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Abstract

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THE AMORPHIZED STATE OF POWDERS OF NATURAL GRAPHITES

(Presented by Academician P. A. Rebinder, 21 V 1963)

X-ray diffraction studies carried out by a number of authors [1–4] on powders of natural graphites subjected to grinding showed substantial changes in their structure depending on the method and duration of dispersion. As was established in [3], during grinding in a ball mill there is observed a sharp decrease and broadening of the interference maxima on the X-ray scattering curve, indicating the transition of graphite from a state of three-dimensional ordering to a two-dimensional one. These structural changes may be regarded as proceeding in the direction of disordering—amorphization of the substance. They proceed most intensively during vibrational grinding [5].

Table 1

Change in the X-ray diffraction characteristics of Taiginsk graphite as a function of its treatment conditions

Vibrational grinding time, h	Specific surface area, m^2/g	Interplanar spacing $d_{(0002)}$, Å	L_c, Å after grinding	L_c, Å after heat treatment*	L_a, Å after grinding	L_a, Å after heat treatment*	$I_{(11\bar{2}2)} : I_{(11\bar{2}0)}$ after grinding	$I_{(11\bar{2}2)} : I_{(11\bar{2}0)}$ after heat treatment*
Initial	15	3.357	310	–	607	–	1.54	–
12	–	3.363	183	200	315	470	0.86	0.89
24	–	3.369	148	150	295	405	0.76	0.79
33	500	3.378	90	100	210	240	0	0.40

* At a temperature of 2500°C.

Thermal treatment of amorphized graphites acts in the direction of restoring the graphite lattice. However, according to the results of [3], this is achieved far from completely.

Fig. 1. X-ray scattering curves as a function of the type of treatment of Taiginskii graphite: a –initial, –treated in vacuum, , , –treated in a vibration mill for 12, 24, and 33 h, respectively.

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The purpose of the present work was to investigate the possible limits of amorphization attainable during prolonged vibrational grinding, the processes of return to the state of three-dimensional ordering during heat treatment of amorphized graphites, and a comparative X-ray structural evaluation of various types of natural graphites.

Graphite powders from the Taiginsk, Noginsk, and Kureisk deposits were taken as the objects of investigation. Powder of Taiginsk graphite was ground for 12-33 hours under isothermal conditions in an M10 vibratory mill, with a volume of 10 dm^3, at an amplitude and oscillation frequency of 3 mm and 25 Hz, respectively. Parallel samples of Taiginsk graphite were ground by abrasion in vacuum (10-12 mm Hg) of pressed specimens during their operation as a sliding electrical contact. After grinding, part of the powder was heated for 10 min at temperatures from 1500 to 3000°C in a graphite crucible placed in the circuit of an LPZ-67 high-frequency furnace. All graphite samples were examined on a URS-50I diffractometer.

The specific surface area of the initial and ground samples was measured on a low-temperature nitrogen adsorption apparatus (BET method) [6].

Fig. 1 shows the intensity curves of X-ray scattering in the angular intervals (2θ) 38–60°, 75–88°. Here one can very clearly see

Fig. 1. X-ray scattering curves as a function of the type of treatment of Taiginskii graphite: a –initial, b –treated in vacuum, v, g, d –treated in a vibration mill for 12, 24, and 33 h, respectively

the gradual broadening and disappearance of the interference maximum ($11\bar{2}2$), as well as the broadening and decrease in the intensity of the lines ($11\bar{2}0$), (0004), ($10\bar{1}1$) with increasing duration of vibrational grinding.

From the data given in Table 1 it is evident that after 33 hours of grinding the ratio of the intensities ($11\bar{2}2$) and ($11\bar{2}0$) becomes equal to zero, which indicates the complete elimination of three-dimensional ordering.

In the curves shown in Fig. 1, the progressive asymmetry of the diffraction maxima with grinding time is noteworthy. The latter indicates an increase in the number of hexagonal networks that are in the most disordered state. Dispersion by wear of the specimen during its rubbing in vacuum is accompanied by practically complete preservation of the lattice parameters characteristic of Taiginskii graphite (Fig. 1). This final product had the following characteristics:

Figure 2. Comparative X-ray scattering curves for natural graphite powders from various deposits.

Figure 2: Figure 2. Comparative X-ray scattering curves for natural graphite powders from various deposits.

specific surface area 325 m^2/g (in the initial state 6.0 m^2/g), interlayer spacing $d_{(002)} = 3.363$ Å, $L_c = 256$ Å, $L_a = 471$ Å, $I_{11\bar{2}2}/I_{11\bar{2}0} = 1.15$.

The X-ray scattering intensity curve shown in Fig. 1 for graphite obtained by dispersion in vacuum shows that the noted changes in the X-ray characteristics are by no means associated only with simple dispersion of the graphite particles.

Thus, only the forceful dynamic action of the balls during treatment in a ball vibration mill causes clearly expressed amorphization of graphite, proceeding in the following sequence (Table 1, Fig. 1):

1) fragmentation of crystallites, causing broadening and asymmetry of the interference maxima; 2) disruption of the order in the alternation of individual layers, their relative mutual displacements; 3) complete transition into a state of two-dimensional ordering; and 4) in the limit —transition into a completely disordered state.

Thermal treatment of amorphized graphites, as is evident from Table 1 and Fig. 3, practically does not increase the values attained during grinding

Fig. 2. Comparative X-ray scattering curves for natural graphite powders from various deposits: **a:** 1—Taiga graphite, treated isothermally in a vibromill for 8 h; 2—natural graphite from the Noginsk deposit, untreated; **b, c, d:** 1—Taiga graphite, treated isothermally in a vibromill for 33 h; 2—natural graphite from the Kureika deposit, untreated. Curves **a, b, c, d** were obtained after heating at temperatures of 2800°, 20°, 1500°, and 2800°, respectively.

of L_c and, in individual cases, contributes to insignificant changes in other indices.

Amorphization of crystalline graphite makes it possible to decipher the structure of graphites that do not have a pronounced crystalline structure.

Figure 2 shows the intensity curves* of X-ray scattering obtained in measurements of powders of Taiginka, Noginsk, and Kureika graphites. From Fig. 2 it is evident that the character of the curves obtained is practically identical. The somewhat greater intensity of the (0004) line for Taiginka graphite is explained by the increased anisotropy of its particles. Heat treatment at 1500—2800° produces identical changes in the intensity curves (Fig. 2). The latter is sufficient proof that the graphite of the Kureika deposit has an amorphized structure very close to two-dimensional ordering.

Fig. 3. X-ray scattering curves as a function of the heat-treatment temperature of amorphized Taiginka graphite: *a* —initial; *b* —treatment temperature 1500°;

Fig. 3. X-ray scattering curves as a function of the heat-treatment temperature of amorphized Taiginka graphite: a —initial; b —treatment temperature 1500°; c —2000°; d —2500°; e —2800°

Figure 3: Fig. 3. X-ray scattering curves as a function of the heat-treatment temperature of amorphized Taiginka graphite: a —initial; b —treatment temperature 1500°; c —2000°; d —2500°; e —2800°

c —2000°; *d* —2500°; *e* —2800°.

A similar convergence is also observed when comparing the intensity curves for Taiginka graphite powder, milled for 8 hours, and graphite from the Noginsk deposit in the initial state and after heating them to 2800°. As can be seen from Fig. 2, upon heating them, the changes in all interference reflections are completely identical.

Thus, by varying the degree of amorphization of natural graphites with a high initial index of three-dimensional ordering, it is possible to obtain an interference pattern similar to those obtained from other types of graphite and, as a result, to decipher their structure.

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* All scattering curves were obtained under identical conditions for recording the intensity.

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