

IMPERFECTIONS IN THE GRAPHITE STRUCTURE

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Much of the crystalline ordering in a graphitizable coke occurs in the range of baking temperatures from 2000–3000°C. Samples of coke baked at a series of temperatures in this range were investigated by X-ray diffraction. All of the available crystalline reflections and the diffuse (h , k) reflections were interpreted by the methods of Fourier analysis of X-ray line shapes. Using models and methods of the type employed by Warren et al. it was possible to reach some conclusions regarding the ordering and growth of graphite crystals. All of the observed broadening of the diffraction lines can be accounted for on the basis of a simple model for the imperfections.

THE ANNEALING OF CARBON

The annealing or graphitization of carbons to graphite is a process of continuous improvement of the crystal structure with increasing temperature at which the material is baked. To determine what imperfections must be annealed to obtain graphite, a series of coke samples was studied after baking at a series of successive temperatures in the range from 2000°C. to 3000°C. This range of baking temperature is where the crystals undergo most of the annealing that can be realized.

Measurements were made of these samples by performing shape analysis of the X-ray powder diffraction line patterns after the coke had been baked sufficiently long to complete the ordering process occurring at each temperature. Figure 1 shows the diffraction patterns of a typical coke baked at successively higher temperatures. The reflections which are sufficiently developed to be useful are the (002), (004), (100), (101), (110), and (112). From the (00 l) lines, after suitable analysis it is possible to determine the c -axis crystal height and the mean displacement of layer planes from the correct graphite spacing. From the (hk 0) lines the mean crystal diameter is de-

termined and from the (hk) diffuse bands the fraction of adjacent mutually oriented layers can be observed.

THE (00 l) LINES

For the coke which was used in these measurements only the (002) and (004) layer lines are useable. The shape of the diffraction lines was measured with a Norelco Diffractometer and corrected for instrumental broadening by the method of Stokes¹. Due to the low absorption coefficient of carbon, the line shapes must be further corrected for finite sample thickness², as well as the Lorentz and polarization factors.

Warren and Averbach³ have shown that use of the Fourier representation makes it possible to separate the particle size broadening of the lines from the strain or distortion broadening if more than one order of the reflection is available. The expression for distribution of intensity across a diffraction maximum is identically a Fourier summation

¹ Stokes, A. R., Proc. Phys. Soc., **61**, 382, 1948.

² Keating, D. T., and Warren, B. E., R. S. I., **23**, 519, 1952.

³ Warren, B. E., and Averbach, B. L., J. A. P., **21**, 595, 1950.

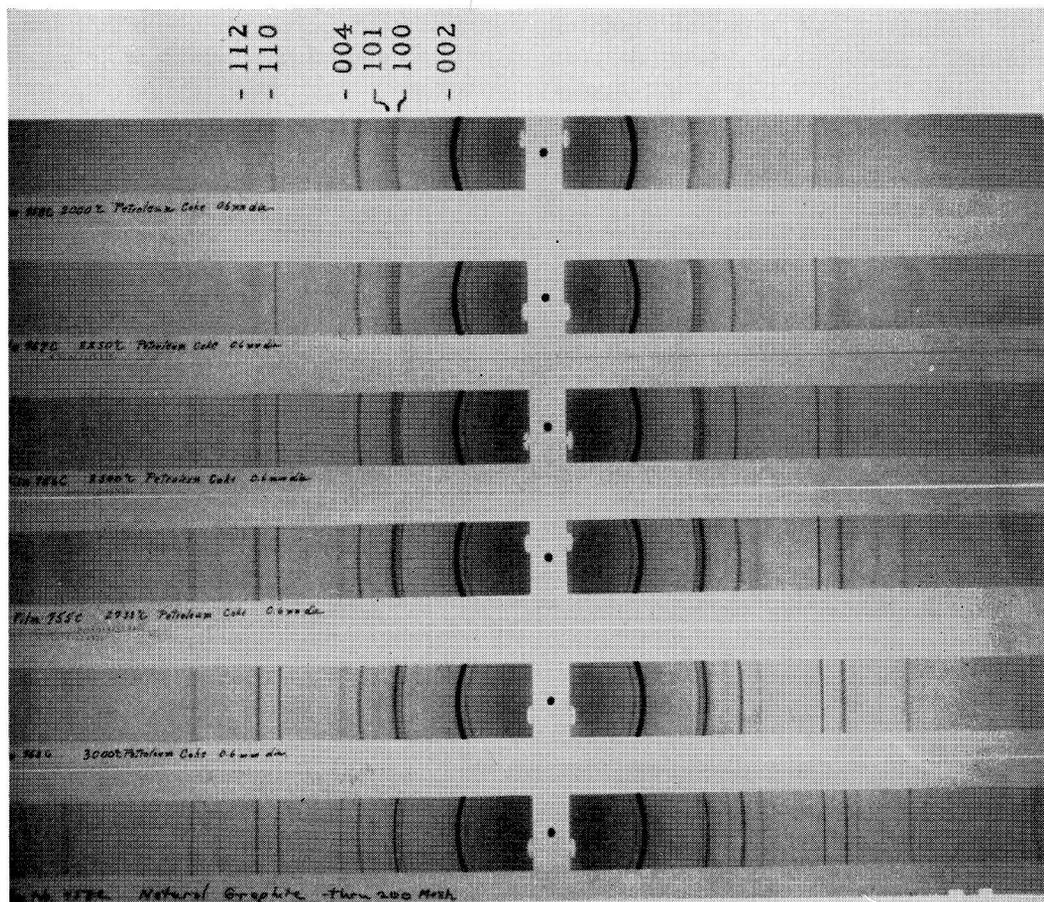


FIG. 1. Typical powder diffraction patterns of petroleum coke heat treated at a series of temperatures.

such that representation of the measured line yields a Fourier series in which the coefficients have real significance and are of the form:

$$A_n(\ell) = \left(1 - \frac{n}{N_3}\right) \langle \cos 2\pi Z_n h_3 \rangle. \quad (1)$$

Here, n is the harmonic of the series representing the reflection of order (ℓ) and only the coefficients of the cosine terms are used here since the shapes of the lines are symmetrical about the peak. The first term in equation (1) is the contribution due to finite crystal height⁴ of N_3 layers and has meaning in terms of real distance. If the period of the

Fourier interval is taken as a unit reciprocal lattice distance, then the harmonics n of the series represent averages over layers nominally n lattice spacings apart. Measured distance in the lattice (L) is then given by $L = na_3$, where a_3 is the unit lattice distance. The second term in equation 1 represents the broadening due to distortion, where the Z_n are the fractional displacements of the layers nominally n spacings distant and $\Delta L = Z_n a_3$. Here, h_3 is the continuous variable measuring distance in the reciprocal lattice in the a_3 direction.

Equation 1 is essentially exact at this point, but, for interpretation, certain approximations must be introduced. To

⁴ Bertaut, E. R., Acta. Cryst., **3**, 14, 1950.

separate the particle size and strain contributions, it is most convenient⁵ to represent the expectation value of the cosine by the exponential approximation

$$\langle \cos 2\pi Z_n h_s \rangle \rightarrow \exp(-2\pi^2 \ell^2 \langle Z_n^2 \rangle), \quad (2)$$

which is valid if the displacements are small or if they are gaussian. Equation 1 then takes the form

$$\ln A_n(\ell) = \ln(1 - n/N_s) - 2\pi^2 \ell^2 \langle Z_n^2 \rangle, \quad (3)$$

and a semilog plot of the measured coefficients $A_n(\ell)$, where ℓ is the order of the reflection, yields curves in which the slope is proportional to $\langle Z_n^2 \rangle$ and have intercepts equal to the particle size coefficients.

As an example, Figure 2 is a semilog plot of a typical set of experimentally measured coefficients for one sample. The Fourier coefficients for each averaging distance of the crystal size contribution can be determined from the intercepts at $\ell^2 = 0$. The mean square displacement $\langle \Delta L^2 \rangle$ of columns of length L is determined from the slopes of the lines. Figure 3 is a plot of A_L^P and $\langle \Delta L^2 \rangle$ as a function of the averaging distance L . It can be seen that $\langle \Delta L^2 \rangle$ has a linear relationship with averaging distance and it is fairly easy to show⁶ that this is the expected behavior. Franklin had proposed that imperfect graphites were made up of a mixture of two layer spacings, 3.35 Å corresponding to the correct graphite orientation and 3.44 Å corresponding to mis-oriented layers. If this model is used, and the assumption is made that the ordering of adjacent layers is statistically independent, the problem becomes one of a "random walk". It is then indicated that the measured mean square displacements, rather than the root mean square displacements, are proportional to the averaging distance. However, for any model which might include

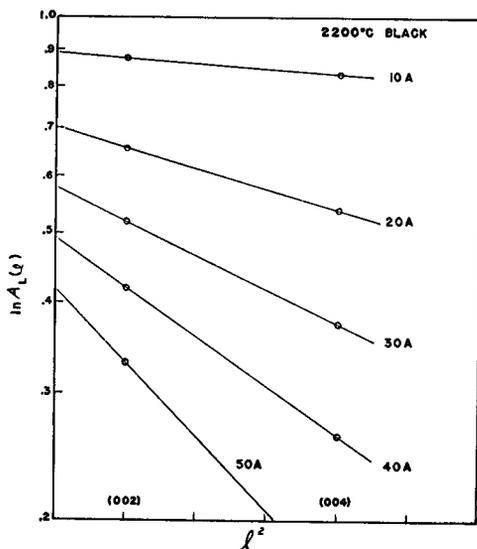


FIG. 2. Plot of $\ln A_L(\ell)$ vs. ℓ^2 for the (002) and (004) reflections from a lamp-black heated at 2200°C.

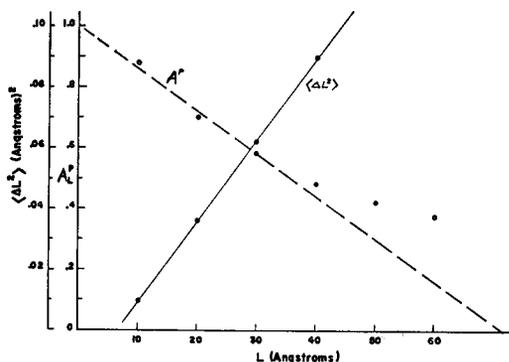


FIG. 3. Plot of the mean square displacements $\langle \Delta L^2 \rangle$ and the particle size coefficients A_L^P vs. the averaging distance L for lampblack heated at 2200°C.

correlation with near neighbors, the effect is noted only over the short averaging distances. Over long averaging distance most models become a random walk arrangement. The linear relationship between $\langle \Delta L^2 \rangle$ and L makes it very convenient for determination of the mean square displacements $\langle Z_1^2 \rangle$ averaged over adjacent pairs of layer planes. Figure 4 is a plot of $\langle \Delta L^2 \rangle$ vs. L for coke samples baked to several temperatures and from the slopes of the lines $\langle Z_1^2 \rangle$ can be

⁵ B. E. Warren and B. L. Averbach, *J. A. P.*, **23**, 497, 1952.

⁶ Bowman, Krumhansl, and Stock, *J. A. P.*, **26**, 1057, (1955).

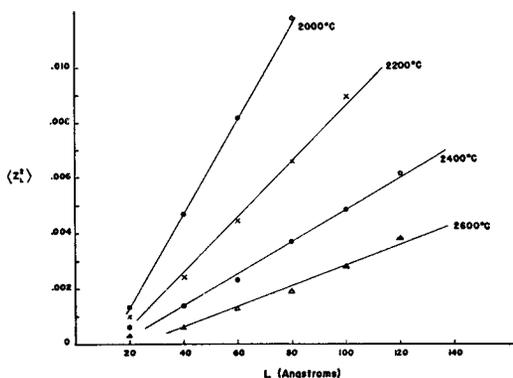


FIG. 4. Plot of the mean square fractional displacements vs. L for petroleum coke samples heat treated at a series of temperatures.

determined for each sample. Méring⁷ has shown that the measured layer spacing \bar{a}_3 is given in terms of the correct spacing a_3 and the mean displacement of layers by the form

$$\bar{a}_3 = a_3(1 + \langle Z_1 \rangle) \quad (4)$$

if the displacements have a discrete value δ but distributed at random in the lattice. Then

$$\langle Z_1 \rangle = P\delta \quad (5)$$

where P is an arbitrary probability distribution. Since it is the mean square displacement which is actually measured, fortunately, for this particular model $\langle Z_1 \rangle$ can be expressed in terms of the next moment

$$\langle Z_1 \rangle = \left\langle \frac{Z_1^2}{\delta} \right\rangle, \quad (6)$$

and Equation (4) becomes

$$\bar{a}_3 = a_3 \left(1 + \frac{\langle Z_1^2 \rangle}{\delta} \right). \quad (7)$$

For each of the cokes there is then a correlation between the distortion broadening and the measured mean spacing of the layers. Figure 5 is a plot of $\langle Z_1^2 \rangle$ as a function of \bar{a}_3 for each coke sample showing very good correlation. From the slope of the line $\delta = .027$ from equation (7) and the spacing of

⁷ Méring, J., Acta. Cryst., **2**, 371, 1949.

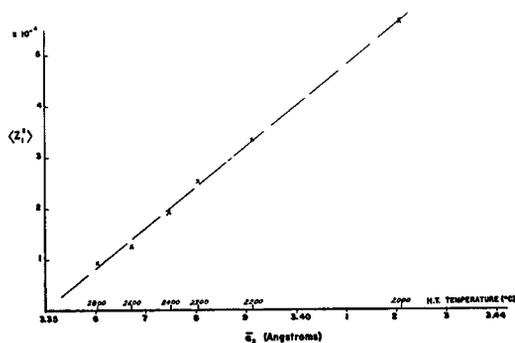


FIG. 5. Plot of $\langle Z_1^2 \rangle$ vs. \bar{a}_3 for samples of petroleum coke heat treated at a series of temperatures.

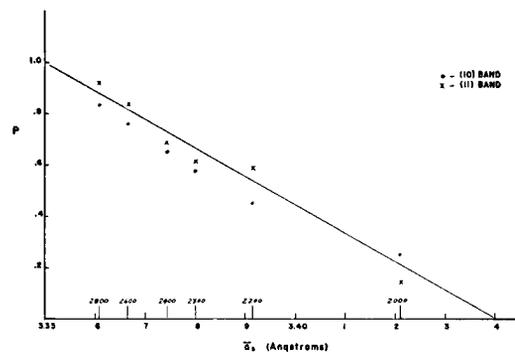


FIG. 6. Plot of P vs. \bar{a}_3 : Points obtained from diffuse (hk) bands, solid line from theory.

misoriented layers is found to be 3.44 \AA . Warren⁸ shows that a convenient index of graphitization is the probability of adjacent layer plane ordering which can be determined from the measured spacing and the discrete allowed spacings for graphite.

$$\bar{a}_3 = Pa_3 + (1 - P)a_3' \quad (8)$$

where $a_3' = 3.44 \text{ \AA}$. This model and the foregoing does not exclude the possibility of coupled pairs of displacements so long as they are distributed at random. However, the ordering parameter P can be obtained independently from the cross-lattice lines. Several workers^{8, 9, 10} have used the modula-

⁸ C. R. Houska and B. E. Warren, J. A. P., **25**, 1503, (1954).

⁹ R. Franklin, Acta. Cryst., **4**, 253, (1951).

¹⁰ G. E. Bacon, Acta. Cryst., **7**, 359, (1954).

tions of the diffuse (hk) bands arising from the random orientation of layers to determine the layer plane ordering. In this process, the distribution of intensity is determined along an (hk) rod in reciprocal lattice space. As graphitization sets in, modulations of the diffuse intensity appear due to some of the layers assuming the correct graphite orientation and spacing. By representing the diffuse intensity with a Fourier series, the probability of adjacent layer plane ordering can be determined from the coefficients of the harmonics. Since the modulations have the lattice periodicity, the coefficients of the harmonics represent the expectation values of finding gratings having 1, 2, 3, etc., lines per grating.

For each of the samples used here, the probability of adjacent layer plane ordering was determined from the (10) and the (11) diffuse bands. There is some difficulty in determining the background accurately which causes more scatter in the results than occurs with those obtained from the layer lines, but the results do appear to confirm the model. Figure 6 is a plot of the ordering parameter P as a function of the mean layer spacing \bar{a}_3 . According to equation 8, P should follow the solid straight line relation obtained from the layer lines. The agreement of the values obtained from the diffuse bands with the values from the layer lines can be taken as good confirmation of Franklin's⁹ theories and the model of statistically independent ordering of layers.

CRYSTAL SIZE

Having determined the modulating factors of the diffuse (hk) bands, they can be used to demodulate the ($hk0$) peaks graphically. The effect of the modulation is to make the (110) sharper than it should be and the (100) broader. After demodulation the ($hk0$) lines are then analyzed to determine the crystallite size by standard line broadening technique from the initial slope of the Fourier transform. These transforms were

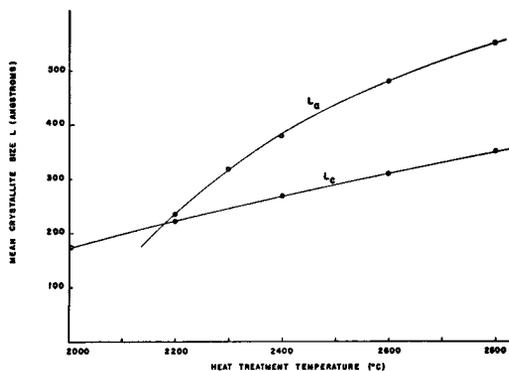


FIG. 7. Mean crystallite dimensions as a function of heat treatment temperatures for petroleum coke treated at a series of temperatures.

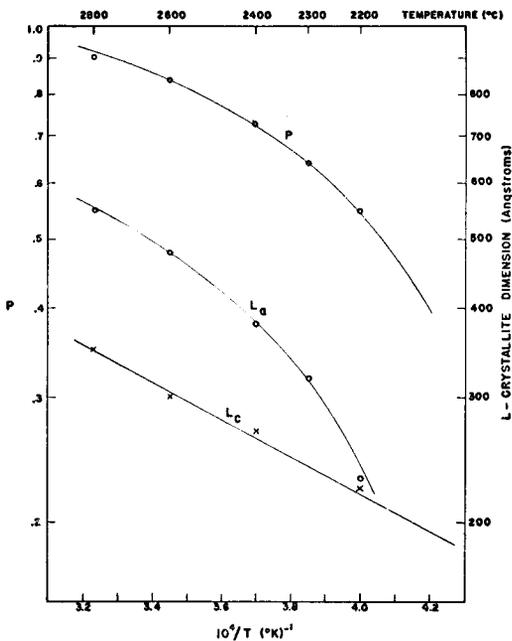


FIG. 8. Comparison of the crystallite dimensions and ordering parameter plotted as a function of reciprocal temperature of treatment for petroleum coke.

found to have initially finite slopes and can, in general, be analyzed for crystal size by the simpler line width methods.

Figure 7 is a plot of the mean crystallite size as a function of the baking temperature. The crystal height (L_c) was determined from the ($00l$) peaks after removal of strain

broadening. It can be seen that the height only increases by a factor of about two, whereas the diameter increases by a factor of five or more.

To summarize these measurements which give a fairly complete description of the crystalline state of the coke, the values of the dimensions and the ordering parameter are plotted on a semilog plot as a function of the reciprocal baking temperature as shown in Figure 8. The growth of the crystal height is the only process which appears to have a simple statistical relationship with temperature. The crystal diameter and the fraction of oriented layers seem to be strongly correlated but these two measurements are not strongly related to the crystal height. The rate of growth in the a -axis direction is a function of the crystal size and proceeds

in a manner which suggests that the growth occurs through a nucleation process. Since all of the diffraction broadening can be accounted for on the basis of misoriented layers and finite crystal size, the imperfections which must be annealed in the graphitization are fairly well characterized. The broadening of lines arising within layers indicates that the individual layers do not contain appreciable distortion. From the layer lines there is no evidence of warping of the layers. It must be concluded then that the ultimate crystal size is determined by previous history and we have shown here that most of the residual distortion can be annealed. The high-temperature annealing removes the residual strain but does not appear to cause growth of crystals by actual mass transfer.