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Effects of boron addition on some properties of hard-type carbons

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The boron-containing hard-type (HT) carbons were prepared by heating the raw coke compacts with 1.6 wt% boron at temperatures ranging from 1000 to 2800° C. Some physical and mechanical properties of boron-doped HT carbons have been measured and compared with those for boron-free materials. It was confirmed that the boron enters the HT carbon at a relatively low temperature of 1400° C and enhances the densification process of compacts during heat-treatment above 1800° C. The addition of boron caused increases in Young's modulus and thermal conductivity, and decreases in hardness and electrical conductivity of HT carbons. The effects are discussed, and compared with those for graphitizable carbons.

1. Introduction

Boron is known as a specific element for carbon or graphite, because a small number of boron atoms enters the substitutional position in the graphite lattice and accelerates the graphitization process of carbon. Lowell [1] has investigated the solid solubility of boron in natural graphite in the range 1800 to 2500° C, and has found that the solubility of boron increased to 2.35 at % with increasing temperatures up to 2350° C. Many investigators have reported the effects of boron addition on some properties of various kinds of graphite materials. Those reports were mainly concerned with X-ray parameters [2–4] and electrical properties [5–8]. A few studies were carried out in regard of other physical properties, elastic modulus and thermal conductivity, etc. [9–13]. In those experiments, the carbon materials used were all graphitizable carbon. However, little work has been reported on the effects of boron addition to non-graphitizable carbon.

A hard-type (HT) carbon, which is classified as non-graphitizable carbon like glassy carbon, is prepared by a unique technique using a ground raw coke powder without any binder materials [14]. In the present work, we examined the effects of boron addition on some properties of HT carbon materials.

2. Experimental procedure

The technique and method of fabrication of the HT carbon with boron were similar to those described in a previous paper [15]. The petroleum coke, industrially manufactured at about 500° C, was used as the starting carbon material; it contained about 14 wt % volatile matter. To enhance the sinterability of the coke powder, raw coke of − 100 mesh was pulverized with a vibratory ball-mill for about 1 h. The mean diameter of the coke after milling was about 8 μm. As a boron source, boron carbide B_4C (Denki Kagaku Kogyo Co.), with a purity of 98% and a mean diameter of 2 μm, was used. The mixing powder, which was prepared by dry blending the mixture of coke and B_4C for 5 h, was pressed unidirectionally to the form of a square plate 30 mm × 30 mm × 6 mm, under a pressure of 200 MPa. The compacts were then heat-treated at temperatures ranging from 1000 to 2800° C, and held for about 1 h in an atmosphere of argon.

The heat-treated samples were examined for bulk density, bending strength, Young's modulus, hardness, electrical resistivity and thermal conductivity. The Young's modulus and electrical resistivity were measured perpendicular to the pressing direction in forming, whereas other properties were measured parallel to the pressing direction. The bulk density was calculated from weight and volume of the specimen. For the measurement of strength, specimens 8 mm wide and 5 mm thick were cut from the samples. The measurement was performed on a testing machine (Shimazu Seisakusho Co., DSC-200) by the three-point method with a span distance of 30 mm and a cross-head speed of 0.5 mm min^{-1}. The Young's modulus at room temperature was calculated from the velocities of pulsed longitudinal and shear waves; the velocities were measured by a sing-around method (Cho-onpa Kogyo Co. UVM-2) using 5 MHz. Hardness was measured with a Shore hardness tester (Masuzawa Seiki Co.), and the electrical resistivity was measured by the constant current potentiometric method. Thermal conductivity was determined at room temperatures by the laser flash method (Sanki Engineering Co. TXP-400) using a ruby laser.

The X-ray diffraction data on (0 0 2) and (1 1 0) spacings of HT carbon were obtained with an X-ray diffractometer (Rigaku Denki Co. RU-200PL) using a graphite monochrometer. In order to determine the concentrations of boron dissolved in HT carbon, the residual B_4C was removed from the pulverized samples using molten sodium carbonate. The residual carbon was suspended in 3 wt % solution of $Ca(OH)^2$, and then was ignited at about 900° C. After the residue was dissolved in water, the solution was titrated with a solution of 0.1 N NaOH using a mannitol. The content of boron presented as a form of B_4C was also determined in a similar manner.

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TABLE I Some properties of the boron-containing HT carbons, fabricated at 2000° C

Boron content (%)	Bulk density ($g\,cm^{-3}$)	Dissolved boron (wt %)	X-ray parameter (nm)		Shore hardness (Hs)	Electrical resistivity (Ωm)	Thermal conductivity ($W\,m^{-1}K^{-1}$)
			(0 0 2)	(1 1 0)			
0	1.88	–	0.3436	0.2442	112	0.45	10
0.4	1.92	0.3	0.3424	0.2448	109	0.22	13
0.8	1.93	0.7	0.3420	0.2452	108	0.16	15
1.6	1.95	1.0	0.3414	0.2456	107	0.16	17
2.4	1.96	1.2	0.3403	0.2459	105	0.16	17
3.3	1.97	1.3	0.3400	0.2459	107	0.16	18
4.8	1.97	1.3	0.3400	0.2459	106	0.17	18
6.4	1.97	1.3	0.3400	0.2460	105	0.17	18

3. Results

3.1. Influence of amount of boron at 2000° C

Some properties of the HT carbon with boron (0 to 6.4 wt %) obtained by heat-treatment at 2000° C are shown in Table I. The HT carbon compacts containing no boron were densified by heating them at 2000° C; this was accompanied by a large volume shrinkage of 43% and a weight loss of 14%. The values of boron content in Table I have therefore, already been corrected by subtracting such a weight loss. It was found that the concentration of boron dissolved in HT carbon increased with increasing amounts of additive up to 3.3 wt %; above this boron level its value was almost constant at 1.3 wt %, but X-ray studies indicated that a part of the B_4C added initially remained undissolved even in the sample with 0.8 wt % boron. The X-ray diffraction studies also showed that the *d*(0 0 2) spacing of HT carbon decreased and the *d*(1 1 0) spacing increased on addition of up to 3.3 wt % boron, but above this level no further change was observed. A similar dependence was observed for hardness, electrical resistivity and thermal conductivity. These results, in which some properties of boron-doped carbon materials were found to have a strong dependence of the content of boron, agreed with other results [10–13]. However, no difference in both the bending strength and the Young's modulus was observed between the samples with and without boron. The boron-doped samples also showed a greater bulk density. It is noteworthy that the boron addition leads to an increase in bulk density of HT carbons, and the change of density revealed a good correspondence with the concentration of boron dissolving in the resultant HT carbon. There is no appreciable difference in the microstructure between the samples with and without boron observable by optical and scanning electron microscopy.

3.2. Influence of heat-treatment temperature

To determine in detail the influence of boron addition on HT carbon, the HT carbons with and without 1.6 wt % boron were prepared by heat-treatment at 1000 to 2800° C. This amount of additive is substantially lower than the maximum solubility of 2.35 at % for natural graphite, reported by Lowell [1].

Fig. 1 shows the changes of bulk density with heat-treatment temperature (HTT). The boron-doped samples obtained at temperatures above 1800° C showed a greater density, compared with those of boron-free samples, but its value appeared to saturate at temperatures above 2200° C. Boron also accelerated the graphitization process of HT carbon, as shown in Fig. 2. Above 1600° C, the boron-doped samples showed a smaller *d*(0 0 2) and a greater *d*(1 1 0) spacing than those of HT carbons without boron, while below this temperature there was no significant difference in X-ray parameters between them. The X-ray study and chemical analysis indicated that a part of B_4C remained undissolved even in the sample heat-treated at 2800° C. The concentration of boron dissolving in HT carbon increased with increasing HTT up to 1800° C, and above this temperature its value appeared to be almost constant at 1.0 ± 0.1, as shown in Fig. 3.

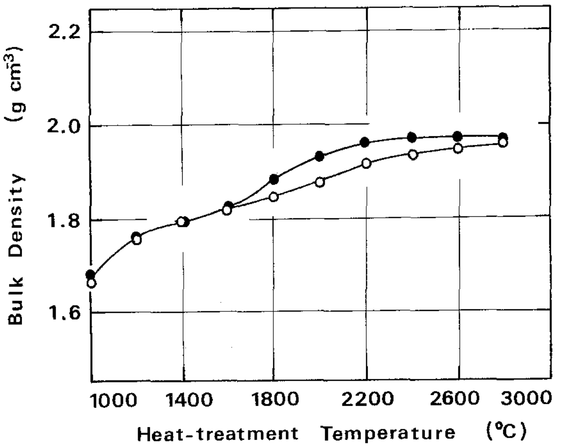

Figure 1 Changes in bulk density of HT carbons with (●) and without (○) 1.6 wt % boron, with heat-treatment temperature.

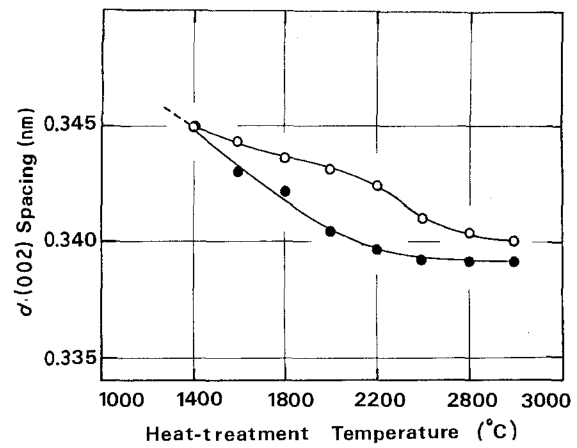

Figure 2 Changes in *d*(0 0 2) spacing of the HT carbons with (●) and without (○) 1.6 wt % boron, with heat-treatment temperature.

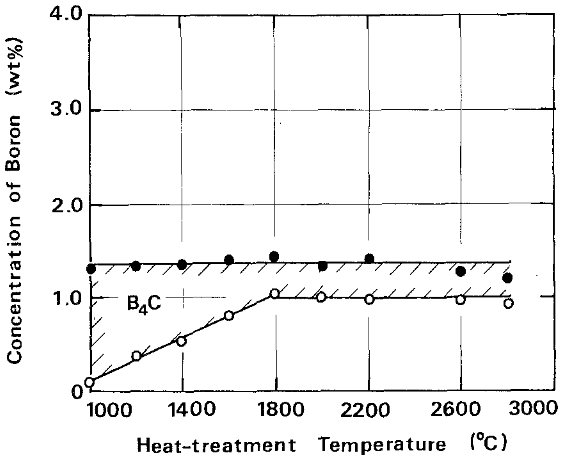

Figure 3 Change in the concentration of boron dissolved in HT carbons with heat-treatment temperature. (●) Total boron; (○) dissolved boron.

Fig. 4 shows the changes of bending strength of HT carbons with and without boron, as a function of HTT. No remarkable difference in bending strength between the samples with and without boron was observed over the entire temperature range. However, the Young's modulus of the boron-doped samples decreased remarkably at 1400° C, in contrast with that of boron-free materials, as shown Fig. 5. A similar result was observed for hardness, electrical resistivity and thermal conductivity, as is evident from Figs 6, 7 and 8, that is, the difference in those properties between the samples with and without boron, developed at the same temperature, at which both hardness and electrical resistivity decreased and thermal conductivity increased. It is noteworthy that boron enters HT carbons even at a relatively low temperature of 1400° C, and leads to the changes of some properties. However, this temperature is below the temperature at which the enhanced densification develops. In general, a significant change in the properties of boron-doped samples was observed in the range 1400 to 2000° C, while it was found that above this temperature those properties changed slowly with increasing HTT, showing no characteristic change. A characteristic behaviour was observed for Young's modulus; the boron-doped samples obtained at temperatures from 1600 to 1800° C showed a smaller Young's modulus, in comparison with those of boron-free materials.

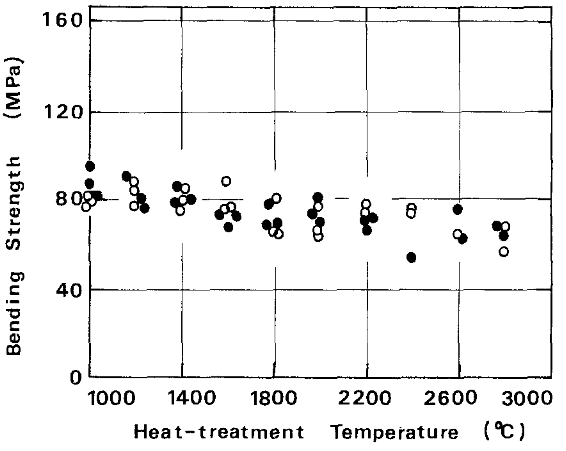

Figure 4 Changes in bending strength of HT carbons with (●) and without (○) 1.6 wt % boron, with heat-treatment temperature.

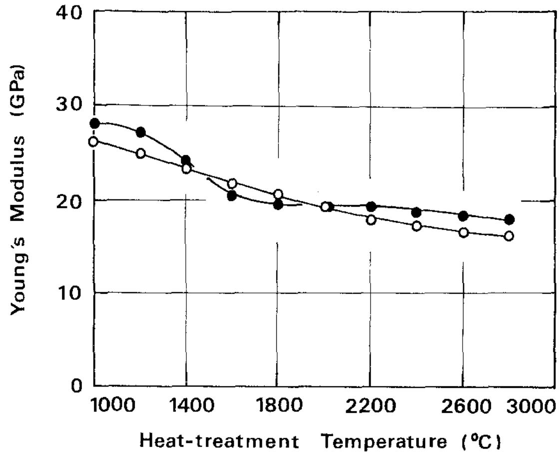

Figure 5 Changes of Young's modulus of HT carbons with (●) and without (○) 1.6 wt % boron, with heat-treatment temperature.

4. Discussion

The boron atoms entered HT carbon even at a temperature of 1400° C and led to changes in some properties of the HT carbons. Addition of boron also caused an increase in density of HT carbon. It was confirmed experimentally that the enhanced densification of HT carbon with boron occurred above 1800° C, and the magnitude of densification depended strongly on the boron level, as shown in Table I. From the results, it was considered that the diffusion of boron (volume diffusion) plays an important role in the densification process of the HT carbon with boron during heat-treatment. There is a considerable difference in the two temperatures for the diffusion of boron and the occurrence of densification. This fact appeared to imply that a different mechanism for the diffusion process (boundary or surface diffusion) occurs at temperatures below 1600° C.

Some physical and mechanical properties of boron-doped HT carbon were strong functions of boron content, as seen from Table I. The HT carbon used in this work is classified as non-graphitizable carbon like glassy carbon [14]. Many investigations concerning the effects of boron addition are made mainly on natural graphite and graphitizable carbon such as pitch coke, in which the doping of boron was achieved by heat-treatment above 2500° C. Therefore, we shall only compare our results obtained above 2200° C with the other results.

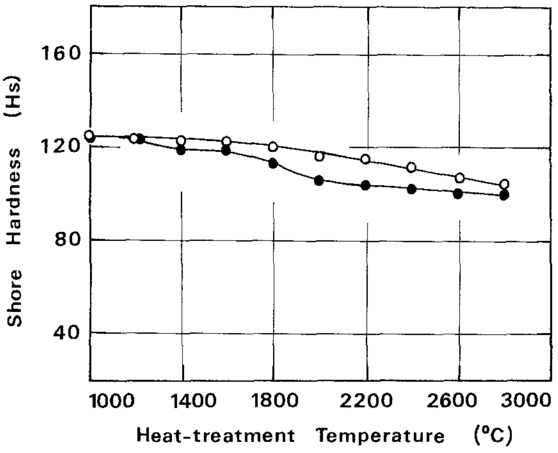

Figure 6 Changes of Shore hardness of the HT carbons with (●) and without (○) 1.6 wt % boron, with heat-treatment temperature.

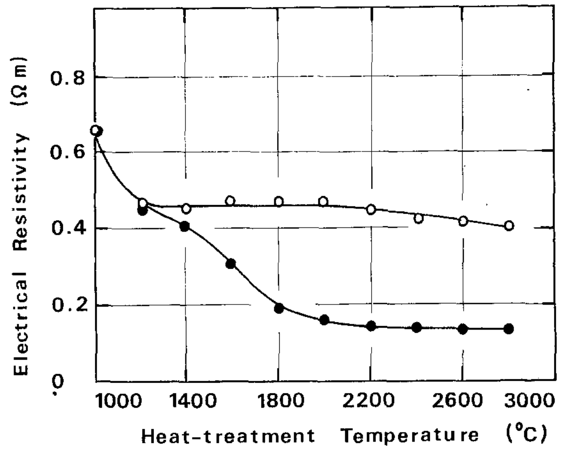

Figure 7 Changes in electrical resistivity of HT carbons with (●) and without (○) 1.6 wt % boron, with heat-treatment temperature.

The decrease in electrical resistivity of HT carbon on doping is in good agreement with that in conventional carbon materials, reported by many investigators [9–13]. On considering the effects of boron, it is necessary to distinguish between the effects only caused by the presence of boron and those caused by the increased degree of graphitization and density, accompanied by boronation. The boron atom which enters the graphite lattice by substituting for carbon at the trigonal site, acts as an acceptor, resulting in a drop in the Fermi level [5].

It was found that a reduction in electrical resistivity of the HT carbon on doping is attributed to the change of electrical structure caused by the boron atoms. The addition of boron led to an increase in the thermal conductivity of HT carbon. In contrast to our results, many investigators [9, 11–13] have reported that a small amount of boron leads to a decrease in thermal conductivity of graphite materials, which has been explained as a decrease in conductivity being caused by the effect of lowering the phonon free path due to the dissolving boron. In the present work, there is not appreciable difference in thermal conductivity between 2800° C HT carbon and 2000° C boron-doped HT carbon, having almost the same densities and X-ray parameters, which appeared to imply that the positive effects, due to increasing density and improved structure, are superior to the negative effects in thermal conductivity due to the dissolving boron atoms. The boron-doped samples showed a greater Young's modulus than the undoped HT carbons. This result agrees with that reported by others [11, 12], and can be explained by the pinning of dislocations due to the dissolving boron atoms. The HT carbon is very hard, like glassy carbon, compared with graphitic carbon. Boron also caused a decrease in hardness of HT carbon, which may also be explained on the basis of the increased degree of graphitization.

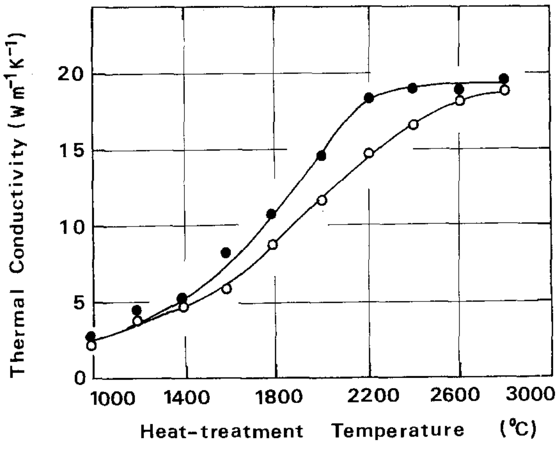

Figure 8 Changes in thermal conductivity of HT carbons with (●) and without (○) 1.6 wt % boron, with heat-treatment temperature.

From the results in these experiments, it was found that except for thermal conductivity, the effects of boron addition on some physical and mechanical properties of non-graphitizable HT carbon are almost the same as those for graphitizable carbons, reported by others [9–13].

5. Conclusion

To examine the effects of boron addition on some physical and mechanical properties of non-graphitizable hard-type (HT) carbon, the boron-containing HT carbon was prepared by heat-treatment of the raw coke compacts with 1.6 wt % boron at temperatures ranging from 1000 to 2800° C.

The results obtained can be concluded as follows:

1. The diffusion of boron began at a relatively low temperature of 1400° C, and also enhanced the densification process of HT carbon during the heat-treatment, at temperatures above 1800° C.

2. The addition of boron caused increases in Young's modulus and thermal conductivity, and the decreases in hardness and electrical conductivity of HT carbon. It was found that such changes are related to the presence of dissolving boron atoms, and the increased density and degree of graphitization of HT carbons, accompanied with boronation.

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