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Small-Angle Scattering from Irradiated Glassy Carbon*

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Synopsis

The small-angle neutron scattering from glassy carbon which had been neutron irradiated at 140°C to a fluence of 1.2×10^{20} n cm^{-2} has been studied. The void in glassy carbon have a spherical shape nearly uniform in size. Irradiation results in a decrease of density of the matrix but size of the voids are unchanged. Slight shrinkage of the voids is occurred during subsequent annealing above 900°C.

I. Introduction

Carbon materials have been extensively used in nuclear reactors because of its excellent nuclear properties. It is essential, therefore, that its response to prolonged fast particle irradiation be well characterized. As a part of study of the irradiation effect on the small angle neutron scattering from carbon materials, the small angle scattering from glassy carbon which had been neutron irradiated at 140°C to a dose of 1.2×10^{20} n cm^{-2} has been studied.

Glassy carbon is a monolithic form of carbon produced by degradation of an organic polymer. The production of this material starts from an organic resin which is put in the desired form and continues with a pyrolysis heat-treatment at temperatures ranging from 500° to 3000°C. The properties of the glassy carbon obtained depend mainly on the final heat-treatment temperature.

The density of pure graphite is 2.15 g/cm^3 while that of glassy carbon is less than 1.50 g/cm^3. This great difference in density (larger than 30%) can not be accounted for by the general observation that density decreases when materials pass from crystalline to amorphous state. Detection of an appreciable small angle scattering from this material suggested the possibility of explaining this

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great density difference by the presence of voids [1].

In the present work, we measured neutron small-angle scattering from neutron irradiated glassy carbon to examine change of pore structure as a result of irradiation. Small-angle scattering techniques have also been employed successfully to determine the pore structure of glassy carbon given different heat treatments [1,2].

II. Experimental

Three kinds of glassy carbon with different heat-treatments at 1300°, 2000° and 3000°C were examined. Samples, square plates 6×6×1 mm, were irradiated in the Japan Material Testing Reactor with fast neutrons (>1 MeV) to a fluence of 1.2×10^{20} n cm^{-2}. As no temperature control was provided, the plates may have been heated to about 140°C during the irradiation.

The neutron small angle scattering measurements were performed on the WIT camera at KENS [3] using the q values ($q = 4\pi\sin\theta/\lambda$, where 2θ is the scattering angle and λ the neutron wave length) over the range 0.02 - 1.0 $Å^{-1}$. The scattering curve was obtained with a point-like collimated beam using ^{6}Li scintillator anular detector. Parastic scattering was determined by counting without sample and subtracted from the total intensity. All measurements were carried out at room temperature.

III. Theory

Let us suppose the particles to be identical and oriented at random. Under these conditions, Guinier[4] gives the following formula for the scattering power I(q) which is applicable to very small angles:

$$I(q) = I(0)\ \exp(-R_g{}^2q^2/3) \qquad (1)$$

where R_g the radius of gyration of the particles with respect to their mass centers.

$$R_g = \frac{\int_V r^2 dV}{V} \qquad (2)$$

where V is the volume of the particles. The intensity at the origin I(0) is related to the structure according to

$$I(0) = N\,\frac{(\rho-\rho_o)^2}{\bar{\rho}}\,V^2 \qquad (3)$$

where N is the number of particles per unit volume. ρ_o the nucleonic density of the particles, ρ the nucleonic density of the matrix and $\bar{\rho}$ the mean density. The value of I(0) is obtained by extrapolation of the experimental curve. If the intensity is isotropic, as in the case under consideration, we have an integral property [4]

$$\int_0^\infty q^2 I(q)\,dq = 2\pi^2 \frac{(\rho-\rho_o)^2}{\bar{\rho}} N V \qquad (4)$$

After obtaining the value of I(0) we can calculate N if we know the densities and volume of the voids. The volume can be obtained by combining eqs.(3) and (4).

$$V = \frac{2\pi^2 I(0)}{\int_0^\infty q^2 I(q)\,dq} \qquad (5)$$

The limit of the large-angle scattering produced by a two-density system is given by Porod's law [5]

$$\underset{q\to\infty}{I(q)} = 2\pi \frac{(\rho-\rho_o)^2}{\bar{\rho}} \frac{S}{q^4} \qquad (6)$$

where S is the surface of the interface per unit volume. Porod has shown that eq.(6) is valid for particles of uniform electronic density of any shape and for any number of particles per unit volume, provided the particles are oriented at random and none of dimension is zero. For identical particles we have

$$q^4 \underset{q\to\infty}{I(q)} = 2\pi \frac{(\rho-\rho_o)^2}{\bar{\rho}} N s \qquad (7)$$

where s is the surface area of the particles.

Systematic deviations from Porod's law can occur when there are density flucuations in the phases or when interface is not well defined. In the case of voids, it is evident that a fluctuation in density can exist only in the matrix. Assuming that there is a step discontinuity of the electron concentration at the interface, we have[6] for one dimensional fluctuations

$$I(q) = \frac{b_o}{q^4} + \frac{b_1}{q^2} \qquad (8)$$

for two dimensional fluctuations

$$I(q) = \frac{b_o}{q^4} + \frac{b_2}{q} \qquad (9)$$

and for three dimensional fluctuations

$$I(q) = \frac{b_o}{q^4} + b_3 \qquad (10)$$

where b_o is the limiting value of $q^4 I(q)$ if Porod's law is satisfied and b_1, b_2 and b_3 are parameters associated with the fluctuation.

The general case of the small angle scattering is best treated by the use of the correlation function $\gamma(r)$ defined as follows

$$\gamma(r) = (\Delta\rho)^2\gamma_0(r); \quad \gamma_0(r) = 1; \quad \gamma_0(r>D) = 0.$$

where $\Delta\rho = (\rho-\rho_0)$ the density difference. As the density difference $\Delta\rho$ is always assumed to be constant here, $\gamma_0(r)$ is only related to the geometry of the particle. As a largest diameter D must exist; γ_0 will vanish for $r \gg D$. According to Debye and Bueche[7], general formula for the scattering intensity of isotropic system is expressed by the correlation function $\gamma(r)$ as

$$I(q) = V\int_0^\infty 4\pi r^2 dr\, \gamma(r) \frac{\sin qr}{qr} . \qquad (11)$$

Thus, $\gamma(r)$ is found by the inversed Fourier transform.

$$V\gamma(r) = \frac{1}{2\pi^2} \int_0^\infty q^2 dq\, I(q) \frac{\sin qr}{qr} \qquad (12)$$

We can obtain the distance distribution function defined below

$$p(r) = \gamma(r)\, r^2 \qquad (13)$$

IV. Results and Discussion

Figure 1 shows the small-angle neutron scattering from unirradiated samples with different heat-treatments at 1300°, 2000° and 3000°C. To show that these results follow Guinier's law, we plotted log I(q) against q^2 in Fig. 2. The fact that the points approximate a straight line over the large range of q^2 values indicates that Guinier's law is obeyed. Applying Guinier's law to the plots of Fig. 2, we obtained the radius of gyration R_g of voids from the slope of the straight lines. R_g values, thus

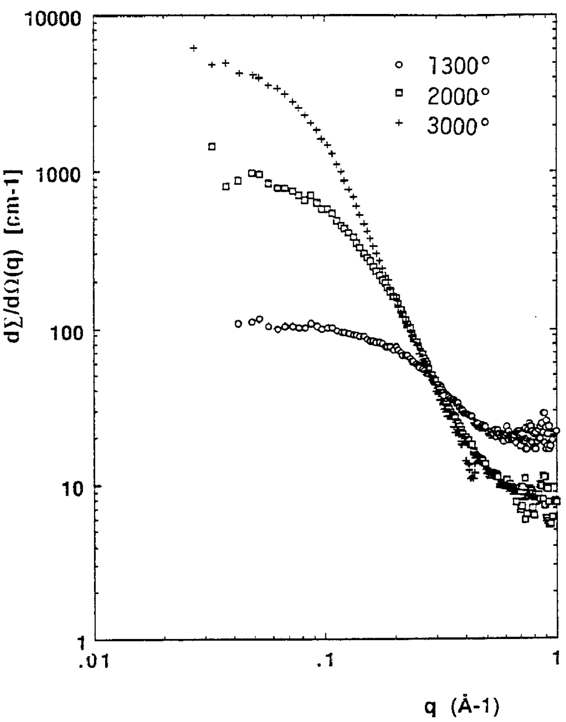

Fig. 1 Scattering curves from unirradiated samples with different heat treatments.

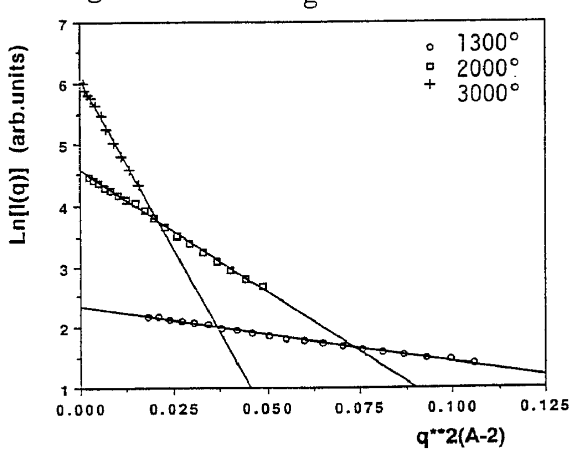

Fig. 2 Guinier's plots showing the linear behavior.

determined, are 6.5, 12.9 and 19.3 Å for the samples heat-treated at 1300, 2000 and 3000°C, respectively.

In Fig. 3, we plotted $q^4I(q)$ against q^2 with the data obtained from the sample of 3000°C heat-treatment. From the plot, we see that Porod's law is not obeyed; the points for high-q region approximate a straight line

$$q^4I(q) = b_o + b_1q^2$$

instead of approaching a constant value. This deviation from Porod's law, according to eq.(8) indicates the presence of one-dimensional fluctuations in the matrix. In the case of graphite, the one-dimensional fluctuations have an appreciable value in the direction perpendicular to the hexagonal planes.

Figure 4 illustrates the effect of irradiation on the small angle scattering from the samples of 3000°C heat-treatment. Also, the scattering curves from samples after subsequent anneals for one hour at 300 and 600°C are shown in this figure. It is evident that the sca-

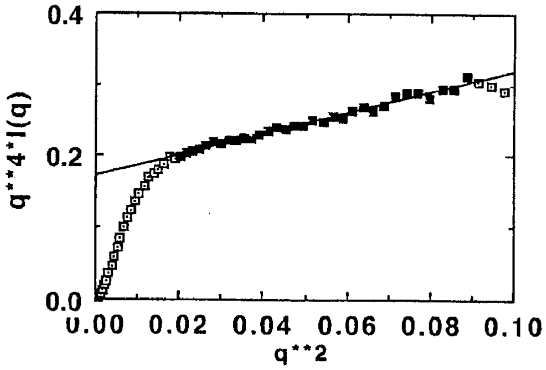

Fig. 3 Variation of $q^4I(q)$ versus q^2 showing positive deviation from Porod's law.

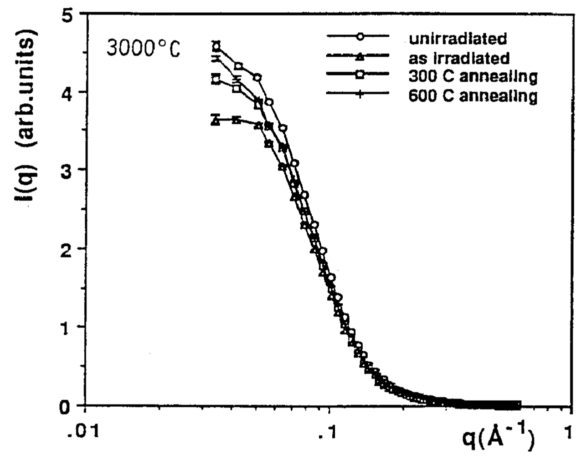

Fig. 4 Effect of irradiation on the small angle scattering from the samples heat-treated at 3000°C.

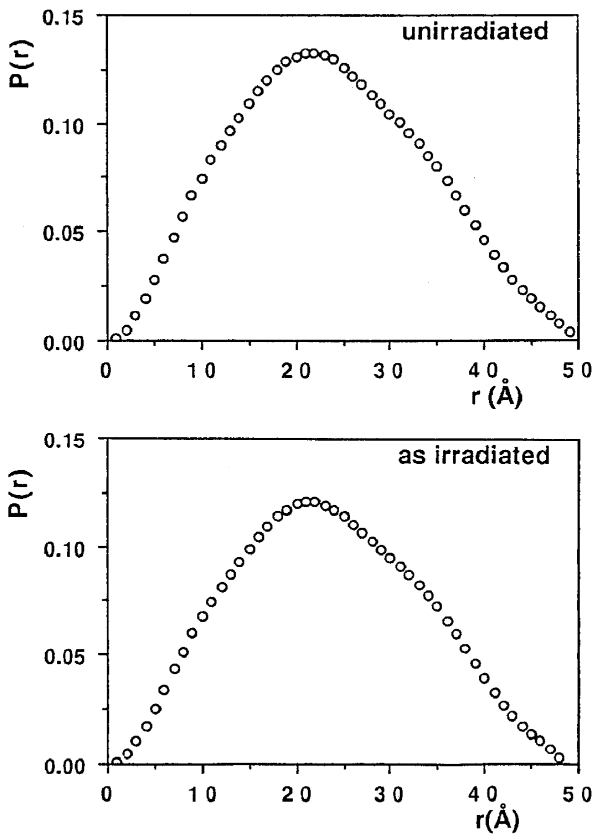

Fig. 5 Distance distribution function for unirradiated and as-irradiated samples of 3000°C heat-treatment.

ttering is decreased at the lower-q values but the slope of curves for the higher-q region is almost identical after the irradiation.

Fig. 5 and 6 give the variation of the normalized distance distribution function p(r) with the irradiation and also after subsequent anneals for one hour, respectively. The shape of p(r) curves is almost unchanged by the irradiation and is similar to that expected from the voids of spherical shape. After the subsequent anneals, the p(r) curves are shifted to the smaller distance as seen in Fig. 6. This fact indicates that the shrinkage of voids due to the migration of vacancies has occurred during subsequent anneals.

The previously developed theory is applied to our experiments to evaluate the numerical values to describe the porosity of glassy carbon. The results are shown in Table 1. The average void diameter increases linearly with heat-treatment temperature from 1300 to 3000°C. The void diameter and the volume of voids are unchanged by the irradiation. However, the decrease of I(0) value suggests that the density of the matrix is reduced by the irradiation.

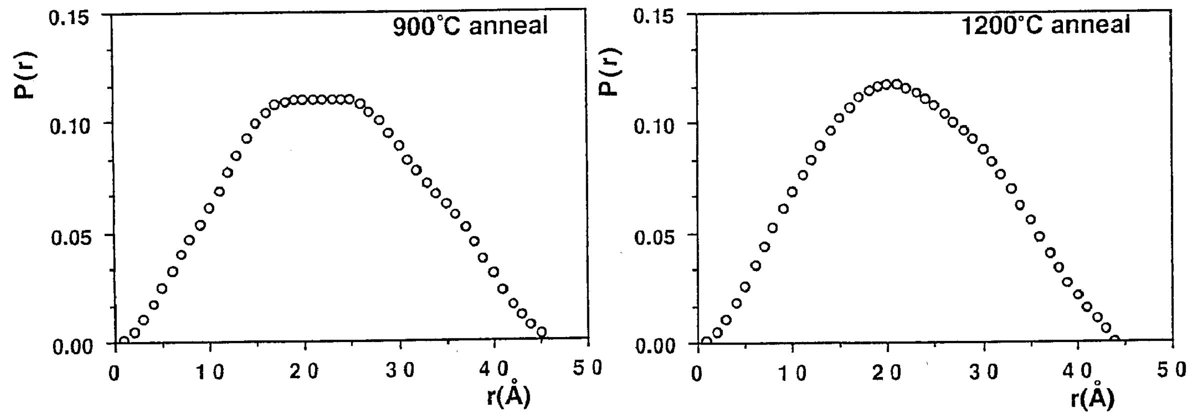

Fig. 6 Distance distribution function after subsequent anneals at 900 and 1200°C.

Table 1 Numerical results.

Samples	1300°	2000°	3000°	as-irr	600°	900°	1200°
R_g(Å)	6.5	12.9	19.3	19.3	19.2	18.7	18.9
V($10^4 A^3$)	0.26	1.05	4.6	4.5	4.6	4.4	4.2
$I(0)/I(0)_{ir}$	-	-	-	0.90	0.91	0.92	0.90

Samples of 1300°, 2000° and 3000° show the heat-treatment temperatures. Also 600°, 900° and 1200° show the annealing temperature after the irradiation.

V. Conclusion

Our results show that glassy carbon contains voids of approximately uniform size. It is apparent that the voids appear to become more spherical and larger with higher temperature heat-treatment. The neutron irradiation up to a fluence of $1.2 \times 10^{20}\, n\, cm^{-2}$, results in a decrease of scattering intensity I(0). This effect suggests that the density of the matrix is reduced due to the disordering caused by the irradiation. Slight shrinkage of the voids is occurred during subsequent annealing above 900°C. The annealing may order the structure at the expense of creating more void volume.

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