxide phase along the pit walls. In this regard, the preferred orientation of the etch-pits in the doped-HOPG may be significant. It suggests that a prevalence of ziz-zag sites on the etch-pit walls can stabilize the pit against further oxidation (or at least slow it down). In a companion study,[8,9] theoretical calculations were used to define the local electron density of zig-zag vs armchair edge sites, and the corresponding influence of boron substitution. These calculations show that boron substitution on armchair sites raises their reactivity (relative to pure carbon), while boron substitution on zig-zag sites lowers the relative reactivity. Consequently, the activation energy for reaction with oxygen is increased on zig-zag sites where boron has substituted for carbon, in general, and in the case of HOPG, the nucleation and/or growth of perpendicular pits limits the overall oxidation rate.

References

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489