Morphological and structural features of materials formed in carbon plasma of arc discharge

A V Zaikovskii*, D V Smovzh, S Z Sakhapov and A V Fedoseev
Institute of Thermophysics SB RAS, Lavrentyev Ave. 1, Novosibirsk 630090, Russia

*E-mail: lexeyza@gmail.com

Abstract. The method of electric arc synthesis is used to obtain nanoparticles encapsulated in a carbon matrix. The properties of the entire material depend on the properties of the carbon matrix. In this paper, the structural characteristics of a carbon material synthesized at various arc discharge parameters are investigated. It is established that in the arc discharge a material containing amorphous and graphite-like carbon structures is synthesized, including in the form of graphene fragments folded into stacks, twisted into rolls and in the form of closed forms. Interplanar distances in graphite-like structures and interatomic distances in amorphous structures are determined. It is established that the pressure of the buffer gas determines the size of the soot globules and the volume fractions of graphite-like and amorphous structures, and the current strength affects the internal structure and determines the size of graphene planes in graphite-like structures.

1. Introduction
After the work of Kretchmer [1] of fullerene synthesis the electric arc method has been developed and widely used for obtaining nanoparticles of various compositions. In the basis of this direction, it is possible to highlight the basic groups of researchers under the leadership of such scientists as Majetich [2], Saito [3], Seraphin [4]. A huge contribution to the study of the electric arc method of synthesis was made by the group of Dyuzhev and Alekseyev [5]. Currently, this direction is actively developed by Keidar [6], Raitses [7] and Schneider [8]. Our scientific group, in particular, studying the synthesis of metallic [9], oxide [10] and carbide [11] nanoparticles, is not the last in this direction. The use of a composite content of sprayed electrodes, including graphite and metal, leads to the formation of a material consisting of metal-containing nanoparticles packed into a carbon matrix [12-14]. The carbon matrix stabilizes the resulting nanostructures, preventing nanoparticles from contacting, coagulating, increasing in size, and oxidizing in the air atmosphere. Nevertheless, a special interest is caused by the structure of the carbon matrix itself, which affects the general properties of the material being synthesized. The carbon structure formed in an arc discharge can take various forms depending on the discharge parameters. At certain parameters of the carbon arc, fullerenes are formed up to 15% of the total produced soot [15]. The presence of catalytic particles leads to the growth of carbon nanotubes [16]. At a certain composition of the discharge atmosphere, or in the presence of catalytic particles, the growth of the graphene structure is initiated [17, 18]. In this paper we present the study of the structure and properties of carbon materials obtained under ordinary arc-discharge conditions for the synthesis of metallic and other nanoparticles.
2. Experimental set-up
In this paper, we study the structure of a carbon material, obtained with different parameters of the arc discharge. The scheme of the electric arc reactor is shown in figure 1. The reactor consists of a sealed chamber (1) in which a movable cylindrical graphite cathode (2) and a rigidly fixed cylindrical anode (3) are coaxially located. The anode is a solid graphite rod. The motion of the cathode is carried out by means of a stepper motor (4). The electrodes are connected to a direct current source (5). The chamber of the reactor is pumped out and purged with helium, and then buffer gas (helium) is injected into it to a certain value. By touching the electrodes, an arc discharge is the same value by the cathode motion with help of the stepping motor (4). In the chamber volume, the atomized electrode components interact with the buffer gas and with each other, forming synthesis products that are deposited on the water-cooled screen (8). Evaporation of the anode material and heating of the buffer gas by the arc discharge lead to an increase in the pressure in the reactor chamber, which is controlled by means of a piezoresistive vacuum gauge (9) and an electromagnetic valve (10). The parameters of the material synthesis process are written to the computer via the microcontroller board (7). Variable discharge parameters are discharge current strength and buffer gas pressure in the reactor chamber. Two series

Figure 1. Scheme of the electric arc reactor.

Figure 2. (a) - SEM image of a layer of C12 material deposited on the walls of the reactor chamber, (b) - SEM image of a individual microagglomerate, (c) - TEM image of chains of carbon globules, (d) - TEM image of individual carbon soot globules in C12 material.
of experiments were carried out: at a constant current of 120 A and a variation in the pressure of the buffer gas, as a result of which the materials designated C3, C6, C12, C25, C50, C100 and C200 were synthesized with the numbers corresponding to buffer gas pressures in Torr and at constant pressure a buffer gas of 12 Torr and variations in arc current strength, which resulted in the synthesis of C60A, C80A, C100A, C120A, C140A, and C150A materials corresponding to the current 61, 79, 100, 123, 134, and 154 Amperes.

3. Results and discussions

The process of formation of the soot carbon structure occurring in an arc discharge is as follows: the graphite constituting the anode, due to high temperatures, is dispersed predominantly in the form of atomic components that enter the hot region of the arc and diffuse into the reactor chamber as a non-isothermal turbulent fan-shaped jet from the interelectrode gap. Turbulent mixing and different temperatures of the jet regions determine various parameters of interaction of carbon components and helium with each other. As a result of interactions, carbon molecules and clusters can form. These components can act as centers of growth of the carbon structure, or collide and unite with each other. In connection with a wide range of energies of interacting components, different carbon structures are formed. In the hotter regions of the jet, the formation of the most thermodynamically stable structure, graphite, consisting of sp2-hybridized carbon atoms, is preferable. In cold regions of the jet, the probability of formation of an amorphous carbon structure having random bonds between sp2-sp3-hybridized atoms is high.

A carbon layer is deposited on the screen for the collection of the synthesis products (figure 2a), which is a conglomerate of hairy agglomerates of micron sizes (figure 2b). Treatment of the material by ultrasound leads to the destruction of the microstructure of the agglomerate into individual chains of soot globules (figure 2c). In figure 2d shows an individual soot globule.

The histograms of the distribution of soot globules in size are lognormal and depend on the synthesis parameters (figure 3). At higher pressures of the buffer globules with a larger size are formed. Such a tendency is observed up to pressures of 100 Torr. Further increase in pressure does not lead to an increase in the size of the synthesized globules (figure 3a). The size of the formed globules weakly depends on the current and is approximately at the same level (figure 3b).

A detailed investigation of the materials showed that the internal structure consists of amorphous and graphitized fragments. Moreover, the graphitized structure can be present in the form of graphene stacks up to 20 pieces, or rolled up into rolls, up to 7 turns, or in the form of closed forms with sizes up to 2 nm (figure 4).

The analysis of the internal structure was carried out using high-resolution transmission electron microscopy images that allows to measure the distances between graphene sheets in graphite-like

![Figure 3](image-url). The histograms of the distribution of globules in size and the dependence of the average globule size on the pressure (a) and current (b).
structure. An example of a histogram of distribution of interplanar distances in C12 is shown in figure 5b. To analyze the amorphous structure from the TEM image, a radial distribution function is constructed

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F(r) = \int_0^{2\pi} \int_{\text{image}} B(x, y, 0, 0) \cdot B(x, y, r, \phi) \frac{dx\,dy\,d\phi}{r},
\]

where \( B \) is the brightness of the image at a particular point of the TEM image. \( x, y \) are the coordinates of the current point (for each point of image), and \( r \) and \( \phi \) are the distance and angle that determine the analyzed point of the image relative to the current point (figure 5a in the inset). For instance, for the image of C12-material the form of the function \( F(r) \) itself is shown in figure 5a. The position of the first maximum gives information on the coordination radius \( (d) \) of the amorphous structure.

Figure 6 shows the arithmetic mean of the parameters of the crystalline and amorphous structures in the synthesized materials, depending on the pressure and current. These parameters are weakly dependent on the synthesis conditions. The average distance between carbon atoms in the amorphous structure is in the range 0.55-0.6 nm. The interplanar spacing in graphite-like structures of synthesized materials is in the range 0.4-0.45 nm, characterizing a highly disordered defective structure.

Another approach to analyzing the structure of synthesized materials is to analyze their physical properties. Electro-resistive measurements, measurements of magnetic susceptibility, and studies of Raman spectroscopy, described in detail in [19], were performed. To identify the structural parameters of the materials under investigation, it is necessary to understand the factors that affect the electrical conductivity, the magnetic susceptibility, and the form of the Raman spectrum of carbon materials.

The synthesized materials consist of highly conductive graphite-like structures and poorly conducting amorphous formations. Also, amorphous carbon can form bonds with the surface of the graphite structure, thereby increasing the contact resistance (figure 7). According to the percolation theory, the electrical conductivity depends on the volume fraction of the well-conducting graphite-like structures in the material \( (\sigma \sim V_{g}/V_{all}) \).

Figure 4. Graphene fragments folded into stacks (a), rolled up into a roll (b), in the form of closed forms (c).

Figure 5. Radial distribution function for analysis of amorphous structure (a) and histogram of distribution of interplanar distances of graphite-like structures in C100A (b).
Virtually all carbon structures, ranging from individual carbon atoms to the graphite structure, have diamagnetic properties. Nevertheless, the edges of the graphite structure possessing the "ZIG-ZAG" shape (figure 7) have a high density of electronic states near the Fermi level, which leads to Pauli paramagnetism on such structures [20]. The overall value of the magnetic susceptibility of a material depends on two factors. The first factor is the fraction of atoms forming the "ZIG-ZAG" edge from the total number of atoms in the graphite structure, that is, it characterizes the size of the graphene planes ($\chi \sim 1/L_a$). The second factor depends on the volume fraction of graphite-like structures in the entire material, since the amorphous material also exhibits diamagnetism ($\chi \sim V_g/V_{all}$).

Raman spectroscopy analyzes molecular vibrations in a material. Raman spectra of synthesized carbon materials have D and G peaks. The D-peak corresponds to the respiratory mode $A_{1g}$ of the vibration symmetry and appears on the defects and boundaries of the graphite structure (figure 7), the G-peak corresponds to the vibrations of the C-C bond of sp2-hybridized atoms, which are also present in amorphous carbon [21]. Thus, the ratio of the intensities of the peaks in the Raman spectrum of D to G ($I_D/I_G$) depends on the number of edge atoms of the graphite-like structure ($I_D/I_G \sim 1/L_a$) and the volume fraction of graphite-like structures in materials ($I_D/I_G \sim V_g/V_{all}$).

As was shown earlier [19], the dependences $\sigma$, $\chi$ and $I_D/I_G$ on the buffer gas pressure correlate with each other, and since all these quantities are proportional to $V_g/V_{all}$. So the information of $V_g/V_{all}$ can be extracted from these dependencies. According to TEM studies, the composition of the C3 material is almost entirely composed of graphite-like structures. Assuming $V_g/V_{all} = 1$ for C3, the dependence $V_g/V_{all}(P)$ was established on the basis of the $\sigma(P)$ dependence (figure 8a).
Correlations of the $\sigma$, $\chi$ and $ID/IG$ dependences on the current are not observed, however, from the data obtained, information on the size of the graphene planes $La$ can be extracted. As was shown above, the electrical conductivity, the magnetic susceptibility, and the ratio of the intensities of the D to G peaks are proportional to the volume fraction of graphite-like structures in the total volume of materials. Nevertheless, only $\chi$ and $ID/IG$ depend on the size of $La$. Then, dividing these values by the value of $\sigma$, we obtain information about $1/La$, or $La \sim \sigma/\chi \sim \sigma/(ID/IG)$. Reliable data on the size of $La$ based on TEM studies were obtained for the C140A material, which contains graphene fragments with an average size of 65 nm. Based on this fact and the dependence $\sigma(I)/\chi(I)$, the dependence $La_{Hi}(I)$ was constructed, and the dependence $La_{ID/IG}(I)$ was constructed on the basis of the $\sigma(I)/(ID/IG)(I)$ dependence. These dependencies are presented in figure 8b.

4. Conclusion
The analysis of the structure of carbon materials obtained in an arc discharge at different synthesis parameters is carried out. It is established that the materials are a homogeneous coating on the screen for collecting the synthesis products. This coating consists of micro-agglomerates with a hairy structure. Microagglomerates consist of chains of soot globules of nanometer sizes. The soot globules consist of graphite-like and amorphous structures. The current strength practically does not affect the size of soot globules, and the use of higher pressures leads to an increase in the size of the globules. The pressure of the buffer gas also affects the volume fractions of graphite-like and amorphous structures in synthesized materials. The discharge current affects the internal structure of the material and determines the size of the graphene planes $La$ in graphite-like structures.

Acknowledgments
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Figure 8. Dependences of $Vg/Vall$ on the pressure of the buffer gas (a) and $La$ on the current (b).
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