Plasma of a vacuum-arc discharge for obtaining carbon-based coatings

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Abstract. Formation of the carbon films and coatings of different structural modifications can be efficiently achieved by sputtering graphite in a vacuum-arc plasma source. In this case the plasma flux is shaped in a form of a current-carrying jet with fairly distinct lateral borders. Spectral analysis shows that this plasma flux contains positively charged, excited and neutral carbon particles. In this paper is shown that for a technological cycle of deposition of a carbon-based coating it is possible to form a sublayer of the substrate material carbide, providing a possibility for the later growth of a well-formed coating.

1. Introduction
Carbon materials and coatings are used in various fields of science and technology. The unique ability of carbon is the possibility of receiving mixed electronic structures, along with the basic $sp^3$, $sp^2$ and $sp$-configurations. Obtaining of the carbon material by sputtering presents an ability of acquiring an infinite number of its condensed forms [1]. Technological methods and conditions of film deposition determine the physical properties of the received materials.

For obtaining materials consisting of carbon atoms the heat treatment of various carbonaceous substances in both the condensed and gas phases is necessary [2]. From the gas phase it is possible to receive soot, fullerenes, pyrocarbon (pyrographite) and diamonds. If soot and fullerenes are the result of processes occurring in the reaction volume, the pyrocarbon and diamonds are formed by deposition of carbon atoms on a solid substrate.

Among the materials built from carbon atoms a special place holds so-called active carbon. It can be represented as a structure made from the condensed carbon atoms, forming a certain pattern. Its distinction from the other known compounds is a different degree of intra- and interlayer disordering of atoms. In this structure, the carbon has a so-called pore space, the volume and pore size of which is determined by the size of the primary crystallites, the nature of their packing and their relative orientation.

2. Features of the coating deposition from a vacuum-arc discharge
Significant progress in the formation of carbon films and coatings of different structural modifications was achieved by sputtering graphite in a vacuum-arc plasma source [3, 4]. The nature of the particle deposition from a plasma flux generated by a vacuum-arc discharge depends on their energy, which
determines not only the adhesion of the formed coating to the substrate, but also the structure and composition of a film and the presence of defects.

When particles contact the surface, their interaction occurs, depending on the energy of the chemical bonds between the atoms in the treated surface, the surface electric fields arising due to the asymmetry of the crystal lattice on the surface, lattice constants and the substrate temperature [5].

If ions interacting with the surface have so high energy that completely free substrate atoms from the chemical bonds, the physical sputtering of the surface is observed. During ion implantation, the ions penetrate into the crystal lattice and remain in it [6]. Upon the surface impact deposited particles are relived from their energy and transferred to the adsorbed state. Further, the process of condensation on the substrate surface is determined by a sufficiently large diffusion mobility of the particles.

In the formation of the coating there are three types of adhesion: mechanical – due to the van der Waals forces; chemical – occurs with the formation of new phases at the interface, its strength is higher, the greater the chemical affinity between the coating and the substrate materials; diffuse – occurs when the substrate temperature is such that there are the processes of materials counter-diffusion.

The quality of the formed coating and the possibility of the textured coating growth are determined by the conditions of condensation, and for each pair condensate–substrate, at a given deposition rate, there is a temperature at which the growth of a crystal-oriented film is observed.

Thus, the process of the coating formation from the plasma of a vacuum-arc discharge includes two stages: heating of the machined part and modification of the structural and phase composition of the surface; condensation of the working substance from the plasma flux. The flow of each process is determined by the energy of deposited ions and the flux density to the machined part [7].

3. Results and discussion

As a coating material in this work was used carbon obtained by a thermal decomposition of a high-density graphite MPG-6 [8] in the plasma of a vacuum-arc discharge, existing in vapors of the eroded cathode. Spraying was carried out from the cathode spot region, which as a heat source on the cathode surface can be modeled in a form of a circle. As movement speed of the cathode spot on the graphite cathode is rather small, significant roles in the spraying process have the temperatures of the cathode and in the region of the cathode spot [9].

Sprayed particles form a directed plasma flux (figure 1) including three groups of particles: charged (ions and electrons that initiate chemical reactions in a working volume), excited and neutral (initial substances, atoms, radicals, intermediate products of the reactions).

![Figure 1. Cathode spot on the working surface of a graphite cathode.](image1.jpg)

![Figure 2. Current-carrying plasma jet providing the shorting of an arc discharge in vacuum.](image2.jpg)

The role of the plasma electron component in the initiation of the reactions is crucial. Distinctive feature of sputtering a graphite cathode in vacuum (10^-3 Pa and below) is that the plasma flux providing shorting of the arc discharge from the cathode to the anode is in a form of a current-carrying
jet with fairly distinct lateral borders (figure 2). The jet in each time point is arbitrarily shorted to the walls of a vacuum chamber, acting as the anode. It is assumed that the kinetic pressure of the plasma \( p = n_e T_e + n_i T_i \) at the flux boundary is balanced by a transverse compression of the cathode plasma jet by an intrinsic magnetic field.

When graphite is sputtered by a cathode spot of a vacuum-arc discharge (\( p = 7.8 \cdot 10^{-3} \) Pa, \( I_{arc} = 80 \) A), in the plasma flux are recorded positively charged (CII, CIII), excited (C*) and neutral (C) carbon particles, as well as molecules having a linear structure, the carbon material conglomerates and the composite particles resulting from the connection of several particles (figure 3).

![Figure 3. Decoding of the plasma flux spectrogram when spraying: (a) – graphite cathode (MPG-6); (b) – graphite cathode with the addition of argon; (c) – graphite cathode with the addition of benzene vapor.](image-url)

Plasma flow was studied using optical spectrometer, developed on the basis of a modified one-dimensional CCD array TCD1304 in Saint Petersburg Electrotechnical University “LETI”. Control of the analyzer is carried out on the emission spectrum of a mercury-quartz low pressure lamp. Spectrometer allows determining the composition of the generated plasma flux in the wavelength range from 220 to 950 nm with optical resolution of 1.5 nm.

Introduction to a working volume of argon (Ar – first ionization potential \( U_{i1} = 15.75 \) V, molecular weight 39.97 g/mol) or helium (He – first ionization potential \( U_{i1} = 24.47 \) V, molecular weight 4 g/mol) increases degree of ionization in the plasma flux, thus in the emission spectrum are observed intense lines in the long wavelength region, for example, CIII – 850.0 nm. Also on the spectrograms
are observed the lines of Balmer series of atomic hydrogen ($H_\alpha$ and $H_\beta$), as well as the emission spectra of $C_2$ (Swan band) and CH (Gere band) molecules.

If carbon conglomerates have a straight trajectory and move with the thermal velocity, the charged particles due to the presence of an external magnetic field are derived from the arc and, while having complex trajectories, move along the field lines.

Modification of the substrate material surface (in this case molybdenum substrate is used) is achieved through the alignment of the following physical processes: sputtering of a graphite cathode by a cathode spot of a vacuum-arc discharge, formation, transportation and extraction of the charged component of the plasma flux, acceleration (bias voltage set at the sample is varied from $-100$ to $-1000$ V) and deposition of the positive carbon ions on the refractory base (substrate temperature range – from 300 to 900 K).

When the equilibrium condition between the receiving of the charged carbon particles ($dn_C/dt$) on the treated surface and the process of material transfer into the depth of the substrate ($dn_{\text{dif}}/dt$) is met, for the multicomponent systems the advantageous is not the coexistence of elements, but the coexistence of the chemical compounds [10]. In this case, simultaneously with the saturation of the surface layer with carbon (diameters of carbon and molybdenum atoms are respectively 0.15 and 0.28 nm) on the substrate takes place the reaction of the formation of a surface carbide compound: $\text{Mo}_{\text{sub}} + 2\text{C} \rightarrow \text{Mo}_{\text{sub}}\text{C} + \text{C}.$

The solubility of carbon in molybdenum in the temperature range 300...1070 K is determined approximately as 0.3 % by weight and at temperatures above 1770 K dramatically increases. Therefore, further penetration of carbon into the surface region is accompanied by the formation in it of a bulk molybdenum carbide ($\text{Mo}_2\text{C}$) having a lattice of a hexagonal structure B$h$. In all X-ray diffraction patterns peaks of the base – molybdenum and the lines of a well-formed $\text{Mo}_2\text{C}$ with preferential orientations (101), (100) and (002), as well as (102), (110) and (103) are observed. From the achieved lines of $\text{Mo}_2\text{C}$ may be marked the lines of maximum intensity: (102) – 2.4595 (ASTM – 2.442) and (103) – 2.2794 (ASTM – 2.292) (figure 4).

![Figure 4. X-ray diffraction pattern of molybdenum carbide ($\text{Mo}_2\text{C}$) on a molybdenum substrate ($\text{CuK}_{\alpha}$ radiation).](image)

![Figure 5. Carbon coating on a molybdenum substrate (a) with the emerging system of crystallites (b).](image)
Thickness of formed carbide is determined by the substrate temperature and the energy of the deposited particles. For the studied samples the layer thickness is 2...3 µm. The increase in the processing time or amplification of the flux of charged carbon particles (\(dn_C/dt > dn_{dif}/dt\)) leads to a formation on the surface of the carbon coating (figures 5, 6), the structure of which is determined by the growth and the mutual orientation of the primary crystallites, the nature and degree of intra- and interlayer ordering of atoms. In turn, the size of the crystallites (figure 5(b)) is determined by the number of initial nuclei, which is greater, the higher is the temperature. In this case, the higher is the temperature the smaller is the size of the crystallites.

**Figure 6.** Distribution of the elements across the thickness (results are obtained using X-ray energy dispersive microanalysis system QUANTAX, defining all the elements, starting from Be (4) and allowing to obtain information on the elemental composition with a spatial resolution of 1 µm).

### 4. Conclusion

Thus, it is shown that stimulation of the growth processes and the ability to control the structure of the various carbon phases is achieved by using ions of plasma flux of a vacuum-arc discharge generated during sputtering of a graphite cathode. In one technological cycle of deposition of a coating based on carbon, it is possible to form sequentially: a sublayer of the carbide substrate material (\(\text{Me}_2\text{C}–\text{MeC}\)) for the future growth of a well-formed coating (figure 5). The presence of the intermediate layer with the agreed properties of the substrate–coating reduces tension and increases the adhesion strength (figure 5).

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