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Crystallite orientation in polycrystalline graphites made from glass-like carbons under high pressure

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The preferred orientation of crystallites was investigated on polycrystalline graphites made from the glass-like carbons with spherical particles under a pressure of 5 kbar at 1300 to 2000°C. The glassy carbon spheres 40 to 70 μm diameter which were pre-heated at 1000°C under normal pressure, gave sintered discs with a bulk density of 1.5 g cm^{-3} and a relatively high degree of orientation. However, spheres of the same type pre-heated at 2000°C gave the high bulk density of 1.9 g cm^{-3} and a very low degree of orientation. The carbon beads 40 to 70 μm diameter gave a relatively low degree of orientation and pre-heating at 2000°C reduced the degree very remarkably. Carbon beads with a smaller particle size, < 20 μm, gave a lower degree of orientation. Pre-heating of the initial carbon of small particle size at temperatures as high as 2000°C resulted in a low degree of preferred orientation of the crystallites in the sintered discs, the temperature dependence being the strongest.

1. Introduction

The effects of the degree of graphitization, density and anisotropy on properties are very important and fundamental characters of polycrystalline graphites. High density has been attained by hot-pressing at relatively low pressures [1, 2]. At higher pressures, above 3 kbar, not only a high density but also high degree of graphitization has been obtained at relatively low temperatures (1600°C) [3-7]. An abrupt graphitization and a remarkable densification have been observed particularly on non-graphitizing glass-like carbons at pressures under 5 kbar [5, 6]. Detailed observation by polarized light microscopy has shown that the nucleation and growth of anisotropic graphite from an isotropic matrix of a glass-like carbon, initiates at contact points of the grains [8].

In the present work, two glass-like carbons, glassy carbon spheres and carbon beads, were graphitized a 5 kbar and the orientation functions of graphite crystallites in the sintered discs measured, as well as the bulk density and degree of graphitization. Both isotropic and anisotropic bodies were obtained from glass-like carbons by selecting grain size and preliminary heat-treatment temperature.

2. Experimental

The samples used are shown in Table I, with the temperature of preliminary heat-treatment under normal pressure, particle size and heat-treatment temperature at 5 kbar. Glassy carbon spheres (Tokai Electrode Mfg Co) were made from furfuryl alcohol condensate, and the carbon beads (Kureha Chemical Co) from pitch materials.

Heat-treatments under a pressure of 5 kbar were performed at temperatures between 1300 and 2000°C for 1 h using a piston-cylinder-type apparatus. Almost all specimens were obtained as sintered discs approximately 8 mm diameter and 5 mm thick. The bulk density of the discs was measured. The fractured surfaces of the discs were observed by scanning electron microscopy. On pulverized specimens, the X-ray diffraction profiles of (002), (004), (10), (11) and (112) lines were measured by using Cu$K\alpha$ radiation. The average c_0-spacing, $\bar{c}_0$, was calculated from the Bragg angles of the (002) and (004) lines, referring to an internal silicon standard.

Small bars, in which the longitudinal direction was perpendicular to the compressing direction, were cut from the sintered discs for use in

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TABLE I The glass-like carbons used

Sample	Carbon	Particle size (μm)	Pre-heat-treatment temperature under normal pressure (° C)	Heat-treatment temperature under 5 kbar for 1 h (° C)
GCS-10	Glassy carbon spheres	40–70	1000	1300–1900
GCS-20			2000	
CB-L-10	Carbon beads	40–60	1000	1300–2000
CB-L-20			2000	
CB-S-10	Carbon beads	< 20	1000	1300–1900
CB-S-15			1500	

measuring the distribution function of the c-axis of graphite crystallites along the compressing direction. The change of maximum intensity of the (002) diffraction line with a rotation angle ϕ of a specimen bar from the compressing direction was recorded by fixing the scintillation counter on the double circled goniometer. The recorded intensities were normalized with respect to that at $\phi = 0$.

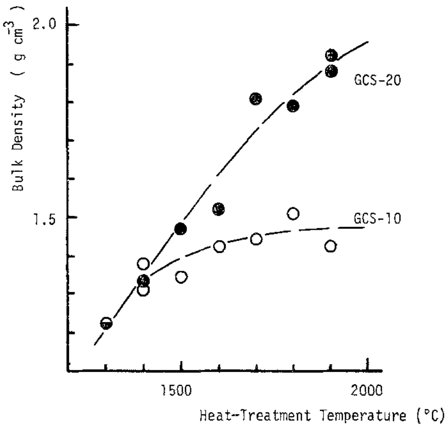


Figure 1 Bulk densities of the sintered discs made from glassy carbon spheres under 5 kbar pressure.

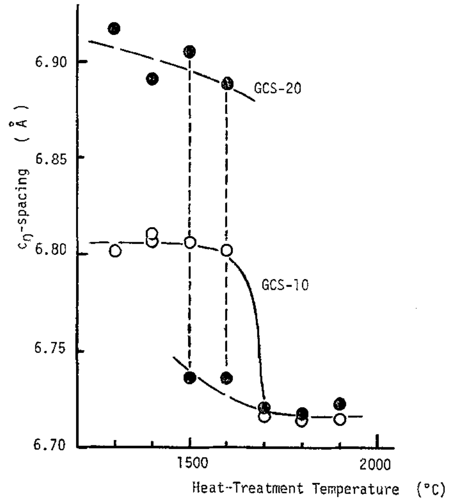


Figure 2 Changes of average c_0-spacing, $\bar{c}_0$, of the glassy carbon spheres with heat treatment temperature under 5 kbar pressure.

3. Results and discussion

3.1. Bulk density and graphitization

The sintered discs made from carbons heat-treated initially at 1000° C have relatively low bulk densities (1.3 to 1.5 g cm^{-3}), as shown on the glassy carbon spheres in Fig. 1. The low values of bulk density are probably caused by the porous structure of these carbons [9] and by large amounts of volatile matter due to the low treatment temperature. On the glassy carbon spheres pre-heated at 2000° C, however, remarkable densification was found, as shown in Fig. 1. The density of the discs heat-treated at 1900° C is comparable to that of the graphitizing carbons. A similar densification was also found for the carbon beads pre-heated above 1500° C, CB-L-20 and CB-S-15 [5, 6].

Graphitization of the glass-like carbons occurred abruptly at 1600 to 1700° C. The changes of $\bar{c}_0$, which is a measure of graphitization degree, with heat-treatment temperature under 5 kbar pressure are shown on the glassy carbon spheres in Fig. 2. Above 1700° C, graphitization of the glass-like carbons used occurs completely, $\bar{c}_0$ reaching about 6.72 Å and three-dimensional diffraction lines of (1 0 1) and (1 1 2) being observed. Before complete graphitization occurs (at 1500 to 1600° C), the co-existence of graphitic and unchanged turbostratic structures were clearly found on the (00l) profiles, for the spheres pre-heated at 2000° C. On both carbon beads CB-L and CB-S, abrupt graphitization was also observed at 1500 to 1700° C. The changes of diffraction profiles and $\bar{c}_0$ with HTT were very similar to those of the glassy carbon spheres.

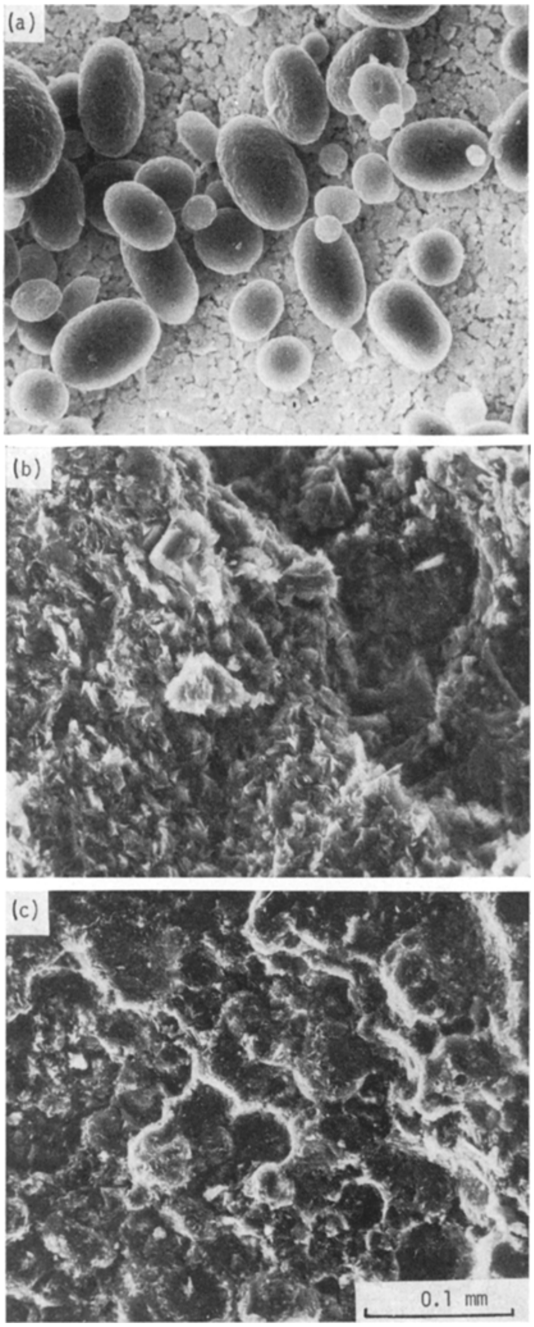


Figure 3 Scanning electron micrographs of the glassy carbon spheres. (a) Original GCS-10; (b) GCS-10 heat-treated at 1800° C under 5 kbar pressure; (c) GCS-20 heat-treated at 1900° C under 5 kbar pressure.

3.2. Scanning electron microscopic observations

The scanning electron micrographs of the fractured surfaces of the sintered discs are shown in Figs. 3 and 4 for the original samples and the samples heat-treated at high temperatures under 5 kbar.

In the case of GCS-10, the spherical shape (mostly ellipsoids) of the original spheres (Fig. 3a) is not retained above 1700° C (Fig. 3b). For GCS-20, however, the spherical shape can be found even after heat-treatment at high temperatures (Fig. 3c), although all spheres were graphitized.

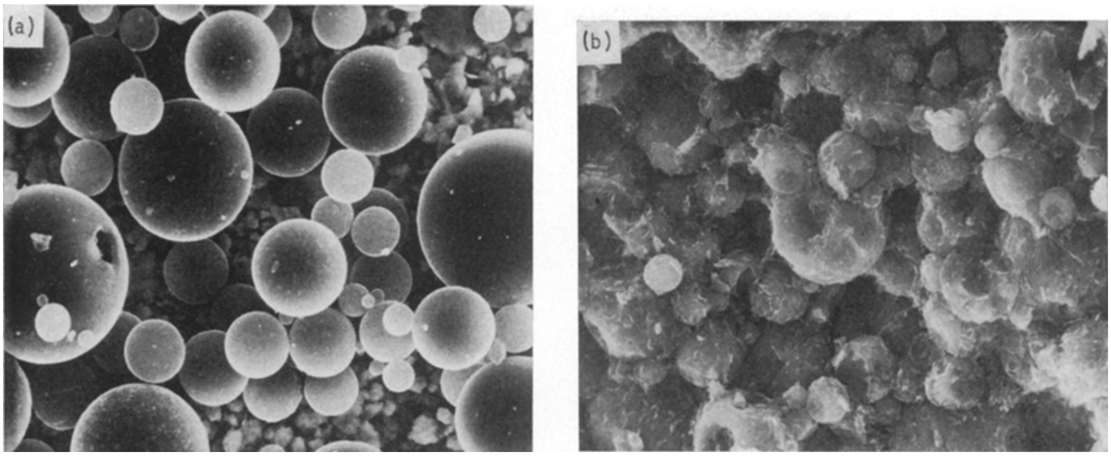
On the carbon beads CB-S, spherical particles similar in size to the original ones, can easily be seen even after heat-treatments at high temperatures under 5 kbar pressure (Fig. 4). For carbon beads CB-L, the spherical shape was also retained at high temperatures, more clearly for CB-L-20 than CB-L-10.

3.3. Preferred orientation of crystallites

Some orientation functions obtained are shown in Fig. 5, with an illustration of the relation between angle ϕ and the compressing direction. From Fig. 5, the value at $\phi = 90°$, $I(90°)$, is found to represent the degree of orientation for each specimen. In Fig. 6, the values of $I(90°)$ are plotted as a function of heat-treatment temperature under 5 kbar pressure, including the results on graphitizing polyvinylchloride coke and non-graphitizing phenol resin char [10].

The $I(90°)$ value, i.e. the degree of preferred orientation, is found to depend strongly on the carbon used as the starting material. Glassy carbon sphere GCS-10 has a relatively low value of $I(90°)$, i.e. a high degree of orientation, which is very close to that of phenol resin char with particles of irregular shape [10]. The destruction of the original spherical shape of GCS-10, described in Section 3.2, seems to be one reason why GCS-10 shows a similar degree of orientation to carbons with irregular particle size. From a flaky graphitized powder of a very small size (5 μm), sintered discs with a similar degree of orientation were obtained by the same heat-treatment [10]. The same glassy carbon spheres pre-heated at 2000° C (GCS-20) show very high value of $I(90°)$, i.e. a very low degree of orientation, probably because they retain their spherical shape even after graphitization at high temperatures under a pressure of 5 kbar (Fig. 3c).

The carbon beads of small particle size pre-heated at 1000° C, CB-S-10, show a much higher value of $I(90°)$ than GCS-10, probably because of their small particle size and retainment of their



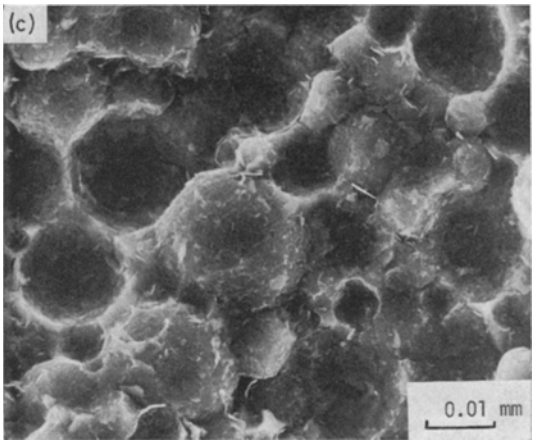


Figure 4 Scanning electron micrographs of the carbon beads with a particle size of < µ20 m. (a) Original CB-S-10; (b) CB-S-10 heat-treated at 1900° C under 5 kbar pressure; (c) CB-S-15 heat-treated at 1900° C under 5 kbar pressure.

original spherical shape after heat-treatments under pressure. The same carbon beads show a little higher value of $I(90°)$ after pre-heating at 1500° C (CB-S-15). Another carbon bead pre-heated at 1000° C (CB-L-10), which has a relatively large particle size, shows a transient from CB-S-10 to GCS-10, $I(90°)$ decreasing from a value similar to CB-S-10 to that of GCS-10. This result may show a gradual destruction of the original particle shape with increase in heat-treatment temperature. However, it was difficult to find any corresponding texture change by scanning electron microscopy. The carbon beads pre-heated at 2000° C (CB-L-20) give very high values of $I(90°)$, i.e. give very isotropic graphite bodies.

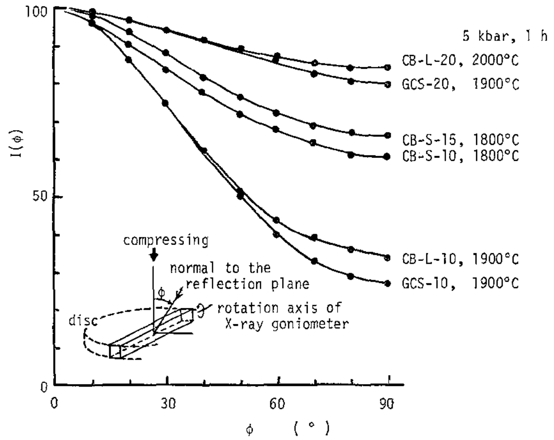


Figure 5 Orientation functions for the discs made from various glass-like carbons under 5 kbar pressure.

The preferred orientation of crystallites in the polycrystalline graphites made by high-pressure graphitization depends strongly on the starting material. From the graphitizing polyvinyl-chloride coke which has particles of anisotropic texture, a very high degree of orientation has been obtained [10, 11]. From the non-graphitizing glass-like carbons with isotropic texture, pre-heated below 1500° C, a relatively high degree of orientation is obtained, although a little lower than that from graphitizing carbons. This may be caused by the drastic change in structure during high-pressure graphitization and also by the lack of exact hydrostaticity of applied pressure. It was previously reported [7] that the preferred orientation in the discs made from graphitizing coke was reduced by the addition of carbon black. The high degree of orientation may

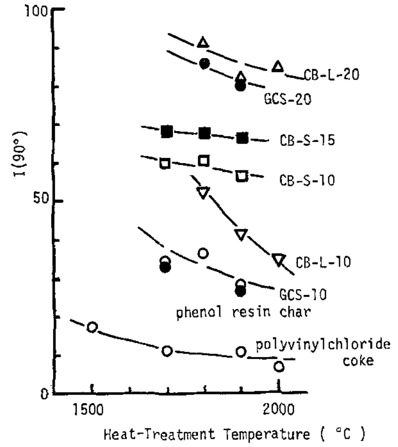


Figure 6 $I(90°)$ as a function of heat-treatment temperature under 5 kbar pressure.

also be reduced by the use of the non-graphitizing carbons pre-heated at high temperatures under normal pressure. Although the carbons with small particle size give a lower degree of orientation, the pre-heating of non-graphitizing carbon at a temperature above 2000° C is more effective for obtaining isotropic graphite bodies by heat-treatments under high pressure. However, it must be mentioned that pre-heating of non-graphitizing carbons increases the graphitization temperature under a pressure of 5 kbar [6]. Pre-heating of glass-like carbons at about 2000° C is suitable for obtaining isotropic graphite bodies as graphitization occurs at about 1700° C under 5 kbar pressure.

Acknowledgements

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References

1. H. BÖDER and E. FITZER, *Carbon* **8** (1970) 453.
2. W. C. CHARD and D. E. NIESZ, 11th Biennial Conference on Carbon, Gatlinburg, 4-8 June (1973).
3. T. NODA and H. KATO, *Carbon* **3** (1965) 289; T. NODA, K. KAMIYA and M. INAGAKI, *Bull. Chem. Soc. Japan* **41** (1968) 485.
4. K. KAMIYA, M. INAGAKI, M. MIZUTANI and T. NODA, *ibid* **41** (1968) 2169.
5. M. INAGAKI, Y. TAMAI, S. NAKA and K. KAMIYA, *Ceram. Bull.* **52** (1973) 856.
6. M. INAGAKI, K. HORII and S. NAKA, *Carbon*, in press.
7. M. INAGAKI, S. HAYASHI and S. NAKA, *High Temp.-High Press.*, in press.
8. K. KAMIYA, M. INAGAKI and T. NODA, *Carbon* **9** (1971) 287; *Idem, High Temp.-High Press.* **5** (1973) 331.
9. R. E. FRANKLIN, *Proc. Roy. Soc. Lond.* **A209** (1951) 196.
10. M. INAGAKI and S. NAKA, *Powder and Powder Met.* to be published.
11. K. KAMIYA, T. NODA, M. INAGAKI and H. SAITO, *J. Mater. Sci.* **7** (1972) 1244.

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