E. A. LEONT' EV and V. M. LUK' YANOVICH

1960

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

E. A. LEONT' EV and V. M. LUK' YANOVICH

ON THE STRUCTURE OF PARTICLES OF GRAPHITIZED THERMAL CARBON BLACK AND THE PRODUCTS OF THEIR SPLITTING

(Presented by Academician M. M. Dubinin on 27 IV 1960)

Electron-microscopic studies in the dark field have shown that, for some carbon blacks, for example thermal black, the images obtained are distinguished by increased brightness at the edges of the particles ([1-3]). Analysis of this phenomenon led to the conclusion that in such carbon blacks their structural elements—parallel-layer groups consisting of 2-4 layers of hexagonally packed carbon atoms—are oriented parallel to the surface of the particles. Upon calcination of thermal carbon black, its particles, which initially had a spherical shape, are transformed into polyhedra. On the basis of electron-microscopic and X-ray data it was suggested that each polyhedron consists of a few pyramid-like graphite crystals, whose apices are oriented toward the center of the polyhedron, while their bases are basal planes of graphite (001) ([4, 3]).

Direct evidence confirming these ideas about the structure of the particles of the initial and calcined thermal carbon black was recently obtained as a result of a microdiffraction study carried out in a high-voltage electron microscope—an electron diffraction instrument ([5]). At the same time it was shown for the first time that, in a particle of calcined carbon black, graphite crystals are separated by interlayers of amorphous carbon with a thickness of the order of 100 Å.

In the present work a different approach was used to reveal the structure of particles of graphitized carbon black—the study in an electron microscope of its oxidized and "exploded" particles. It is known that, when graphite is treated in a liquid medium with strong oxidizing agents, oxygen atoms penetrate into the interplanar spaces of the lattice and chemically bond with carbon atoms ([6]). When the dried product is heated to 180-200°, an explosive evolution of CO and CO_2 occurs, leading to splitting of the crystal along the c axis into packets consisting of a comparatively small number of basal planes. A polycrystalline graphite body subjected to such treatment will be "exploded," i.e., split into individual crystals deformed (elongated) along the c axis, but retaining their dimensions in the directions of the a and b axes. This method was used to reveal the crystals forming the spheroids of nodular graphite in cast iron ([7]).

Figure 1. Particles of thermal carbon black: a—initial; b—calcined at 3200°; c—calcined and oxidized in a liquid medium

Figure 1: Figure 1. Particles of thermal carbon black: a—initial; b—calcined at 3200°; c—calcined and oxidized in a liquid medium

Figure 2. "Exploded" particles of thermal carbon black

Figure 2: Figure 2. "Exploded" particles of thermal carbon black

The object of study was thermal carbon black calcined at 3200° in an inert atmosphere for 20 min. (the same sample as in work ([5])). After calcination the particles acquired the form of polyhedra (Fig. 1a,b). To obtain an oxidized sample, 1 g of carbon black was poured with a mixture of concentrated acids: 30 ml H_2SO_4 ($d = 1.84$) + 10 ml HNO_3 ($d = 1.40$). Then, with stirring over 15-20 min., 10 g of finely ground $KClO_3$ was added, and the mixture was kept for 1.5-2 hours. The carbon black was washed with water until there was no reaction for Cl^-. The oxidized carbon black was readily wetted by water, so that specimens for observation in the electron microscope could easily be prepared from its aqueous suspension. As can be seen in Fig. 1c, as a result of oxida-

Fig. 1. Particles of thermal carbon black: **a**—initial; **b**—calcined at 3200°; **c**—calcined and oxidized in a liquid medium

Fig. 2. "Exploded" particles of thermal carbon black

particles swell, the shape of the polyhedron is smoothed, and around some particles a shell that has separated from their surface is noticeable. It is characteristic that predominantly large particles swell, whereas the majority of small ones do not change.

To obtain "exploded" particles, small amounts of dried oxidized soot were heated in air, and the products scattered by the explosion were collected on grids covered with a film substrate. In some cases, specimens were prepared from particles of oxidized soot already deposited on a quartz film by splitting them in vacuum from an incandescent spiral.

Typical micrographs of "exploded" particles are shown in Fig. 2. As can be seen in the photographs, the "exploded" particles are elongated formations; moreover, study of stereomicrographs shows that they are three-dimensional formations, and not flat ribbons. In accordance with what was said above, these formations can consist only of graphite layers, split and deformed by the force of the explosion, but nevertheless connected with one another.

Fig. 3

Figure 3: Fig. 3

Fig. 3. Schematic representation of the structure of a particle of calcined thermal soot (a) and of the products of its splitting—an "exploded" particle (b). 1—graphite crystals; 2—interlayer of amorphous carbon; 3—deformed graphite crystals; 4— "seam" in the "exploded" particle. The plane of splitting of the initial particle is shown by a dotted line.

The considerable width of the "exploded" particles is noteworthy: their cross section often corresponds to the diameter of the oxidized soot particle (Fig. 2a) or even exceeds it (Fig. 2b). It is not excluded that calcined soot contains graphite crystals whose dimensions in the directions of the axes a and b correspond to the width of the exploded particle shown, for example, in Fig. 2a.

However, it seems to us more probable that in most cases the "exploded" particles consist of several mutually connected deformed graphite crystals. Interlayers of amorphous carbon may serve as the binding material, since, as is known, amorphous carbon does not swell or split when treated with liquid oxidizing agents. Indeed, in many micrographs paired "exploded" particles are visible, fastened in the middle by a "seam" (Fig. 2b serves as an example). It is natural to assume that the appearance of this "seam" is due to the presence of amorphous interlayers in the particle of calcined soot. In Fig. 2v it can be distinguished that the wide "exploded" particle consists of several narrower formations.

The schematic structure of calcined and "exploded" particles of thermal soot is shown in Fig. 3. If the splitting of a calcined particle occurs along the plane shown by the dotted line in Fig. 3a, then two formations arise (Fig. 3b). In the diagram the length of the products of splitting is greatly reduced: in reality this length exceeds the diameter of the initial particle by an order of magnitude and more. The diagram makes it possible to understand why exploded particles can have a shape widening toward one end, and why their cross section may be greater than the diameter of the initial soot particle. Dark

inclusions at the narrower end of the exploded particle (Fig. 2b) are evidently remnants of unsplit material from the central part of the soot particle.

Thus, taking into account the presence of amorphous interlayers between graphite crystals in the particles of calcined soot makes it possible to explain the specific morphology of the exploded particles. The shells separated from the oxidized particles (Fig. 1b) are apparently surface layers of graphite crystals, fastened by the same interlayers of amorphous carbon.

The present work confirms that the shape and dimensions of the products of splitting of a graphite body are a function of the body' s structure, and their study, in our opinion, can provide additional information about this structure. The splitting method may be especially useful for investigating polycrystalline graphite bodies formed from such large crystals that their analysis by the X-ray method becomes difficult.

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
22 IV 1960

CITED LITERATURE

[1] U. Hofmann, A. Ragoss, et al., *Zs. anorg. Chem.*, **255**, 195 (1947).
[2] C. E. Hall, *J. Appl. Phys.*, **19**, 271 (1948).
[3] H. P. Boehm, *Zs. anorg. Chem.*, **297**, 315 (1958).
[4] E. A. Kmetko, *Proceedings of the First and Second Conferences of Carbon*, Buffalo, N. Y., 1956, p. 21.
[5] H. M. Popov, V. I. Kasatochkin, V. M. Lukyanovich, *DAN*, **131**, 609 (1960).
[6] U. Hofmann, *Ergebn. exakt. Naturwiss.*, **18**, 229 (1939).
[7] E. A. Leont' ev, V. M. Lukyanovich, B. S. Milman, *DAN*, **112**, 461 (1957).

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