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Effect of Pressure on Graphitization of Carbon. I. Heat Treatment of Soft Carbon under 1, 3 and 5 kbar

Tokiti NODA,*1 Kanichi KAMIYA and Michio INAGAKI

Faculty of Engineering, Nagoya Universisty, Nagoya

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Polyvinylchloride coke was heat-treated under the quasi-hydrostatic pressure of 1, 3, and 5 kbar by using a simple piston cylinder type high pressure apparatus. The process of graphitization under pressure was studied kinetically by analyzing the profile of the (002) diffraction line. It was found that the accelerating effect of pressure on the graphitization of carbon became more pronounced at higher pressure. The process of graphitization under 3, and 5 kbar seemed to take place in at least two stages. In the first stage, the profile of the (002) line shifted simply from the position of the original line to 26.0° in 2θ, which corresponded to a c_0-spacing of 6.85 Å. In the next stage, a new component, having a c_0-spacing of about 6.72 Å, appeared in addition to the first component, having a c_0-spacing of 6.85 Å. Therefore, the profiles of the (002) line became composite. Under 1 kbar, however, no composite profiles were observed and the c_0-spacing decreased gradually with heat treatment. Approximate values for the activation energy and activation volume for graphitization under 3—5 kbar were estimated to be 80—120 kcal/mol, and −7—−9 cc/mol, respectively.

It has been reported that the graphitizing cokes, such as petroleum coke and polyvinylchloride coke, graphitized very rapidly at around 1500°C under a pressure of 10 kbar.1) Profiles of the (002) diffraction line of the cokes heat-treated at 1400—1500°C under 10 kbar were found to be composite, while no composite profiles were found with heat treatment of the same cokes under a reduced pressure of 10^{-2} Torr.1) A kinetic study of the graphitization could not be carried out at a pressure as high as 10 kbar, because of the high rate of graphitization.

In the present work, the heat treatment of polyvinylchloride coke under pressures of 1, 3, and 5 kbar was carried out for various durations at various temperatures, in order to learn the effect of pressure on the graphitization of carbon, and also to obtain more precise information on the composite profile of (00*l*) diffraction.

Experimental

Sample and Apparatus. The sample used was a graphitizing coke PV-7, which was also used in previous work.1) The coke was prepared by carbonizing polyvinylchloride at 680°C, and was examined spectroscopically and found to contain only negligible amounts of inorganic impurities. The coke had a paricle size in the range of 0.1 to 0.4 mm.

The high pressure apparatus used was of a simple piston-cylinder type. It was made of tool steel, having a hardness of R. C. 64, and a bore diameter of 24 mm.

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*1 Present address: Mie University, Tsu, Mie-ken.

1) T. Noda and H. Kato, *Carbon,* **3**, 289 (1965).

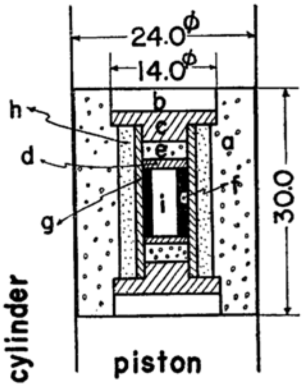

Fig. 1. Arrangement of the specimen cell.
a : pyrophyllite holder, b : metal disk (14ϕ-3 mm), c : graphite terminal plate (14ϕ-2mm), d : graphite plate (6ϕ-1mm), e : pyrophyllite disk (6ϕ-2.5mm), f : glassy carbon tube (6ϕ·4ϕ-10mm), g : graphite heater (8ϕ·6ϕ-21mm), h : boron nitride, i : sample

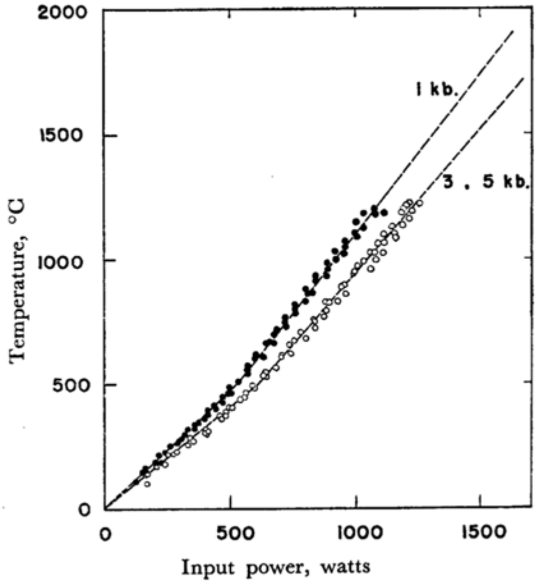

Fig. 2. Relations between input power and temperature under different pressures.

Such a piston-cylinder type apparatus made of tool steel has been known to last up to 10 kbar at room temperature.2) The whole apparatus was immersed in water for cooling during the experiment. The arrangement of the specimen cell is shown in Fig. 1. Boron nitride (h in the figure) was placed between a graphite heater and pyrophyllite in order to prevent chemical reaction between them. A glassy carbon tube (f in the figure) played the role of preventing contamination of the sample. A heating current was passed through the pistons into a graphite tube heater. The pistons were insulated from the cylinder by a composite sheet of asbestos and Myler film. The temperature of the central part of the sample was evaluated from the relation between heating input power and temperature, which had been determined beforehand up to about 1200°C using a chromel-alumel thermocouple. The relations between input power and temperature were determined at different pressures and are shown in Fig. 2. A thermocouple inserted in the specimen probably makes a heat sink which may cause a small decrease in the temperature of the specimen. In most of the actual runs, no thermocouple was inserted in the specimen, and therefore the heat treatment temperature of the specimen could be a little higher than the temperature estimated from the input power. However, the difference may be within the error of temperature measurement, because the input power for the melting of platinum under 5 kbar (1800°C3)) with in same arrangement was exactly on the extrapolated straight line of the upper part of the curve for 5 kbar.

There was a very large temperature gradient in the specimen along the axial direction of the graphite heater, the temperature of the end part of the specimen being about 10% lower than that of the central part. The temperature of the specimen was controlled manually by regulating the input power. The error in the determination of the heat treatment temperature was estimated to be ±50°C at 2000°C from the scattering of the points in the relation between input power and temperature, and from the variation of input power regulation. The heating rate was about 1000°C/min and the specimen was cooled down to room temperature within a few minutes by cutting off the power. The maximum temperature which was attainable depended strongly on the arrangement of the specimen cell. By using the arrangement shown in Fig. 1, a temperature up to 1800°C was attained under 1 kbar, and 2000°C under 5 kbar.

The pressure was transmitted through pyrophyllite, so that quasi-hydrostatic pressure was applied to the sample. The pressure was calibrated by use of the phase transition of neutral ammonium fluoride, which occurs at 3.7 kbar with a volume change of about 28%,4) The error in the pressure measurement was estimated to be ±0.2 kbar from the scattering of four independently measured values of the phase transition.

The heat treatments of the sample were carried out at temperatures ranging from 1100°C to 1900°C for 3 to 90 min under 1, 3, and 5 kbar. The central part (about 1 mm thick) of the heat-treated specimen was used for the X-ray diffraction analysis, in order to avoid ambiguity caused by the temperature gradient along the specimen.

Analysis of X-Ray Diffraction Profiles. The profiles of the (002), and (004) diffraction lines for the heat-treated specimen were measured by using a recording X-ray diffractometer and Ni-filtered Cu$K\alpha$ radiation. Most of the profiles obtained were composite, as can be seen in Figs. 3b), and c). All the composite profiles appear to have two peaks at around 26.0° and 26.5° in 2θ. The occurrence of a composite profile indicates that there must be more than one independent range to produce coherent scattering of X-rays,

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2) T. Noda, H. Kato, T. Takasu, A. Okura and M. Inagaki, This Bulletin, **39**, 829 (1966).

3) W. Paul, "Solid under Pressure," McGraw-Hill, New York (1963), p. 175.

4) R. Stevenson, *J. Chem. Phys.*, **34**, 346 (1963).

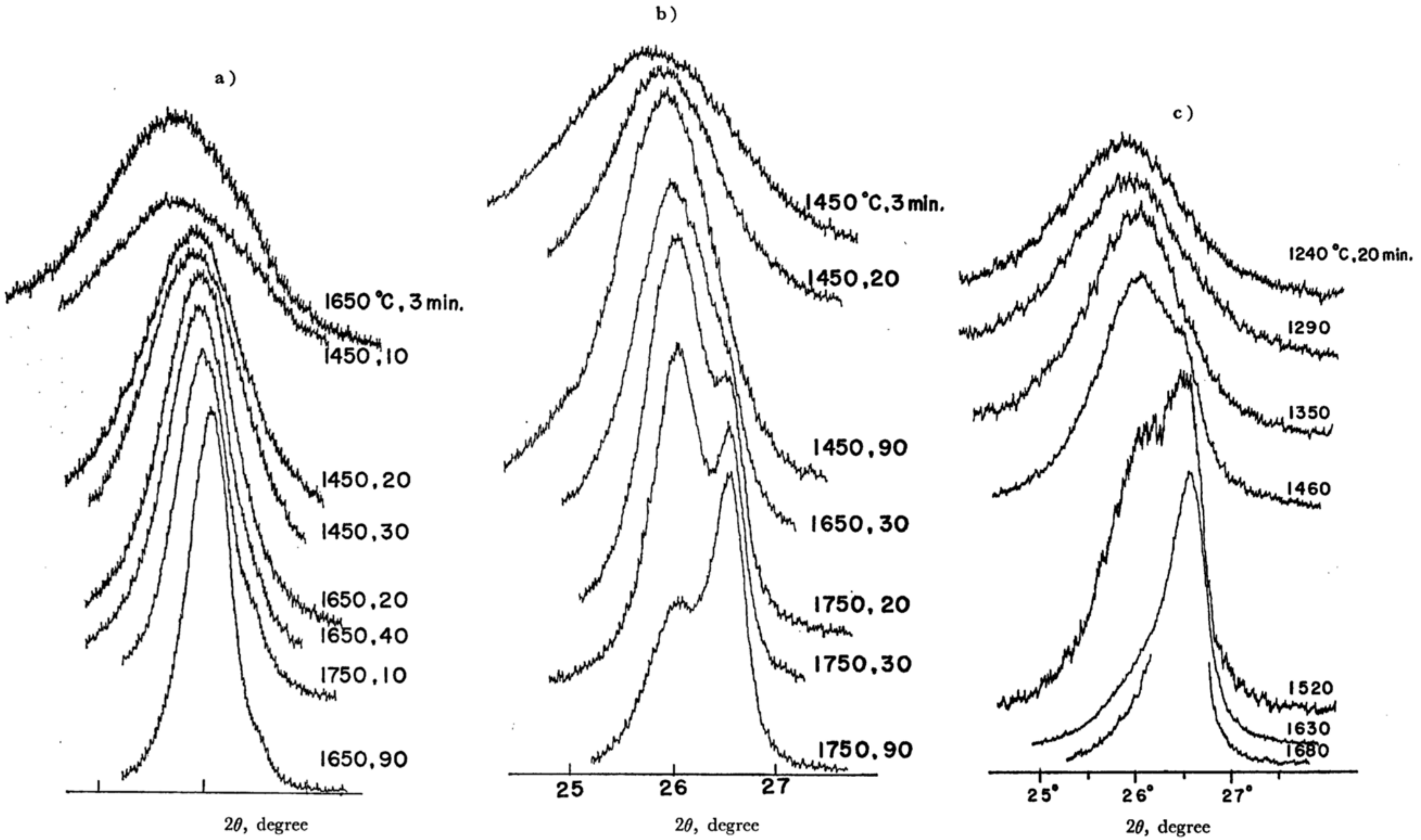

Fig. 3. Changes of the profile of (002) diffraction line a) under 1 kbar, b) under 3 kbar, c) under 5kbar.

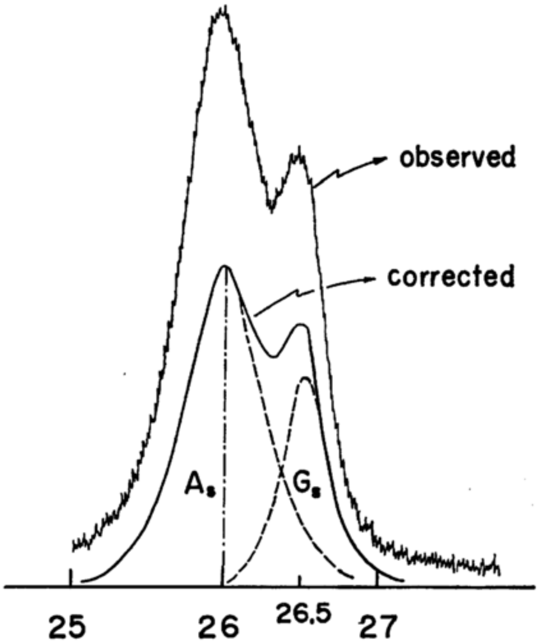

Fig. 4. Schema of separation of composite profile.

and therefore the composite profile can be separated into its component profiles.[5] The procedure for the separation of an observed composite profile into its component profiles is illustrated in Fig. 4. After correction for the Lorentz-polarization, atomic scattering and absorption factors by the conventional method,[6] the profile on the low angle side is folded at 26.0°, the reason for which will be described later. When the component profile at 26.0° is subtracted from the composite profile, the balance gives an almost symmetrical and sharp peak at around 26.5°. The components, correspond to the separated profiles at 26.0°, and at 26.5°, are designated as A_S, and G_S, respectively.[*2] The areas under the separated component profiles were measured by using a planimeter, and the ratio of the area of the profile of the component G_S to the total area of the composite profile was calculated. This area ratio is sensitive to the preferred orientation of the crystallite in the specimen used for X-ray measurement. The correction of the area ratio for the preferred orientation was carried out by using the calibration curve, because the quantity of specimens for X-ray measurement was so small that direct measurement of the preferred orientation of crystallites in the specimen could not be carried out. The calibration curve was determined by using known mixtures of two kinds of petroleum cokes, one treated at 1600°C, and the other treated at 3200°C, which have the same diffraction angles as those of the component profiles, 26.0°, and 26.5°, respectively.

Results

Profiles of the (002) diffraction line for specimens heat-treated under 1 kbar are shown in Fig. 3 a). The diffraction angle of the line increased and its half-width decreased with increase in heat treatment temperature (HTT) and residence time, similar to the changes for heat treatments under room or reduced pressure. Changes of the (002) profile under 3 kbar are shown in Fig. 3 b). At low temperature and short residence time for heat treatment, the diffraction angle and half-width of the line changed the same as in the case of 1 kbar. When the diffraction angle of the line reached to

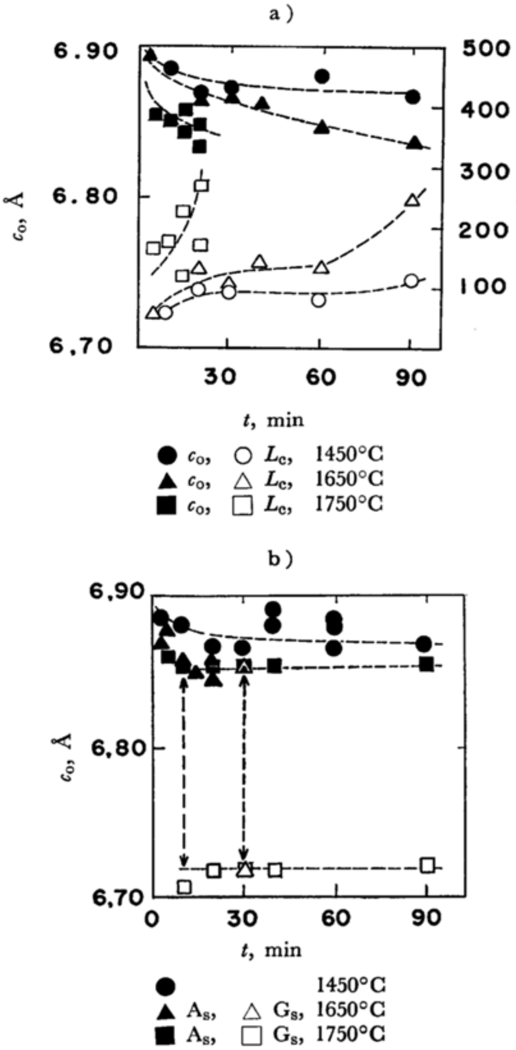

Fig. 5. Changes of c_0-spacing and crystallite size L_c with residence time.
a) under 1 kbar, b) under 3 kbar.

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5) T. Noda and M. Inagaki, "Proceedings of the Fifth Conference on Carbon Vol. I," Pergamon Press, London (1962), p. 559.

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

[*2] For a hard carbon heat-treated under 5 kbar, the authors found a similar composite profile, which seemed to consist of two components. In the present work, the components of soft carbon were distinguished from those of hard carbon by using a suffix "s," because they might not have the same structures.

26.0°C, however, a new sharp peak for the component G_s appeared at 26.5°, overlapping the profile for the component A_s. With further heat treatment, this sharp profile for G_s developed without appreciable change in the diffraction angle. Almost the same changes in the profile of the (002) diffraction line were observed under 5 kbar (Fig. 3 c)), but the change occured at lower temperature, or in a shorter time than in the case of 3 kbar. In the heat treatments under 3, and 5 kbar, the diffraction angle of the profile for the component A_s stayed unchanged at 26.0° after the appearance of the profile for the component G_s. This is the reason why the position of the profile for A_s was fixed at 26.0° when the observed composite profile was separated into its component profiles, as illustrated above.

Changes in the c_0-spacing and crystallite size L_c of the specimens heat-treated under 1 kbar with residence time are shown in Fig. 5 a). Comparing these changes with those of the same coke under reduced pressure,[1] the accelerating effect of pressure on graphitization of carbon becomes very evident. In Fig. 5 b), the changes in the c_0-spacing of the specimens heat-treated under 3 kbar with residence time are shown. Under 3 kbar, the component G_s was observed to appear in 30 min at 1650°C, and in 10 min at 1750°C, while at 1450°C no indication of the component G_s was observed in 90 min. The crystallite size of the component A_s increased gradually from 100 to 200 Å, while that of the component G_s was about 300 Å. Change in the content of the component G_s with residence time is shown in Fig. 6. The content of G_s increased to about 50% in 90 min at 1750°C. Changes in the c_0-spacing of the components A_s and G_s of the specimens heat-treated under 5 kbar with HTT for various residence times are shown in Fig. 7 a). The c_0-spacing of the component A_s decreased to 6.85 Å around 1600°C in 3 min, around 1350°C in 20 min, and around 1300°C in 60 min. Changes in the content of the component G_s with HTT under 5 kbar are shown in Fig. 8 a) The intersection of these curves with the abscissa, or the temperature at which the component G_s begins to appear, should be about the same as those at which the c_0-spacing of the component A_s reaches 6.85 Å. The shape of the curves appears to be the same for different residence times, and they may be superimposed by translation along the abscissa. Such a superimposed curve for a residence time of 10 min is shown in Fig. 8 b). It is evident that the superimposition works quite well. Therefore, the curves for c_0-HTT and L_c-HTT were translated by the same amount. The superimposed curves make it easier

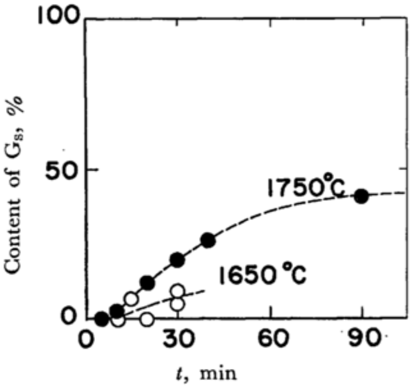

Fig. 6. Changes of content of the component G_s with residence time under 3 kbar.

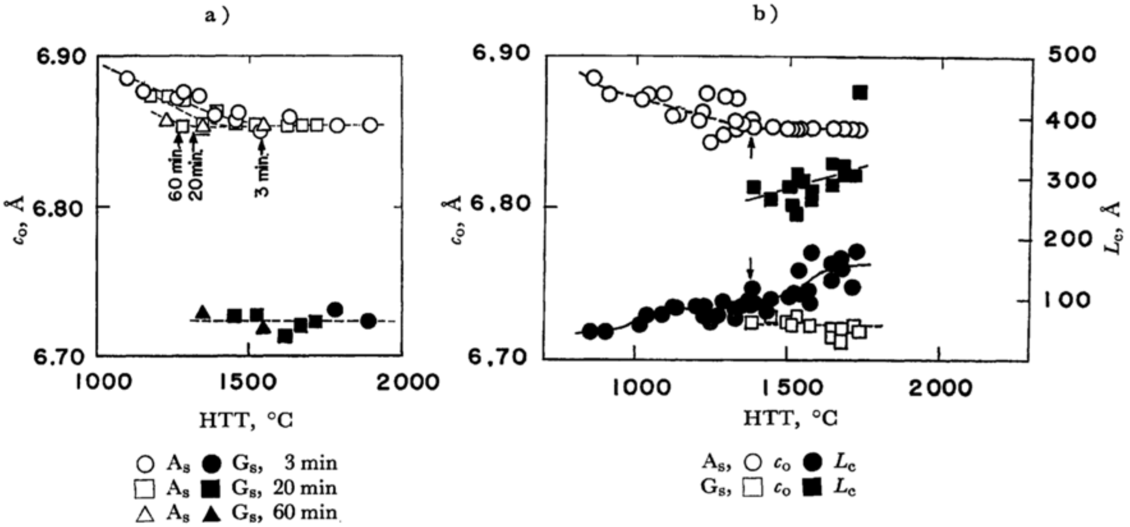

Fig. 7. Changes of c_0-spacing and crystallite size L_c with HTT under 5 kbar.
a) for different residence times, b) superimposed curve for the residence time of 10 min

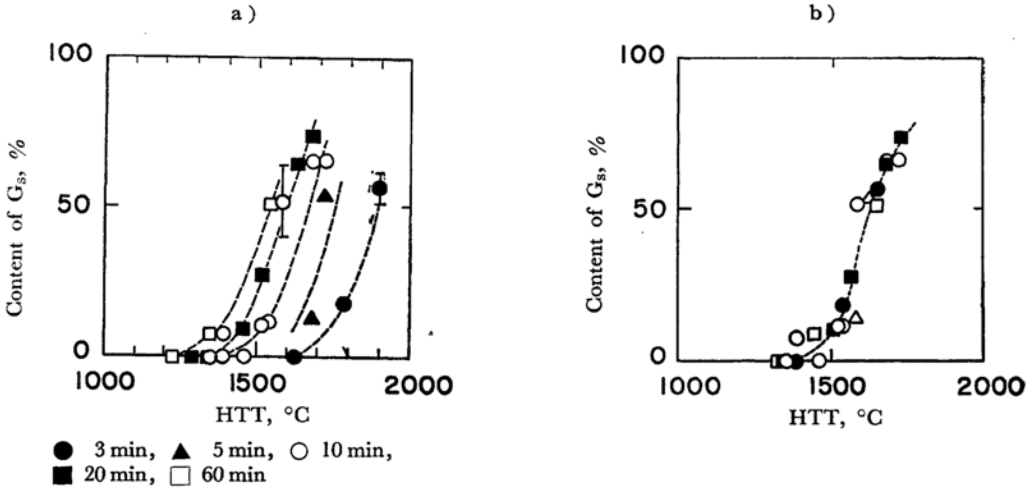

Fig. 8. Changes of content of the component G_s with HTT under 5 kbar.
a) for different residence times b) superimposed curve for the residence time of 10 min

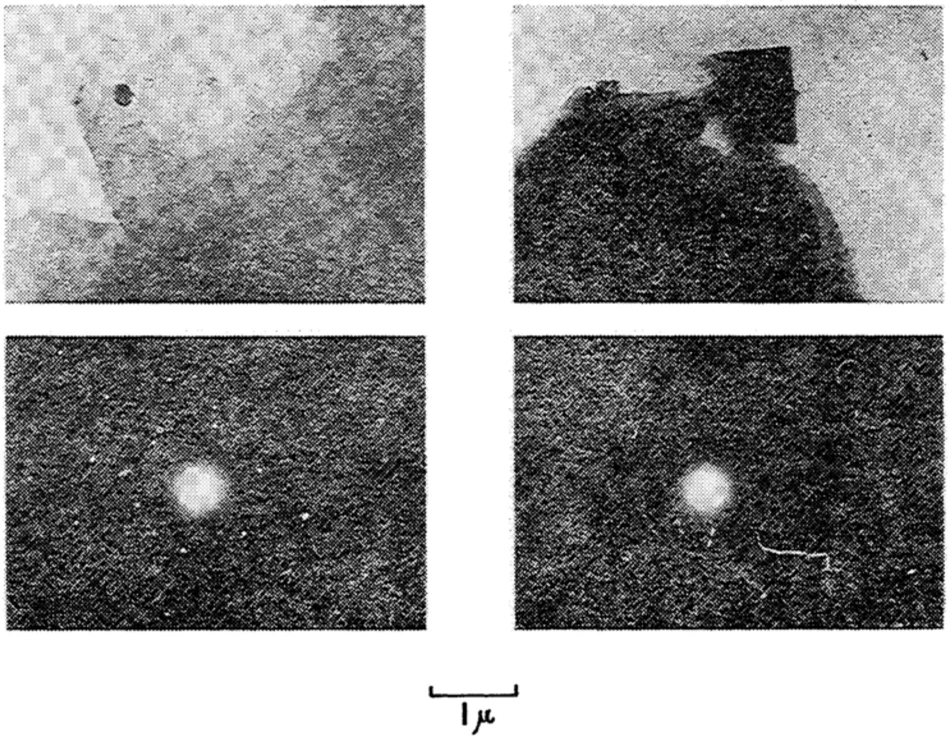

Fig. 9. Electron micrographs and electron diffraction patterns for the specimen heat-treated at 1720°C under 5 kbar.

to view the general trends of the changes in c_o and L_c with HTT (Fig. 7 b)).

From these figures, it can be seen that the graphitization of carbon under 3, and 5 kbar seems to proceed as follows. In the early stage of graphitization, there is one component A_s, of which the c_o-spacing decreases from the original value of 6.91 Å to 6.85 Å, and the crystallite size L_c increases to about 100 Å. In the next stage, the component G_s appears, and its content increases rapidly with increase in temperature and residence time for heat treatment. The c_o-spacing of the components A_s, and G_s remain unchanged at 6.85, and 6.72 Å, respectively. The crystallite sizes L_c of the components A_s, and G_s are about 150—200 Å, and 300 Å, respectively.

Discussion

In a previous work,[1] composite profiles were also obtained in cases where a rapid change in the c_0-spacing was observed. It was suggested that there might be a possibility that each specimen used for X-ray study was a mixture of carbons heat-treated at different temperatures because of the steep temperature gradient in the specimen In the present work, pyrophyllite disks (e in Fig. 1) were inserted between the specimen chamber and the graphite terminal plates in order to minimize the temperature gradient in the specimen. Even in this modified arrangement a temperature difference was observed between the end and the central parts of the specimen, the temperature of the end part being about 10% lower than that of the central part, as mentioned previously. In addition to the temperature gradient, the pressure gradient along the specimen must be taken into account. The pressure at the end part of the specimen may be a little higher than that at the central part. The (002) profile of the end part of the specimen of which the central part had a composite profile was also composite, and its only difference from the central part was the degree of the developement of the component G_s, the content of G_s for the end part being smaller than that for the central part. This seems to show that temperature and pressure gradients along the specimen were not the cause of the occurence of a composite profile. The temperature difference itself affected the content of the component G_s. In other words, the structural change in the specimen under pressure was properly reflected in the diffraction profile.

In the graphitization process of PV-7 under a pressure of 3—5 kbar, there exist the components G_s and A_s side by side in the one specimen. In the early stage, there is only one component A_s, of which the mean c_0-spacing gradually decreases to 6.85 Å and the crystallite size L_c increases a little. In the next stage, in which the c_0-spacing of the component A_s has reached 6.85 Å, the component A_s begins to transform into the component G_s, and the main change at this stage is the increase in the content of the component G_s. The c_0-spacing of the component A_s stays unchanged at 6.85 Å, and its crystallite size L_c also remains unchanged at around 150—200 Å through this stage. The c_0-spacing of 6.85 Å is a little but evidently smaller than that of the so-called turbostratic structure, 6.88 Å. If the c_0-spacing of one component is assumed to be 6.88 Å, the balance of the profile becomes strongly un-symmetrical, and it is necessary to assume it consists of more than two components. The c_0-spacing of the component G_s is 6.72 Å and its crystallite size L_c is around 300 Å. The spacing of the component G_s measured from the (004) diffraction line is also 6.72 Å, and is clearly not 6.71 Å. Even though this spacing of 6.72 Å is a little larger than the spacing of natural graphite, 6.708 Å, specimens having a high content of the component G_s were found by X-ray diffraction to have a three dimensional structure, and by electron microscope and microdiffraction to contain flaky particles of which diffraction pattern was of the perfect six-fold symmetry of single crystal (Fig. 9a)). In the same specimen, however, some other particles showed continuous diffraction rings (Fig. 9b)). It is known that the c_0-spacing of the cokes graphitized as highly as possible can hardly be reduced to that of natural graphite.[7]

Phenomenally, the change in profile in the second stage of graphitization under a pressure of 3—5 kbar is similar to the so-called two-, or three-phase graphitization of non-graphitizing or hard carbons. The occurence of a composite profile,

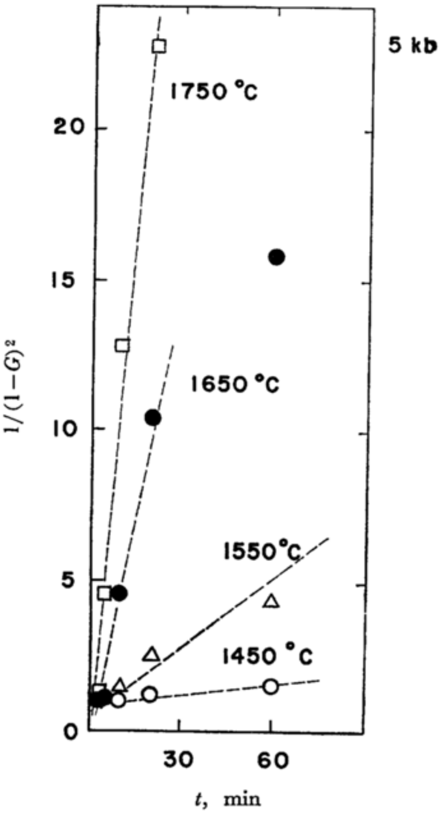

Fig. 10. Relations between content G of the component G_s and residence time t.

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[7] T. Noda and M. Inagaki, This Bulletin, **37**, 1709 (1964); T. Noda and H. Matsuoka, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **63**, 465 (1960); P. L. Walker and G. Imperial, *Nature*, **180**, 1184 (1957).

which was composed of the components G_s and A_s, indicates that ranges having graphitic and non-graphitic structures have a sufficient extent to produce independent coherent scattering of X-ray in one specimen.

Under 1 kbar, no composite profile was observed and the c_0-spacing decreased continuously to 6.78 Å without the appearance of the second peak for the component G_s. This means that not a sufficient extent of lattice, having graphitic structure to produce coherent X-ray scattering, was formed in the specimen by the treatment, so that only a homogeneous decrease of the c_0-spacing was observed.

From these experimental results, it can be concluded that the accelerating effect of pressure on the graphitization of carbon increases with pressure. However, the graphitization process above 3 kbar seems to be different from that below 3 kbar. For experiments under 3, and 5 kbar, an approximate relation between the content, G, of the component G_s, and residence time t was investigated, although the accuracy of the measurements of temperature and pressure of heat treatment were not good enough, and also experimental data was not abundunt enough for a quantitative kinetic analysis of graphitization under pressure. A relatively good linearity between $1/(1-G)^2$ and t was obtained (Fig. 10). By using the experimental rate constant, the activation energy was calculated to be 80—120 kcal/mol, and the activation volume -7—-9 cc/mol at temperature of 1650—1750°C.

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