Reports of the Academy of Sciences of the USSR

G. M. PLAVNIK, L. A. FEIGIN

1965

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1965. Volume 161, No. 2

PHYSICAL CHEMISTRY

G. M. PLAVNIK, L. A. FEIGIN

APPLICATION OF THE METHOD OF SMALL-ANGLE X-RAY SCATTERING TO THE STUDY OF THE DISPERSE STRUCTURE OF FINELY GROUND GRAPHITE

(Presented by Academician P. A. Rebinder on September 1, 1964)

The study of the structure of highly disperse graphite preparations is a very complex problem, requiring for its solution the application of various physicochemical methods. The most widespread methods have been adsorption methods for surface investigation, analysis of the profile of X-ray diffraction reflections, and sedimentometric analysis. Measurement of adsorption makes it possible to determine only one characteristic of the system—its specific surface area; sedimentometric analysis in a number of cases cannot be carried out at all because of the aggregative instability of colloidal-graphite preparations. Analysis of the form of the interference lines on the X-ray pattern of highly disperse graphite samples, while in principle making it possible to obtain the most complete information on the disperse structure (⌒1), is in practice limited to a very narrow range of dispersity (⌒2). Thus, on the side of large particles this method is limited by the small broadening of the lines in comparison with a standard, and at high degrees of dispersity—by the superposition of neighboring lines on one another, the weakening of their intensity, and the impossibility of unambiguously separating them from the "background." It should also be borne in mind that from the profile of diffraction lines one determines the sizes of crystallites, which at the initial stages of grinding are much smaller than the sizes of the particles. If to this is added the further fact that the crystallite sizes determined by X-ray methods often turn out to be larger than the average size corresponding to the value of the specific surface area, whereas the opposite would have been expected, then, naturally, the need arises for the application of new methods.

In this respect, analysis of X-ray scattering in the region of small angles, i.e., in the immediate vicinity of the primary beam, appears very promising. This method, taking into account the concepts developed in recent years ($^{3-}$5), suc-

Fig. 1

Figure 1: Fig. 1

cessfully combines the capabilities of adsorption and X-ray (at large angles) methods and makes it possible, by means of a single procedure, to obtain the principal characteristics of disperse systems—the specific surface area, average sizes and shape of the particles, and degree of polydispersity.

We investigated samples of natural Taiginsk graphite, ground in a laboratory vibrational mill for 1, 3, 10, and 26 hours. Weighed portions of the powder were placed in cuvettes whose windows were sealed with a thin polymer film (20 μ), transparent to X-rays. The weighed portions were selected in such a way that the mass of powder per unit area was strictly identical in all samples. Measurement of the intensity of small-angle X-ray scattering was carried out on an apparatus whose optical scheme included five slits: three collimator slits and two receiving slits. As the source of X-rays, filtered copper radiation was used at a tube voltage of 18 kV. The scattered radiation was recorded by the ionization method. For each sample, two overlapping scattering curves were measured: one with collimator slit widths of 50 and 20 μ, the other with ···

slot width of 100 μ. This made it possible to cover a range of scattering angles from $1'$ to 5°. To check the data obtained from small-angle scattering, measurements of the specific surface area by low-temperature nitrogen adsorption were carried out, and the crystallite sizes were determined by X-ray diffraction at large angles.

Figure 1 presents the scattering curves for four comminuted samples, plotted in logarithmic coordinates. From these data it follows that, as the duration of dispersion increases, the intensity of small-angle scattering increases sharply. This may serve as experimental proof that the observed effect is caused by "true" scattering from inhomogeneities, and not by double diffraction reflections, since in the course of grinding, as a result of amorphization of the substance, the intensity of interference lines (single reflections) decreases sharply ([6],[7]). This conclusion is also confirmed by Warren' s data ([8]), which showed that in powdered graphite-like materials the intensity of double reflections is at least two orders of magnitude lower than that of "true" scattering.

Fig. 1. Intensity curves of small-angle X-ray scattering of graphite.
1—sample T_1, grinding duration 1 h; 2—T_3, 3 h; 3—T_{10}, 10 h; 4—T_{26}, 26 h; the origin of curve 4 is shifted to the right along the abscissa axis. The dashed lines indicate straight lines whose slope tangent is equal to 3.

From the nature of the scattering curves one can judge the shape of the scattering particles. At the initial stages of dispersion (within 1 hour), the system still contains a significant amount of large particles. As the grinding duration increases, the "head part" of the curves (the region of the smallest angles) becomes increasingly gentle. Such a course of the curves indicates a plate-like

Fig. 2

Figure 2: Fig. 2

shape* of the scattering particles ([3],[4]). The formation of graphite particles of plate-like shape during grinding is also confirmed by electron-microscopic data ([6]). The "tail part" of all the scattering curves consists of straight lines whose slope tangent is very close to 3 (Fig. 1). Such a course of the curves makes it possible to conclude that the scattering intensity per unit mass in this region is proportional to the specific surface area of the particles ([9],[10])

$$I = kS/s^3, \tag{1}$$

where k is a proportionality coefficient; $s = 2\pi\varphi/\lambda$; λ is the wavelength of the X-ray radiation, φ is the scattering angle, and S is the specific surface area. Formula (1) was obtained as applied to slit collimation. Since in our experiments the intensity of the incident beam was strictly constant and the mass of graphite per unit area was unchanged, the relative change in intensity on the rectilinear section corresponds to the change

---

* A gently sloping section in scattering curves may also arise from scattering by rod-shaped particles; however, the formation of such particles in graphite, which has a clearly expressed layered structure, appears unlikely.

of the specific surface area of graphite during dispersion. If the absolute value of the surface area of at least one specimen is known, then the specific surface areas of all specimens can be determined. In the present case, specimen T_3, with a specific surface area of 90 m^2/g (adsorption data), was chosen as such a standard. The surface-area values calculated in this way (Fig. 2, curve 1) are very close to the adsorption data.

It was also of interest to determine the absolute values of the specific surface area on the basis of small-angle data alone ([3,4]):

$$S = \frac{1}{\rho} \frac{4(1-w)\lim_{s\to\infty}[I(s)s^3]}{\displaystyle\int_0^\infty I(s)s\,ds}, \tag{2}$$

where ρ is the density; w is the relative volume of the disperse phase; the remaining notation is the same as in formula (1). It turned out that the surface-area values calculated from (2), although strictly proportional to the adsorption measurements, are, in absolute magnitude, approximately a factor of two smaller (Fig. 2, curve 2).

Fig. 2. Comparison of specific surface areas according to adsorption and small-angle scattering data: 1 —from intensity ratios; 2 —from absolute measurements

The use of the commonly applied Guinier tangent method for determining particle size appears unjustified in the present case, owing to the considerable polydispersity and anisometry of the particles. Apparently, this explains the almost complete absence of work on the application of the small-angle method to the study of the particle sizes of finely ground graphite. We attempted to circumvent these difficulties by applying the method proposed at one time by Hosemann (^{5,11}), who showed that various kinds of particle-size distributions can be approximated by means of a generalized Maxwell distribution

$$M(x) = (x/c)^n e^{-(x/c)^2} K(n) c, \tag{3}$$

where M is the density of the volume distribution of particles with respect to their radii x; $1/K(n) = \Gamma((n+1)/2)/2$ is the normalization factor expressed through the gamma function. This formula includes both the Gaussian distribution ($n = 0$) and various types of asymmetric distributions.

Table 1

Particle sizes calculated from X-ray measurements at small and large angles

Specimen	Small angles	Small angles	Small angles	Large angles	Large angles	Large angles
Specimen	σ	$\overline{R}$	$2\overline{R}$	L_a	L_c	R
T_{10}	1.04	53	150	150	54	53
T_{26}	0.95	35	98	84	42	32

Using this distribution, one can, by constructing for the small-angle scattering intensity curve $I(\varphi)$ the moment function $f(\varphi) = I(\varphi)\varphi^2$, directly determine the mean sizes and the degree of polydispersity.

Table 1 gives, determined from the moment curve, the values of the mean radii of inertia

$$R = \left[\int_v r^2 \, dv \Big/ \int_v dv\right]^{1/2}$$

(a characteristic of the linear dimensions of a body of arbitrary shape) and, calculated from them under the assumption that the particles have the shape of flat disks, the diameters $2R$, as well as the parameter

$$\sigma = \left[(\overline{R^2} - \overline{R}^2)/\overline{R}^2\right]^{1/2},$$

which characterizes the polydispersity of the system. The table also gives values obtained from analysis of the profile of diffraction reflections, $L_a = 2R$ and L_c —the crystallite dimensions in the directions of the a and c axes—as well as the corresponding values of the radii of inertia R.

It follows from the data in the table that the size values calculated from measurements at small and large angles are in good agreement with one another. It should be borne in mind, however, that the crystal sizes were determined, as in most other studies, without allowing for the influence of lattice distortions on the width of the interference lines. If these distortions were taken into account, the calculated crystal sizes would evidently be larger. In this sense the small-angle data are in better agreement with the adsorption data than are the results of measurements at large angles.

The results obtained show that, in the process of dispersing graphite materials, very fine (R_i = 35–50 Å) flat particles are formed, characterized by a high degree of polydispersity ($\sigma \simeq 1$). At the same time the surface area reaches several hundred square meters per gram. Thus, the method of small-angle X-ray scattering makes it possible to reveal a sufficiently complete picture of the disperse structure of colloidal systems and, in many cases, can provide information that usually requires the use of at least two methods—adsorption and X-ray diffraction at large angles.

Institute of Physical Chemistry
Academy of Sciences of the USSR

Institute of Crystallography
Academy of Sciences of the USSR

Received
19 VIII 1964

REFERENCES CITED

1. A. I. Kitaigorodskii, *X-ray Structural Analysis of Fine-Crystalline and Amorphous Bodies*, Moscow, 1952.
2. L. A. Feigin, V. N. Rozhanskii, *Doklady Akademii Nauk SSSR*, **113**, No. 5, 1102 (1957).
3. G. Porod, *Kolloid Zs.*, **124**, 83 (1951); **125**, 51 (1952).
4. A. Guinier, *Small-Angle Scattering of X-Rays*, N. Y., 1955.
5. R. Hosemann, S. N. Bagchi, *Direct Analysis of Diffraction by Matter*, Amsterdam, 1962.

6. L. A. Feigin, Dissertation, Moscow, 1958.

7. G. M. Plavnik, L. A. Plutalova, B. M. Rovinskii, *Izv. AN SSSR, Mekhanika i mashinostroenie*, No. 4, 179 (1963).

8. E. Warren, *Proc. Fourth Conf. on Carbon*, University of Buffalo, 1960, p. 351.

9. V. N. Filippovich, *ZhTF*, **26**, No. 2, 398 (1956).

10. A. Guinier, *X-ray Crystallography*, Moscow, 1961.

11. R. Hosemann, *Zs. Phys.*, **113**, Heft 11–12, 751 (1939).

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