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A Study of Pore Growth in Glassy Carbon
Using Small-Angle X-ray Scattering

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Abstract

Small angle x-ray scattering was used to study the average pore size in glass-like carbon as a function of both heat treatment time and heat treatment temperature. A pore growth model based on graphitization processes is presented. The simple mechanism shows that the change in the average radius of gyration with time is related to the total number of pores as a function of time, which in turn depends on the irreversible thermal expansion phenomenon. The results of this study are inconsistent with a vacancy migration pore growth mechanism proposed earlier.

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Introduction

Glassy carbon is a disordered, nongraphitizing carbon with a structure composed of entangled laths of graphitic ribbons [1]. Glass-like carbon is a very porous material with the pore volume accounting for about one-third of the microstructure. It has been shown [2] that the total pore volume of glassy carbon depends only on heat treatment temperature (HTT) and not heat treatment time (HTt). In addition, it is well-established that the pore size increases [3,4] and specific surface area decreases [2] with HTt. It was proposed that, due to an overall decrease in surface energy, pore growth occurred by the migration of vacancies such that larger pores grow at the expense of smaller pores in the system. However, when one considers the disordered microstructure of glassy carbon, it is difficult to conceive of such a simple vacancy diffusion model as being the dominant mechanism of pore growth. Pores in glassy carbon are typically small, lenticular shaped, and located between the tangled graphitic laths. Voids of this type are bounded by very low energy (002) crystallographic planes, and thus a surface energy controlled growth would seem unlikely. Clearly, the size and shape of the pores depends on inherent strains present in the material. Also, glassy carbon contains a high concentration of structural defects which would act as excellent sinks for migrating vacancies. A more realistic model for pore growth would emphasize structural changes and reduction in strain energy with HTt.

In previous work, Bose and Bragg [2] used small angle x-ray scattering to study the growth of voids in glassy carbon by determining the radius of gyration from a method first proposed by Guinier [5]. In this technique, the radius of gyration is calculated from a plot of

$\ln I$ (intensity) vs h^2 (magnitude of the scattering vector = $4 \sin \theta / \lambda$). In this study, a kinetic analysis was not possible because the radius of gyration measured by the Guinier method is not representative of the average particle size, but rather is heavily weighted toward the larger particles in the system.

Hosemann [6] outlined a method of determining the average radius of gyration from small angle x-ray data by assuming a Maxwellian distribution of particle sizes and a Guinier scattering function of the form $\exp[-h^2 R_g^2/3]$. In this technique, the data plotted as $h^2 I(h)$ vs h gives the parameters, h_m , which represents the scattering vector at the maximum of the curve, and h_T , which is defined by the intersection with the h -axis of the tangent of the curve at the inflection point on the high angle side of the curve. Then, the average radius of gyration is given by

$$\overline{R_g} = \frac{1}{h_m} \sqrt{\frac{6}{n+2}} \frac{\Gamma(n+2/2)}{\Gamma(n+1/2)}$$

where the parameter n is found from the relation:

$$\frac{h_T}{2h_m} - 1 \cong \frac{1}{\sqrt{2(n+1)}}$$

The $h^2 I - h$ analysis has been used in the study of carbon blacks by Matzkus and Hosemann [7], Matzkus [8], and Kuroda [9].

In the present work, small angle x-ray scattering is employed to determine the average pore size in glass-like carbon as a function of HTT and HTt. The results are discussed in terms of possible void growth mechanisms which may take place at high temperatures.

Experimental

Material. Glassy carbon in the form of plates (10.3x5.1x.16 cm) was obtained from Polycarbon, Inc., North Hollywood CA. The as-received material was processed at 1000°C for 1 hour. Samples of dimensions 5.1 cm x 1.8 cm (2" x 11/16") were cut from the plates and ground to a thickness of .13 cm (.05") using a diamond wheel. The specimens were then heat treated in a graphite Astro furnace at 1600°C, 1800°C, 2100°C, and 2500°C for times ranging from 1 to 48 hours. An inert atmosphere of either pure helium or pure argon was employed during all the heat treatments. Temperatures were measured with a Leeds and Northrup optical pyrometer calibrated in the 1000-3000°C temperature range. The precision of measurements was about $\pm 10^\circ\text{C}$.

Small Angle X-ray Scattering. The small angle x-ray scattering apparatus used is shown schematically in Fig. 1. The system consists of a doubly bent graphite crystal monochromator, two apertures placed 27 cm apart, a flight path of 161 cm, and a linear position sensitive detector. The detector is a gas-filled ($\text{Ar} - \text{CH}_4$ at 45 psi) proportional counter with delay line read out. The entire system is evacuated to avoid air scatter. A point collimated beam 1.1 mm in diameter of CuK_α x-ray radiation was used throughout the investigation. Small angle scattering spectra in the angular range $.2^\circ < 2\theta < 3.5^\circ$ was

collected for 500 seconds. A more detailed description of the small angle scattering system can be found elsewhere [10].

Results

The scattering curves for glassy carbon heat treated at 2100°C are shown in Fig. 2. The similar form of the curves for different heat treatment times indicates that to a first approximation the pore shape remains roughly constant.

Figure 3 shows typical $h^2 I$ vs h data (HTt = 15 hrs, HTT = 2100°C). It can be seen that the shape of the curve agrees quite well with that predicted by Hosemann's theory. From the values $h_m = .095 \text{ \AA}^{-1}$ and $h_T = .368 \text{ \AA}^{-1}$, the average radius of gyration was found to be $\approx 7.9 \text{ \AA}$. It should be noted that effects due to interparticle interference can be neglected if the quantity g , the polydispersity, defined as $g = h_T/h_m - 1$, is greater than or equal to the packing density of the particles in the specimen [9]. This was found to be the case for all samples studied.

A determination of the average radius of gyration of voids in glassy carbon can be used to test the vacancy migration growth mechanism first proposed by Bose and Bragg [2]. Lifshitz and Slyozov [11] showed that the bulk diffusion controlled growth of precipitates in alloy systems can be described by:

$$\bar{r}^3 - \bar{r}_1^3 = \frac{9 \gamma D C_0 \Omega^2}{8RT} t$$

where $\bar{r}$ is the radius, $\bar{r}_i$ the initial average radius, γ is the interfacial energy between matrix and solute, C_o is the equilibrium solubility of precipitates, D is the diffusion coefficient of the precipitate species, Ω is the molar volume of solute, and RT has the usual meaning. Assuming that the aspherical pores grow such that their shape, due to an anisotropy in γ , is preserved, then the average radius of gyration of the pores raised to the third power will be proportional to RTt according to the model. In addition, the slopes of these lines are proportional to $D_{vac} C_{o,vac}$. Thus, a plot of $\ln[\bar{Rg}^3 - (\bar{Rg}_i^3)]$ vs $1/t$ should yield the activation energy $\Delta H_m + \Delta H_f$, which is on the order of 260 kcal/mole for carbon materials.

An analysis of this type is depicted in Figs. 4,5,6, and 7 which plot Rg^3 vs RTt for 1600°C, 1800°C, 2100°C, and 2500°C. It can be seen that the data fit reasonably well to a linear relationship; however, because of the scatter in the data points, the results are by no means conclusive. The activation energy determination is illustrated in Fig. 8. The value $\Delta H = 51$ kcal/mole is very much lower than the predicted value. This suggests that the simple model of vacancy migration from small voids to large voids is not valid for glassy carbon.

As disordered carbons are heat treated at high temperatures, the material tends toward the ordered graphite structure. This process is known as graphitization. The rate of graphitization in glassy carbon is very slow, hence it is classified as a hard carbon. This transformation to a more ordered structure has been generally attributed [12] to the annealing out of structural defects which are present in high

concentrations. As a result, the activation energy has been found to be about 260 kcal/mole for most disordered carbons.

One characteristic of graphitization is an increase in the parameters L_a and L_c . L_a represents the "apparent" crystallite size (or regions of near-perfect graphite) in a direction parallel to the layer planes, and L_c is the "apparent" crystallite dimensions measured perpendicular to the layer planes. Saxena and Bragg [13] used the changes in the L_a and L_c dimensions to study the kinetics of graphitization in glassy carbon. Physically, an increase in L_a and L_c in glassy carbon indicates the tangled graphitic ribbons are gradually straightening out.

Clearly, any process which alters the characteristics of the lath-like ribbons must necessarily change the structure of the pores which they enclose. Thus, pore growth would appear to be related to the graphitization process taking place. For example, lenticular-shaped voids enclosed by the bends in a graphite ribbon would tend to close up as the layer planes straightened, whereas other pores, perhaps situated between many tangled laths, may be oriented such that their sizes increase with increasing L_a and L_c . According to the above scenario, the rate of change of the dimensions of any individual pore will be proportional to the rate of graphitization. However, graphitization kinetics cannot be derived from changes in the average pore size as measured by small angle x-ray scattering. The change in the average pore size with time is a function of both the pores that are increasing in size, as well as those which are decreasing in size.

Following Bose [2], the average radius of gyration as a function of time can be written in the form of a first-order rate equation as:

$$\overline{Rg} = \overline{Rg}_0 \exp(k_R t)$$

where it is assumed that the measured times are short compared to any saturation in the pore size that may take place. The rate constant k_R depends on temperature according to:

$$k_R = k_0 \exp(-\Delta H/RT)$$

where ΔH is the activation energy for the process. The kinetic analysis is shown in Fig. 9, and the Arrhenius plot to determine the activation energy is shown in Fig. 10. The observed value of $\Delta H \approx 30$ kcal/mole is much lower than the ΔH for graphitization (≈ 215 kcal/mole) found for glassy carbon [13]. A possible explanation for this effect is discussed below.

The expression for the average radius of gyration can be written explicitly as:

$$Rg(t) = \frac{\sum_i^k n_i Rg_i(t)}{N(t)} \quad (1)$$

where n_i is the number of pores with radius of gyration Rg_i and N is the total number of voids in the sample. With heat treatment, Rg_i will be a function of time and, due to the fact that many pores are closing up, N will also be a function of time.

It is now assumed that approximately one-half the distribution of pores are oriented in the material such that growth will take place and

half the distribution is oriented favorably for a decrease in size. In particular, Rg_i is expressed as $Rg_i \exp(\pm kt)$, where k is now related to the rate of graphitization with the sign of k describing the direction of dimension change. The process is shown schematically in Fig. 11. The sum over Rg_i can then be expressed:

$$\sum_i^k n_i Rg_i = \frac{1}{2} \sum_i^k n_i Rg_i \exp(kt) + \frac{1}{2} \sum_i^k n_i Rg_i \exp(-kt) \quad (2)$$

A bimodal distribution of pore sizes, which would be predicted from this mechanism (Fig. 11), has been found in glassy carbon by Jenkins, Wang, and Walker [14].

At later heat treatment times, pores begin to disappear. If $c(t)$ represents the fraction of particles remaining as a function of time Eq. (2) can be rewritten as:

$$\sum_i^k n_i Rg_i = \frac{1}{2} \sum_i^k n_i Rg_i \exp(kt) + \frac{1}{2} c(t) \sum_i^k n_i Rg_i \exp(-kt) \quad (3)$$

The number of pores n_i is assumed to remain constant as the radius of gyration of the i^{th} pore decreases. As Rg_i reaches a very small value, defined as the point at which the pore disappears, the total n_i pores vanish simultaneously. As a result, $c(t)$ can be expressed explicitly as $c(t) = \exp(-kt)$. Substituting and rearranging, Eq. (3) becomes:

$$\sum_1^k n_1 Rg_1(t) = \frac{1}{2} \sum_1^k n_1 Rg_1 [\exp(kt) + \exp(-2kt)] \quad (4)$$

Graphitization in glassy carbon is a very slow process (for example, k at 2500°C for L_a increase $\sim 0.005 \text{ hr}^{-1}$ [13]); thus the quantity kt is small. As a result, the quantity in brackets on the righthand side of Eq. (4) can be approximated as a constant numerically equal to 2, which means the time dependence of the sum $\sum_1^k n_1 Rg_1(t)$ can be removed. This result can be seen intuitively by careful examination of Fig. 11.

The important result can then be obtained that:

$$Rg(t) N(t) = \text{const.} \quad (5)$$

Approximate data for relative changes in $N(t)$ with time can be calculated by writing:

$$N = \frac{\text{total volume of pores}}{\text{ave. volume of pore}}$$

and noting that the numerator is proportional to one plus the percentage increase in total pore volume and the denominator is proportional to Rg^3 assuming constant pore shape with HTt. The volume fraction of pores in glassy carbon can be determined by:

$$\text{vol. fr. of pores} = \frac{\rho_{\text{graphite}} - \rho_{\text{gc}}}{\rho_{\text{graphite}}}$$

where the density of perfect graphite $\rho_{\text{graphite}} = 2.27 \text{ gm/cm}^3$. Consequently, the changes in total pore volume can be found by monitoring changes in density of the glassy carbon with HTt. The results are plotted in Figs. 12 and 13. These findings conflict with an earlier study [2] which found no change in total pore volume with HTt. Figures 15 and 16 provide further evidence that the mechanism for pore growth in glassy carbon is not one of vacancy diffusion.

The data for $N(t)$ is plotted in Fig. 14. Here $N(t)$ was given by $N(t) = N_0 \exp(-k_N t)$ which is valid for relatively short times. Equation (5) predicts that k_N and k_R should differ by a constant and the activation energies should be the same. This is shown in Fig. 10. Due to the fact that the change in total pore volume is small compared to the change in R_g^3 the function $N(t)$ will be dominated by $R_g^3(t)$ (in fact, it predicts $3k_N = k_R$ which is observed in Fig. 10) and a comparison of $N(t)$ and $R_g(t)$ has little meaning. Experimental support of Eq. (5) will only be realized through a calculation of N as a function of time which is independent of a $R_g(t)$ measurement.

Discussion

As one can deduce from Fig. 11, the change in the total number of pores with time will depend on the specific shape of the distribution of pore sizes present in the material. Mathematically, this can be shown as follows. Assume, for simplicity, a Gaussian distribution of pore sizes

$$n(X) = Q \exp \left[- \frac{(\overline{Rg}_0 - X)^2}{2\sigma^2} \right]$$

where Q is a constant. The total number of pores after the distribution has shifted is given by:

$$N = \int_x^{\infty} Q \exp \left[- \frac{(\overline{Rg}_0 - X)^2}{2\sigma^2} \right] dX \quad (6)$$

where x is essentially the distance of the shift. N is thus a function of the lower limit of the above integral, and one can write:

$$\frac{dN}{dx} = -Q \exp \left[- \frac{(\overline{Rg}_0 - x)^2}{2\sigma^2} \right] \quad (7)$$

According to the pore growth model presented, x will vary with time as $x = x_0 \exp(kt)$ where x_0 is an arbitrarily small pore size defining the disappearance of pores. By the chain rule:

$$\frac{dN}{dt} = \frac{dN}{dx} \frac{dx}{dt} = -Q k x_0 \exp \left[- \frac{(\overline{Rg}_0 - x_0 \exp(kt))^2}{2\sigma_0^2 \exp(2kt)} \right] \exp(kt) \quad (8)$$

where the time dependence of σ has also been included. Approximating, for example, $\exp(kt)$ as $1 + kt$ and multiplying out Eq. (8) one finds:

$$\frac{dN}{dt} = -Q k x_0 \exp \left\{ - c \left[\left(\frac{2Rg_0^2}{2} - \frac{6Rg_0 x_0}{2} + \frac{4x_0^2}{2} + 1 \right) kt \right] \right\}$$

where c is a constant.

Integrating, the expression for N becomes:

$$N(t) = K \exp [-(c + c'kt)] \quad (9)$$

and thus from Eq. (5):

$$R_g(t) = K' \exp (c + c'kt) \quad (10)$$

or, writing natural logs:

$$\ln R_g(t) = K'' + c'kt \quad (11)$$

where K'' is yet another constant.

Although many simplifications were made in the derivation of Eq. (11), many important qualitative ideas can be deduced. Equation (11) shows that the slope of the curve $\ln R_g(t)$ vs t will be modified by the factor c' . The parameter c' depends on quantities such as σ_o^2 and R_g^2 , which describe the initial pore size distribution. Thus, if the initial pore size distribution is the same for all temperatures, then the activation energy for pore growth should be the same as the ΔH for graphitization (≈ 215 kcal/mole). However, in glassy carbon the initial pore size distribution does, in fact, depend on temperature due to an irreversible volume expansion which has been observed in heat-treated glassy carbon samples. After heat treating and cooling to room temperature, the material experiences a considerable decrease in density. This permanent dimensional change depends on heating rate, temperature, and sample size. In the present

investigation, this effect can be observed as a change in the intercept with temperature of the curves in Figs. 4-7, 9, 12, and 13.

Presently, there exist two explanations of the density-loss phenomenon. Mehrotra et al. [15] hypothesize the density decrease is due to the large difference in thermal expansion coefficients in the c and a directions of the glassy carbon matrix. This anisotropy leads to microcracking, which irreversibly increases the internal pore size. Fishbach and Rorabaugh [16] have proposed that the volume expansion occurs by the internal pressure exerted from the evolution of pyrolysis gases within the pores. The effects of heating rate and sample size are thus explained by the fact that pyrolysis gases are slow in diffusing out of the material.

The change in R_g with time is in reality due to two effects: one is the initial distribution of pore sizes which depends on the irreversible thermal expansion of the material, and the second is the graphitization of the sample which occurs at high temperatures. Consequently, the activation energy measured by R_g kinetics cannot be related to physical processes taking place in the material such as the motion of vacancies or interstitials.

The plots of percentage increase in total pore volume vs HTt (Figs. 12 and 13) show a very interesting phenomenon. From 1600°C to 1800°C the total pore volume decreases (after the initial increase), the amount of decrease being greater at the higher temperature. At 2500°C, however, the trend is completely reversed and the total pore volume is observed to increase with time. This effect can also be explained in terms of the graphitization process.

In addition to an increase in the L_a and L_c parameters, graphitization will result in a decrease in the d_{002} layer spacing in a typical soft carbon. The larger d_{002} spacing is generally associated with a reduced van der Waals attraction due to the disordered stacking of layers [12]. One can readily see that as the layer spacing decreases, the pores, which are enclosed by layers, must increase in size. The situation for glassy carbon, however, is more complex. Saxena and Bragg [13] and Henry and Bragg [16] have shown that a decrease in d_{002} does not occur in glassy carbon below heat treatment temperatures of about 2200°C. Thus, at temperatures greater than 2200°C there exists a second contribution to pore growth which everywhere increases the pore size; namely, a decrease in the layer plane spacing. The rate constants observed in this case will differ in that a term k_d , the rate constant for d_{002} decrease, is added to the rate constant governing pore growth at lower temperatures, and the kinetics of the two temperature regimes cannot realistically be compared.

The growth due to d_{002} decrease can be significant. For a typical L_a dimension of ten layer planes [13] and a decrease in d_{002} of .01 Å, the change in R_g will be about .1 Å. For an average pore size of 10 Å, this represents a 3% increase in the total pore volume which is comparable to Fig. 16.

Conclusions

Vacancy migration from small pores to large pores with an overall decrease in surface area does not appear to be a realistic pore growth mechanism for glassy carbon. This conclusion is based on the

nonconstancy of total pore volume with HTt and a measured activation energy much lower than that predicted by a coarsening process.

A model of pore growth based on the graphitization process is proposed. The increase in the L_a and L_c dimensions, as well as a decrease in the layer plane spacing at temperatures $> 2200^\circ\text{C}$, both lead to a change in pore size. A simple mechanism is suggested which shows that the low activation energy measured here and in a previous investigation [2] are in fact due to the irreversible thermal expansion which takes place in glassy carbon.

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Figure Captions

- Fig. 1. Schematic of small angle x-ray scattering system.
- Fig. 2. Scattering curves ($\ln I$ vs $\ln h$) for glassy carbon heat treated at 2100°C.
- Fig. 3. $h^2 I - h$ analysis due to Hosemann [6] for glassy carbon heat treated at 2100°C for 15 hrs.
- Fig. 4. Pore size R_g^3 vs heat treatment time for 2500°C.
- Fig. 5. Pore growth at 2100°C.
- Fig. 6. Pore growth at 1800°C.
- Fig. 7. Pore growth at 1600°C.
- Fig. 8. Activation energy determination assuming a Lifshitz-Slyozov [11] coarsening behavior.
- Fig. 9. Kinetics of pore growth assuming an exponential law.
- Fig. 10. Activation energy determination from the data of Fig. 9 (k_R are the slopes of Fig. 12 and k_N are the slopes of the lines in Fig. 14).
- Fig. 11. Schematic of pore growth model showing change in the distribution of pore size.
- Fig. 12. Change in total pore volume with heat treatment time at 1800°C and 1600°C. The curves demonstrate a decrease in total pore volume after an initial irreversible thermal expansion induced volume expansion.
- Fig. 13. Change in total pore volume with heat treatment time at 2500°C showing an opposite behavior to the curves of Fig. 12.
- Fig. 14. Relative change in the total number of pores with heat treatment time.

Fig. 1. Schematic diagram of the small-angle x-ray scattering system.

XBL 821-7772

XBL 822-5227

fig. 2

XBL 8110-6800

fig. 3

fig. 4

X BL 8110-6801

fig. 5

XBL823-5349

fig. 6

fig. 7

XBL 823-5352

fig. 8

XBL825-5662

fig. 9

XBL825-5664

fig. 10

XBL 825-5661

fig. 11

XBL 825-5660

fig. 12

XBL 825-5659

fig. 13

XBL825-5663

fig. 14