SYNTHESIS AND CHARACTERIZATIONS OF NOVEL BORON CONTAINING CARBON (B/C) MATERIALS PREPARED BY 9-CHLOROBORAFLUORENE
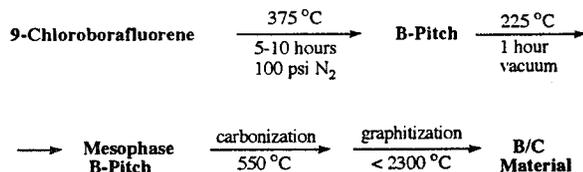
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Introduction

Boron is one of the few elements that can be substituted into the carbon structure. The presence of the electron deficient boron alters the electronic structure of the substrate and leads to many interesting effects on the thermal, electrical as well as chemical properties of the carbon[1,2]. Although the properties of boron doped carbons have been studied, the process of synthesizing these materials has not been improved upon. The method of doping carbon with substitutional boron via solid state diffusion has many drawbacks. The diffusional process requires very high temperatures as well as long residence times. As the result of the additional heat treatment during doping, it is often very difficult to separate the effect of boron from the effect of the increase in graphitization. This uncertainty hinders the characterization and the understanding of B/C materials. Furthermore, the concentration of the dopant is limited by the temperature of the reaction and the dispersion of the dopant is often inhomogeneous. Lowell[3] determined that the solid solubility of boron in carbon approached a maximum value of 2.35 atomic % at 2350 °C.

Experimental

Our research approach has been concentrating on a new synthetic route to prepare B/C materials by using specifically designed boron containing carbon precursors. The focus of this paper is on heterocyclic aromatic boron containing hydrocarbons, specifically 9-chloroborafluorene (9-CBF) which was synthesized by a published method[4]. The general process for the heat treatment of the boron containing precursor can be summarized by the following diagram:

9-Chloroborafluorene $\xrightarrow[\substack{\text{5-10 hours}\\\text{100 psi N}_2}]{375\,°C}$ B-Pitch $\xrightarrow[\substack{\text{1 hour}\\\text{vacuum}}]{225\,°C}$

$\longrightarrow$ Mesophase B-Pitch $\xrightarrow[550\,°C]{\text{carbonization}}$ $\xrightarrow[<2300\,°C]{\text{graphitization}}$ B/C Material

Results and Discussion

The polarized micrograph of B/C pitch that had been carbonized at 500 °C shows 100 % homogeneous and has complete optical activity. It has the appearance of a coke produced from Brooks and Taylor (BT) meosphase, in which there is complete local anisotropy while the material as a whole is statistically isotropic. The B-pitch mesophase is highly graphitizable with high yield (> 85%). The resulting B/C materials (thin films) were examined by X-ray diffraction. Pure silicon (NBS SRM 640) was the internal standard for the accurate determination of d spacing. Sp-1 graphite was used as the standard for detemining instrument broadening in the calulation of crystallite size. Figure 1 depicts the x-ray diffraction patterns of the B/C materilas at different heat treatment tempeartures.
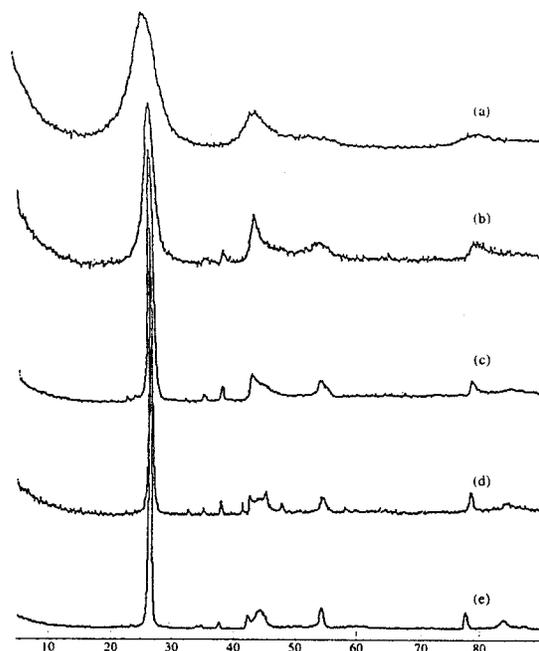

Figure 1, X-ray diffractions of B/C materials prepared at (a) 1000 °C, (b) 1500 °C, (c) 1800 °C, (d) 2100 °C and (e) and 2300 °C.

Clearly, there is significant development of the (100) and (101) peaks as the temperature increased from 1800 to 2300 °C. Table 1 summarizes the x-ray

crystallite parameters of interlayer spacing, d, crystallite size, Lc and crystallite width, La. The d spacing decreases with heat treatment tempeature and time, both Lc and La increase with temperature. Apparently, only 2300 °C was necessary to obtain x-ray crystallite parameters that typically require much higher temperature (> 3000 °C) to achieve in traditional carbons. Clearly, the in situ boron is catalyzing graphtization of the B/C material.

Closer examination of the secondary peaks shows that there is significant development of the (100) and (101) peaks as the temperature increased from 1800 to 2300 °C. The (101) peak is traditionally broader than the (100) peak since it is as much a measure of Lc as a gauge of La. Although the increase in graphitization temperature has an augmenting effect on the crystallite size and width, the enlargement of La and Lc at such low temperatures can positively be attributed to catalysis by boron. Higher values of La and Lc were observed in the 2300 °C B/C material even though the lattice spacing (3.347 A) was well below that of graphite. As shown in Table 1, the dimensions for Lc and La for the 2300 °C B/C material are 456 and 689 A respectively. Interestingly, the improvement of crystallite size was more pronounced in the a direction than in the c direction. If the mechanism of catalysis is base on enhanced diffusivity as is widely believed, then one would expect the faster growth of crystallite width (La), since the diffusion constant of boron parallel to the layer planes (6320 cm^2/sec) is much greater than that in the perpendicular direction (7.1 cm^2/sec)[5]. The activation energy for these two processes are almost equal, 157 kcal/mole for parallel and 153 kcal/mole for perpendicular. The result of this study provides the first evidence that support the anisotropy in the catalysis of graphitization.

Conclusion

This paper has shown a new synthetic route to prepare boron containing carbon (B/C) material with high boron content and well ordered crystalline structure. By virtue of the fact that boron is chemically bonded to the aromatic carbons of the 9-CBF precursor, an in situ boron catalyzing carbonization and graphitization reactions can effectively take place at relatively low temperature to form a uniform B/C material with the substitutional boron in the graphilic structure. The knowledge of boron and carbonization chemistry allows us to develop the intermediate of mesophase B-pitch, which by its nature should be processable. In addition, the new B-pitch allows us for the first time to evaluate the catalytic effect of boron on the graphitization process, without the effects of high temperatures (>2500 °C). Interestingly, x-ray diffraction analysis demonstrated anisotropy in the catalysis of graphitization reactions by boron where La grows preferentially over Lc.

References

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Table 1. X-ray crystallite parameters and boron content as function of graphitization temperature and time

Sample	Pyrolysis conditions		X-ray results			
	Temp. (°C)	Time (hours)	d002 (A)	Lc (A)	La (A)	Boron content(wt%)
BC-1	1000	1	3.461	–	–	7.65
BC-2	1500	1	3.411	–	–	11.39
BC-3	1800	1	3.383	88	–	7.42
BC-4.1	2000	1	3.379	177	336	6.96
BC-4.2	2000	5	3.363	168	297	5.62
BC-4.3	2000	8	3.356	270	321	8.21
BC-5	2300	1	3.347	456	689	3.46