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Effect of Coexisting Minerals on Graphitization of Carbon. I. Heat Treatments of Carbon under 3 kbar in the Presence of Limestone

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The effect of the presence of limestone on the graphitization of carbon was investigated by the heat treatments of the carbon sample under the quasi-hydrostatic pressure of 3.2 kbar. The carbon sample used was a coke (PV-7) prepared by carbonization of polyvinylchloride up to 680°C. It was placed between two disks of limestone so as to make a sandwich-type specimen. The heat treatments were performed in a simple piston-cylinder type vessel at various temperatures of 800—1300°C for 20—240 min. Above 1000°C, the carbon specimens were obtained as caked tablets. The profiles of (002) diffraction line of these carbon tablets were found to be composite, consisting of a sharp component profile at 26.5° and a broad one at lower angle than 26.2°. The component G_M corresponding to the sharp component profile seemed to have the graphite structure. The content of the component G_M increased very rapidly with the increase in heat treatment temperatures above 1000°C. Phenomenally, the developement of the graphite structure seemed to be closely related to the recrystallization and the melting of coexisting limestone, but some chemical effects should not be excluded.

In the nature, a good quality of graphite crystals has been found in beds of metamorphic rocks, such as limestone. The temperature-pressure condition of the graphite formation was estimated geologically as the temperature of several hundreds degrees and the pressure of several kilobars. On the other hand, it has been found in a laboratory that the carbon is graphitized very rapidly at around 1500°C under the pressure of 10 kbar[1] and even under 5 and 3 kbar.[2] However, any indication of the presence of graphite structure could not be found by X-ray diffraction at temperatures lower than 1300°C. Therefore, the limestone might have some effect on graphitization, like the pressure and the temperature have.

The purpose of the present work is to see the effect of the presence of limestone on the graphitization of carbon under the pressure.

Experimental and Results

The carbon sample used was a coke (PV-7) prepared by carbonization of polyvinylchloride and consequently heated up to 680°C. The grain size of the sample was limited in the range between 0.1 and

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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).

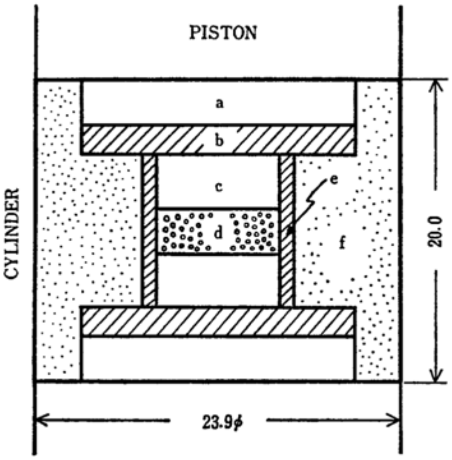

Fig. 1. Arrangement of the pressure cell used for heat treatments of carbon in the presence of limestone.

a: steel disk, b: graphite disk, c: limestone, d: carbon specimen, e: graphite tube heater, f: pyrophyllite

0.4 mm. Limestone disks of 3.5 mm thick and 8.0 mm in diameter were cut out from Fusulina limestone from Akasaka, Gifu-ken, Japan. The carbon sample of 180 mg was placed between two disks of limestone so as to make a sandwich-type specimen as shown in Fig. 1. A high pressure apparatus used was a simple piston-cylinder type one, which was made from a tool steel. The bore and outer diameter were 24 and 50 mm, respectively, and the cylinder was protected by a soft steel guard ring. The heat treatments were performed at various temperatures between 800 and 1300°C for 20—240 min under the quasi-hydrostatic pressure of 3.2 kbar. The heat treatment temperature (HTT) was estimated from input power using the relation between temperature and input power, which was determined beforehand using a chromel-alumel thermocouple inserted in the carbon specimen arranged in the same way as in the heat treatments. The temperature was controlled by adjusting the input power. The pressure was calibrated by using KNO_3 and AgI.[3)]

In comparison, the carbon sample was heat-treated under the same pressure without limestone, replacing limestone disks (in Fig. 1) by glassy carbon plates and pyrophyllite disks. Glassy carbon plates were used to prevent the direct contact of carbon specimen with pyrophyllite disks.

Profiles of (002) diffraction line of the heat-treated specimens were measured by a recording X-ray diffractometer using Ni-filtered Cu$K\alpha$ radiation. Specimens for X-ray diffraction were taken from the central part of heat-treated carbon tablets.

Above 1000°C, the carbon specimens heat-treated with limestone were obtained as caked tablets. In the tablets, appreciable amounts of calcium carbonate were detected by X-ray diffraction method and the amounts increased with HTT. Limestone disks themselves were found to have recrystallized above 1000°C. The thickness of recrystallized part of limestone increased with the increase in HTT and residence time. Grains of recrystallized limestone grew along the axial direction of the heater (Fig. 2), to which the temperature gradient was parallel. Limestone was found to have melted above 1250°C.

Higher temperature

Lower temperature side

Fig. 2. Growth of grain of recrystallized calcite in contact with carbon sample treated at 1120°C for 60 min under 3.2 kbar (under polarized light).

Profiles of (002) diffraction line of the carbon samples heat-treated with linestone above 1000°C were found to be composite, consisting of a relatively sharp profile at 26.5° in 2θ (6.72 Å in the c_0-spacing) overlapping on a broad profile at an angle lower than 26.2°. With the increase in HTT and residence time, the sharp profile at 26.5° became stronger and narrower, while the broad profile shifted to higher angles. The profile of (002) diffraction line of the carbon sample heat-treated without limestone had only a hump at about 26.5° above 1300°C. The representative changes of the profiles with HTT are shown in Fig. 3 a) and b).

The composite profiles were graphically separated into two component profiles. The schema of the separation is shown in Fig. 4: After the observed composite profile (1) is corrected for the Lorentz-polarization, atomic scattering and absorption factors by conventional methods[4)] (the profile (2)), the high angle side of the sharp profile is folded to the low angle side and the profile (3) is obtained. Subtracting the profile (3) from the composite profile (2), the balance profile (4) is obtained. Since the profile (4) is not symmetrical usually, however, the profile (5) for the broad component is obtained by folding the low angle side of the profile (4) at the angle of the maximum intensity. Finally, the profile (6) for the sharp component is obtained by subtracting the profile (5) from the profile (2). Some trial and error

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3) M. Inagaki, S. Hirano and H. Saito, to be published.

4) W. R. Ruston, *Fuel*, **32**, 53 (1953).

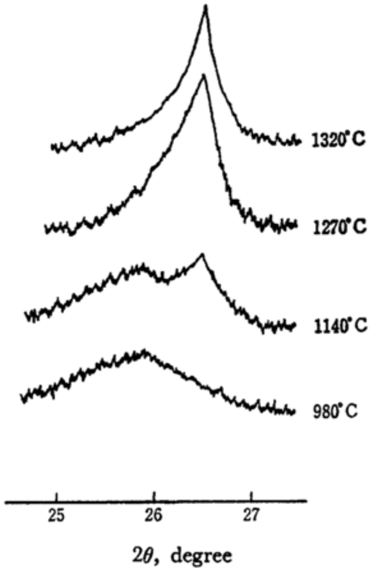

Fig. 3 (a).

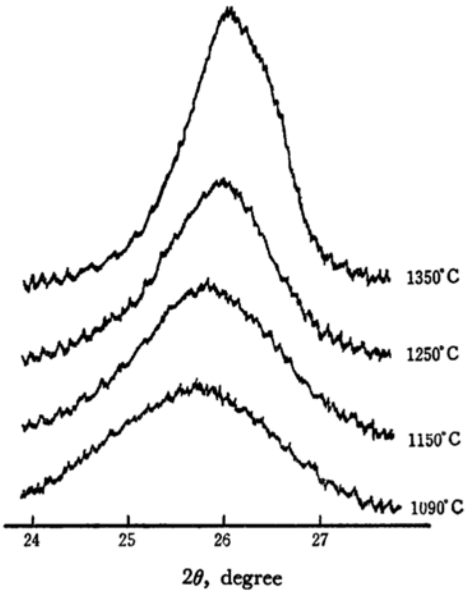

Fig. 3 (b).

Fig. 3. Changes of profiles of (002) diffraction line with HTT for 60 min.

a) treated in the presence of limestone
b) treated without any minerals

adjustments are needed in order to obtain the symmetrical component profiles and to fit the profile composed from the component profiles satisfactorily well with the original composite profile. The components which correspond to the sharp and broad component profiles are designated as G_M and A_M, respectively.[*2]

The c_0-spacing of the two components was measured from the separated profiles (5) and (6), and the result is shown in Fig. 5. The c_0-spacing of the component G_M is almost constant and around 6.72 Å, while the c_0-spacing of the component A_M decreased

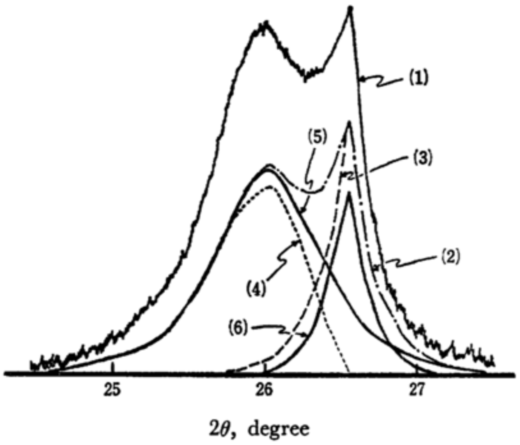

Fig. 4. Schema of separation of the composite profile.

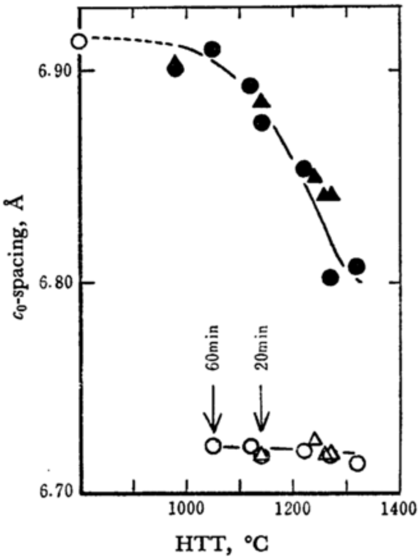

Fig. 5. Variation of c_0-spacing of two components, G_M and A_M, with HTT.
Above the temperature marked by the arrow, the component G_M could be observed on the diffraction profile.

G_M	A_M	
△	▲:	20 min
○	●:	60 min

[*2] For the soft and hard carbons heat-treated under pressure without any minerals, the composite profiles were observed and separated into two components G_S and A_S, and G_H and A_H, respectively. In the present work, the suffix " M " was used for each component in order to distinguish from the components reported previously.[2,5)]

5) M. Inagaki, K. Kamiya, M. Mizutani and T. Noda, to be published.

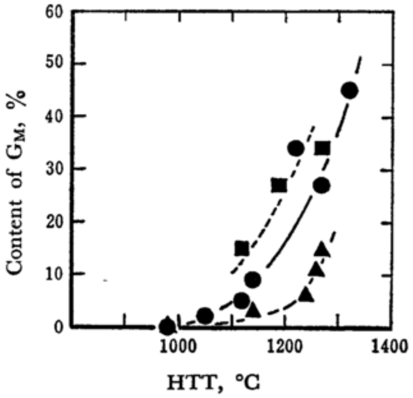

Fig. 6. Variation of content of the component G_M with HTT.
▲, 20 min ●, 60 min ■, 240 min

gradually from 6.91 to 6.80 Å. It is reasonable to take the component G_M as the graphitic component, because the component G_S having the c_0-spacing of 6.72 Å was reported to have the graphite structure.[2,6] Therefore, the content of the component G_M was used as a measure of graphitization of the sample. The content of the component G_M was obtained from the ratio of the area under the profile of the component G_M to the total area under the composite profile. The ratio of areas was corrected for the preferred orientation of crystallite in the specimens for X-ray diffraction, when the ratio was converted to the content of the component G_M. Changes of the content of the component G_M with HTT are shown in Fig. 6 for several residence times.

Discussion and Summary

The graphitization of carbon under pressure is evidently accelerated by limestone. Under 3 kbar in the presence of limestone, the component G_M, which seems to have the graphite structure, begins to appear just above 1000°C. This temperature is much lower than that in the case of the heat treatment of the same sample PV-7 under the same pressure without limestone.

The content of the component G_M increased very rapidly with the increase in HTT. The content was about 45% with the heat treatment at 1300°C for 60 min. However, with a longer treatment as 240 min, only a small increase in the content was observed.

Phenomenally, the developement of the graphite structure seems to be closely related to the recrystallization and the melting of the coexisting limestone, but some chemical effects should not be excluded. In order to know the mechanism of the effect of limestone on the graphitization of carbon under pressure, more precise experiments are needed.

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6) M. Inagaki, K. Kamiya and T. Noda, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind.Chem. Sect.*), **71**, 652, 812 (1968).