A Comment on the Structure of Glassy Carbon

Tokiti NODA,* Michio INAGAKI** and Shigehiko YAMADA***

** Mie University, Tsu, Mie-Ken*

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

**** Nagoya Plant, Tokai Electrode Mfg. Co., Showa-ku, Nagoya*

Department of Applied Chemistry, Aichi Institute of Technology, Chikusa-ku, Nagoya

(Received June 4, 1968)

Glassy carbon is an apparently isotropic, continuous and non-porous material, showing conchoidal surface of fracture. It has a similar spectral dependence of reflectance to that of graphite.[1] Its electrical resistivity is of the same order as that of regular carbon materials and its thermal conductivity is relatively high compared with that of common ceramic materials.[2] The changes in Hall coefficient and magnetoresistance of glassy carbon with heat treatment temperature (HTT) resemble those of very hard carbon.[3] Its high strength, high Young's modulus, high hardness and also high impermeability to gases[2] suggest that glassy carbon must have a unique structure different from those of regular carbons.

The first proposal concerning the structure of glassy carbon was made with the aid of radial distribution function by two of the present authors.[4] Two other models of the structure of glassy carbon have been proposed since then.[5,6] Noda and Inagaki[4] proposed the contribution of tetrahedral bond together with trigonal bond as the principal bonds to the construction of glassy carbon. The extension of region consisting of only trigonally-bound carbon atoms or only tetrahedrally-bound carbon atoms can not be known by the radial distribution analysis. From the observation that the X-ray diffraction pattern of glassy carbon is very similar to that of turbostratic carbons,[4] it was deduced for the structure of glassy carbon that trigonal carbon atoms make small domains of two-dimensional graphite-like arrangement and that these domains are linked by tetrahedral bonds, while tetrahedral carbon atoms themselves make no domain of regular arrangement.

Furukawa[5] composed a model of three-dimensional irregular network configuration which contains all kinds of C–C bonds, *i. e.*, tetrahedral, planar double, linear triple and also conjugated C–C bonds. This model has no repetition of hexagonal rings of trigonal carbon atoms more than three. Insofar as glassy carbon heat-treated at such a low temperature as 800°C is concerned, the above two models are similar to each other, because the model of Noda and Inagaki consists of a large amount of tetrahedral carbon atoms and a number of small domains of trigonal carbon atoms, and Furukawa's model mainly consists of carbon atoms bound by tetrahedral and planar double bonds. According to Noda and Inagaki,[4] the content of trigonal carbon atoms increases and so the content of tetrahedral carbon atoms decreases with rise of HTT, and the X-ray diffraction band of (00*l*) becomes narrower with rise of HTT. These changes may be attributed to the increase in the size of the domains of trigonal carbon atoms. Takahashi and Westrum[7] measured the specific heat of glassy carbon, which was heat-treated at 3000°C, by adiabatic calorimetry from 6 to 350°K and found its T^2-dependence. This result suggests that glassy carbon mainly consists of two-dimensional layer lattice. Furukawa's model is not in harmony with this suggestion.

Kakinoki[6] proposed a model which consists of two kinds of domains, which are respectively composed of tetrahedral and trigonal carbon atoms and linked to neighboring domains by oxygen bridges. In his model, the oxygen bridges are responsible for the low density of glassy carbon and for the fact that the carbon is hardly graphitized at temperatures as high as 3000°C.[2,4] The oxygen content of glassy carbon directly determined by chemical analysis[8] was found to be about 1.2 per cent for 900°C-treated and about 0.3 per cent for 1200°C-treated glassy carbons, and 0.1—0.2 per cent for glassy carbon heat-treated at 1300—3000°C, respectively, the last value was determined by activation analysis.[9] The porosity of glassy carbon changes with HTT. Glassy carbon heat-treated at 600—700°C has the maximum apparent porosity (10—11%) and absorbs moisture of about 10 per cent by weight.[10] The oxygen

1) E. A. Taft and H. R. Philipp, *Phys. Rev.*, **138A**, 197 (1965).
2) S. Yamada and H. Sato, *Nature*, **193**, 261 (1962); *Carbon*, **2**, 253 (1964).
3) T. Yamaguchi, *Carbon*, **1**, 47 (1963).
4) T. Noda and M. Inagaki, This Bulletin, **37**, 1534 (1964).
5) K. Furukawa, *Nihon Kessho Gakkai Shi*, **6**, 101 (1964).
6) J. Kakinoki, *Acta Cryst.*, **18**, 578 (1965).
7) Y. Takahashi and E. F. Westrum, Jr., presented at the First Japanese Calorimetry Conference, Osaka, Nov., 1965.
8) K. Imaeda, private communication.
9) I. Fujii, mentioned in Ref. No 5.
10) H. Sato and S. Yamada, presented at Symposium on Carbon, Tokyo, July, 1964.

content as high as about 5—6 per cent, which was mentioned by one of the present authors (S. Y.) at an informal meeting of the Symposium on Carbon in Tokyo (1964) and was used by Kakinoki for construction of his model, was found later by Yamada to be mainly due to the moisture absorbed in glassy carbon. Fitzer, Schäfer and Yamada also obtained similar results on moisture absorption[11] and oxygen content[12] in the cases of glass-like carbons obtained from phenolic and furan resins. Therefore, Kakinoki's model seems to be inappropriate, because it has been derived from the presumption that glassy carbon contains several per cent of oxygen.

Ergun and Tiensuu[13] pointed out that X-ray diffraction study is not sufficient to ascertain the presence of diamond-like structures in amorphous carbons, but other properties of carbons such as hardness, density, electronic properties, graphitizability, *etc.*, must be considered. From the above discussions and also by considering the properties of glassy carbon,[2,3] the structural model of Noda and Inagaki, *viz.*, trigonal carbon atoms make small domains of two-dimensional graphite-like arrangement and these domains are linked by tetrahedral bonds, may be considered to be the most probable for the structure of glassy carbon. The possibility, that some kinds of bonds other than the tetrahedral one contribute to the linking of graphite-like layers, may not be ruled out.

Small graphite-like layers linked by C–C bonds three-dimensionally without any ordering make a continuous and low-density glassy carbon body which is isotropic and homogeneous in the long range ordering. In low-temperature-treated glassy carbons, the size of graphite-like layers is small and the percentage of linking carbon atoms is relatively high, but the size of layers increases and the percentage of linking carbon atoms decreases with rise of HTT. Insofar as to the structure that graphite-like layers are linked by so-called criss-cross linkages, glassy carbon is basically similar to regular carbons. The characteristics of glassy carbon, such as high strength, high hardness, impermeability, *etc.*, are mostly due to the high content of carbon atoms linking graphite-like layers successively in the three-dimensional way without any ordering. The high content of linking carbon atoms is also the main reason for non-graphitizability of glassy carbon.

11) E. Fitzer, W. Schäfer and S. Yamada, presented at the Eighth Conference on Carbon, Buffalo, June, 1967.
12) E. Fitzer, W. Schäfer and S. Yamada, unpublished.
13) S. Ergun and V. H. Tiensuu, *Acta Cryst.*, **12**, 1050 (1959).