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Effect of Pressure on Graphitization of Carbon. VIII. Effect of Water on the Graphitization of Carbon under High Pressure

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It has been reported[1-3] that the graphitization of carbon is promoted remarkably by pressurizing and that the heterogeneous graphitization, in which one domain in coke or char particle is completely graphitized and the other part remains ungraphitized, is observed under high pressure. The pyrophyllite, $Al_2O_3 \cdot 4SiO_2 \cdot H_2O$, which has been used as a pressure transmitting material, begins to be dehydrated around 400°C.[4] The water derived from pyrophyllite was found to accelerate the graphitization of carbon under pressure in the presence of calcite or

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[1] T. Noda and H. Kato, *Carbon*, **3**, 289 (1965).

[2] T. Noda, K. Kamiya, and M. Inagaki, This Bulletin, **41**, 485 (1968).

[3] K. Kamiya, M. Inagaki, M. Mizutani, and T, Noda, *ibid.*, **41**, 2169 (1968).

[4] C. O. Hulse and R. B. Craft, *J. Appl. Phys.*, **36**, 1593 (1965).

calcium carbonate.[5]

In the present work, the effect of water on graphitization of carbon under pressure was investigated by comparing results obtained in experiments of dry system in which calcined pyrophyllite was used as a pressure transmitting material and those in a wet system in which a small amount of water was added to carbon specimen.

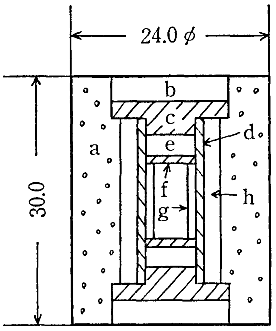

Fig. 1. Pressure cell arrangement

a. pyrophyllite
b. metal disk
c. graphite plate
d. graphite heater
e. pyrophyllite disk
f. graphite plate
g. glass-like carbon
h. boron nitride

Pressurizing of the specimen was carried out by using a piston-cylinder type vessel. The details on experimental apparatus and procedure were reported previously.[2,3] The high pressure cell arrangement used is shown in Fig. 1. In the experiments of dry system, calcined pyrophyllite disks were inserted into the artificial graphite heater (e, in Fig. 1) in place of raw pyrophyllite disks which had been used in previous works. Calcination of pyrophyllite was performed at 970°C in air. The completion of dehydration was confirmed by measuring ignition loss (about 6.2%). The mechanical strength of pyrophyllite was found to increase rapidly when calcined above 1000°C.[4] Pyrophyllite calcined at 970°C maintained the original texture, but was a little harder than the raw material. The other parts of cell arrangement were exactly the same as in the previous one. The sample used was a typical soft carbon, the polyvinyl chloride coke, PV-7, carbonized to 680°C. Heat treatment temperature of specimen (HTT) was determined from the consumed electric input-power by using the relation between temperature and consumed power established beforehand. Heat treatments were carried out at several temperatures between 1200°C and 1800°C for various residence times under 5 kbar. The carbons heat-treated under pressure showed a composite profile of (00 *l*) diffraction lines. The content of the graphitic component G_S was evaluated for the heat-treated carbon by the same procedure as reported in details previously.[1-3]

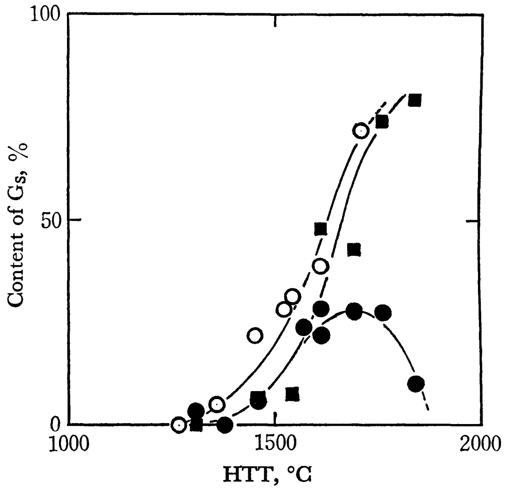

Fig. 2a. Variation of content of the component G_s with HTT for 60 min under 5 kbar.

○ with raw pyrophyllite
● with calcined pyrophyllite
■ with calcined pyrophyllite and water of 20 mg.

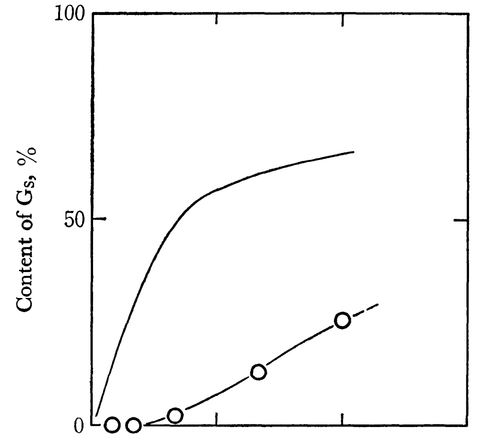

Fig. 2b. Variation of content of the component G_s with residence time at 1590°C under 5 kbar.

— with raw pyrophyllite
○ with calcined pyrophyllite

The variation of content of G_S with HTT for a constant residence time of 60 min is shown in Fig. 2a). In comparison with results of experiments where raw pyrophyllite disks were used in the graphite heater, the development of the component G_S with respect to HTT was found to be depressed in the present experiments where calcined pyrophyllite disks were used. Above 1700°C, content of G_S decreased with the increase in HTT. The decrease in the content of G_S was assumed to be due to the fact that, above this HTT, homogeneous graphitization occurred more easily than the heterogeneous one.[6] The variation of content of G_S with residence time at 1800°C under 5 kbar is shown in Fig. 2b). The variation of content of G_S in the case where raw pyrophyllite has been used is also shown. It is clear that heterogeneous graphitization was depressed without any water which originated from the dehydration of pyrophyllite. Even though the pyrophyllite disks in the heater were calcined, there remains the possibility that water might

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[5] S. Hirano, Thèses (March, 1970) Nagoya University.

[6] K. Kamiya, M. Inagaki, H. Saito, and T. Noda, This Bulletin, **43**, 926 (1970).

come into the specimen through a boron nitride sleeve from the pyrophyllite cylinder surrounding the graphite heater. In order to eliminate the possibility, the whole pyrophyllite cylinder was calcined at 970°C. Since it became harder with calcination, a part of applied load may have been supported by the cylinder and the pressure in the specimen might be much lower than expected. No exact value of pressure was figured out in this case. The heterogeneous graphitization, however, seemd to occur because a small amount of the graphitic component could be detected on (004) diffraction profile.

In the experiments of wet system, distilled water of about 20 mg was added to the sample and the heat treatments were carried out by using the same pressure cell arrangement as that shown in Fig. 1. The amount of water corresponded roughly to that derived from the complete dehydration of two disks of raw pyrophyllite in the graphite heater and was about 20 weight percent of carbon specimen. Almost the same results as those with raw pyrophyllite were obtained with this arrangement as shown in Fig. 2a).

From the results, it can be said that water accelerates heterogeneous graphitization under pressure, but has nothing to do with the occurrence of heterogeneous graphitization. Heterogeneous graphitization or two-phase graphitization, was found to be possibly caused by the stress-concentration at the contacts between the coke particles.[7]

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7) K. Kamiya, M. Inagaki, and T. Noda, *Carbon*, in press.