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Abstract

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ON THE POSSIBILITY OF A COMPLETE X-RAY DIFFRACTION DISPERSION ANALYSIS OF GRAPHITE POWDERS AND COLLOIDAL PREPARATIONS

(Presented by Academician P. A. Rehbinder on 6 XI 1956)

X-ray diffraction methods for measuring the dispersity of solids have been developing for 30 years already. In this work, as a rule, only the average dimensions of a single-crystal grain are estimated, on the basis of the so-called "width" of the diffraction line. In recent years the fundamental possibility has been demonstrated ([1,2,7]) of finding the distribution function of crystallite sizes by investigating the shape of the diffraction line of a powder X-ray pattern. This method is based on harmonic analysis of the intensity of a diffraction reflection and makes it possible to estimate separately the magnitude of the strains and the grain sizes for crystals of any symmetry ([3]).

In the absence of microstrains, the intensity $I(\theta)$ of the hkl reflection can be represented in the form of a Fourier integral

$$I(\theta) = \int_{-\infty}^{+\infty} h(n) e^{2\pi i n \omega(\theta)}\, dn, \tag{1}$$

where n is a parameter linearly related to the grain size; θ is the diffraction angle; ω is a variable in reciprocal space.

The function $h(n)$ is related to the grain-size distribution curve $g(M)$ by the relation

$$h(n) = K \int_{|n|}^{\infty} (M - |n|) g(M)\, dM. \tag{2}$$

Differentiating equation (2) with respect to n, we obtain

Figure 1

Figure 1: Figure 1

$$-\frac{dh}{dn} = K\int_{|n|}^{\infty} g(M)\,dM; \qquad \frac{d^2h}{dn^2} = Kg(n), \tag{3}$$

i.e., the first derivative dh/dn gives the integral function, and the second derivative d^2h/dn^2 gives the differential distribution function. Thus we obtain exhaustive information on the dispersion composition of the sample. Investigation of different reflections also makes it possible to study the shape of the crystallites.

However, the practical application of this method encounters considerable difficulties. Thus, in the case of metals (and it is precisely for them that this method has been applied up to now), it becomes necessary to separate the effects of dispersity and microstrains on line broadening, which cannot always be done. In practice, by this route it has not yet been possible to construct distribution functions. It may be assumed that in the case of brittle bodies dis—

blurring of the lines due to microstresses should be absent. This circumstance substantially facilitates the investigation of the dispersion composition of such specimens.

We have made an attempt to find the particle-size distribution function for highly dispersed graphite systems. This problem arose in connection with the introduction into practice of new types of colloidal graphite preparations produced by mechanical dispersion of graphite powder in a vibratory mill (^{4}). By varying the grinding time, we were able to obtain graphite preparations with a very wide range of particle sizes. It is interesting to note that, usually, inert graphite under prolonged grinding (up to 30 hours) reaches an extremely high degree of dispersion, which makes it similar to soot, and upon discharge from the vibratory mill it heats in air to a temperature of $\sim 700°$.

Graphite, as is known, readily cleaves along the cleavage planes without substantial distortion of the lattice. The bonding forces between atoms in the basal plane are very large; therefore graphite is often classified as a valence crystal (of the diamond type). Graphite flakes perpendicular to the basal plane split off, breaking down analogously to brittle bodies without significant distortions of the crystal structure. It is therefore natural to expect that, during mechanical dispersion of graphite, microstresses should not arise in it to any appreciable extent; this is confirmed by our results.

Fig. 1. Function $h(n)$ of the $(11\bar{2}2)$ line for ground graphite powders: *a*—experimental data, *b*—calculated from formula (5)

Determination of the true line shape was carried out by us using Stokes' objective method (^{5}), which consists in comparing, by harmonic analysis, the

Figure 2

Figure 2: Figure 2

Fig. 3. Differential distribution curves for graphite powders; a—5 h of grinding; b—15 h of grinding. The functions were constructed under the assumption of the existence of a logarithmically normal distribution, the parameters of which were determined from experiment. The calculation was performed for the $(1\bar{1}52)$ line.

Figure 3: Fig. 3. Differential distribution curves for graphite powders; a—5 h of grinding; b—15 h of grinding. The functions were constructed under the assumption of the existence of a logarithmically normal distribution, the parameters of which were determined from experiment. The calculation was performed for the $(1\bar{1}52)$ line.

intensities of lines obtained under identical conditions for a sufficiently coarse-crystalline specimen (standard) and for the object under study. As the standard we used graphite powder that had not been subjected to vibratory grinding. This method directly gives the desired Fourier coefficients of the true line profile. Such a transformation can be performed with satisfactory accuracy only when the line of the specimen is considerably broader than the line of the standard. To reduce the instrumental line width, we prepared sufficiently thin specimens (diameter 0.25 mm), used narrow diaphragms (diameter 0.2-0.25 mm), carried out exposures in large-diameter cameras (86 and 114 mm), and selected the wavelength of the X-radiation so that the lines under study fell in the angular interval θ near 45° (since in this case blurring due to the finite height of the specimen disappears). Photographic processing of the X-ray diagrams was carried out simultaneously under strictly standardized conditions. The X-ray diagrams were carefully photometered with allowance for the blackening curve.

Fig. 2. Integral distribution curve of graphite particle sizes after 15 hours of vibratory grinding. The calculation was made from the $(11\bar{2}2)$ line

The lines $11\bar{2}0$ and $11\bar{2}2$ were subjected to harmonic analysis (as the most convenient for photometry and allowing one to estimate the particle shape—

types) of radiographs of graphite powders of various degrees of dispersion. The curves of the Fourier coefficients as functions of the parameter n, proportional to the crystallite size, proved to be close to the theoretical curves for the case of absence of stresses (Fig. 1). To find the integral particle-size distribution function it is sufficient to differentiate the experimentally found function $h(n)$ (Fig. 2). The accuracy achieved in this way naturally cannot be very high, and the distribution curve can be constructed only over a narrow interval of dispersion (in our case, for powders after 15-20 h of vibratory grinding).

Fig. 3. Differential distribution curves for graphite powders; *a*—5 h of grinding; *b*—15 h of grinding. The functions were constructed under the assumption of the

existence of a logarithmically normal distribution, the parameters of which were determined from experiment. The calculation was performed for the $(11\bar{5}2)$ line.

The accuracy can be increased and, at the same time, the size interval in which the distribution curve can be determined can be widened by introducing special assumptions about the character of the particle-size distribution. A. N. Kolmogorov (^{6}) showed that the size distribution of particles of a solid formed as a result of a random crushing process obeys a logarithmically normal law of the form

$$g(x) = \frac{1}{\sqrt{2\pi}\sigma x} \exp\left[-\frac{1}{2}\left(\frac{\ln x - \ln \xi}{\sigma}\right)^2\right], \tag{4}$$

where x is the particle size, and ξ and σ are constants of the distribution. There are grounds to expect that, in the systems we have studied as well, such a logarithmically normal distribution is realized. Then the problem reduces to finding the median ξ and the dispersion σ from the experimental curve. Substituting the expression for the distribution function into equation (2), we obtain:

$$h(x) = h(0)\Phi(\eta - \sigma) - \frac{h(0)x_i}{\xi e^{\sigma^2/2}}\Phi(\eta), \tag{5}$$

where

$$\eta = \frac{1}{\sigma}\ln\frac{x}{\xi}, \qquad \Phi(z) = \int_z^\infty \frac{1}{\sqrt{2\pi}} e^{-z^2/2}\,dz.$$

For the logarithmically normal distribution law the relations

$$\bar{x} = \xi e^{\sigma^2/2}, \qquad \overline{x^2} = \xi^2 e^{2\sigma^2}, \tag{6}$$

hold, where $\bar{x}$ is the mean size and $\overline{x^2}$ is the mean square of the size.

From the experimental curve $h(x)$, $\bar{x}$ and $\overline{x^2}$ are easily found (^{1}). After this, the median ξ and dispersion σ are determined from relations (6). The curves $h(\eta)$ calculated from these parameters (by formula (5)) agreed satisfactorily with the experimental data (see Fig. 1), which may be regarded as experimental confirmation of the possibility of applying the logarithmically normal law to describe the particle-size distribution of graphite. Use of this assumption made it possible to extend the range of dispersions for which a complete distribution curve can be obtained toward larger sizes (Fig. 3).

Investigation of lines with different indices also makes it possible to estimate the shape of the crystallites. It turned out that graphite grains can represent them in the form of disks whose height is several times smaller than the diameter.

Determinations of the specific surface area by low-temperature nitrogen adsorption using the Brunauer, Emmett, and Teller method are in satisfactory agreement with the X-ray data. This indicates that in our samples the regions of coherent scattering apparently coincide with graphite particles whose size is determined from the adsorption of nitrogen vapor.

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Note: Figure translations are in progress. See original paper for figures.