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Abstract

Full Text

{Physical} Chemistry

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ELECTRON-MICROSCOPIC STUDY OF THE STRUCTURE OF SPHEROIDAL GRAPHITE IN CAST IRON

(Presented by Academician M. M. Dubinin, 30 VII 1956)

The introduction into cast iron of certain elements (in particular Mg, Ce, Ca) in amounts of several hundredths of a percent causes the crystallization of graphite inclusions not in the usual lamellar form, but in the form of spheroidal formations—spherulites with varying degrees of roundness. This makes it possible to increase the strength limits of cast iron by a factor of 2–3 and to impart ductility to it while preserving a number of technological advantages and the economy of the methods of its production. In many cases the new high-strength cast iron fully replaces steel, malleable cast iron, and nonferrous alloys, so that the problem of further improving the properties and technology of such cast iron acquires great significance for the national economy.

In this connection, recently a large number of works have been devoted to the study of spheroidal graphite, and a number of hypotheses have been put forward concerning its structure ([1]–[5]). However, because of the limited experimental material, this question has not been finally resolved. In electron-microscopic studies ([2], [4], [5]) the authors confined themselves to the investigation of ordinary metallographic polished sections; however, since the surface of the graphite inclusions is inevitably strongly deformed in the course of its preparation, such studies could not provide sufficient information for understanding the structure of graphite. An exception is the work ([6]), in which, by means of cathodic etching of polished sections, valuable information on the structure of graphite was obtained.

We carried out an electron-microscopic study of the undeformed surface of graphite inclusions by the replica method, as well as of their internal structure by means of chemical splitting and photographing of the decomposition products. For the study, spheroidal graphite separated from Mg-containing cast iron by electrolytic dissolution was used (Fig. 1). The electrolyte was a 20% HCl solution; the current was 5 A. The separated graphite was washed with an alkaline solution, water, and dried.

Obtaining replicas from the surface of the separated spheroidal particles with a diameter of about 100 μ was a difficult methodological problem. After a number of attempts we adopted the following method. A thin layer of a 0.1% collodion solution was applied to the surface of a glass plate and, after 1-2 min., powdered graphite was sprinkled on it. The excess was shaken off, so that the collodion film was covered with a single-grain layer. The conditions were selected (by observation in a stereomicroscope) so that (1/3)—(1/4) of the height of the globules was wetted by the solution. After a day, upon completion of the hardening of the film, the object was covered with molten sulfur. Sulfur wets graphite well but does not wet the film, and therefore after solidification the sulfur layer, together with the globules adhering to it, was easily separated from the plate. On the latter there remained the collodion film, which had retained the impressions of the graphite grains. By thermal decomposition in vacuum, the final quartz replica was applied to it ([7]), which

was strengthened by applying a layer of gelatin 0.1-0.2 mm thick. Then the lower collodion layer was dissolved in acetone, and the separated quartz replica with the gelatin layer was washed and placed on the surface of water with the gelatin downward. After the gelatin had dissolved, the quartz film was washed with water and caught on a specimen-holder grid. A drop of alcohol, and then ether, was immediately applied to the film, the excess liquid being drawn off with filter paper. Strengthening the quartz replica with gelatin and replacing the water by a liquid of lower surface tension during drying of the replica must be carried out in order to avoid its rupture.

Photography was carried out with a UEM-100 electron microscope at a magnification of 8200.

Examination of stereophotographs of quartz replicas (Fig. 2) shows that the surface of the graphite has a rough relief: it appears nodular, covered with rounded protrusions ranging in size from one to several microns.

To study the internal structure, the graphite was first ground in an agate mortar, and the comminution products were examined in the electron microscope. In this case a picture typical of ordinary graphite was observed—thin semitransparent plates formed as a result of the separation of crystals along cleavage planes. These data are in agreement with the results of X-ray studies, according to which spheroidal graphite contains well-formed crystals.

Of greatest interest was the attempt to determine the dimensions of these crystals; for this it was necessary to isolate them, as far as possible each separately, from the spherical grain. The mechanical comminution described above did not solve the problem, since in this process uncontrolled deformations of the crystals are inevitable. We therefore applied vigorous oxidation of the graphite in a liquid medium; as a result, oxygen atoms penetrate into the interplanar spaces of the graphite lattice and combine chemically with carbon atoms to form graphite oxide ([8]). Upon subsequent heating to 180–200° there occurs an explosive evolution of carbon monoxide and dioxide, leading to splitting of the crystal along the (c) axis into packets consisting of a comparatively small number of basal planes. When observed in the electron microscope, the splitting product of ordinary graphite resembles sheets of crumpled paper ([9]).

The oxidation of graphite was carried out as follows. Graphite (0.1 g) in a porcelain cup was covered with a mixture of concentrated acids: 3 ml (H_2SO_4) + 1 ml (HNO_3). Then, while stirring for 15–20 min, 1 g of finely ground and thoroughly dried ($KClO_3$) was added, and the mixture was kept for ($2^{1/2}$)-3 hours. The graphite was washed with water until a negative reaction for (Cl') and dried in a desiccator over (P_2O_5). When heated to 180–200°, the graphite was destroyed, forming a product externally resembling soot, which in the optical microscope appeared to consist of elongated worm-like particles with a cross-section of several microns.

The specimen was placed on a specimen-holder grid and examined in the electron microscope. One of the typical photographs is shown in Fig. 3. Here part of a worm-like particle is visible, evidently representing a not very strongly destroyed graphite crystal; in places, dark bands are noticeable (indicated by arrows), which can only be comparatively thick packets of unsplit basal planes of the graphite lattice. A higher degree of splitting of the graphite crystal is shown in Fig. 4. According to the literature, in this case, as a rule, rupture of the basal planes themselves does not occur, so that the cross-section of the formations observed in the photographs (several microns in size) must correspond to the width of the original graphite crystals (dimensions in the direction of the (a) and (b) axes). Thus, the picture observed in the photograph must be analogous to that which would be observed when rubbing

Fig. 1. Spheroidal inclusions of graphite, isolated from cast iron by electrolytic dissolution. Optical microscope. (110×)

Fig. 2. Stereoscopic photograph of a quartz replica from the surface of spheroidal graphite. (8200×)

Fig. 3

Fig. 4

Fig. 3. Product of chemical splitting of spheroidal graphite. (8200×)

Fig. 4. Product of chemical splitting of spheroidal graphite. A higher degree of splitting than in Fig. 3. (8200×)

a stack of weakly glued sheets of paper, when the force is applied in a direction perpendicular to the plane of the sheets. The apparent fibrousness of the structure observed in Fig. 4 is most likely explained by the formation of folds on the basal planes of the crystals deformed during splitting. When photographed in a transmitted electron beam, the presence of folds similar to those on crumpled tissue paper will create the impression of a fibrous structure.

Attention is drawn to the fact that the elongated formations in Figs. 3 and 4 correspond in cross section (several microns) to the round protrusions observed in the stereophotograph (see Fig. 2). It may be assumed that these protrusions are graphite crystals emerging onto the surface of the spherulite, and that the

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transverse dimensions of the protrusions correspond to the dimensions of the crystals in the directions of the (a) and (b) axes. This assumption agrees with ideas about the radial direction of growth of graphite crystals in the spherulite and with the data on the dimensions of these crystals presented in ({}^{6}).

Final conclusions about the structure of spheroidal graphite cannot be drawn on the basis of electron-microscopic photographs alone—here the use of various research methods is necessary. However, in our opinion, the data set forth above open up new possibilities for solving this problem. By applying oxidation of graphite of different intensity, it is possible to carry out successive splitting of its inclusions and, by observing this process with optical and electron microscopes, to obtain deeper information about their structure.

This method may also be applied to the study of the structure of other polycrystalline graphite bodies.

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