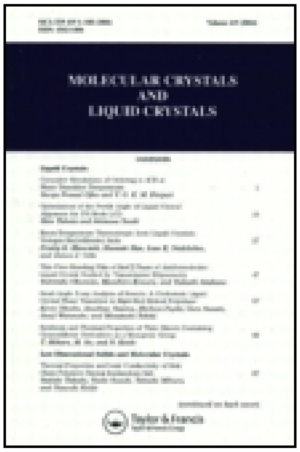

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Structure and Properties of Boronated Graphite

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Structure and Properties of Boronated Graphite

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Boronated natural graphite compacts were prepared at a temperature of 1750°C under pressures between 0.1 and 0.5 GPa with a nominal B_4C content of 2 wt.% and at 2200°C under a pressure of 19.8 MPa with nominal B_4C contents of 1, 2.5 and 50 wt.%. Their interlayer spacing d_{002} and lattice constant a_0 were determined. The measurements of the electrical resistivity, magnetoresistance and Hall coefficient for the compacts were carried out mainly at liquid nitrogen temperature. With the increased substitution of boron atoms, the interlayer spacing d_{002} decreases from the values of the reference natural graphite compacts, showing a trend of the lattice constant a_0 to increase slightly. At liquid nitrogen temperature, all of the boronated compacts show the positive Hall coefficient decreasing with the increase in substituted and ionized boron atoms. Below liquid nitrogen temperature, the boronated compacts except the slightly boronated ones exhibit the negative magnetoresistance and almost temperature independent resistivity.

Keywords: Boronated natural graphite compact; interlayer spacing d_{002}, lattice constant a_0; electrical resistivity; magnetoresistance; Hall coefficient

INTRODUCTION

When some amount of B_4C was mixed with pure natural graphite powder and heated at temperatures between 2200 and 2300°C under a pressure of 19.8 MPa, boronated graphite compact could be obtained[1]. A pronounced effect of boronation was to decrease the interlayer spacing d_{002} with increasing nominal content of B_4C molecules. On the other hand, when a very small amount of boron atoms was substituted into the graphite lattice, the Fermi level was depressed and the related electronic properties changed notably[2]. When a large amount of boron atoms was substituted, a negative magnetoresistance was observed at room and liquid nitrogen temperatures[3]. The aim of the present study is to prepare boronated natural graphite compacts under pressures and to examine changes in lattice parameters, such as d_{002} and lattice constant a_0, and in electronic properties, such as the electrical resistivity, magnetoresistance and Hall coefficient, on boronation.

EXPERIMENTAL

Natural graphite compacts and boronated graphite compacts were prepared from mixtures of natural graphite and B_4C powder under pressure. As listed in Table I, the samples were prepared in two series; to study the effect of pressure at the same nominal B_4C content and the same heat treatment temperature (HTT) of 1750°C (B-18 series) and to examine the effect of B_4C content at the same HTT and heating time (HTt), i.e. at a heat treatment at 2200°C for 1 hr under a pressure of 19.8 MPa (B-2 series).

X-ray diffraction measurements were made on powdered samples of the compacts, mixed with pure silicon powder as an internal standard, employing CuKα radiation. The interlayer spacing d_{002} and lattice constant a_0 for the samples were determined from the 006 and 110 lines, respectively. For the measurements of electrical resistivity, magnetoresistance and Hall coefficient, bridge-shaped specimens with about 0.5 mm in thickness with flat surfaces perpendicular to the pressing direction were used. The measurements were mainly made at liquid nitrogen temperature. For the measurements of magnetoresistance and Hall coefficient, the magnetic fields up to 1 T were applied perpendicular to the specimen surfaces.

TABLE I Preparation condition for natural graphite compacts and boronated natural graphite compacts

Sample Code	Nominal wt.% of B_4C	Pressure (GPa)	HTT (°C)	HTt (hr)
B-18-0	0	0.5	1750	2.0
B-18-1	2.0	0.1	1750	2.0
B-18-3	2.0	0.3	1750	2.0
B-18-5	2.0	0.5	1750	2.0
B-2-0	0	0.0198	2200	1.0
B-2-1	1.0	0.0198	2200	1.0
B-2-2.5	2.5	0.0198	2200	1.0
B-2-50	50.0	0.0198	2200	1.0

RESULTS AND DISCUSSION

For boronated samples in B-18 series, the 110 and 006 diffraction lines were so sharp that the lines due to $K\alpha_1$ and $K\alpha_2$ radiations were clearly separated, suggesting very high crystallinity. For the samples of B-2-1 and B-2-2.5, the 110 and 006 lines were sharp, but the separation of the 110 line due to $K\alpha_1$ and $K\alpha_2$ was not so distinct.

In the B-2-50 sample, crystallites of the primary solid solution of boron atoms into graphite lattice and those of B_4C were found to coexist, i.e. diffraction lines due to the crystallites of the primary solid solution and those of B_4C were observed. The interlayer spacing d_{002} and lattice constant a_0 obtained for the samples are listed in Table II, showing a trend in B-2 series to decrease d_{002} gradually with the increase in nominal B_4C content, and then to increase. The trend suggests that the boronation proceeds in two steps; substitution of boron atoms into the graphite lattice and then intercalation into interstitial sites (i.e. graphite gallery). Boronation seems to be effective under rather lower pressure (B-18 series).

In Table III, the room temperature resistivity ρ_{RT}, resistivity ratios ρ_{RT}/ρ_{77K} and $\rho_{RT}/\rho_{4.2K}$ are listed, where ρ_{77K} and $\rho_{4.2K}$ are the resistivities at liquid nitrogen and liquid helium temperatures, respectively. It must be noted that samples of B-18-1, B-2-1, and B-2-2.5, i.e. those with d_{002} values smaller than those of non-boronated samples, show the resistivities to be almost temperature independent.

TABLE II The interlayer spacing d_{002} and lattice constant a_0 for the samples

Sample code	a_0 (nm)	d_{002} (nm)
B-18-0	0.24620	0.33545
B-18-1	0.24624	0.33526
B-18-3	0.24612	0.33538
B-18-5	0.24623	0.33560
B-2-0	0.24610	0.33541
B-2-1	0.24636	0.33510
B-2-2.5	0.24658	0.33485
B-2-50	0.24658	0.33608

TABLE III Room temperature resistivity ρ_{RT}, resistivity ratios ρ_{RT}/ρ_{77K} and $\rho_{RT}/\rho_{4.2K}$ for specimens

Sample code	$\rho_{RT} \times 10^6$ (Ωm)	ρ_{RT}/ρ_{77K}	$\rho_{RT}/\rho_{4.2K}$
B-18-0	5.1	0.642	0.5495
B-18-1	6.4	1.016	1.0129
B-18-3	7.6	0.705	0.6589
B-18-5	6.8	0.678	0.6209
B-2-0	13.5	0.727	0.6670
B-2-1	6.6	1.012	1.0081
B-2-2.5	8.5	1.004	0.9929
B-2-50	18.6	1.005	0.9992

In B-18 series, at liquid nitrogen temperature, field dependent positive Hall coefficient and positive magnetoresistance were observed for the specimens B-18-3 and B-18-5 and field independent Hall coefficient and negative magnetoresistance for B-18-1, as shown in Fig. 1. In B-2 series, field independent Hall coefficient and negative magnetoresistance were measured at liquid nitrogen temperature, the results on magnetoresistance being plotted in Fig. 2 together with that for B-18-1.

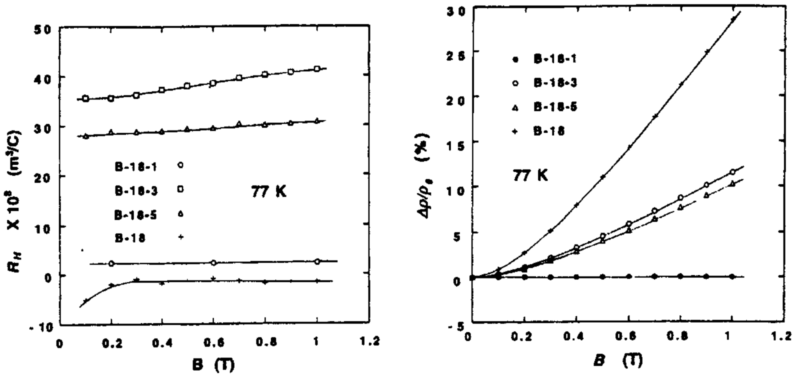

FIGURE 1 Hall coefficient R_H and magnetoresistance $\Delta\rho/\rho_0$ for specimens in B-18 series at liquid nitrogen temperature plotted as a function of magnetic field B.

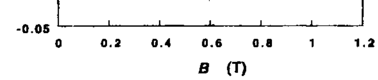

FIGURE 2 Dependence of magnetoresistance $\Delta\rho/\rho_0$ on magnetic field B for B-18-1 and specimens in B-2 series at liquid nitrogen temperature.

The values of the Hall coefficient and magnetoresistance obtained at liquid nitrogen temperature in a magnetic field of 1 T for the specimens are listed in Table IV. The concentration of boron atoms n_B substituted into graphite lattice and ionized can be estimated for the boronated specimens of B-18-1, B-2-1, B-2-2.5 and B-2-50 from the Hall coefficient data, because in these specimens the conduction carriers are only positive holes. The values are also listed in Table IV. Almost constant values of n_B in boronated specimens in B-2 series suggest the value of the concentration of substituted and ionized boron atoms at the phase boundary of the primary solid solution to be about 0.4 %.

TABLE IV Magnetoresistance $(\Delta\rho/\rho_0)_{77K,1T}$ and Hall coefficient $(R_H)_{77K,1T}$ measured at liquid nitrogen temperature and in a field of 1 T and concentration of substituted and ionized boron atoms n_B for specimens

Sample code	$(\Delta\rho/\rho_0)_{77K,1T}$ (%)	$(R_H)_{77K,1T} \times 10^8$ (m^3/C)	n_B (%)
B-18-0	28.46	-1.60	0
B-18-1	-0.0428	2.31	0.24
B-18-3	11.49	41.3	----
B-18-5	10.21	30.8	----
B-2-0	22.45	-7.38	0
B-2-1	-0.0391	1.44	0.37
B-2-2.5	-0.0396	1.29	0.41
B-2-50	-0.0242	1.30	0.40

At liquid helium temperature, the specimens B-18-1, B-2-1 and B-2-2.5 show an enhanced negative magnetoresistance. The resistivities of these specimens show a shallow minimum at a temperature around 130 K.

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