EFFECT OF BORON ADDITION AND HEAT TREATMENT ON MICROSTRUCTURE OF PETROLEUM PITCH AND PITCH-DERIVED CARBON

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Introduction

The much study has been tried to investigate the suitability of pitches as a matrix precursor for carbon-carbon (C/C) composites. To obtain the C/C composites with excellent mechanical properties, the matrix pitch is required to have high carbon yield and to be a fine mosaic texture during carbonization and graphitization [1]. It is known that the texture of pitch-derived carbon can be controlled by adding carbon black and some compounds in early stages of pitch carbonization. In graphitization stages, there are some reports described about an effect of boron addition on texture and structural changes, and mechanical properties of C/C composites [2,3]. But, there is no report on the effect of boron powder addition on the textural and structural changes for the pitch-derived carbon during early stages of pitch carbonization and graphitization totally. The aim of this study is to clarify the effect of boron additive and heat treatment temperature on textural and structural changes of pitch-derived carbon.

Experimental

Some properties of petroleum pitch (Maruzen Petroleum Chemical Co.; MP-N) used in this study are listed in **Table 1**. A metallic boron powder (Rare Metallic Co.; 1.3 μm) or a B_4C powder (Denka Co.; 1.3 μm) was added to the pitch and they were ground by an agate mortar for 1h. The boron content of the mixed powder was adjusted in the range from 0 to 10 mass%-B. The mixed powders, which was stuffed in a alumina crucible, were heat-treated at 1000°C for carbonization in N_2 gas. After heat treatment at 1000°C, a carbonaceous block was heat-treated at 2000°C for 1 hour in Ar gas. The heat-treated samples were investigated by XRD analysis for identification and quantification of graphite crystallinity. The peak separation using the Voigt function was carried out for the asymmetric peak of the graphite (004) profile. Polarized microscopic observation was also carried out for the polished section of the carbonaceous block heat-treated at 400, 425 and 450°C in N_2 gas for 1h. Average number of mesophase spheres in the carbonaceous block was counted at 9 sections of randomly selected area of 100 μm x 100 μm on the polished sample.

Results and Discussion

1. Textural changes

Figure 1 shows morphology changes with amount of boron additive for the samples heat-treated at 425°C by polarized microscopic observation. Growth of mesophase spheres were suppressed by boron addition, but the number of mesophase spheres in the samples heat-treated at 400°C, which was in the stage of mesophase nucleation, was increased with the increase of B_4C addition (**Table 2**). **Figure 2** shows amount of boron additive dependence of morphology of the samples heat-treated at 2000°C. The texture of carbonized pitch changed from flow type texture to fine mosaic one by B_4C addition. The sample with metallic boron showed almost the same tendency as the sample with B_4C.

2. Structural changes

From the XRD analysis, B_4C was identified in the sample heat-treated at 2000°C with more than 3 mass%-B additive. For the metallic boron-contained samples with 3 and 5 mass%-B and the B_4C-contained sample with 2.1 mass%-B, graphite (004) profile showed remarkable asymmetric peak, and it was found that the samples contained well-orientated graphite (**Fig. 3**).

Figure 4 shows amount of boron additive dependence of $c(002)$, $c(004)$ and $a(110)$ of the samples heat-treated at 2000°C. The c values of the samples with metallic boron and B_4C decreased and the a values of the sample increased with the increase of boron additives in the range of 0 to 3 mass%-B. In the range of 3 to 10 mass%-B, slight increase of the c values was observed and the a values of the samples with B_4C powder were smaller than that of the samples with metallic boron powder. These results indicated that 1. active boron atom diffused into carbon and rearranged graphite structure, 2. the critical values of c and a were thought to be due to the solubility limit of boron in graphite and 3. activity of boron atom in the metallic boron and B_4C was different.

Conclusions

An addition of metallic boron powder or B_4C powder into the petroleum pitch is one of the effective method for textural and structural control of the pitch-derived carbon and graphite materials.

References

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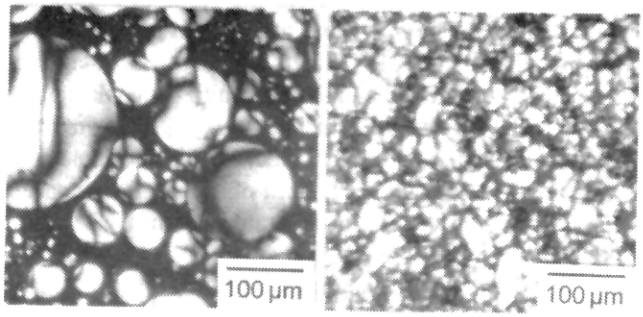
Table 1 Characteristics of petroleum pitch

xylene insoluble / mass%	63.1
pyridine insoluble / mass%	17.4
quinoline insoluble / mass%	0
softing point / °C	250
melt viscosity / poise	100 (289.4℃)

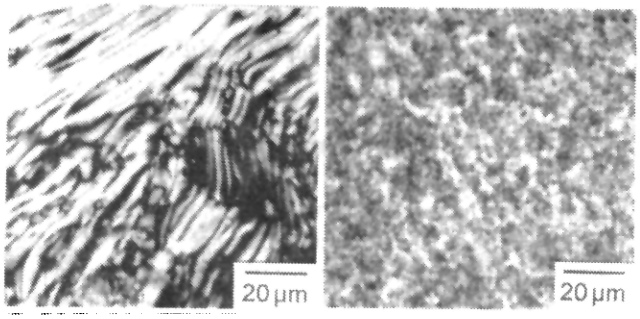
Table 2 The number of spheres in the pitch

B_4C addition / mass%	spheres x 10^3 / mm^2	
	400°C	425°C
0	2.2	1.4
1	2.3	1.5
3	4.5	1.3
5	5.1	2.9
8	4.9	4.9
10	4.9	3.9



a) 0 mass%-B **b)** 5 mass%-B (B_4C)

Fig. 1. Morphology changes with amount of boron additive for the samples heat-treated at 425°C by polarized microscopic observation.



a) 0 mass%-B **b)** 5 mass%-B (B_4C)

Fig. 2. Amount of boron additive dependence of morphology of the samples heat-treated at 2000°C.

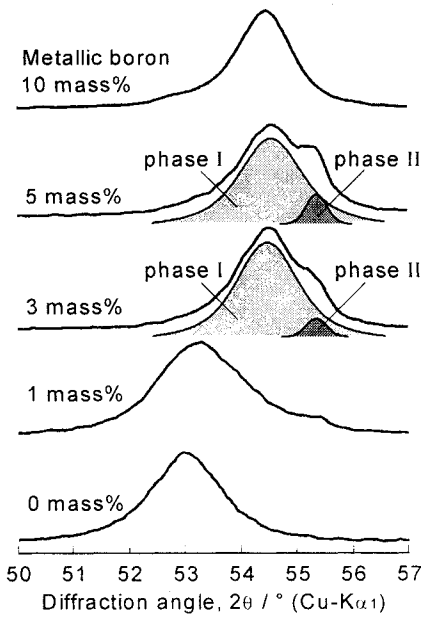


Fig. 3. Graphite (004) profile of the samples heat-treated at 2000°C.

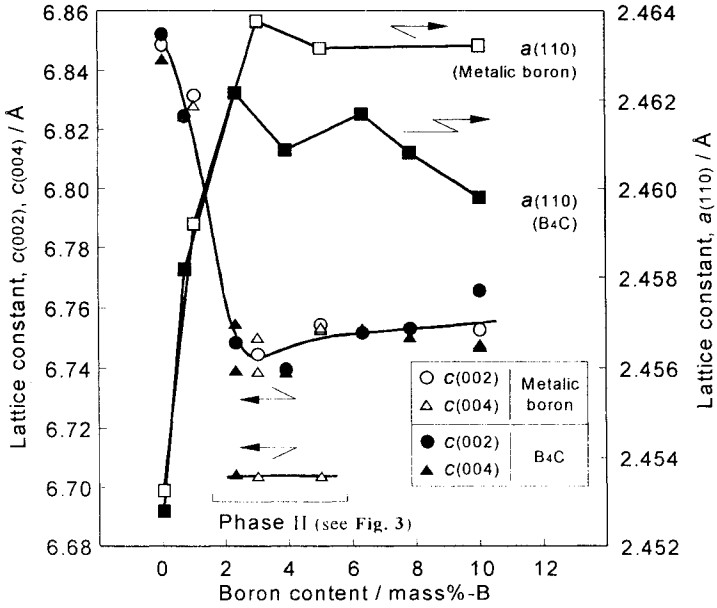


Fig. 4. Amount of boron additive dependence of $c(002)$, $c(004)$ and $a(110)$ values of the samples heat-treated at 2000°C.