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MECHANISM OF FORMATION OF A CATHODE COATING IN A CARBON ARC

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The structure and properties of carbon materials formed in an arc between graphite electrodes in the case of decreased pressure of a buffer gas are considered. A mechanism of formation of a cathode coating by positively charged carbon macroparticles is proposed. The particles melt upon collision with the cathode surface and then the stage of growth of a coating from a liquid phase occurs.

After the development of the technology of production of fullerenes in a heterogeneous plasma by spraying of a graphite anode in an arc in an inert atmosphere, it became possible to actively study their properties and mechanism of formation [1]. Simultaneously it became easier to investigate carbon nanotubes and nanoparticles formed in a cathode coating [2, 3]. Great hardness of the coating is of interest for the synthesis of superhard materials [4, 5].

The physicomechanical properties of a cathode coating were studied in [3, 6]. Based on the results obtained, Grushko et al. made assumptions on the mechanism of formation of a cathode coating without account taken of the processes in a heterogeneous arc plasma that are determining ones in the formation of the coating. In [3], it is assumed that the particular features in the properties of the cathode coating are assigned by the conditions of its formation and the appearance of specific structures and microdistortions in it.

The abbreviated description of the experimental conditions along with the failure to cite all of the parameters of production of the coating samples limits the possibility of comparing the results of [3, 6] with other investigations.

In the present work, the kinetics of formation of a cathode coating is considered as a function of the discharge parameters and the observed structure of the coating is related to the processes in the plasma. The investigations were carried out for an arc discharge of direct current I = 80–100 A at a pressure of a buffer gas (helium) of P = 1–500 torr. Spectrally pure graphite rods with a 6-mm diameter, a discharge gap of L = 3–5 mm, and an arc voltage of U = 20–40 V were used as the electrodes. The destruction rate of the anode was R_a = 2–5 mg/sec. The discharge occurred in a steel water-cooled cylindrical chamber with a diameter of 110 mm and a volume of ~2 liters. Fullerene-containing soot (FCS) was deposited on the walls of the chamber; the amount of fullerenes in the soot, depending on the discharge regime, amounted to 1–15%. The structure of the cathode coating and its properties are considered for P = 100 torr.

The experiments [7, 8] performed earlier made it possible to obtain information on the space-time structure and the temperature fields of the generated heterogeneous plasma and the magnitude of anode erosion. For the indicated range of working regimes, from 30 to 50% of the mass of the anode sprayed in the arc is deposited on the cathode. The large share of carbon arriving at the cathode demonstrates that in this case we have the deposition of a particle flux that is not distributed uniformly in space but is directed from the anode to the cathode. One reason for the existence of this direction can be a gasdynamic force arising due

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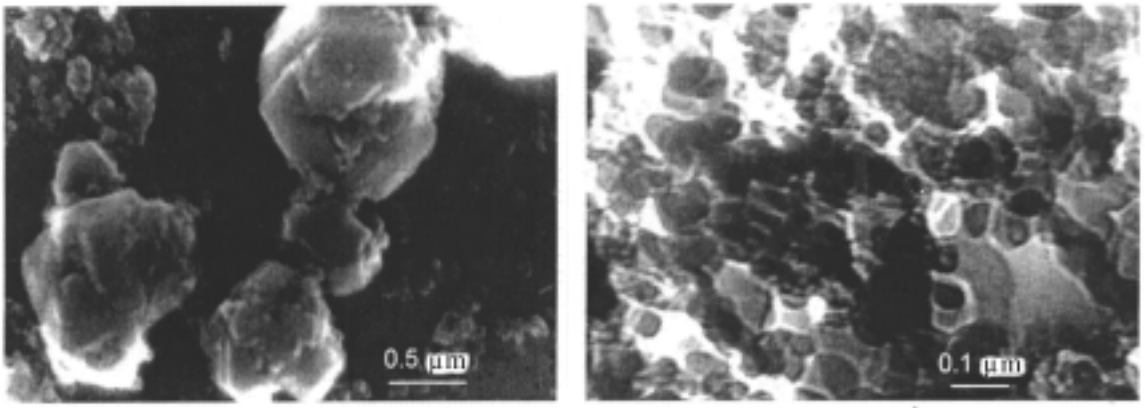

Fig. 1. Photographs of the sample of fullerene-containing soot obtained with a scanning microscope (a) and a transmission electron microscope (b).

to the rotation of a spiral arc [9]. However, it is likely that the influence of the electric field between the anode and the cathode that accelerates positively charged carbon micro and macroparticles toward the cathode is the most significant.

It follows for the data of [7, 8] that the time of the particles' stay in the region of high temperatures of the arc is practically the same in motion toward both the cathode and the wall of the chamber. Therefore, one can assume that the structure and size of the microparticles at the cathode surface and at the outlet of the arc plasma will be similar. The particles, as they move in the buffer gas toward the chamber walls, are at a temperature lower than that in the plasma and must not experience noticeable structural transformations at this stage. Therefore, the characteristics of the fullerene-containing soot deposited on the chamber wall will be close to the characteristics of the material participating in the production of the cathode coating.

The study of the properties of carbon soot for the regime discussed in the work was carried out by the methods of x-ray and electron diffractions and electron microscopy [5]. In the x-ray diffraction spectra of fullerene-containing soot, a broadened reflex appears at $2\theta = 26.6^{o}$, which corresponds to a graphite interplanar spacing of 3.36 Å. In the regions $2\theta = 5–6^{o}$ and $10–11^{o}$, one observes greatly broadened reflexes that demonstrate the presence of weakly ordered structures.

The electron-diffraction patterns that are taken for reflection from fullerene-containing soot samples prepared by deposition from an aqueous suspension indicate the presence of crystalline graphite in the soot. The electron-diffraction patterns obtained by transillumination (in transmitted light) reveal greatly diffused diffraction rings or halos characteristic of amorphous materials. Diffraction reflexes corresponding to the crystalline phase are not recorded. The absence of graphite reflexes in the electron-diffraction patterns obtained by transillumination indicates a significant (of the order of microns) size of these crystals.

Investigations by the method of electron microdiffraction make it possible to draw the conclusion of the presence of an insignificant amount of a non-graphite crystalline phase in the soot. The obtained pictures of microdiffraction are determined either by the presence of randomly distributed crystallites of a single phase in the sample or by the presence of different phases each of which corresponds to a certain set of point reflexes. Furthermore, crystallites of fullerite C_{60} are recorded.

The morphology of large particles of fullerene-containing soot has been studied with a scanning electron microscope (Fig. 1a). The maximum observed particle size is 4–10 μm; the particles have a pronounced laminar structure. There are also plane hexagonal particles ~1.5 μm in size and particles of a complex rounded shape which consist of smaller ones (0.2–0.4 μm in size). The size of the smaller particles was determined using a transmission electron microscope and was 0.02–0.05 μm (Fig. 1b).

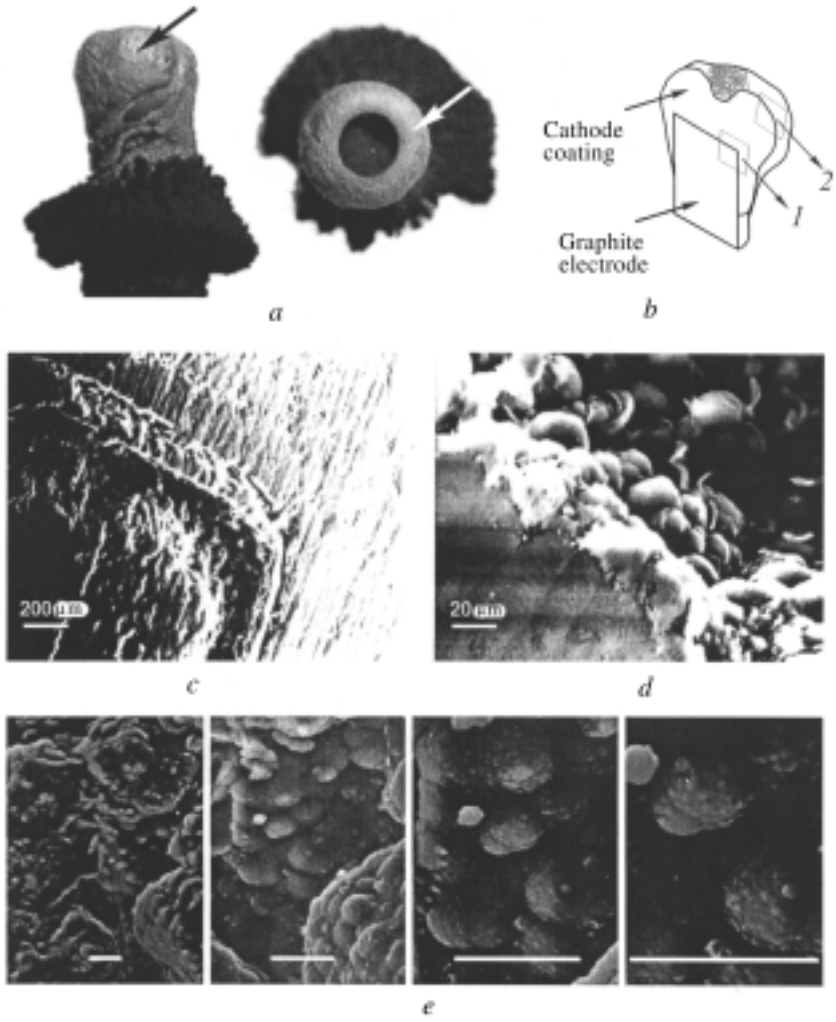

Fig. 2. Structure of a cathode coating after 10 min of operation of the arc for I = 80, L = 5 mm, and P = 100 torr: (a) external view of the cathode coating on a graphite rod 6 mm in diameter (side view and end view); (b) scheme of the microsection of the coating (figures 1 and 2 denote the portions that correspond to photographs (c) and (d); (c) transition layer between the coating and the graphite cathode; (d) microsection of the coating and its exterior surface; (e) exterior surface of the coating for different magnifications (the mark size is 20 μm) in the zone marked by the arrow in Fig. 2a.

Thus, from the results of the x-ray structural and electron-diffraction investigations and data obtained using the electron microscope it follows that fullerene-containing soot consists of carbon particles 0.02–0.05 μm in size, micron graphite particles, and crystallites of small size comparable with the size of soot particles and referred to fullerite C_{60}. Furthermore, the presence of other phases and clusters is not excluded.

The carbon macroparticles mentioned above and carbon ions, apparently, provide a basis for the formation of a cathode coating. In several seconds after firing the arc, a homogeneous thin layer is formed on the cathode. At the subsequent stages of the discharge, the coating is produced at the periphery of the end of the cathode and its lateral surface. It has a symmetric shape and is weakly related to the cathode. Then the coating acquires the shape of a cylinder with a diameter nearly equal to the anode diameter.

Figure 2a shows an external view of a coating formed on the cathode after 10 min of operation of the arc at a rate of destruction of the anode of ~3 mg/sec. The coating has two characteristic regions. The interior of the coating 2–5 mm in diameter with a loose structure consists of a mixture of nanoparticles, nanotubes, and amorphous carbon [2]. The hard exterior coating of gray metallic color is formed of needle-shaped and fan-shaped structures oriented predominantly in the direction of their growth. For certain regimes of the arc, a hollow crater 2–5 mm in diameter is observed in the axis region of the cathode coating.

Figure 2c shows a screen photograph of the microsection of a graphite cathode and a carbon coating. It is seen that the transition layer between the cathode and the coating has a column structure. Figure 2d shows a photograph of the microsection of the cathode coating and its exterior surface. The structure of the untreated exterior surface of the coating is shown in Fig. 2e.

The observed structure of the cathode coating can be determined by the following set of physico-chemical processes. The temperature of the plasma in the larger part of the arc exceeds 4000 K. The carbon crystallites arriving from the anode are heated approximately to the same temperature. The thermoemission of electrons from the surface of heated macroparticles determines their significant positive charge. Based on the data of [10], one can consider that the charge of a submicron carbon particle in the plasma of an electric arc may exceed 10^3 e. Under the action of the electric field (the average intensity of the field between the anode and the cathode is ~50 V/cm) highly heated crystallites and carbon ions move toward the cathode. The counterflow of the plasma from the cathode with high concentration of electrons significantly decreases the charge of macroparticles, especially in the axis zone of the discharge. As a result, in this zone the cathode surface can be reached mainly by atoms and neutral macroparticles with small velocities forming a loose interior of the coating, and the cross section of the flux of positively charged carbon particles acquires the shape of a ring symmetric to the cathode counterflow of the plasma. The estimates show that in the region that is insignificantly shifted from the cathode axis the velocity of positively charged macroparticles can exceed 1 km/sec in accordance with the realized values of the intensity of the electric field in the axis region.

At the initial stage of the discharge, a transition layer is formed from carbon crystallites on the surface of the cathode. Then the stage of quasi-epitaxial growth of the cathode coating begins. Carbon macroparticles, upon collision with the cathode, are additionally heated and melt as a result of transition of their kinetic energy to thermal energy. Figure 2e shows a thin layer of a melt in the zone of contact of the particles with the coating. The possibility of obtaining such a state of carbon was discussed in [11, 12].

In our opinion, the formation of a graphite melt on the cathode is demonstrated by helical lines on the exterior surface of the coating. They can appear due to the rotation of the melt layer under the action of either the magnetic field of the arc or a nonuniform electric field because of the movement of the cathode binding of a rotating spiral arc.

The cathode coating and the graphite rods used as the electrodes, as the x-ray structural investigations have shown, are identical in phase composition. The bar x-ray photograph (Fig. 3a) of the initial graphite electrode shows the presence of several weak unidentified reflexes. The degree of graphitization that characterizes the closeness of the crystal lattice of the sample to the lattice of graphite [13] is 0.87. The analysis of the texture maxima (peaks) according to the Harris method [14] has shown that it is plane (002) that is predominantly located in parallel to the direction of extrusion.

The intensities of practically all reflexes from the exterior untreated surface of the coating (Fig. 3b) and from the polished surface of its microsection (Fig. 3c) are much lower than those observed in the initial graphite. At the same time, one can note the redistribution of the intensity of reflexes (100) and (101). The profiles of diffraction lines (002) and (004) of the graphite and the coating are given in Fig. 3d. Just as in [3], the reflexes of the coating are shifted toward smaller angles and are greatly broadened. The increase in the interplanar spacing for the cathode coating in relation to the initial graphite amounts to 2–3%, which demonstrates the turbostratum structure of the material [15].

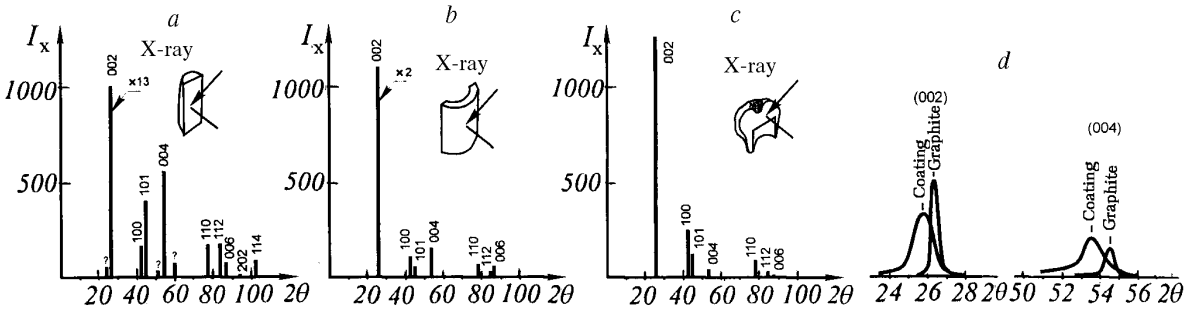

Fig. 3. Bar x-ray photographs of the initial graphite (a), the exterior surface of the cathode coating (b), and its microsection (c), and also profiles of diffraction lines (002) and (004) of the graphite and the coating (d). θ, °; I_x, rel. units.

The broadening of the diffraction lines was used to determine the values of intensities of the second kind (microintensities) — $8 \cdot 10^{-3}$ and the size of the regions of coherent scattering — 200 Å. The values of the microintensities coincide with the data given in [3], and the size of the regions of coherent scattering is approximately five times smaller. In [3] it is noted that whereas the microintensities are determined by the presence of dislocations, their density should be of the order of 10^{11}–10^{12} cm^{-2}. For our case the density of dislocations found from the size of the regions of coherent scattering turned out to be $\rho_1 = 8 \cdot 10^{11}$ cm^{-2}, and that calculated from the data on the size of the blocks given in [3] is $\rho_2 = 3 \cdot 10^{10}$ cm^{-2}. Such a difference can be related to the character of distribution of dislocations in the material. In [16] it is shown that if the values of the density of dislocations determined from the size of the regions of coherent scattering (ρ_1) and microstresses (ρ_2) coincide, the latter are distributed in a random manner in the sample and the large difference in ρ_1 and ρ_2, ρ_1 being less than ρ_2, is related to the formation of plane dislocation pileups.

The microhardness H of the characteristic zones of the microsection of the cathode coating does not exceed 8 GPa. However, there are zones where $H \sim 50$ GPa or where the hardness cannot be measured by ordinary methods of microhardness measurement. The small values $H \sim 0.4$ GPa correspond to the microhardness of the graphite. The increase in H in comparison with [3, 6] can be determined by the random distribution of dislocations over the volume of the coating that indicates its uniform growth. The high density of dislocations leads to a reduction in the length of their mean-free path, which improves the strength characteristics of the material.

The identity of the phase compositions of the material of the cathode coating and of the graphite rod was confirmed by electron-diffraction investigations. At the same time, the electron-diffraction patterns for the reflection from the exterior surface of the coating indicate the presence of a crystalline phase with high values of interplanar spacings characteristic of fullerite C_{60}. This is consistent with the results of [17], according to which bundles of 10^2–10^3 single-shell nanotubes can represent a quasicrystal made up of nanotubes whose lattice constant will be equal to the lattice constant of fullerite C_{60} [18].

The material of the cathode coating reveals diamagnetic properties with a magnetic susceptibility of $\chi \sim -5 \cdot 10^{-6}$ characteristic of the volume material of the initial graphite electrode. When ground to powder to a size of the order of 10 μm, graphite becomes a paramagnetic due to the appearance of a large number of broken bonds. The magnetic susceptibility of the material of the cathode coating, when it is ground, practically does not change. This seems to be due to the cathode-coating material containing elements with closed carbon particles linked to each other by a small number of chemical bonds.

A reliable comparison of the physicochemical properties of the cathode coating with the data of [3, 6], as has been noted above, is impossible because of the incomplete description by Grushko et al. of the parameters of the experiment. The results obtained in the present work refer to the regime that is most fre-

quently used in practice for the synthesis of fullerenes. The data of [3, 6], as we assume, refer to somewhat differing regimes, although it is possible to produce fullerenes for them, too. Moreover, in [6] the cathode coating is considered at the initial stage of formation. The similarity of the physicochemical properties of the cathode coating in the above works shows that the properties of the coating depend little on the specific regime of the discharge.

Based on the results of the present work and of the investigations carried out earlier, we can propose the following model of formation of a cathode coating in an arc discharge in the regime of fullerene formation:

(1) the strongly heated anode supplies micro- and macroparticles of carbon to the arc plasma: amorphous particles 0.02–0.05 mm in size, micron graphite particles, and crystallites of small size and different phases;

(2) carbon macroparticles in the arc plasma are heated to a high temperature and acquire a positive charge due to the thermal emission of electrons;

(3) carbon particles accelerated by the electric field of the arc melt upon collision with the cathode surface, and then we have the stage of coating growth from a liquid phase.

The results obtained in the work are of interest for creating new materials. The coating formed on the cathode in a carbon arc in helium at low pressure is a promising carbon material of high strength and hardness.

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NOTATION

I, current strength; U, voltage; P, pressure; L, length of the discharge gap; R_a, rate of destruction of the anode; θ, angle of scattering of x-rays; I_x, intensity of scattered x-ray radiation; ρ_1 and ρ_2, dislocation densities determined from the size of the regions of coherent scattering and microstresses respectively; H, microhardness; χ, magnetic susceptibility.

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