

Preferred orientation of crystallite in carbons heat-treated under high pressure

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A soft carbon and a hard carbon which were prepared from polyvinylchloride and phenolformaldehyde resin, respectively, both by carbonizing to about 700°C, were obtained as sintered cakes by heat-treatment up to about 1800°C under the quasihydrostatic pressure of 5 kbar. Preferred orientation of crystallites relative to the compressing direction in these cakes was determined by X-ray diffraction technique by using the (004) or (002) diffraction line. The soft carbon showed remarkable preferred orientation of crystallites, but the degree of orientation was dependent only a little on heat-treatment temperature (HTT). At 1200°C under 5 kbar, the hard carbon gave a sintered cake which had no appreciably preferred orientation. The degree of preferred orientation of crystallites in the cake of the hard carbon greatly increased with the increase in HTT. The difference in the dependence of preferred orientation of crystallites in the soft and hard carbons on HTT was interpreted by referring to the texture of the original carbons.

1. Introduction

It has been found that either soft carbons [1, 2] or hard carbons [1, 3] were graphitized very rapidly around 1500°C under quasihydrostatic pressures of 3 kbar and higher. The (00 l) diffraction lines of the carbons heat-treated under high pressure had so-called composite profiles which consisted of two component profiles, one having the c_0 -spacing of 6.72Å and the other of 6.86Å [2, 4, 5]. Electron microscopic observation revealed that graphitized domains existed along with ungraphitized domains. The former seemed to correspond to the component profile with $c_0 = 6.72\text{Å}$ and the latter with $c_0 = 6.86\text{Å}$. Each was named the graphitic and the turbostratic component, respectively [2, 4, 5]. Electron spin resonance measurement also showed the existence of two components for the carbon heat-treated under high pressure [6]. In heat-treatment of the carbons under high pressure some domains of original ungraphitized carbon particle change to graphitic phase and the other domains of the particle remain unchanged. It was proposed that this type of graphitization process be called the heterogeneous graphitization [7]. The heterogeneous graphitization of soft

carbons was shown experimentally to occur only under high pressure [7, 8]. Microscopic observation of a hard carbon heat-treated under high pressure showed that the graphitic domain was initiated at contact points of particles of the original carbon and grew into the ungraphitized matrix [9].

Carbon specimens heat-treated under high pressure were obtained as sintered cakes without any binder and their bulk densities were relatively high as 1.8 ~ 1.9 g cm⁻³ [10]. Results of measurements of electronic properties of these cakes were already reported [11]. In the present paper the preferred orientation of crystallites in the cakes is reported.

2. Experimental

The carbons used were the polyvinylchloride coke PV-7 and phenolformaldehyde resin char PH-7, both of which were carbonized to about 700°C. The carbon PV-7 is known to be a soft carbon or a graphitizing carbon, and the carbon PH-7 is a hard carbon or a non-graphitizing carbon.

A piston-cylinder type high pressure apparatus was used to perform the heat-treatments under

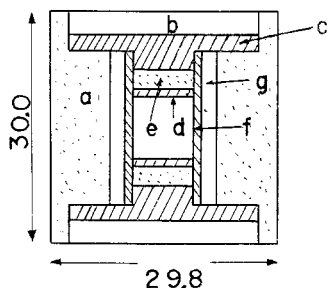


Figure 1 High pressure cell arrangement. (a) pyrophyllite; (b) metal disk; (c) artificial graphite; (d) artificial graphite; (e) pyrophyllite; (f) artificial graphite heater; (g) boron nitride.

the pressure of 5 kbar. High pressure cell arrangement used is shown in Fig. 1, which is almost the same as reported previously [2, 3], except that the graphite heater is larger than the previous one. Pyrophyllite and boron nitride have the roles of the pressure transmitter and the electrical and thermal insulators. The heat-treatment temperature (HTT), or specimen temperature, was determined from the consumed electric power input by using the relation between temperature and power input which was established beforehand. The procedures for the heat-treatment have been previously reported in detail [2-5]. The heat-treatments were carried out at various temperatures between 1200 and 1800°C for 60 min under 5 kbar.

A disk of about 2 mm thick was cut out of the central part of each sintered cake of carbon, where almost no temperature gradient was observed along the axial direction [5]. For the measurement of the preferred orientation of crystallites, a specimen bar of cross section 1×1 mm and length about 6 mm, was cut out from this disk, a pair of longitudinal side planes being perpendicular to the direction of compression. The remaining part of the disk was pulverized in an agate mortar and used for X-ray powder diffraction. On the pulverized specimen, the diffraction profile of the (004) or (002) line was measured. The composite profile was separated into two symmetrical component profiles, which corresponded to the turbostratic and graphitic components, after correcting the diffracted intensity for atomic scattering, Lorentz polarization and absorption factors. The overall content of the graphitic component G was evaluated as the ratio of the area under the separated component profile of the graphitic component to the total area of the composite

profile, which was corrected for the preferred orientation of crystallites in pulverized specimen. The procedure for separation of composite profile and the determination of content of the graphitic component were reported previously [2, 4, 12]. The preferred orientation of crystallites in the specimen bar was measured by using a double circled goniometer. The specimen bar was set up against the goniometer head, so that its longitudinal direction was perpendicular to the base of the goniometer. The diffraction profile of the (004) or (002) line was recorded at every 5 or 10 degrees of specimen rotation, α , and the integrated intensity for the diffraction line was determined by measuring the area under the profile. The observed integrated intensity was plotted as a function of rotation angle of specimen α to obtain a so-called rocking curve. The rocking curve was normalized with respect to the maximum intensity at $\alpha = 0$, in other words, to the concentration of crystallites having their c -axes parallel to the compressing direction. In addition to the overall values of preferred orientation of crystallites and of content of the graphitic component, on the composite profiles, the rocking curves for both graphitic and turbostratic components, which were separated by the same procedure as described above, were measured, and the content of the graphitic component was determined as a function of rotation angle α from the compressing direction.

3. Results and discussion

The diffraction profiles of the (004) line of the soft carbon heat-treated at different temperatures are shown in Fig. 2a and those of the (002) line of the hard carbon in Fig. 2b. Changes of content of the graphitic component (G) for both carbons with HTT are shown in Fig. 3. For the soft carbon the graphitic component had a constant c_0 -spacing of 6.72Å and its amount increased with increase in HTT, while the turbostratic component remained unchanged in its X-ray characteristics. Those results agree well with those reported previously [2]. The graphitic component began to appear at as little higher temperature of heat-treatment as 1500°C than that previously reported [2]. This may be caused from the small modification in the pressure cell which was made in order to obtain larger specimen size for the preferred orientation measurement. Because the position of the profile of the graphitic component of the hard carbon was not as distinct as that of the soft carbon, the

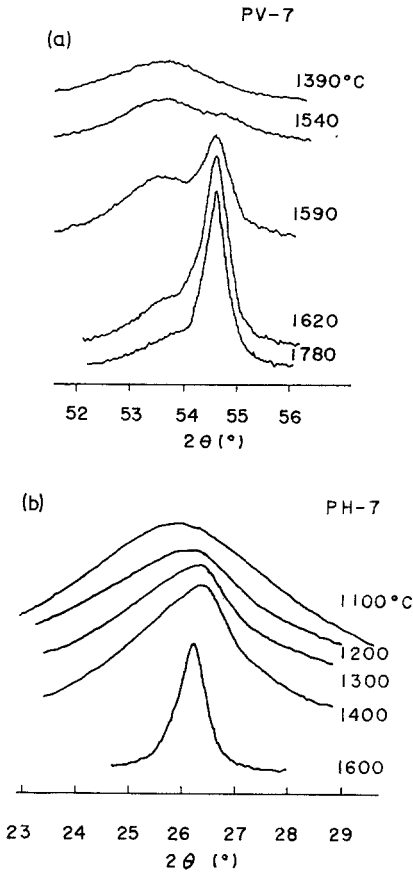


Figure 2 (a) Change of (004) diffraction profile for soft carbon PV-7 with HTT under 5 kbar. (b) Change of (002) diffraction profile for hard carbon PH-7 with HTT under 5 kbar.

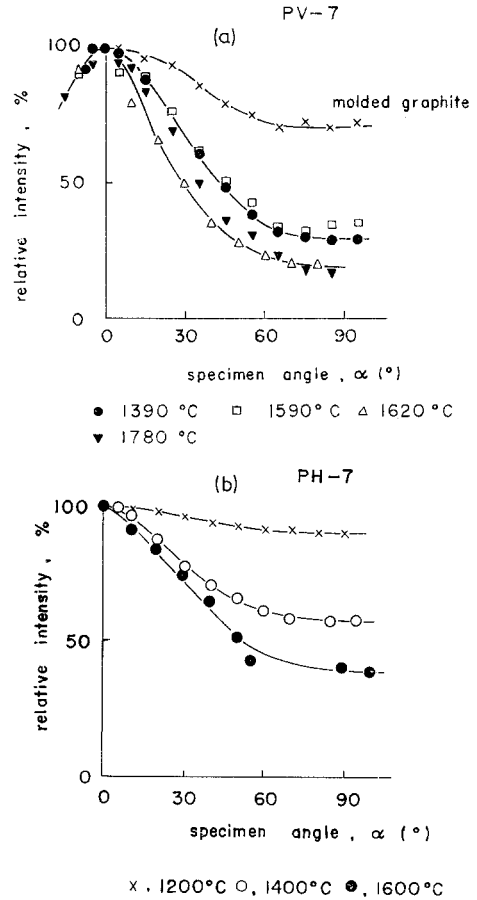


Figure 4 Overall rocking curves of (a) soft carbons and (b) hard carbons heat-treated at various temperatures under 5 kbar.

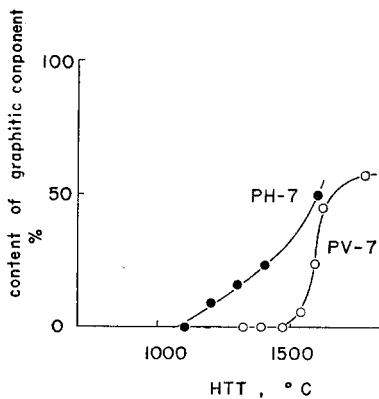


Figure 3 Variation of content of the graphitic component G with HTT.

carbon. However, it was again observed, as previously noted [2], that the hard carbon was graphitized rather easier than the soft carbon under high pressure.

The overall rocking curves of the soft and hard carbons are shown in Figs. 4a and b, respectively. The preferred orientation of crystallites in the soft carbon was very remarkable even for low temperature-treated specimens, but the degree of preferred orientation increased only a little with increase in HTT. In the hard carbon, on the other hand, the specimen heat-treated at 1200°C showed almost no preferred orientation, but the change of orientation with HTT was quite large and at 1600°C the rocking curve was approximately the same as that of the soft carbon heat-treated at the same temperature. The large difference in the change of preferred orientation with HTT between the soft and hard

probable error of content of the graphitic component may be larger than that of the soft
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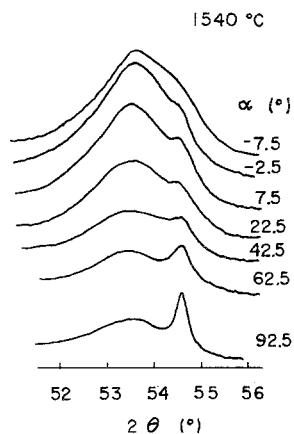


Figure 5 Change of (004) diffraction profile with rotation angle, α , for the soft carbon heat-treated at 1540°C under 5 kbar.

carbon is caused from the difference in the texture of the original particles. On soft carbon, graphite-like layers orientate roughly parallel to each other in flakey particles [13], but the layers of hard carbon are small and orientate at random, and so the particles of hard carbon were optically isotropic, and had irregular shape and sharp edges [9, 14].

The diffraction profiles at different rotation angles, α , of the soft carbon specimen heat-treated at 1540°C are shown in Fig. 5. From these profiles the content of the graphitic component at each rotation angle, α , was determined. The area under the profile, i.e., integrated intensity is plotted as a function of rotation angle, α , in Figs. 6a, b and c for 1540, 1590 and 1780°C treated specimens, respectively, by histogram. The curves in these figures correspond with the overall rocking curves which are shown in Fig. 4a. The content of the graphitic component is represented by shadowed area and the percentage of the graphitic component on the amount of crystallites, of which c -axes make an angle of α with the compressing direction, is shown as a numerical value. It can be seen that the content of the graphitic component of which the c -axis is parallel to the compressing direction, increased with HTT. However, attention should be drawn to the fact that the turbostatic component of which the c -axis was perpendicular to the compressing direction, transformed to the graphitic component easier at low temperature than that parallel, and at temperatures as high as 1780°C no difference

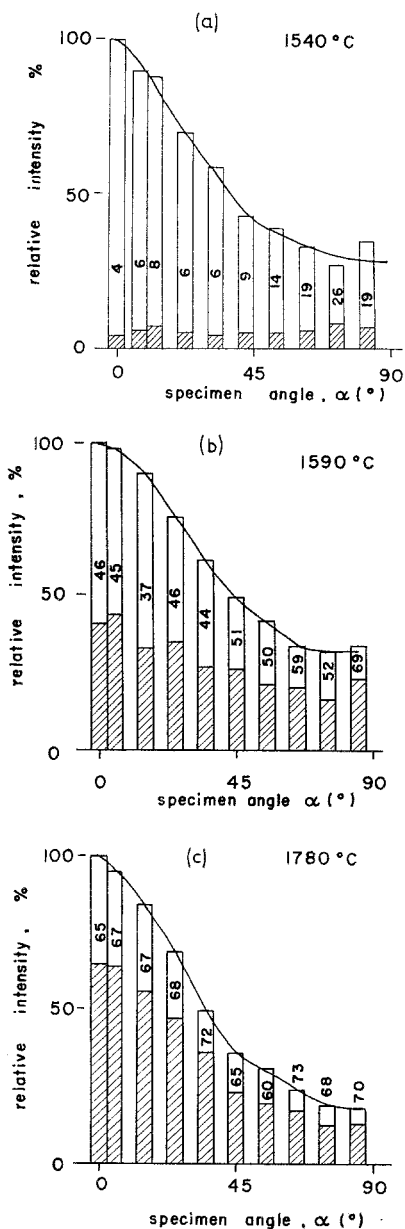


Figure 6 Changes of integrated intensity of (004) diffraction with rotation angle, α , treated at (a) 1540°C; (b) 1590°C; and (c) 1780°C. The content of the graphitic component at every α was shown by shadowed area and in numerical value.

was observed in the percentage of the graphitic component among different rotation angles.

It was already reported [9, 14] that by optical microscopic observation the graphitic component was found to nucleate at contact points of angular particles of hard carbon and grew into

ungraphitized matrix. The present result and the results of microscopic observations may contribute to the understanding of the mechanism on the formation of the graphitic component at high pressure and relatively low temperature. However, more detailed and elaborated investigations on the growth of the graphitic component should be done for the complete understanding of the mechanism.

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