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Abstract

Full Text

Physical Chemistry

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On the Influence of Adsorption Layers on the Dispersion of Graphite

(Presented by Academician P. A. Rebinder, 14 III 1957)

The problems of the physicochemical influence of the medium on the processes of graphite dispersion have been studied quite insufficiently, which is connected, above all, with the difficulties of dispersion analysis in the region of colloidal particle sizes. In our work we used measurement of the specific surface by the method of low-temperature nitrogen adsorption (¹), the X-ray diffraction method developed by us earlier (²), and electron-microscopic investigation.

Vibrational grinding of graphite (^{2,3}) makes it possible to obtain highly dispersed colloidal-graphite preparations with an average size of the primary particles of 100 Å and less; the specific surface in these cases reaches 600 m²/g. At the same time, the finest vibrational milling of dry graphite proceeds 10–20 times more intensively than grinding in an aqueous medium.

It is important to note that, in the vibrational grinding of a number of solids (quartz, cement, etc.), it is not possible to exceed specific-surface values on the order of several tens of m²/g. It is therefore natural to relate such a high dispersity of ground graphite powders to the layered structure of the graphite lattice. The considerable distances between layers of carbon atoms (3.37 Å), in comparison with the corresponding distance in the basal plane (1.41 Å), determine the low bonding energy of the layers, which explains the perfect cleavage of graphite, the sharp anisotropy of the bonding forces, and the easy dispersion along the basal planes. This is confirmed by X-ray diffraction and electron-microscopic studies, which show that graphite particles are flakes whose size in the basal plane is considerably greater than their height. In Fig. 1 the semitransparent (for the electron beam) particles of graphite are clearly visible.

To elucidate the mechanism of graphite dispersion, we carried out experiments introducing small additions of water during grinding, as well as certain other substances. The experiments were performed mainly on a laboratory mill*, which makes it possible to carry out simultaneous grinding under completely identical conditions in 4 chambers—drums of 100 cm³ capacity each. The drums were carefully sealed. It was shown (⁴) that in a vibrational mill rather small average pressures are produced, so that the dispersion process proceeds mainly at the expense of surface abrasion of the particles during their relative displace-

Figure 1. Thin semitransparent flakes of graphite ground in an aqueous medium. Electron micrographs.

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ments and, consequently, the frictional force between particles determines to a significant extent the degree of grinding.

Figure 2 presents curves of the dependence of the increase in the specific surface of graphite on grinding time with various additions of water. From these data it is seen that the dispersion of dry graphite proceeds most intensively: the specific surface increases at a constant rate of $30 \text{ m}^2/\text{g} \cdot \text{min}$, up to a value of $300 \text{ m}^2/\text{g}$. (The indicated rate was determined by the choice of the parameters of the vibrational mill; changing these parameters

* The mill was designed by M. I. Aronov and L. M. Morgulis.

Fig. 1. Thin semitransparent flakes of graphite ground in an aqueous medium. Electron micrographs.

within sufficiently broad limits has essentially no effect on the established regularities; at the same time, the intensity of dispersion changes by tens of times.) On the other hand, when water is added in amounts on the order of 3% relative to the graphite, the increase in specific surface area with time also proceeds linearly, but at a rate approximately 10 times lower, i.e., about $2 \text{ m}^2/\text{g} \cdot \text{min}$. With smaller additions of water, two regions can be distinguished that differ sharply in the rate of formation of new surfaces of the graphite particles.

Knowing the true value of the specific surface area enabled us to calculate the number of saturated monolayers of water formed on the surface of the graphite particles, and also to estimate the decrease in the number of these layers during dispersion of the powder with a definite amount of water. (In view of the hydrophobicity of graphite, it makes sense to speak of layers only when their number does not exceed 3-4; however, as will be clear from what follows, precisely this case is of greatest interest to us.) It was found that the change in the rate of increase of the graphite surface occurs at a water content corresponding to the formation of a saturated adsorption monolayer. This circumstance should be attributed to the sharp increase in the coefficient of friction of the pure, freshly formed surfaces of graphite particles in comparison with the friction of graphite surfaces covered with adsorbed moisture.

Fig. 2. Kinetics of graphite dispersion with the introduction of small additions of water.

1 —dry dispersion, 2 —0.35% water, 3 —0.7% water; 4 —1% water, 5 —3% water

In light of this, the kinetics of dispersion of graphite with small additions of

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Fig. 3. Kinetics of graphite dispersion with the introduction of additions of butyl alcohol. 1 —dry dispersion, 2 —0.8% butyl alcohol, 3 —2.4% butyl alcohol, 4 —8% butyl alcohol

Figure 3: Fig. 3. Kinetics of graphite dispersion with the introduction of additions of butyl alcohol. 1 —dry dispersion, 2 —0.8% butyl alcohol, 3 —2.4% butyl alcohol, 4 —8% butyl alcohol

water can be explained as follows. At the beginning of the dispersion process, the surface of the graphite particles is small, so that even the smallest additions of water provide a sufficient number of layers of adsorbed moisture (in this case adsorption of water molecules takes place from saturated vapor), and the grinding rate corresponds to the “wet” dispersion regime. Then, as the surface area increases, the number of water layers decreases, and after the available amount of water becomes less than is required for the formation of a saturated monolayer, the grinding rate approaches that for the case of “dry” comminution.

Fig. 3. Kinetics of graphite dispersion with the introduction of additions of butyl alcohol.

1 —dry dispersion, 2 —0.8% butyl alcohol, 3 —2.4% butyl alcohol, 4 —8% butyl alcohol

It is clearly evident from our experiments that small amounts of moisture or other substances always present in the surface layer of the initial graphite specimen can influence the dispersion process only at the very initial stage, since in the course of vibrational comminution of graphite its specific surface area increases by hundreds (and even thousands) of times, and impurities contained in the graphite will, during comminution, have a negligible surface density. This circumstance was checked by us, in particular, by different drying of the graphite specimen before comminution. Drying of graphite at 100°, and heating of the drum with graphite to 200° directly—

but before the experiments and drying of the graphite at 300° in a stream of nitrogen did not lead to the detection of any noticeable difference in the course of the grinding curves, whereas the introduction of 1% water reduced the rate of dispersion severalfold.

Fig. 3 gives data on the kinetics of grinding graphite with small additions of butyl alcohol, which show the same course of the curves as in the case of water. Calculation shows that the formation of a monolayer of butyl alcohol is also

sufficient for a sharp decrease in the coefficient of friction. Experiments with the introduction of benzene vapor qualitatively confirm the same picture. Our results showed the identical influence of additions of water on the grinding of both natural graphite and artificial graphite obtained from anthracite at high temperature.

The results obtained agree with the data of Bowden and co-workers⁽⁵⁾, who established a smooth increase in the coefficient of friction of the graphite-graphite system with increasing temperature of degassing of graphite (in high vacuum) up to 1000°, as well as with data obtained in the study of the increased wear of carbon and graphite brushes of electrical machines at high altitudes under conditions of reduced atmospheric humidity^(6,7).

For comparison we carried out similar experiments on the dispersion of mica (a hydrophilic material), whose crystal lattice also has a layered structure. In this case, on the contrary, we found an increase in the rate of grinding in the presence of additions of water (Table 1), which is in accord with the general phenomenon of adsorption lowering of the strength of solids, discovered by P. A. Rehbinder^(8,9). The change in the picture on passing from graphite to mica is analogous to an inversion effect—the transition from lubricating action to wear with increasing pressure during friction in a surface-active medium.

Table 1

Effect of small additions of water on the acceleration of the process of dispersion of mica
(specific surface area in m^2/g)

Amount of water, %	Grinding duration, min.	Grinding duration, min.	Grinding duration, min.	Grinding duration, min.
	1	2	4	6
0.0	7.0	14.5	21.0	23
2.5	9.3	14	22	—
5.0	11.2	16	30	34

Very recently Eichborn⁽¹¹⁾, studying the grinding of cement, quartz, and marble, showed that the process of dispersion is facilitated in vapors of adsorption-active substances. An analogous phenomenon was also observed by I. L. Ettinger and M. M. Protod' yakov⁽¹²⁾. Thus, the results obtained by us testify to a sharply expressed specificity of graphite dispersion and to the adsorption lubricating action of monomolecular layers.

In conclusion, the authors express their sincere gratitude to P. A. Rehbinder, A. A. Zhukhovitskii, V. I. Likhtman, and D. S. Sominskii for discussion of the results and valuable comments.

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