Relations between the Degree of Orientation and the Conditions of the Deposition of Pyrolytic Graphite

By Tokichi NODA, Michio INAGAKI and Hajime KATO

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Pyrolytic graphite is produced by the thermal decomposition of a carbonaceous gas. Recently, this graphite has attracted considerable attention and has been widely studied because it possesses many interesting physico-chemical properties. In a number of investigations concerning pyrolytic graphite, it has been found that its electrical, thermal, and mechanical properties are extremely different from those of ordinary graphitized products. Its tensile strength along a deposition surface is about ten times higher than that of ordinary graphitized products1), and its strength-to-weight ratio is the highest of all high-temperature materials2). This graphite has a high density and a high impermeability to gases. In addition, it is more resistant to oxidation. Its thermal and electrical conductivities are strongly anisotropic, higher in a plane parallel to the deposition surface than in a plane perpendicular to it, because the crystallites in pyrolytic graphite are highly oriented in placing their layer-planes parallel to the deposition surface. It can be said that many interesting physico-chemical properties of pyrolytic graphite are largely dependent upon the orientation of the crystallites. However, the direct

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1) H. E. Martens and J. D. Jaffe, *J. Appl. Phys.*, **31**, 1122 (1960).

2) Anon., *Industrial Heating*, **27**, 593 (1960).

measurement of the orientation for pyrolytic graphite had not yet been carried out. Therefore, the present work was carried out to discover the relations between the degree of orientation and the conditions of the deposition, such as the rate of flow of hydrocarbon gas and the temperature of the deposition. The degree of orientation was directly measured by means of the X-ray diffraction method. The graphitizability of pyrolytic graphite is also discussed on the basis of X-ray diffraction profiles.

Experimental

Preparation of Pyrolytic Graphite. — Pyrolytic graphite was prepared by passing gaseous hydrocarbons on the heated surface of an electrographitized carbon rod. The rod was 9 mm. in diameter and had a reduced central part 9 mm. wide, 1 mm. thick and 60 mm. long; it was placed in a bell-jar type metallic chamber. The rod was heated by the passage of electric current directly through it, and the temperature of the surface of the reduced part was measured with the aid of an optical pyrometer. The pressure of gas in the chamber was measured with a mercury manometer, and the rate of gas flow, with a flowmeter. The gas used was a commercial propane gas which was a mixture of light hydrocarbons, such as propane, propyrene, butane, and butene. After the chamber had been evacuated, the propane gas was admitted at a constant rate of gas flow—45, 115, 330, 665 or 1110 cc./min., and then the rod was heated to the desired temperature of deposition—1600, 1800, 2000, 2200 or 2400°C. The heating of the rod was performed in a moment. Deposition was carried out at a constant temperature of the deposition surface and at a constant rate of gas flow until the deposited graphite had thickness enough.

The Anisotropy Factor and the X-Ray Diffraction Profile.—The orientation function, $I(\phi)$, of graphite crystallites in a specimen was obtained from a (002) diffraction ring[3] taken by using unfiltered CuK radiation. In order to make a specimen, the deposited graphite was sliced in the direction perpendicular to the deposition surface.

The orientation anisotropy factor (σ_{oz}/σ_{ox}) proposed by Bacon[3] can be calculated as

$$\sigma_{oz}/\sigma_{ox}=2\cdot\frac{\int_0^{\pi/2} I(\phi)\cdot\cos^2\phi\cdot\sin\phi\cdot d\phi}{\int_0^{\pi/2} I(\phi)\cdot\sin^3\phi\cdot d\phi} \qquad (1)$$

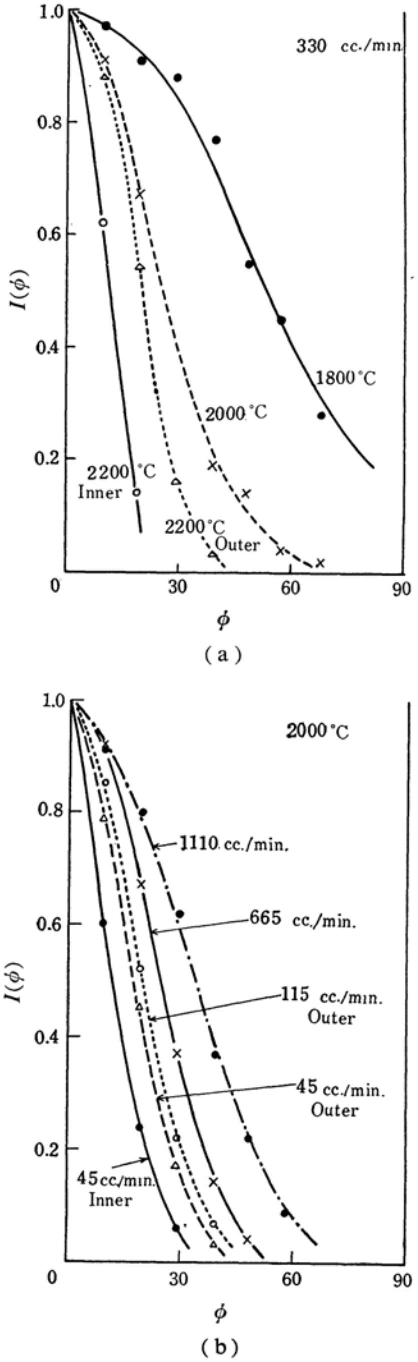
The orientation functions of all slices could well be approximated to curves of $\cos^n\phi$, that is to say, $I(\phi)=\cos^n\phi$. Therefore, Eq. 1 can be reduced to

$$\sigma_{oz}/\sigma_{ox}=n+1 \qquad (2)$$

The profiles of the (002) or (004) diffraction of the deposited graphites were obtained by using a recording diffractometer.

Results and Discussion

Relations between the Anisotropy Factor and the Conditions of Deposition.—The orientation functions of the deposited graphites, which were produced at a constant rate of gas flow, i. e., 330 cc./min., and at various temperatures of deposition, are shown in Fig. 1a. The



(a)

(b)

Fig. 1. Orientation functions of pyrolytic graphites.

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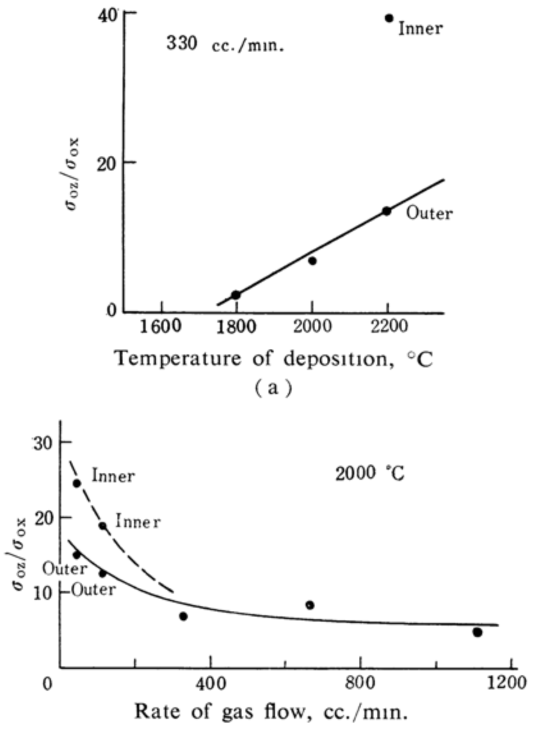
[3] G. E. Bacon, *J. Appl. Chem.* (*London*)., **6**, 477 (1956).



(a)

(b)

Fig. 2. Anisotropy factors (σ_{oz}/σ_{ox}) of pyrolytic graphites.

anisotropy factor, which was calculated from the orientation function, is shown in Fig. 2a as a function of the temperature of deposition. From the two figures, it can be seen that the degree of crystallite orientation in the pyrolytic graphite increases with the increase in the temperature of deposition and that the anisotropy factor is directly proportional to the deposition temperature between 1800 and 2400°C, when the anisotropy factor is taken as a measure of the crystallite orientation. Brown and Watt⁴⁾ reported that the electrical resistivity of pyrolytic graphite decreases in the direction parallel to the deposition surface and increases in the direction perpendicular to it as the temperature of deposition rises. This strong dependence of the electrical resistivity on the temperature of deposition has been explained on the assumption that the graphite crystallites are more highly oriented as the temperature of deposition increases. In the present work, this assumption is experimentally verified by the direct measurement of the orientation.

The orientation functions of deposited graphites which were produced at a constant temperature, i. e., 2000°C, and at various rates of gas flow are shown in Fig. 1b. The variation of the anisotropy factor with the rate of gas flow is shown in Fig. 2b. On the basis of the two figures, it can be said that the degree of crystallite orientation increases and that, accordingly, the anisotropy factor becomes larger as the rate of gas flow decreases.

A cross-section of the deposited graphite, which was produced at a temperature above 2000°C, consisted of two or three layers. These layers were easily distinguishable from one another on the basis of their lusters. An inner layer, which was closer to the graphite substrate, had more metallic luster than an outer one.

The anisotropy factor of an inner layer was found to be larger than that of an outer one. These large anisotropy factor values of the inner layer have never been found in ordinary graphitized products³,⁵⁾. It has been previously reported, however, that graphite crystallites in carbon which had been obtained by vacuum evaporation were highly oriented with their layer-planes parallel to the evaporated surface and that the degree of orientation increased with the increase in the temperature of the heat-treatment⁶⁾.

X-Ray Diffraction Profiles.—As is shown in Fig. 3, almost all the (002) or (004) diffraction profiles of the deposited graphites have been found to be asymmetrical and to be apparently composed of two kinds of profiles, whose values of c_0 are 6.72 and 6.86 Å. Similar phenomena have been observed with charcoals heat-treated at various temperatures⁷,⁸⁾. The similarity of the asymmetrical diffraction profile of pyrolytic graphite to that of charcoal is of great interest in regard to their graphitization.

Diefendorf reported that soot particles, produced in a gas phase by the thermal decomposition of methane, were incorporated in pyrolytic graphite when the pressure of the gas was above 5 mmHg⁹⁾. The observed asymmetry of the diffraction profile of the pyrolytic graphite may be caused by the incorporation of these soot particles.

The profile of an inner layer of the deposited graphite was sharply defined, and its c_0 value was 6.71～6.72 Å; i. e., the inner layer of the deposited graphite was highly graphitized. Because the crystallites were strongly oriented, the thermal conductivity in a direction perpendicular to the deposition surface was very

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4) A. R. G. Brown and W. Watt, "Industrial Carbon and Graphite", Society of Chemical Industry, London (1958), p. 85.

5) T. Noda and M. Inagaki, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **62**, 1300 (1959).

6) T. Noda and H. Matsuoka, ibid., **64**, 2083 (1961).

7) T. Noda, M. Inagaki and N. Fusisawa, ibid., **64**, 1370 (1961).

8) R. E. Franklin, *Proc. Roy. Soc.*, **A209**, 196 (1951).

9) R. J. Diefendorf, *J. Chim. Phys.*, **4**, 815 (1960).

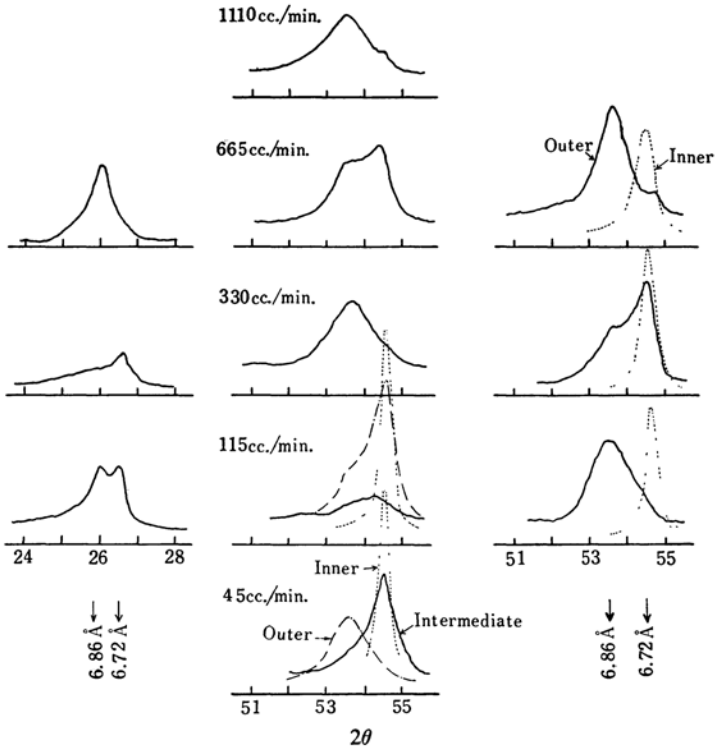

Fig. 3. X-Ray diffraction profiles of pyrolytic graphites.

low[2] and a large temperature gradient seemed to be produced in the deposited graphite. Therefore, it is thought that the temperature of an inner layer is higher than that of the deposition surface.

Petroleum coke is the most easily graphitizable carbon of all raw carbon materials, but the c_0 value of one sample of petroleum coke (Greate Lake Co.) was not less than 6.718Å, even when it was heat-treated at 3400°C[7]. It has also been reported that vacuum-evaporated graphite had a c_0 value of 6.710Å when it was heat-treated at 2800°C under atmospheric pressure[6]. The inner layer of pyrolytic graphite had a c_0 value of $6.71\sim6.72$Å. It can be said that a carbon in which graphite crystallites are strongly oriented, such as pyrolytic graphite and evaporated graphite, is much more graphitizable than ordinary raw carbon materials, for instance, coke and carbon black.

Summary

Pyrolytic graphites were deposited on carbon rods by the thermal decomposition of a commercial propane gas at various temperatures and at various rates of gas flow. The orientation functions of the graphite crystallites in the deposited graphites were measured by means of the X-ray diffraction method. It was shown that the degree of orientation in the deposited graphites increased with the increase in the temperature of deposition and decreased with the increase in the rate of gas flow. The graphites deposited at temperatures above 2000°C were composed of two layers; the inner layers had a larger degree of orientation and a higher graphitizability than the outer layers. Almost all the $(0\,0\,l)$ diffraction profiles of the deposited graphites were found to be asymmetrical and to the apparently composed of two kinds of profiles, whose c_0 values were 6.72 and 6.86Å.

Department of Applied Chemistry
Faculty of Engineering
Nagoya University
Chikusa-ku, Nagoya