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Effect of Pressure on Graphitization of Carbon. VI. Normal Pressure Heat Treatment of Soft Carbon Pre-Heat-Treated under High Pressure

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Three different samples of polyvinylchloride coke (designated as N-1, N-2, and N-3 which were pre-heat-treated at 1470, 1590, and 1620°C, respectively, under 5 kbar) were heat-treated in a flow of nitrogen under normal pressure. Process of graphitization in these samples was investigated by analyzing (004) diffraction profile. Sample N-1 has a symmetrical profile and consists only of the trubostratic component A_S. Samples N-2 and N-3 have a composite profile and are composed of the turbostratic component A_S and the graphitic component G_S. Only the profiles corresponding to the turbostratic component A_S of these samples shift gradually to higher angle together with sharpening when the heat treatment temperature under normal pressure increases. Changes in c_0-spacing and crystallite size L_C of the component A_S with heat treatment temperature follow the same course of change as in those of the original polyvinylchloride coke. However, heat treatment of the sample under normal pressure did not affect the quality and quantity of the component G_S which had been formed by the pre-heat-treatment under high pressure. These results indicate that the pre-heat-treatment of soft carbon under high pressure has no accelerating effect on the graphitization of the carbon in the subsequent heat treatment under normal pressure.

Polyvinylchloride coke PV-7, a soft carbon, has been found to be graphitized very rapidly at as relatively low a temperature as 1400—1500°C under high pressure above 3 kbar.[1–3] The process of its graphitization is divided into two stages on the basis of the change in the profile of (00*l*) diffraction line.[2,3] In the first stage, the structural component of the carbon is the turbostratic one A_S, of which the c_0-spacing is larger than 6.85 Å. In the second stage, however, two components A_S and G_S, having the turbostratic and graphitic structures, respectively, coexist in the sample and no component having an intermediate structure is observed. In this stage, the graphitization proceeds through the direct transformation from turbostratic carbon to graphite, which can be detected by the composite structure of the profile of (00*l*) diffraction line.[2,3] Such a change in the profile of (00*l*) diffraction line contrasts with that observed by the heat treatment under normal pressure.[4] It was confirmed that the composite profile observed in the sample heat-treated under pressure was not due to the temperature and pressure gradients in the specimen.[5] A similar abrupt transformation was also observed on a hard carbon PH-7 prepared from phenolformaldehyde resin.[6,7]

In the present work, in order to know whether the after-effect of high pressure heat treatment of carbon can be detected in the graphitization under normal pressure, the soft carbon PV-7 pre-heat-treated at several temperatures under 5 kbar was re-heat-treated under normal pressure. Structural changes by the re-heat-treatment were followed by X-ray diffraction.

Experimental

Pre-heat-treatment under High Pressure. A simple piston-cylinder type high pressure vessel made of tool steel was used. Its bore diameter was 30 mm. The pressure cell arrangement was similar to that previously reported,[2] except that the graphite tube heater used was larger, *i. e.* inner diameter 8 mm, outer diameter 10 mm and length 21 mm, and that the glassy carbon tube in the graphite heater was not used. The weight of the sample was about 450 mg, almost four

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

[4] M. Inagaki, K. Kamiya and H. Saito, TANSO No. 54, 84 (1968).

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

[6] K. Kamiya, M. Inagaki, M. Mizutani and T. Noda, This Bulletin, **41**, 2169 (1968).

[7] K. Kamiya, S. Yugo, M. Inagaki, H. Saito and T. Tsuzuku, *ibid.*, **41**, 2782 (1968).

times the previous one. The contamination of the heat-treated samples was scarcely detected by X-ray analysis. Heat treatment temperature was estimated from the input power by using the relation between input power and temperature, which was determined especially for the present cell arrangement.

The coke PV-7 was heat-treated at three different temperatures of 1470, 1590, and 1620°C for the residence

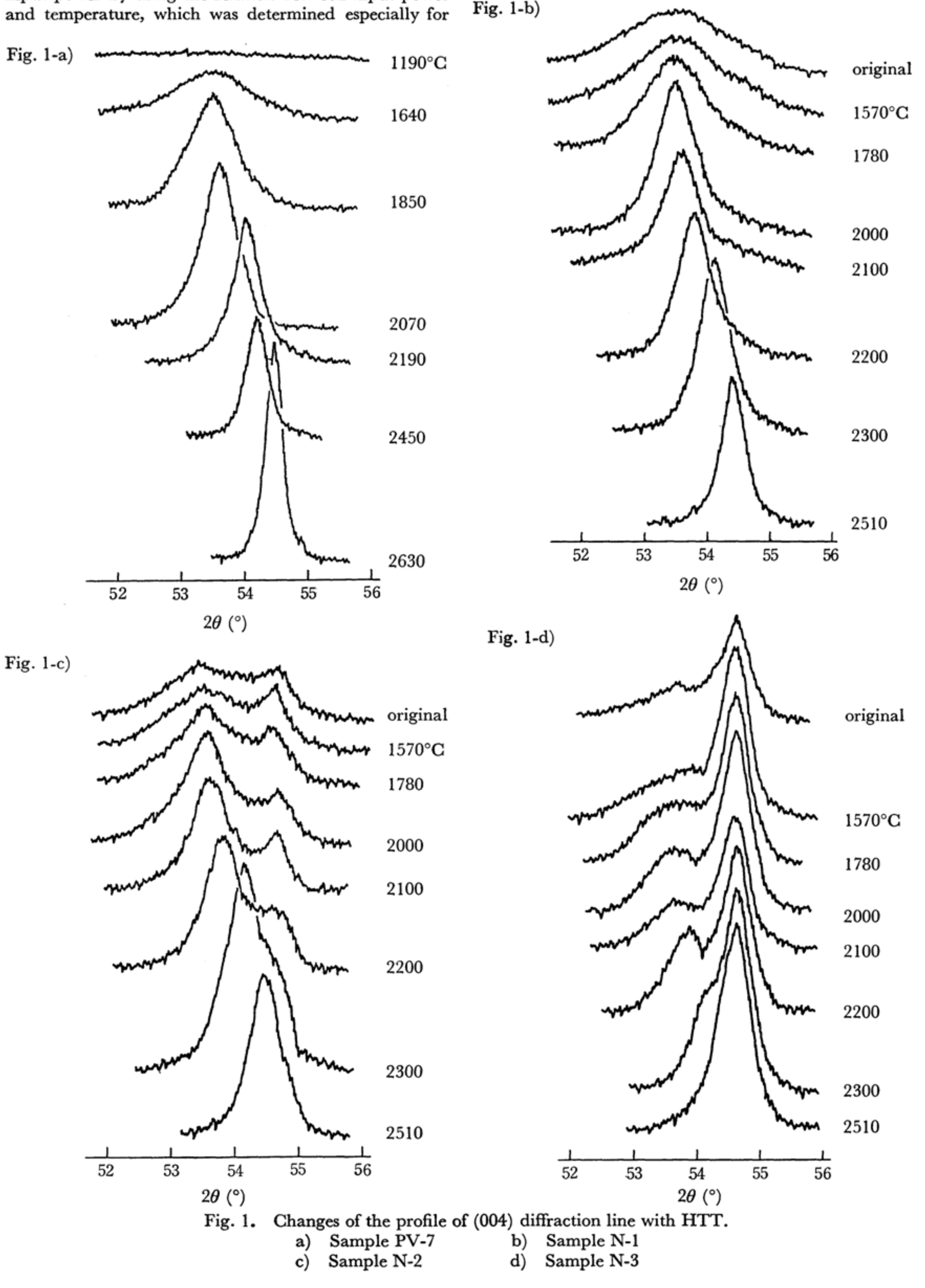

Fig. 1. Changes of the profile of (004) diffraction line with HTT.
a) Sample PV-7 b) Sample N-1
c) Sample N-2 d) Sample N-3

time of 20 min under a quasi-hydrostatic pressure of 5 kbar. The heat-treated specimens were obtained as sintered cakes *ca.* 8 mm in diameter and *ca.* 6 mm long. A tablet 8 mm in diameter and 2 mm thick was sampled from the central part of the sintered cake of each heat-treated specimen. For this central part, temperature gradient during the heat treatment under 5 kbar was scarcely observed.[5] To minimize the effect of the possible gradients of temperature and pressure along the radial direction of the tablet on the final results, each tablet of the specimen was cut into eight small pieces through the center of the tablet and these small pieces were used for the re-heat-treatment under normal pressure at different temperatures. The 1470°C-, 1590°C-, and 1620°C-treated samples were designated as N-1, N-2, and N-3, respectively, in the present work.

Re-heat-treatment under Normal Pressure. The re-heat-treatment under normal pressure was conducted at temperatures ranging from 1190 to 2630°C for the residence time of 60 min in a flow of nitrogen by using a graphite tube resistance furnace. During the heat treatment, small pieces of the samples N-1, N-2, and N-3, and the original coke PV-7 were placed in graphite crucibles separately and the crucibles were put in a large graphite container.

Heat treatment under normal pressure was performed as follows. After the central part of the graphite heater was heated to a desired temperature, the graphite container, which contained the four samples and was placed beforehand in a cold part of the heater, was pushed into the central part. It required about 10 min to heat the crucible to the desired temperature. After 60 min residence, the graphite container was pushed out to a cold part on the opposite side of the heater and then the temperature of the furnace was raised in order to perform another heat treatment. The temperature of heat treatment was determined by focusing an optical pyrometer on the surface of the graphite crucible through a hole drilled in the container wall. The optical pyrometer used was calibrated to the standard lamp for pyrometry. The temperature of the furnace was kept constant within ±10°C by adjusting the input power manually.

X-Ray Analysis. The profiles of (004) diffraction line of all heat-treated samples were measured by using Ni-filtered Cu*Ka* radiation and a recording goniometer. The specimens for X-ray analysis were 0.2 mm thick. The heat-treated samples of PV-7 and N-1 had symmetrical profiles of (004) diffraction line, as can be seen in Fig. 1-a) and b). For the sample producing such a symmetrical profile, c_0-spacing and crystallite size L_c were measured by the usual method[8] referring to the inner standard of silicon. However, profiles of all samples derived from N-2 and N-3 had a composite structure, as can be seen in Fig. 1-c) and d). The composite profile was separated into the profiles of two components A_S and G_S, which were on low and high angle side, respectively.[*1] A similar procedure to that reported previously[3] was applied to the separation of the composite profile. In the present work, the angular position of the component profile on low angle side could not be fixed at a constant value, but estimated very easily because the separation of two component profiles was relatively large. Almost all the composite profiles could be separated into two symmetrical component profiles after one or two trials. For each separated component profile, c_0-spacing and crystallite size L_c were measured by referring to the inner standard of silicon. The content of the component G_S was evaluated by measuring the ratio of area under the profile of G_S to the total area of the composite profile and correcting it for the crystallite orientation.[2,3]

Results

Changes of the profile of (004) diffraction line with temperature of heat treatment under normal pressure (HTT) for the samples PV-7, N-1, N-2, and N-3 are shown in Figs. 1-a), b), c) and d), respectively. For the sample PV-7, all the profiles are symmetrical and shift to a higher angle together with sharpening as HTT increases. Sample N-1 is found to have almost the same tendency of change in the profile as that of the sample PV-7. For samples N-2 and N-3 of which the originals have composite profiles, only the profile corresponding to the component A_S shift to a higher angle with sharpening as HTT increases, but the profile corresponding to the component G_S does not seem to change in position, relative intensity and sharpness with heat treatment.

Changes of c_0-spacing and crystallite size L_C with HTT for the samples are shown in Figs. 2-a) and b), respectively. Sample PV-7 becomes to have almost the same values of c_0 and L_C as those of the component A_S of the other samples at about 2000°C and above that temperature the changes in c_0 and L_C of A_S of the samples N-1, N-2, and N-3 as well as PV-7 follow the same course of change with HTT. On the other hand, the graphitic component G_S which has been formed by the pre-heat-treatment under high pressure has the constant c_0-spacing of 6.72 Å and the crystallite size L_C of around 300 Å during the heat treatment under normal pressure.

Changes of content of the component G_S with HTT are shown in Fig. 3. The content of the component G_S does not change by the re-heat-treatment under normal pressure. Sample N-1 does not have any amount of the component G_S originally.

Discussion

The graphitization under pressure above 3 kbar proceeds in two stages.[2,3] In the first stage the c_0-spacing of carbon decreases to *ca.* 6.85 Å and in the second stage a new component having graphitic structure develops in the original turbostratic car-

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[8] M. Inagaki and T. Noda, This Bulletin, **35**, 1652 (1962).

[*1] In a previous work,[2] the component A_s had the c_0-spacing larger than 6.85Å. In the present work, however, the component corresponding to the separated profile on low angle side was designated as A_s, even if it has the c_0-spacing smaller than 6.85 Å.

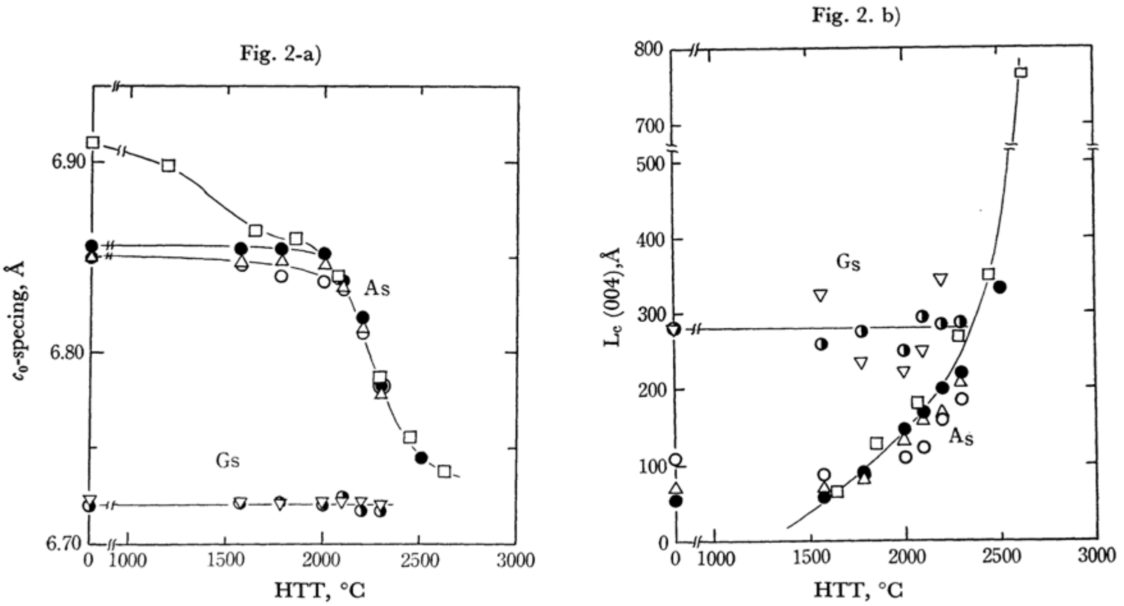

Fig. 2. Changes of the X-ray parameters of the component As and Gs with HTT.
a) c_0-spacing, b) crystallite size L_c
As □: PV-7, ●: N-1, △: N-2, ○: N-3
Gs ▽: N-2, ◑: N-3

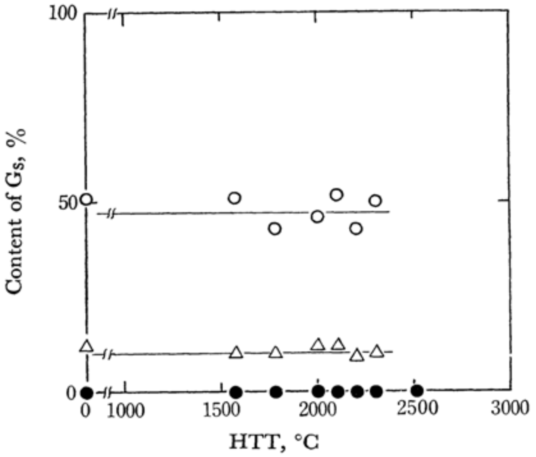

Fig. 3. Change of content of the graphitic component Gs with HTT.
●: N-1, △: N-2, ○: N-3

bon, *i.e.*, a sharp peak corresponding to c_0 of 6.72 Å develops besides the original broad peak of turbostratic carbon, making (00*l*) diffraction profile composite. This direct transformation of turbostratic carbon to graphite indicates that graphitization under high pressure proceeds heterogeneously on the scale of crystallite and can be called a heterogeneous graphitization. On the other hand, the graphitization under normal or reduced pressure proceeds homogeneously. The c_0-spacing decreases continuously to the value of graphite, and this change is detected as a continuous shift of a symmetrical profile of (00*l*) diffraction line to higher angle.

The sample N-1 has a symmetrical profile and its c_0-spacing is 6.856 Å, *i.e.*, it is on the first stage of graphitization process and consists only of turbostratic component A_S. The samples N-2 and N-3 give composite profiles and consist of turbostratic component A_S and graphitic component G_S, *i.e.*, they are on the second stage of graphitization process. The component A_S, which did not transform directly to graphitic component during the pre-heat-treatment under high pressure, was found to be graphitized homogeneously when the samples N-1, N-2 and N-3 were re-heat-treated under normal pressure. However, the re-heat-treatment of the samples under normal pressure did not affect the quality and quantity of the component G_S which has been formed by the pre-heat-treatment under high pressure.

These results indicate that the pre-heat-treatment of a soft carbon under high pressure has no accelerating effect on the graphitization of the carbon in the subsequent heat treatment under normal pressure, and that the direct transformation of the turbostratic component to graphitic component by the application of external stress causes the observed heterogeneous graphitization of soft carbon.

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