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Effect of Pressure on Graphitization of Carbon. IV. Abrupt Graphitization of Hard Carbon under 5 kbar

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A hard carbon, phenolformaldehyde resin char carbonized to 700°C, was heat-treated under a quasi-hydrostatic pressure of 5 kbar at various temperatures between 1100—1800°C for the residence times of 3, 20 and 60 min. The graphitization process of the hard carbon under pressure consisted of three stages. In the first stage of the graphitization, the profile of (002) diffraction line was symmetrical. It means that there is only one component A_H in the sample. In the second and third stages of graphitization, the (002) profile became composite. In the second stage, three components A_H, G'_H and G''_H coexisted in the sample. The sum of the contents of the components G'_H and G''_H was less than 20% and increased gradually with heat treatment temperature. In the third stage, two components A_H and G''_H coexisted. The content of the component G''_H increased abruptly up to more than 70% at about 1400, 1500 and 1700°C for the residence time of 60, 20 and 3 min, respectively. The components A_H and G''_H have the turbostratic and graphitic structures, respectively. The component G'_H seemed to have the intermediate structure between turbostratic and graphitic structures.

Hard carbons or non-graphitizing carbons are hardly graphitized even at very high temperatures such as 3000°C. So-called two- or three-phase graphitization was often observed for hard carbons at high temperatures of heat treatment.[1-4] Recently, Oberlin and Rousseaux gave a beautiful representation of two-phase graphitization of a sugar charcoal by means of dark field electron micrographs and electron microdiffraction.[5] On the other hand, soft carbons are easily graphitized under the same condition and multi-phase graphitization has never been observed. Under high pressure above 3 kbar, the graphitization of soft carbons was found to proceed very rapidly at relatively low temperatures as 1500°C and the phenomenon similar to the two-phase graphitization was observed.[6,7] It was found that even glassy carbon, a typical hard carbon, was graphitized around 1500°C under 10 kbar.[6] In the present work, phenolformaldehyde resin char, one of hard carbons, was heat-treated under the pressure of 5 kbar at various temperatures for three different residence times. The graphitization process of the sample was precisely followed by analyzing the profile of (002) diffraction line and was compared with that of soft carbon under the same pressure.

Experimental and Results

The sample used was a carbon prepared at 700°C from phenolformaldehyde resin, which was made by a conventional method using ammonium hydroxide as catalyst. The sample was a hard carbon and was

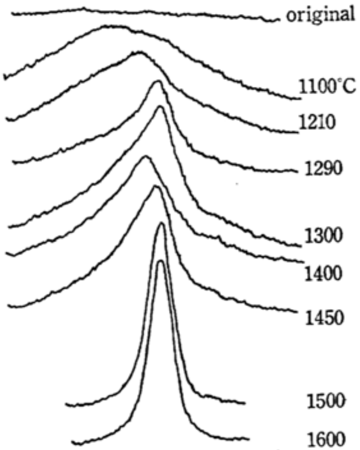

Fig. 1. Change of profile of (002) diffraction line of the hard carbon, heat-treated under 5 kbar for 60 min, with HTT.

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1) R. E. Franklin, *Proc. Roy. Soc.*, **A 209**, 196 (1951).
2) H. Akamatu, H. Inokuchi, H. Takahashi and Y. Matsunaga, This Bulletin, **29**, 574 (1956).
3) M. Inagaki and T. Noda, *ibid.*, **35**, 1652 (1962).
4) H. Honda and K. Kobayashi, private communication.
5) A. Oberlin and F. Rousseaux, *Compt. Rend.*, **265**, C 436 (1967).
6) T. Noda and H. Kato, *Carbon*, **3**, 289 (1965).
7) T. Noda, K. Kamiya and M. Inagaki, This Bulletin, **41**, 485 (1968).

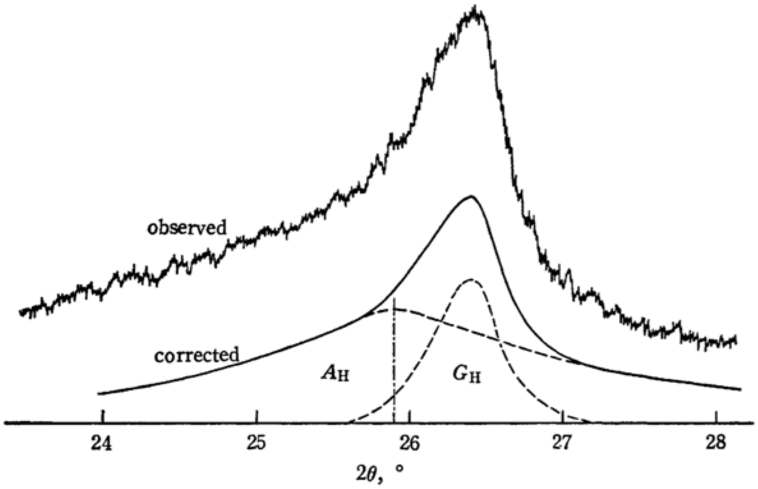

Fig. 2. Schema of separation of composite profile observed on the hard carbon.

named as PH-7 in order to make easy to distinguish from the sample of a soft carbon PV-7, which was used in the previous works.[6-9] The particle size of the sample was limited in the range of 0.1—0.4 mm. The used high pressure apparatus and the arrangement of specimen cell were the same as reported previously.[7] The heat treatments of the sample were performed under a quasi-hydrostatic pressure of 5 kbar at various temperatures between 1100—1800°C for residence times of 3, 20 and 60 min. The heat treatment temperature (HTT) was evaluated from the electric input power by using the relation between temperature and input power, which was determined beforehand for the same arrangement and sample. For the heat-treated sample, the profile of (002) diffraction line was measured by using Ni-filtered Cu*Kα* radiation and a recording goniometer.

Change of (002) diffraction profile with HTT for the residence time of 60 min. is shown in Fig. 1. Above 1200°C, the profile appeared to be composite, consisting of at least two component profiles. Such a composite profile was separated into the component profiles by almost the same procedure as previously described.[7,8] In the present work, however, the profile on the low angle side is folded at the angular position where the tail of the folded profile coincides well with the tail of the composite profile on the high angle side (Fig. 2). When this profile on the low angle side is subtracted from the composite profile, the balance gives another component profile, which is on the high angle side. In the present work, these two components corresponding to the profiles on the low angle side and high angle side are designated as A_H and G_H, respectively.*2

For each separated profile, the c_0-spacing was measured by referring to the inner standard of silicon and the area under the profile was measured by using a planimeter. In order to obtain the content of the component G_H, the ratio of the area under the profile for the component G_H to the total area of the composite profile was obtained and then corrected for the preferred orientation of crystallite in the specimen by using the same calibration curve as reported previously.[8] Changes of c_0-spacing of two components with HTT are shown in Fig. 3 and the

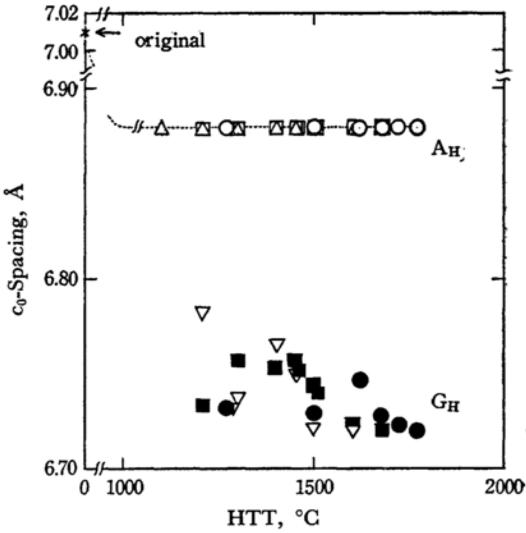

Fig. 3. Changes of c_0-spacing of two components A_H and G_H with HTT.

A_H	G_H	
○	●	3 min
□	■	20 min
△	▽	60 min

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

9) M. Inagaki, K. Kamiya and T. Noda, *ibid.*, **71**, 812 (1968).

*2 The suffix " H " stands for the component observed on hard carbon.

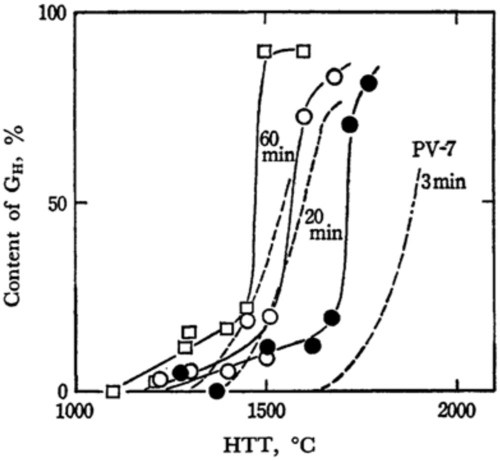

Fig. 4. Changes of content of the component G_H with HTT
● 3 min ○ 20 min ☐ 60 min
Changes of content of the component G_S of the soft carbon PV-7[7] were shown by the broken lines.

change of content of the component G_H with HTT is shown in Fig. 4.

Discussion and Summary

On the graphitization process of the hard carbon PH-7 under 5 kbar, the profile of (002) diffraction line showed the composite one. Similar composite profiles of (00 *l*) diffraction line had been observed on the soft carbon PV-7 heat-treated under the same pressure.[6-9] The graphitization process of PH-7 under pressure seemed to be composed of two stages; in the early stage the (002) profile of the heat-treated sample being symmetrical and in the later stage it consisting of two component profiles A_H and G_H. However, the later stage could be divided into two more stages from the view points of c_0-spacing, symmetry of the profile and content of the component G_H, which will be described below. Therefore, the graphitization process of PH-7 under pressure was considered to consist of three stages. On the soft carbon PV-7, the graphitization process under the same pressure was divided into two stages.

In the first stage of the graphitization, the (002) profile is symmetrical though being very broad. It means that there is only one component A_H in the sample. The presence of the high angle component G_H was not indicated. The c_0-spacing of the component A_H decreases from the original value to 6.88 A with the increase in HTT.

In the second stage of graphitization (above 1200°C), the (002) profile becomes composite, consisting of the components A_H and G_H. The content of the component G_H increases gradually up to about 20% and its apparent c_0-spacing decreases from about 6.79 to 6.72 Å with the increase in HTT. The profile of the component G_H in this stage is not exactly symmetrical and therefore may consist of two components G'_H and G''_H. Assuming that the component G'_H has a relatively large c_0-spacing as 6.78 Å and the component G''_H has 6.72 Å and that the component G'_H transforms to G''_H, the gradual decrease of the apparent c_0-spacing and the lack of symmetry of profile of the component G_H may be explained. On the other hand, the component A_H becomes to have a constant c_0-spacing of 6.88 Å through this stage, though the angular position of this component profile has not been assumed as constant before the separation of the composite profile. On the soft carbon PV-7,[7] the component A_S on the low angle side had a little smaller c_0-spacing and its profile was much sharper than that of the compoent A_H observed on the hard carbon PH-7 in the present work.

In the third stage of graphitization, the content of the component G_H increases abruptly to more than 70% at about 1400, 1500 and 1700°C for the residence time of 60, 20 and 3 min, respectively. The profile of the component G_H is almost symmetrical

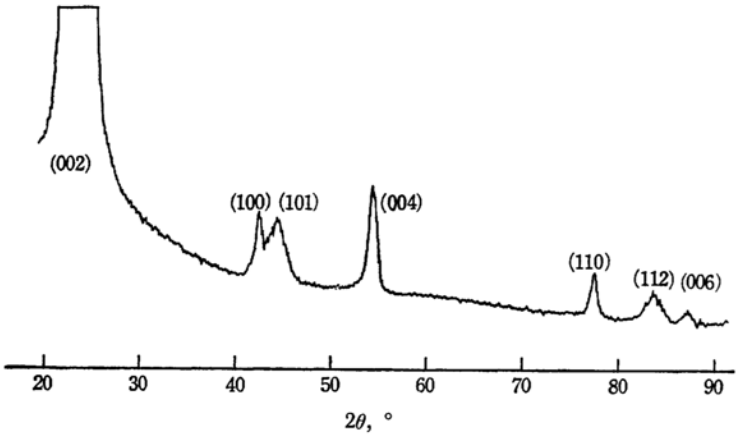

Fig. 5. Diffraction pattern of the hard carbon heat-treated at 1500°C for 60 min under 5 kbar.

and has the c_0-spacing of around 6.72 Å. Therefore, component G_H may consist of only one component the G''_H in this stage. The c_0-spacing of the component A_H is also constant at 6.88 Å through stage. The sample obtained in this stage (the content of G_H is more than 70%) was found to have the three-dimensional diffraction lines such as (101) and (112) lines (Fig. 5).

These experimental facts suggest the followings; The component A_H has turbostratic structure and its c_0-spacing in the second and third stages is the same as that has been assigned for this structure by others.[1,10] The component G_H is considered to consist of two components G'_H and G''_H. The component G''_H, which has the c_0-spacing of 6.72 Å and shows the three-dimensional diffraction lines, corresponds to graphitic structure and it may be the same as the component G_S observed on the soft cabon PV-7. The component G'_H, whose c_0-spacing is between 6.72 and 6.88 Å, corresponds to the intermediate structure between turbostratic and graphitic structures. The component G'_H is observed only in the second stage of graphitization and its content is much less than 20%. No component having such an intermediate structure as G'_H was observed on the soft carbon PV-7.

As shown in Fig. 4 (for the convenience of comparison the change of content of the component G_S in the soft carbon PV-7 are also shown), it is surprising that the hard carbon PH-7 is graphitized as abruptly as the soft carbon PV-7 at low temperature as 1500°C under 5 kbar. For the residence time of 3 min, the hard carbon PH-7 seems to be graphitized somewhat faster than the soft carbon PV-7.

From the results of the present work, it is deduced that the hard carbon heat-treated under pressure consists of two or three components, each of which has enough extent to produce the coherent X-ray scattering. Such a constitution of the structural components is very similar to that oberved on the soft carbon.[7]

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10) B. E. Warren, " Proceedings of the Conferences on Carbon, " Univ. of Buffalo (1956), p. 49.