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Effect of Coexisting Minerals on the Graphitization of Carbon under Pressure. V. Distribution of Calcium and Graphitic Components in Heat-Treated Carbon Specimens

Shin-ichi HIRANO, Michio INAGAKI and Hajime SAITO

Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya

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The accelerating effect of coexisting calcium compounds on the graphitization of carbon under pressure has been reported.[1-4] The mechanism of the accelerating effect on the graphitization seems to consist of the formation and the successive decomposition of calcium carbide and/or the formation and the successive reaction of calcium metal and carbon monoxide.

In the present work, the distribution of calcium in carbon specimens heat-treated in the presence of calcium compounds under pressure was determined by using an electron microprobe analyser. The distribution was compared with that of the graphitic component G_M which was determined by the X-ray diffraction method.[1]

Specimens were prepared from a polyvinylchloride coke, carbonized at 680°C (PV-7) by heat treatment under 3.2 kbar for 60 min at 1090 and 1360°C in the presence of calcium carbonate, and at 1100, 1400 and 1500°C in the presence of calcium oxide precalcined at 920°C. All the five specimens were obtained as caked pieces.

Details on the apparatus and the procedure for the preparation of the caked specimens were reported previously.[2,4] The size of the caked specimens was about 7.6 mm in diameter and 2.5 mm in thickness.

The specimens were cut into halves (a) and (b) across their diameter, one half for the electron microprobe analysis and the other for the X-ray diffraction analysis.

Sample (a) was mounted in resin. The surface of the cross section was ground on an abrasive paper and finished to a very flat surface by polishing on a felt with very fine corundum powder dispersed in ethanol in order to avoid reactions between calcium compounds and water. Electron beam of 100μ width was scanned along the thickness (h-direction) and also along the radial direction (r-direction) on the polished section of the caked specimen (Fig. 1).

For X-ray diffraction analysis, sample (b) was cut down to pieces along the thickness and also

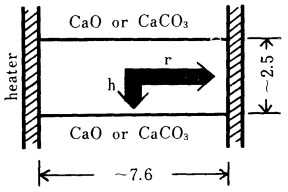

Fig. 1. Scheme of direction scanning electron beam.

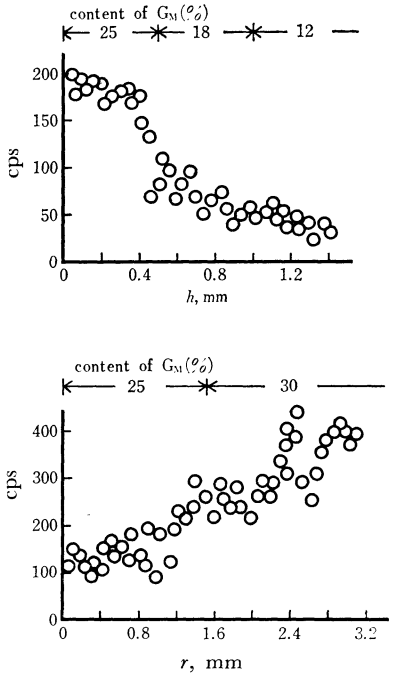

Fig. 2. Relation between distribution of calcium and content of graphitic component G_M in the specimen heat-treated at 1360°C under 3.2 kbar in the presence of calcium carbonate.

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*, **72**, 643 (1969).

3) T. Noda, M. Inagaki, S. Hirano and H. Saito, This Bulletin, **42**, 1738 (1969).

4) S. Hirano, H. Saito and M. Inagaki, *ibid.*, **43**, 2599 (1970).

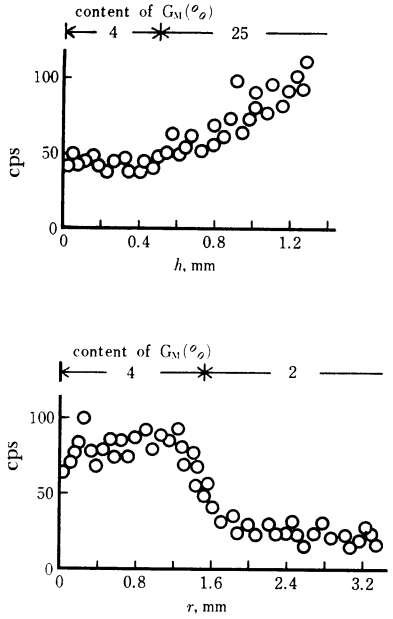

Fig. 3. Relation between distribution of calcium and content of graphitic component G_M in the specimen heat-treated at 1100°C under 3.2 kbar in the presence of calcium oxide.

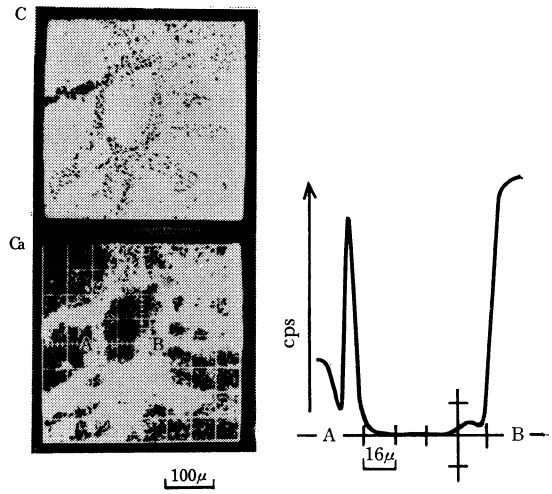

Fig. 4. a) X-ray fluorescence photograph of carbon in the central area of the specimen heat-treatd at 1360°C under 3.2 kbar in the presence of calcium carbonate.
b) X-ray fluorescence photograph of calcium in the same area as in Fig. 4a.
c) Concentration variation of calcium scanned from A to B in Fig. 4b.

along the radial direction, and the content of graphitic component G_M was measured for each piece.

Two examples of results are shown in Figs. 2 and 3. In the presence of calcium carbonate, the content of graphitic component G_M was found to be larger in the central part of the specimen than in the peripheral part which was close to carbonate layer. This distribution of graphitic component was attributed to a temperature gradient in the specimen.[2] In the presence of calcium oxide, however, the reverse distribution of graphitic component G_M was observed,[4] that is, the content of graphitic component was smaller in the central part than in the peripheral part. The reason for this difference in the distribution of graphitic component in the heat-treated carbon specimens is not clear. However, in both cases the part having a larger content of graphitic component G_M has larger calcium concentration. The same relation was observed for all the specimens.

X-ray fluorescence photographs of carbon and calcium in the central area ($400\,\mu \times 400\,\mu$) of a specimen are shown in Figs. 4a and 4b. The concentration variation of calcium scanned with electron beam width of $10\,\mu$ from A to B (Fig. 4 b) across a carbon grain is shown in Fig. 4c. From the figures we see that calcium was accumulated in the boundaries of carbon grains. The concentration of calcium in the carbon grain decreased very steeply in the layer about $10\,\mu$ from the boundary and only a minute amount of calcium was detected in the inner part.

The fact that the content of graphitic component G_M and the concentration of calcium were closely related to each other supports the proposed mechanism of the acceleration of graphitization in the presence of calcium compounds,[4] *viz.*, the intermediate formation of calcium carbide and/or calcium metal.

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