The Structure of Glassy Carbon

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It has already been reported that the properties of glassy carbon are remarkably different from those of usual electrographitized carbons.[1,2]

In this work, the structure of glassy carbon will be investigated by determining the interlayer spacing, the crystallite size, the disorganized carbon content and the radial distribution function of glassy carbon by means of X-ray diffraction techniques, and a structural model of glassy carbon will be proposed.

Experimental and Results

Two groups of glassy carbon, A and B, were used as the samples in this work. The samples of both groups were heat-treated at temperatures ranging from 500° to 3000°C.

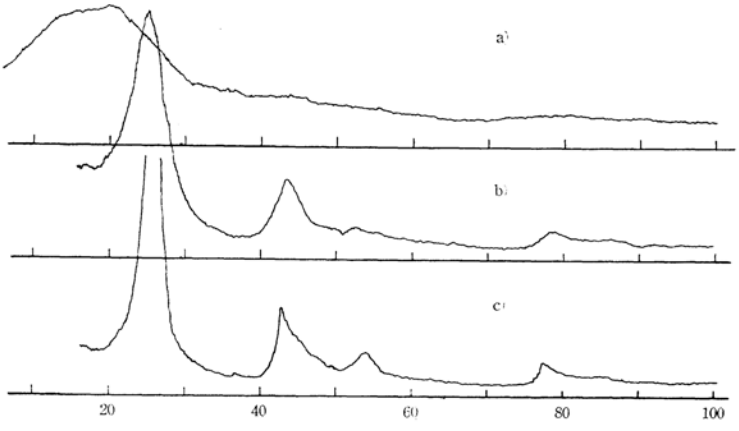

Fig. 1. X-Ray diffraction patterns of glassy carbon treated at a) 500°C, b) 1500°C, and c) 3000°C.

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[1] S. Yamada and H. Sato, *Nature*, **193**, 261 (1962).

[2] S. Yamada, H. Sato and T. Ishii, presented at the Sixth Biennial Conference on Carbon, Pittsburgh, 1963.

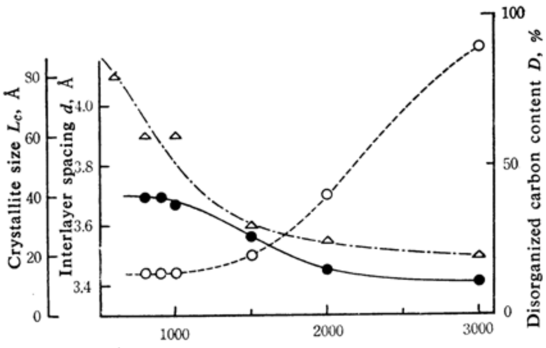

Fig. 2. Variations in the interlayer spacing d, the crystallite size L_c and the disorganized carbon content D with the heat-treatment temperature.
●: Interlayer spacing d
○: Crystallite size L_c
△: Disorganized carbon content D

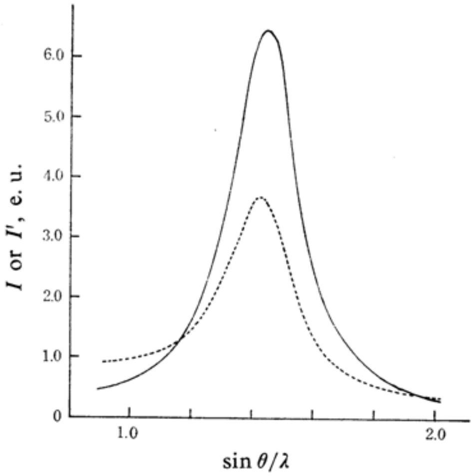

Fig. 3. Determination of the disorganized carbon content D.
……: I-profile, ——: I'-profile which corresponds to the D value of 30%.

The X-ray diffraction patterns are shown for the samples in the A group in Fig. 1. In Fig. 2, the variations of the interlayer spacing, d, the crystallite size, L_c, and the disorganized carbon content, D, are shown as functions of the heat-treatment temperature. The interlayer spacing and the crystallite size were measured from the observed (002) diffraction profile. With the sample heat-treated at 3000°C, the lattice constants, c_0 and a_0, and the crystallite sizes, L_c and L_a, were measured from (002) and (10) diffractions using an extra-pure silicon powder as an inner standard. It was found that $c_0=6.810\,\text{Å}$, $a_0=2.418\,\text{Å}$, $L_c=82\,\text{Å}$ and $L_a=39\,\text{Å}$. The content of disorganized carbon, which did not participate in the graphite-like layer structure, was determined using the same method as Franklin.[3] The method consists of the determination of the most pertinent D value which makes the I'-profile symmetrical. For the glassy carbon heat-treated at 1500°C, the original I-profile and the symmetrical I'-profile, which corresponds to the D value of 30%, are shown in Fig. 3. The value of I' is calculated from Eq. 1:

$$I'=\frac{s^2}{0.0606}\cdot\frac{I-D}{1-D} \tag{1}$$

where $s=2\sin\theta/\lambda$

$$I=\frac{I_{\text{obs}}-I_{\text{inc}}}{I_{\text{co}}}$$

In the above equation, I_{co} and I_{inc} are the intensities of the coherent and incoherent scattering of carbon respectively. The observed intensity, I_{obs}, of (002) diffraction had been corrected for the various intensity factors, such as absorption and Lorentz-polarization factors, and then normalized to electron units by fitting the theoretical and experimental intensities in the range of s from 1.00 to 1.20 Å^{-1}. The measurement of the diffraction intensity was made by means of point-by-point fixed counting at an angular interval of 0.5° and using CuK_α radiation.

In the variations of the interlayer spacing, the crystallite size and the disorganized carbon content with heat treatment, no remarkable difference was found between the samples in the A and B groups.

For each sample, the radial distribution

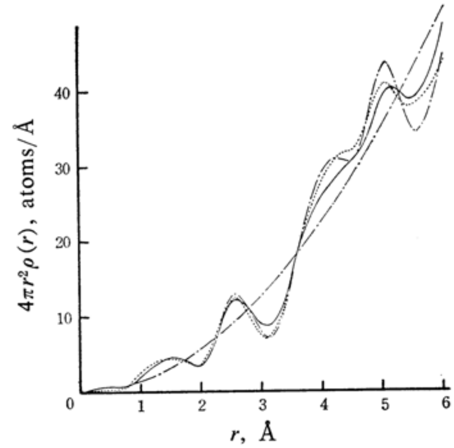

Fig. 4. Radial distribution curve of glassy carbon.
——: Treated at 900°C
……: Treated at 1500°C
–-–-: Treated at 2000°C
—·—: Mean electron density $4\pi r^2\rho_0$

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[3] R. E. Franklin, *Acta Cryst.*, 3, 107 (1950).

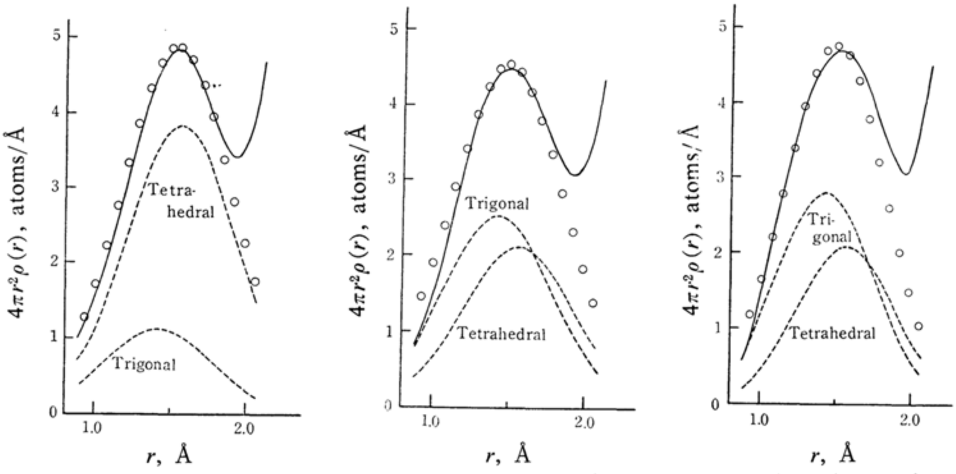
function, $4\pi r^2\rho(r)$, was calculated by means of the summation of Eq. 2:

$$4\pi r^2\rho(r)=4\pi r^2\rho_0 + 8\pi r\sum_{s=0.08}^{1.60} s\cdot i(s)\cdot \mathrm{e}^{as^{-2}}\cdot\sin(2\pi rs)\varDelta s \qquad (2)$$

where $s=2\sin\theta/\lambda$

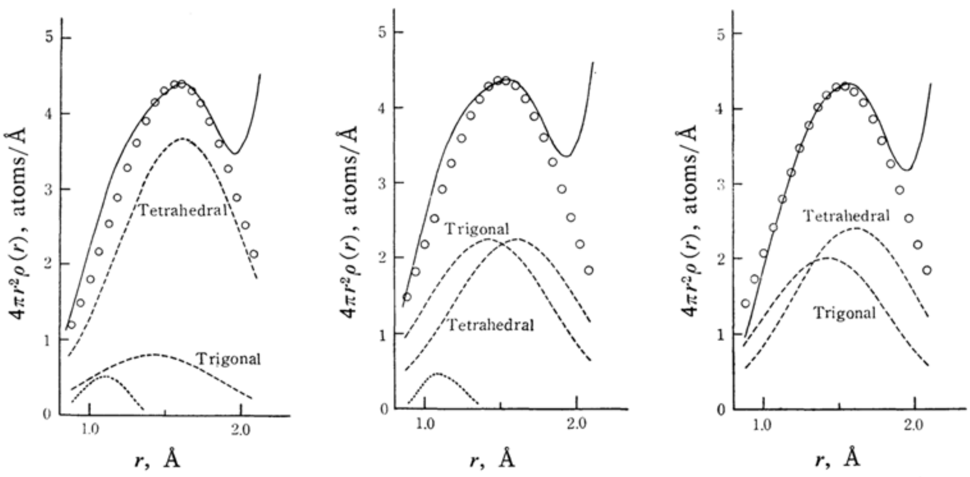
$$i(s)=\frac{I_{\mathrm{obs}}-(I_{\mathrm{co}}+I_{\mathrm{inc}})}{I_{\mathrm{co}}}$$

In the above equation, the value of ρ_0 was calculated as 0.113 atoms/Å^3 using the theoretical density of graphite of 2.25 g./cm^3. The interval, $\varDelta s$, of the above summation was 0.02 Å^{-1}. The factor e^{-as^2} was the artificial temperature factor, and the value of a in this factor was determined as 0.90 so that the value of this factor would be equal to 0.10 at the upper limit of s. The observed intensity, I_{obs}, had been corrected for the various intensity factors and then normalized to electron units on the basis of the range of s from 1.50 to 1.60 Å^{-1}. The measurement of the diffraction intensity was made by means of point-by-point fixed counting and using CuK_α radiation in the range of s from 0.08 to 1.20 Å^{-1} and by using MoK_α radiation in the range of s from 1.20 to 1.60 Å^{-1}. The radial distribution curves for three samples of the B group are shown in Fig. 4.



a) 850°C-treated b) 1500°C-treated c) 2000°C-treated

Fig. 5. Separation of the first peak of the radial distribution curve into component curves with the glassy carbons in the A group.
——: Observed curve ------: Component curve ○○○○: Composite curve



a) 800°C-treated b) 1500°C-treated c) 2000°C-treated

Fig. 6. Separation of the first peak of the radial distribution curve into the component curves with the glassy carbons in the B group.
——: Observed curve ------: Component curve
○○○○: Composite curve ……: Remainder curve

The first peak of the radial distribution curve, whose position corresponds to the distance to the nearest neighbour atoms, is represented by the solid line in Figs. 5 and 6. Since the mean co-ordination number obtained from the area under the observed curve was in the range of 3∼4 and since the first peak was located at around 1.5∼1.6 Å, it was assumed that glassy carbon is mainly composed of two types of carbon atoms, one having a tetrahedral relation to its neighbours, like diamond, and the other having a trigonal relation to its neighbours, like graphite. In this paper, these two types of carbon atoms are called tetrahedral and trigonal carbon atoms respectively. Therefore, the first observed peak was separated into two component curves corresponding to trigonal and tetrahedral carbon atoms on the assumption that the curve for each carbon atom had the Gaussian form. For example, the first observed peak for the glassy carbon heat-treated at 850°C could be separated with a negligible remainder when the two component curves were expressed as follows:

For tetrahedral carbon atom

$$\frac{9.6}{\sqrt{2\pi}}\cdot\exp\left\{-\frac{1}{2}\cdot\left(\frac{r-1.56}{0.36}\right)^2\right\}$$

For trigonal carbon atom

$$\frac{2.8}{\sqrt{2\pi}}\cdot\exp\left\{-\frac{1}{2}\cdot\left(\frac{r-1.42}{0.36}\right)^2\right\}$$

The separated curves are shown by the broken lines in the figures. With several samples of the B group, particularly with samples heat-treated at low temperatures, the remainder between the observed curve and the composite curve was not negligible, as is shown by the dotted line in Fig. 6.

Discussion

The X-ray diffraction pattern for glassy carbon is very similar to that for a carbon black. The interlayer spacing decreases and the crystallite size increases with an increase in the heat treatment temperature. These variations are also similar to the variations with heat treatment for usual carbon materials. It can be said that graphitization, that is to say, the developments of a graphite-like layer structure, proceeds in glassy carbon. The deduction that the graphite-like layer structure is developed in glassy carbon with heat treatment could be drawn from the variations in other properties,2,4) such as electrical resistivity and the Hall coefficient, with heat treatment. However, glassy carbon is a typical non-graphitizing carbon because the progress of its graphitization is very little in comparison with that of graphitizing carbons, as can be seen in Fig. 2. The degree of graphitization for the glassy carbon heat-treated at 3000°C was almost the same as that for the petroleum coke heat-treated at about 1900°C. With the glassy carbon heat-treated at low temperatures such as 500∼600°C, the (002) diffraction was not well-defined, and the disorganized carbon content was as large as 80%. The glassy carbon heat-treated at a low temperature should be called an organic solid. The radial distribution curve for the glassy carbon heat-treated at 500°C converged to the mean electron density, $4\pi r^2\rho_0$, beyond $r=4$ Å. With an increase in the heat treatment temperature, the values of r at the maxima on the observed radial distribution curves approach those for graphite; that is to say, $r=1.4$, 2.6, 4.0 and 5.0 Å. This result is consistent with the variations in the interlayer spacing, the crystallite size and the disorganized carbon content with the heat treatment temperature.

With the samples of the A group, the curve which is composed of two component curves, corresponding to trigonal and tetrahedral carbon atoms, coincides quite well with the observed curve. The content of the tetrahedral carbon atom was calculated from the mean co-ordination numbers of the component curves, taking into consideration the fact that the theoretical co-ordination numbers for tetrahedral and trigonal carbon atoms are 4 and 3 respectively. It was found that the calculated content of the tetrahedral carbon atom is in good coincidence with the disorganized carbon content. With the samples of the B group, particularly with the samples heat-treated at low temperatures, the coincidence between the observed curve and the composite curve was not as complete as with the samples of the A group. A small number of carbon atoms with another relation to their neighbours may also exist in glassy carbon. From the remainder curve, which is located at around 1.1 Å, the carbon-hydrogen bond can be expected. However, the carbon-carbon triple bond and the carbon-oxygen double bond might be assumed because such a separation procedure of the first peak is not very accurate.

As has been described above, the graphite-like layer structure was developed in glassy carbon with heat treatment, and no diffraction line which corresponds to that of the other structures was detected in the X-ray diffraction pattern of glassy carbon. Therefore, it can

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4) T. Yamaguchi, *Carbon*, **1**, 47 (1963).

be assumed that the trigonal carbon atoms form the graphite-like layer structure and that the tetrahedral carbon atoms form no regular structure. From these results, a structural model of glassy carbon can be proposed, in which tetrahedral carbon atoms form the main part of the criss-cross linkages which link the graphits-like layers in a random way. Furukawa[5] has proposed a somewhat different structural model of glassy carbon, a three-dimensional irregular network configuration of carbon atoms without assuming a significant graphite-like layer structure.

The reason why the structure of glassy carbon is somewhat different in the A and B groups has not yet been made clear. However, it can be said that the conditions of the production of glassy carbon may have a certain effect on its structure. Yamaguchi[4] also used two types of glassy carbon, one impermeable to gas and the other rather porous.

Summary

The structure of glassy carbon has been investigated by determining the interlayer spacing, crystallite size and disorganized carbon content, and by an analysis of the radial distribution function.

Glassy carbon has been found to be a typical non-graphitizing carbon. From the analysis of the first peak of the radial distribution curve, it has been assumed that not only trigonal but also tetrahedral carbon atoms exist in glassy carbon. A structural model of glassy carbon has been proposed; in this model tetrahedral carbon atoms form the main part of the criss-cross linkages which link graphite-like layers in a random way.

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[5] K. Furukawa, Private communication.