BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1738—1740 (1969)

Effect of Coexisting Minerals on Graphitization of Carbon under Pressure. III. Accelerating Effect of Calcium Hydroxide

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(Received October 18, 1968)

The polyvinyl chloride coke was heat-treated under the pressure of 3.2 kbar at 600—850°C for 20—240 min in a simple piston-cylinder type vessel, being sandwiched between two disks of calcium hydroxide. By electron microscopic observations, particles having the six-fold symmetry diffraction pattern of graphite single crystal were found besides particles of amorphous carbon even in the specimen heat-treated at temperature as low as 600°C. Above 800°C, the sharp peak corresponding to the graphitic component appeared on (002) diffraction profiles, overlapping with the broad band of the turbostratic component. The formation of the graphitic component seems to be related to the recrystallization of coexisting calcium hydroxide, as in the case of limestone and calcium carbonate. However, the fact that a small amount of free calcium oxide formed by the decomposition of calcium hydroxide was detected in the heat-treated carbon specimens suggests a chemical theory for the accelerating effect of calcium compounds on the graphitization of carbon under pressure.

It has been found in the previous works[1,2] that the graphitization of carbon is accelerated by the heat treatments under pressure in the presence of limestone or calcium carbonate. The beginning of graphitization, that is the appearance of the component having the graphitic structure, was found to be closely related to the recrystallization of coexisting minerals.[2]

According to Wyllie and Tuttle,[3] the melting point of calcium carbonate is lowered by the addition of water. For example, the melting point of calcium carbonate, 1310°C at 1 kbar, is depressed to 1130°C by the addition of only 8 wt% of water. In our preliminary experiment, a soft carbon was heat-treated under pressure in the presence of calcium carbonate disks, which absorbed about 8 wt% of water. The graphitization of carbon was found to start at about 1000°C, about 100°C lower than that in the case of dry calcium carbonate.[2] However, we could not draw any conclusion at that time, because the exact control of the water content of calcium carbonate disks was experimentally difficult and also it was not known whether water vapor affects the graphitization of carbon or not.

In the present work, heat treatments of carbon were performed under pressure by using disks of calcium hydroxide, whose melting point is 840°C at 3 kbar,[3] in order to confirm the relation between the graphitization of carbon and recrystallization of coexisting minerals.

Experimental and Results

The carbon sample used was the polyvinyl chloride coke (PV-7) which was used in the previous works.[1,2] Disks of calcium hydroxide, 8.0 mm in

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1) T. Noda, M. Inagaki, S. Hirano and K. Amanuma, This Bulletin, **41**, 1245 (1968).

2) T. Noda, M. Inagaki, S. Hirano and H. Saito, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **72**, 643 (1969).

3) P. J. Wyllie and O. F. Tuttle, *J. Petrology*, **1**, 1 (1960).

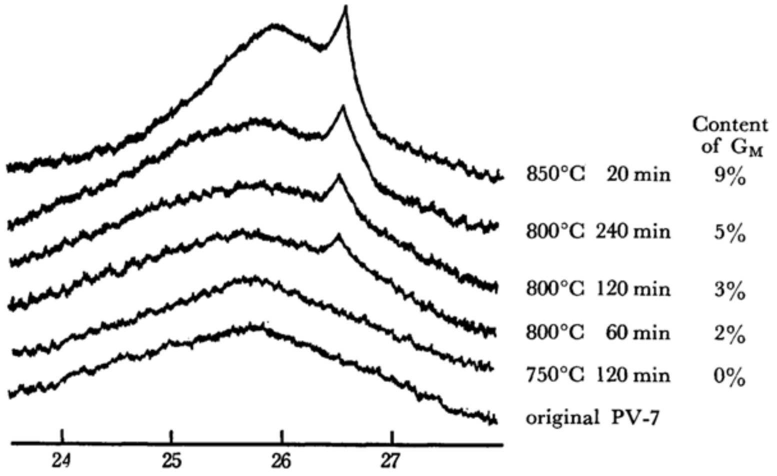

Fig. 1. Change of observed profile of (002) diffraction line with heat treatment

diameter and 3.5 mm thick, were made by compressing calcium hydroxide powder (chemical reagent grade) under 3.5 kbar. The bulk density of the disks was about 2.2 g/cm^3 (*ca.* 15% porosity). The disks and powder of calcium hydroxide were kept in an evacuated desiccator to avoid the absorption of carbon dioxide during the stroage. The heat treatments were performed at temperatures between 600 and 850°C for residence times of 20—240 min under the quasi-hydrostatic pressure of 3.2 kbar in a simple piston-cylinder type vessel. The arrangement of the pressure cell and the procedure for the heat treatments were exactly the same as used previously.[1,2] Temperature of heat treatment (HTT) was determined from input power by using the relation between temperature and input power. Pressure was calibrated by using the transition points of KNO_3 and AgI.[4]

The profile of (002) diffraction line of the central part of the heat-treated specimens was measured by using Ni-filtered Cu$K\alpha$ radiation. The same part of the specimen was dispersed in trichloroethylene by ultrasonic vibration, then supported by an evaporated carbon film, and observed by transmission electron microscope.

The carbon specimens heat-treated above 600°C were obtained as sintered cakes. In the cakes, calcium hydroxide was detected by X-ray diffraction method. The disks of calcium hydroxide recrystallized above 600°C, and were found to melt above 800°C at the part in contact with carbon specimen. Above 800°C, a small amount of calcium oxide was detected by X-ray diffraction method not only in the disks of calcium hydroxide but in the carbon specimen.

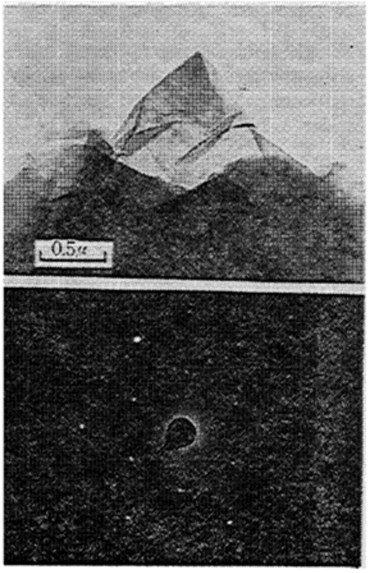

Fig. 2. Bright-field micrograph and selected area diffraction pattern of graphitic particle in carbon specimen heat-treated at 600°C for 60 min under 3.2 kbar.

Figure 1 shows the change of observed profile of (002) diffraction line with heat treatment. Above 800°C, a sharp peak is observed on a broad band. According to the same procedure reported previously,[1] the composite profile was separated graphically into two profiles for the graphitic component G_M and the turbostratic component A_M. The component G_M had almost constant c_0-spacing of 6.72 Å, and the component A_M of 6.90Å which was not so different from the original value. The content of the graphitic component G_M was obtained from the ratio of the area under the profile of G_M to the total area under the composite profile after the correction for the preferred orientation of crystallites in the specimen used for the X-ray measurement. The measured content of the component G_M is given for each profile in Fig. 1.

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[4] M. Inagaki, S. Hirano and H. Saito, *Yogyo Kyokai Shi,* **76,** 264 (1968).

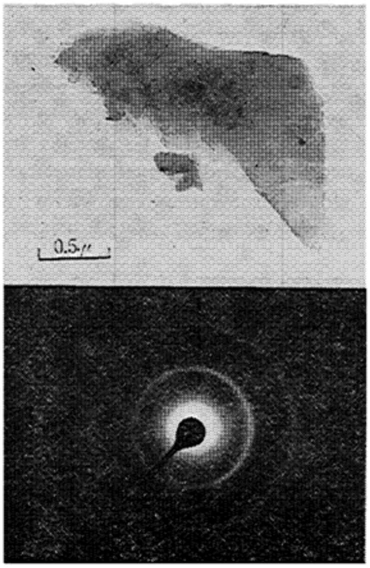

Fig. 3. Bright-field micrograph and selected area diffraction pattern of turbostratic particle in carbon specimen heat-treated at 600°C for 60 min under 3.2 kbar.

By electron microscopic observation, particles having the diffraction pattern of six-fold symmetry of graphite single crystal, were found besides particles having the turbostratic structure even in the specimen heat-treated at 600°C for 60 min. Bright-field micrographs and selected area diffraction patterns of graphitic and turbostratic particles are shown in Figs. 2 and 3, respectively.

The heat treatment above 900°C was difficult to carry out because the calcium hydroxide melts and reacts with graphite heater.

Discussion and Summary

The accelarating effect of coexisting calcium hydroxide on graphitization of carbon is more remarkable than that of calcium carbonate.(2) Even at HTT as low as 600°C, particles having the graphitic structure were found with electron microscopy. The temperature of the beginning of formation of the graphitic component is much lower than those found in the heat treatments of the same coke in the presence of limestone and calcium carbonate,(2) as well as without any minerals.(2,5) The content of the component G_M increases slightly with the increase in residence time. However, the increase in HTT seems to be more effective than the increase in residence time, when the result at 850°C for 20 min is compared with that at 800°C for 60 min.

A close relation seems to be present between the graphitization of carbon under pressure in the presence of foreign minerals and the recrystallization of the coexisting minerals, when a conclusion can be drawn from the present result together with the results of the works on the effect of calcium carbonate previously reported.(1,2) However, the fact that a small amount of free calcium oxide was found in the heat-treated specimens suggests a chemical theory of acceleration of graphitization. Active calcium oxide formed by the decomposition of calcium hydroxide can react at relatively low temperatures, *vis.*, 600°C, with amorphous carbon to form an intermediate compound, probably calcium carbide, which decomposes inversely to form stable graphite and calcium oxide. In order to verify this theory, more detailed and extensive experiments will be needed.

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