BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 926—930 (1970)

Effect of Pressure on Graphitization of Carbon. VII. Effect of Pre-Heat-Treatment on Graphitization of Carbon under High Pressure

Kan-ichi KAMIYA, Michio INAGAKI, Hajime SAITO and Tokiti NODA

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

(Received September 24, 1969)

The soft carbon samples PV-15, -17 and -20, and the hard carbon samples PH-15 and -20, which were prepared by pre-heat-treatment of a polyvinylchloride coke PV-7 at 1500, 1700 and 2000°C and a phenolformaldehyde resine char PH-7, at 1500 and 2000°C, respectively, under reduced pressure, were re-heat-treated under quasi-hydrostatic pressure of 5 kbar. The structural changes in these carbons by the re-heat-treatment under pressure were studied by X-ray diffraction analysis. On the soft carbons, the rate of development of graphitic component was found to become small with the increase in temperature of pre-heat-treatment. On these samples, especially on PV-20, the normal homogeneous graphitization of turbostratic component was observed above about 1700°C besides the heterogeneous graphitization. However, the hard carbon samples PH-15 and PH-20 showed the same abrupt heterogeneous graphitization at around 1500°C as the original PH-7. These results suggest that the structure of carbon sample is related to the heterogeneous graphitization under high pressure. One can deduce a conclusion from the results of this series of experiments that the heterogeneous graphitization is more dominant in a carbon sample having a lower degree of graphitization, for example, a larger c_0-spacing and a smaller crystallite size.

Both soft and hard carbons have been found to be graphitized very rapidly around 1400—1500°C under high pressure.[1-5] Under high pressure, the graphitization proceeds heterogeneously, that is a part of original carbon transforms directly to graphite having three dimensional ordering, while the other part of the specimen remains almost unchanged. The direct transformation of turbostratic structure to graphitic structure occurs in whole domain without going through intermediate state of graphitization. This heterogeneous graphitization under high pressure is reflected in the composite (00*l*) diffraction profile of the sample. The observed composite profile consists of two kinds of component profiles which correspond to turbostratic and graphitic components.

Under normal or reduced pressure, however, the graphitization proceeds homogeneously as being demonstrated by the continuous shift of almost symmetrical (00*l*) diffraction line toward higher angle side.

In the preliminary experiment,[1] the carbons pre-heat-treated above 1500°C under reduced pressure was found not to show any abrupt graphitization around 1400—1500°C under the pressure of 10 kbar. The purpose of the present work is to investigate more precisely the effect of pre-heat-treatment on graphitization of carbon under high pressure.

Experimental

Preparation of Samples. The original samples used were a polyvinylchloride coke (PV-7), which was carbonized to 680°C[1] and a phenolformaldehyde resine char (PH-7), which was carbonized to 700°C. Pre-heat-treated soft carbons PV-15, -17 and -20 were prepared by the heat-treatment of PV-7 at 1500, 1700 and 2000°C, respectively, for 60 min under the reduced pressure of 10^{-2} Torr. The c_0-spacings of these samples were 6.885, 6.858 and 6.845 Å, respectively. Pre-heat-treated hard carbons PH-15 and PH-20 were prepared at 1500 and 2000°C, respectively, from PH-7, through the same procedure as the soft carbons. The c_0-spacing of the samples PH-15 and -20 was 6.959 and 6.927 Å, respectively. Only the c_0-spacing of PV-20 was smaller than 6.85 Å and those of the other samples were larger. Therefore, PV-20 was on the second stage[6] of graphitization process and the other samples were on its first stage.

The furnace and the procedure used for the pre-heat-

---

[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*, **71**, 652 (1968).

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

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

[6] M. Inagaki, *Tanso*, No. **53**, 61 (1968); M. Inagaki Y. Murase and T. Noda, *ibid.*, No. **54**, 80 (1968).

treatments were the same as those reported in detail elsewhere.[7] Time necessary for heating and cooling to and from pre-heat-treatment temperature was both less than a few minutes.

Heat-Treatment under High Pressure and X-Ray Diffraction Analysis. A piston-cylinder type high pressure apparatus,[2,3] made from tool steel, was used for heat-treatments of the samples under 5 kbar. The pressure cell arrangement used was exactly the same as reported previously.[2] The heat-treatment temperature (HTT) was determined by using the relation between specimen temperature and consumed electric input power, which was established beforehand for each sample from the measurement of temperature by using a thermocouple inserted into the specimen under 5 kbar. The heat-treatments under 5 kbar were performed at various temperatures ranging from 1200 to 1900°C.

The central part of the heat-treated specimen was sampled for X-ray diffraction analysis. In this part, the temperature gradient along axial direction has been hardly observed.[4]

Profiles of (004) and (002) diffraction lines of the heat-treated samples were measured by using Ni-filtered Cu $K\alpha$ radiation and a recording goniometer. The composite profile observed was graphically separated by trial and error method into two component profiles which corresponded to the graphitic component G and turbostratic one A. The details of the separation procedure were reported previously.[2,5,8] The c_0-spacing and crystallite size L_c were measured for each separated component profile by referring to the inner standard of silicon, and the content of the graphitic component $G_S{}^*$ or $G_H{}^*$ was obtained from the ratio of the area under the profile of the graphitic component to the total area of the composite profile. The area ratio was corrected for crystallite orientation in the X-ray specimen.[3]

Results

Soft Carbon Samples. Change of (004) diffraction profile of the sample PV-15 with HTT under 5 kbar is shown in Fig. 1a). Above 1500°C, a profile corresponding to the graphitic component G_S appeared on the high angle side of the profile of the turbostratic component A_S. The intensity of diffraction of the component G_S gradually increased

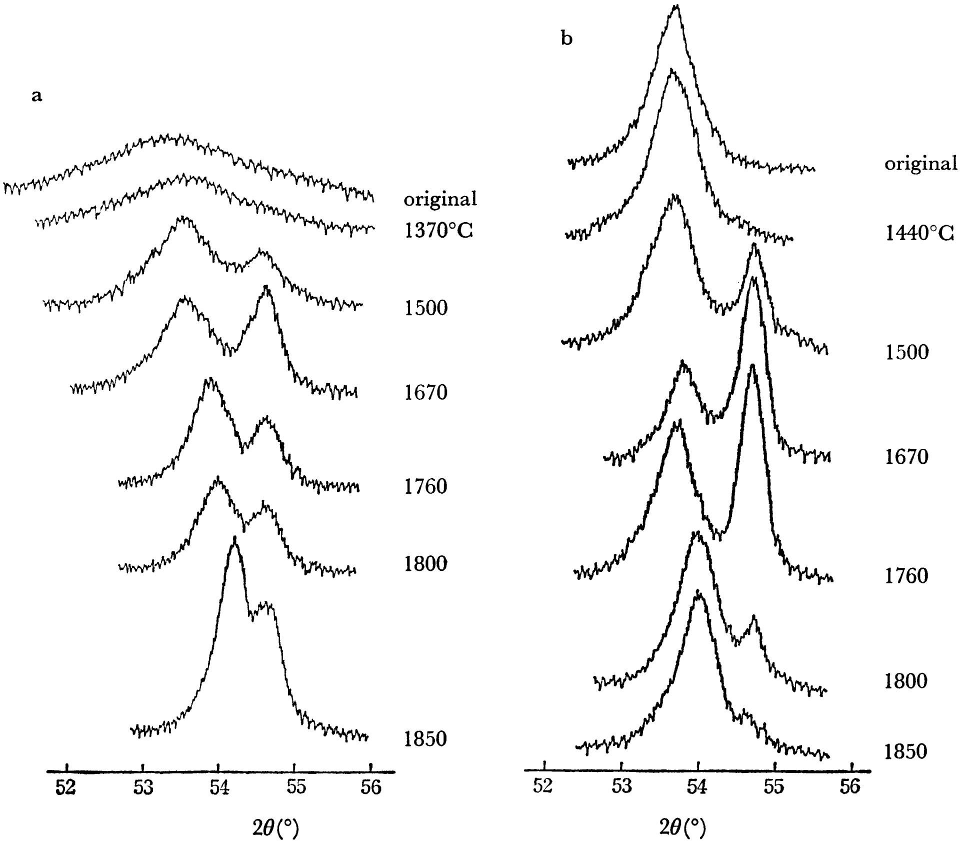

Fig. 1. Changes of Profile of (004) diffraction line with HTT under 5 kbar for 60 min.
a) PV-15 b) PV-20

---

7) M. Inagaki, Y. Murase and T. Noda, *Yogyo Kyokai Shi*, **76**, 184 (1968).

8) K. Kamiya, M. Inagaki and H. Saito, This Bulletin, **42**, 1425 (1969).

*1 Suffixes S and H show whether the original sample is soft carbon (PV-7) or hard one (PH-7).[5]

up to 1670°C. This change in profile had the same trend as that observed previously for the original sample PV-7,[2] except that the temperature of appearance of the component G_S in PV-15 was somewhat higher than that in PV-7. Above 1670°C, the intensity of diffraction of the component G_S did not increase or rather decreased gradually and the profile of the component A_S began to shift to higher angle side together with sharpening. For the sample PV-17, change of (004) diffraction profile with HTT was similar to that observed for the sample PV-15. The same but more marked trend of change in diffraction profile with HTT can be seen in the case of PV-20, which is shown in Fig. 1b). The component A_S had a little higher diffraction angle, that is, a smaller c_0-spacing than those of the sample PV-7, -15 and -17. The profile of the component G_S appeared at 1500°C and developed gradually with the increase in HTT. Above 1800°C, it became markedly small, and the profile for the component A_S began to shift to higher angle side.

The content of the component G_s for the samples PV-15, -17 and -20 is plotted against HTT in Fig. 2. The variation of content of the component G_S for the original sample PV-7 is shown in the same figure. An anomalous change of content of G_S for the sample PV-20 is seen in this figure. In the case of PV-20, the content of the component G_S increased gradually up to 1700—1800°C and became small above this temperature. The similar but small decrease in the content of the component G_S was also observed in the cases of PV-15 and -17 above about 1700°C. The point marked by solid square in Fig. 2 represents the content of G_S for the sample PV-20 which was heat-treated at 1740°C for 60 min and then, without cooling, heat-treated further at 1880°C for 60 min under 5 kbar. It shows a large content of G_S which corresponds to the value for the temperature of the first heat-treatment, that is, 1740°C.

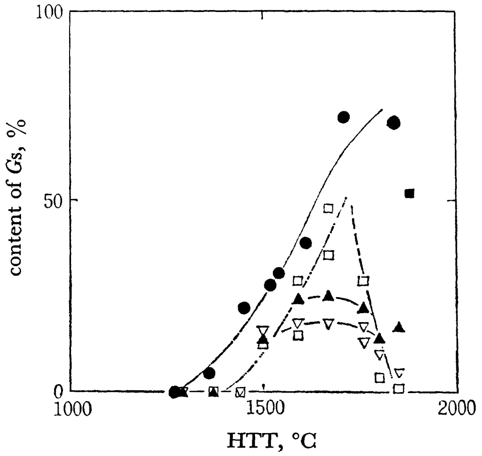

Fig. 2. Variations of content of G_S with HTT under 5 kbar for 60 min for pre-heat-treated soft carbons. ●; PV-7, ▲; PV-15, ▽; PV-17, □; PV-20, ■; PV-20 heat-treated at 1740°C and then at 1880°C under 5 kbar.

The variations of content of the component G_s with residence time at 1590 and 1800°C under 5 kbar are shown in Figs. 3a) and 3b). In the case of PV-7, the content of G_S increased very rapidly with residence time. In the cases of PV-17 and -20, the rate of development of the component G_S was depressed and seemed to approach a small limiting value.

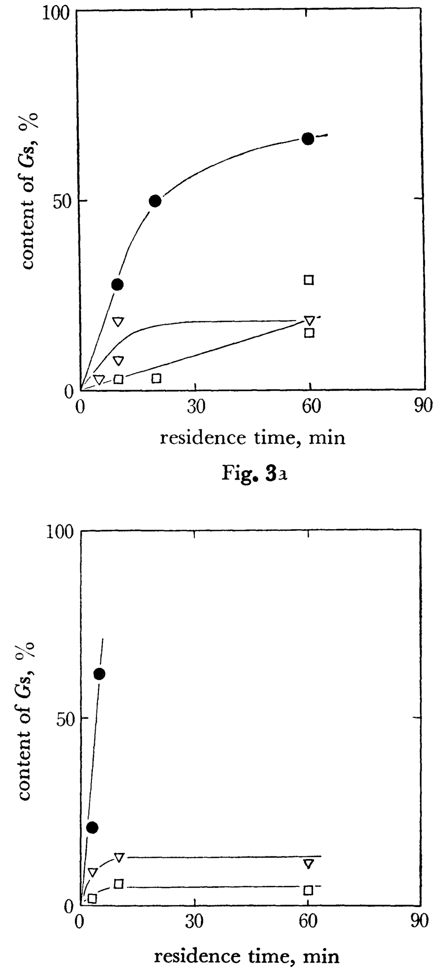

Fig. 3a

Fig. 3b

Fig. 3. Variations of content of G_S with residence time of HTT under 5 kbar for pre-heat-treated soft carbons.
●; PV-7, ▽; PV-17, □; PV-20
a) at 1590°C under 5 kbar, b) at 1800°C under 5 kbar

The variations of the c_0-spacing of the component A_S and G_S with HTT are shown in Fig. 4. The

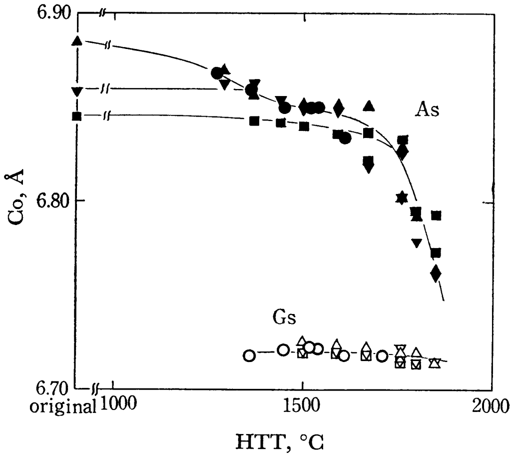

Fig. 4. Variations of c_0-spacing of the component A_S and G_S with HTT under 5 kbar for 60 min for pre-heat-treated soft carbons.

	PV-7	PV-15	PV-17	PV-20
A_S	●	▲	▼	■
G_S	○	△	▽	□

samples PV-15 and -17 showed gradual decrease in the c_0-spacing of the component A_S down to about 6.85 Å. After the c_0-spacing of the component A_S reached about 6.85 Å, it remained almost constant and the component G_s, whose c_0-spacing was about 6.72 Å, began to appear. Above around 1700°C, however, the c_0-spacing of the component A_S decreased rapidly. The sample PV-20, whose c_0-spacing was smaller than 6.85 Å, showed no change in the c_0-spacing of the component A_S until about 1700°C, while the component G_S was detected even at 1500°C. Above about 1750°C, the c_0-spacing of the component A_S for PV-20 decreased rapidly along the same line as PV-15 and -17.

The mutual relation in the change of crystallite size L_c of the component A_S with HTT among the four soft carbon samples PV-7, -15, -17 and -20 was the same as that in the c_0-spacing and is shown in Fig. 5.

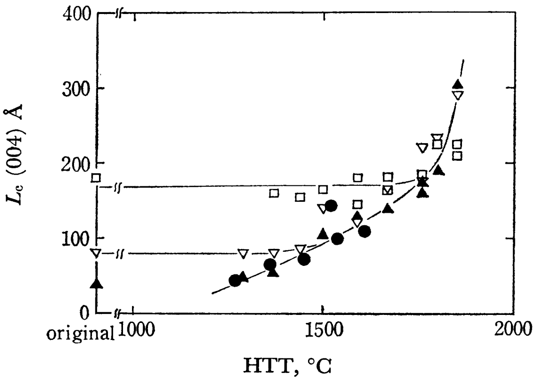

Fig. 5. Variations of crystallite size $L_c(004)$ of the component A_S with HTT under 5 kbar for 60 min for pre-heat-treated soft carbons.
●; PV-7, ▲; PV-15, △; PV-17, □; PV-20

Hard Carbon Samples. Changes of (002) diffraction profile with HTT for the samples PH-15 and PH-20 were almost the same as that for the original sample PH-7, which was previously reported.[5] The variations of content of the graphitic component G_H with HTT for the samples PH-7, -15 and -20 are shown in Fig. 6. No appreaciable difference in the change of content of the component G_H among three samples can be made, because there was a relatively large error in the determination of HTT in the case of the hard carbon.[9] The c_0-spacing of the turbostratic component A_H had a constant value of about 6.88 Å and the graphitic component G_H of about 6.72 Å.

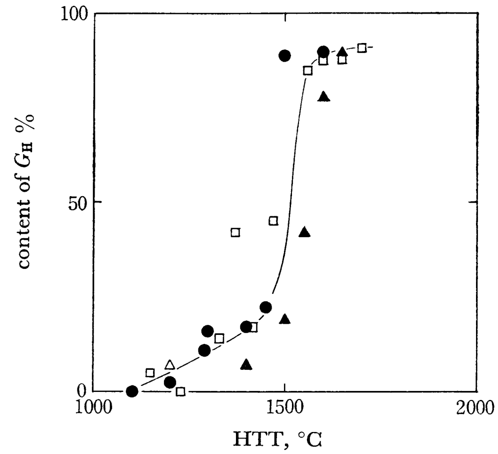

Fig. 6. Variations of content of G_H with HTT under 5 kbar for pre-heat-treated hard carbons
●; PH-7, ▲; PH-15, □; PH-20

Discussion

The starting of the heterogeneous graphitization under pressure, that is, the first appearance of the graphitic component G_S, of the pre-heat-treated soft carbons was retarded about 100°C from that of the original un-treated carbon sample PV-7. In the case of the sample PV-7, the content of the component G_S increased with increase in HTT, but in the cases of the pre-heat-treated carbons, a maximum value at about 1700°C was observed in the plot of the content of G_S against HTT. The apparent decrease of the content of G_S dose not mean the actual disappearance of the graphitic component once formed, but it comes from the fact that the formation of G_S largely depressed at higher HTT in the cases of the pre-heat-treated carbons, as it can be seen from Fig. 3. This conclu-

---

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

sion is also confirmed by an experimental result represented by a solid square mark in Fig. 2. The sample PV-20 was first heat-treated at 1740°C for 60 min and then further at 1880°C for 60 min. The content of G_S of the sample after these heat-treatments was about 50%. This value corresponds to the one which can be obtained by the first heat-treatment at 1740°C. This suggests that the high content of G_S formed by the heat-treatment at 1740°C remained unchanged by the subsequent heat-treatment at 1880°C.

For the sample PV-15 and -17, the heterogeneous graphitization process was dominant in the range around 1400°C to 1700°C, in which the c_0-spacing of the structural components A_S and G_S remained unchanged at 6.85 and 6.72 Å, respectively. However, above 1700°C the homogeneous graphitization process became dominant and the profile of the turbostratic component A_S shifted to higher angle side. For the sample PV-20, the heterogeneous graphitization process began from about 1500°C and was dominant up to about 1800°C. It seemed that the direct transformation of the turbostratic component A_S to the graphitic component G_S, without having the intermediate structure, was slowed down when the c_0-spacing of the component A_S decreased below 6.85 Å. For the sample PV-7, only the heterogeneous graphitization has been observed by the heat-treatment under pressure, because it proceeded so rapidly that almost all of the component A_S transformed to the component G_S at temperatures below about 1700°C. For the pre-heat-treated carbons, one could observe the homogeneous graphitization of the component A_S, because the rate of the direct transformation of A_S to G_S was slowed down by the pre-heat-treatment.

In the previous work,[1] it was reported that the pre-heat-treated soft carbons showed no heterogeneous graphitization under 10 kbar. The residence time in that work was 3 min, but this residence time seems not to be enough for the graphitic component to develope, as it can be deduced from Fig. 3. Therefore, heterogeneous graphitization under pressure was probably not detected. It has been also mentioned that the graphitization of carbon under high pressure might be related to the dehydrogenation of carbon. This assumption was deduced from the fact that, under high pressure, carbon containing hydrogen, such as PV-7, was graphitized more rapidly than pre-heat-treated carbons which had been deprived of hydrogen. In the present work, however, the pre-heat-treated hard carbons PH-15 and PH-20 were shown to be graphitized as rapidly as original un-treated hard carbon sample PH-7. The sample PH-20 seemed to be almost completely dehydrogenated. This suggests that the dehydrogenation of the sample is not important factor for the rapid graphitization under high pressure.

The c_0-spacing of the samples, PH-7, PH-15, PH-20, PV-7, PV-15, PV-17 and PV-20, used in the present work was 7.01, 6.96, 6.93, 6.91, 6.885, 6.858 and 6.845 Å, respectively and the crystallite size $L_C(002)$ was 17, 17, 21, 28, 72, 150 and 260 Å, respectively. Among these seven samples PH-7, PH-15, PH-20 and PV-7 showed only heterogeneous graphitization under high pressure. However, for other samples, which had smaller c_0-spacings and larger crystallite sizes than the above four samples, the homogeneous graphitization was observed to occur side by side with the heterogeneous one even under high pressure. From this fact one can conclude that the heterogeneous graphitization is more dominant in a carbon sample which has a lower degree of graphitization.

The course of developement of the component G_S and A_S of the sample PV-20 was a little different from the other pre-heat-treated samples as shown in Figs. 1b) and 2. It seems to be related to the fact that the sample PV-20 was already on the second stage of normal graphitization process, while the others were on its first stage. However, the reason why the maximum value of the content of G_S was so large for PV-20 can not be understood.

The authors wish to thank Mr. M. Mizutani for his assistance. The carbon materials used were supplied by Tokai Electrode Mfg. Co.