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Effect of carbon cathode plasma parameters on the structure and properties of deposited coatings

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Abstract. The results of studying the structure and mechanical properties of the coatings deposited with the use of a pulsed carbon cathode-arc plasma in vacuum are presented. An original technique for evaporating a graphite cathode under the influence of a pulsed discharge with a variable structure (shape, amplitude, and pulse duration) has been developed. The generation parameters of pulsed cathode plasma have been determined, at which carbon diamond-like coatings with higher mechanical properties are formed.
Keywords: amorphous carbon coatings, pulse shape, cathode-arc evaporation, hardness, wear resistance.

1. Introduction

The interest in carbon (a-C) coatings is due to their unique optical, electrical and tribological properties [1, 2]. Pulse cathode arc evaporation of graphite is known to be the most promising method for the formation of a-C coatings, which makes it possible to obtain coatings with a high content of carbon atoms in the state of sp^3-bond hybridization and characterized by high mechanical and tribological properties [6]. The growth kinetics and phase composition of a-C coatings deposited from a pulsed cathode plasma are largely determined by the energy and the incidence angle of ions, the ion current density, the duration and frequency of the pulses, and the substrate temperature [3, 4]. It has been established that a decrease in the substrate temperature is highly desirable to reduce the number of C–H and C–O bonds in the coating, which are formed due to interaction with residual hydrogen and oxygen in the volume of the vacuum chamber and reduce the operational properties of the coatings [5].

Our previous studies have shown that for a given energy of carbon ions, the highest coating properties are achieved when pulsed flows of carbon plasma are generated by a discharge with an optimal frequency [1, 6, 7]. Note that the pulse shape, the electron energy distribution within the pulse determine the thermal effect on the target, the plasma generation kinetics, and the composition of the resulting volatile products. As a consequence, there are changes in the conditions and modes of interaction of carbon plasma flows with the substrate surface and, accordingly, in the structure and properties of the deposited coatings. It is possible to expect that the use of a given pulse structure will make it possible to realize the evaporation mode that ensures the generation of carbon ions with the specified energy and cluster composition, and, hence, to form coatings with high performance properties.

This paper aims at determining the effect of the energy and time parameters of the pulsed discharge, which is used to create carbon plasma flows, on the phase composition, morphology, and mechanical properties of the resulting coatings in order to establish its optimal structural characteristics.

2. Experimental

The method of forming carbon (a-C) coatings from the plasma of a pulsed cathode-arc discharge has been implemented on a number of commercially available vacuum installations and consists in evaporation of a graphite cathode by a high-current arc pulse discharge [6], which generates a flow with almost constant ion energy (Fig.1b). This research deals with a modified UVNIPA-1-001 vacuum deposition installation (Fig.1) to obtain a-C coatings. The installation used a power supply unit for a carbon plasma generator, which allows forming discharge pulses with different energy distribution within one pulse. A schematic representation of the oscilloscope records of the discharge pulse current is shown in Fig.1b, 1c and 1d.

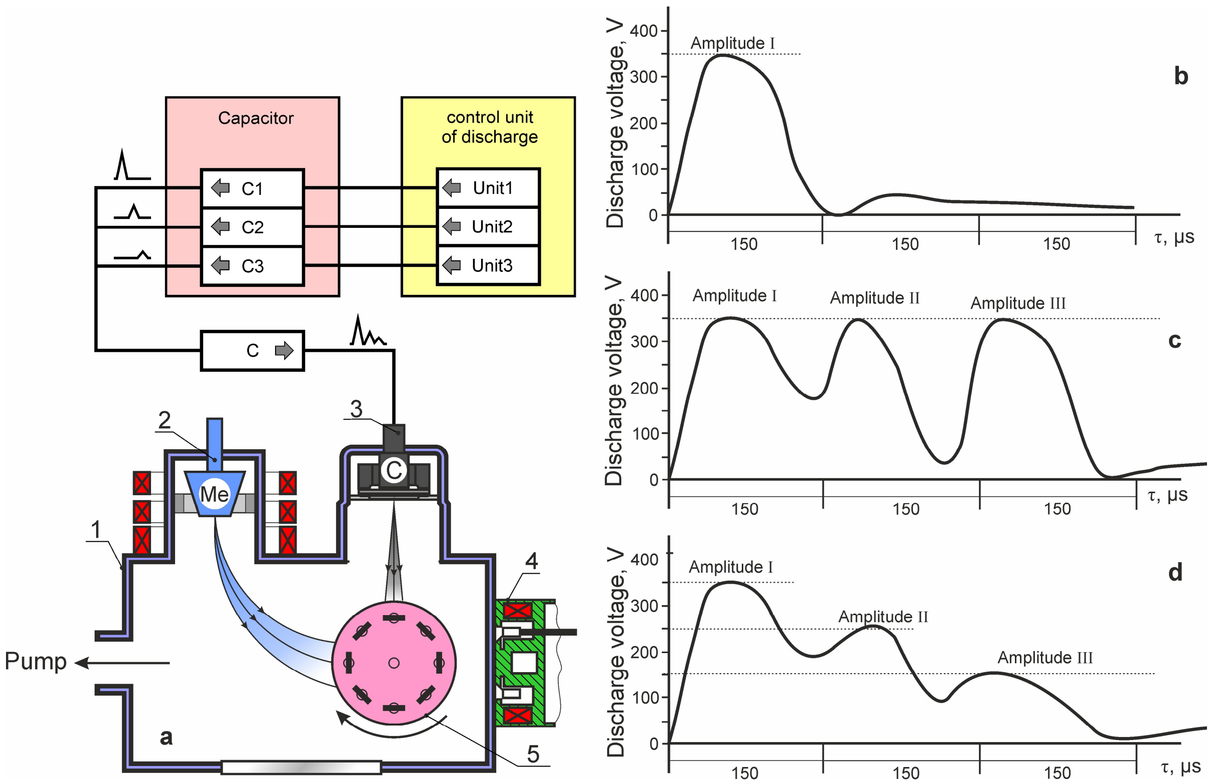

Fig.1. Scheme of a-C coating deposition (a), oscilloscope record of cathode-arc discharge voltage single-pulse (b), oscilloscope record of discharge voltage pulse with different component ratio (c, d).

Table 1 shows the discharge parameters and their corresponding deposition rates of the a-C coating. The pulse repetition rate was 5 Hz.

Table 1. Formation modes of carbon coatings

Sample		**Discharge voltage by pulse components, V**			**Discharge energy *E*, J**	**Growth rate *V*, × 10^{-5} μm/imp**	**Evaporation efficiency, *V/T*, × 10^{-5} μm/J**
		I	**II**	**III**			
a-C_I	Carbon coating	350	0	0	294	3.2	0.0108
a-C_{II}		350	350	350	882	8.6	0.0097
a-C_{III}		350	250	150	498	6.4	0.0128

Changing the voltage amplitude of pulse components I, II, and III while keeping the discharge duration constant makes it possible to control the average discharge current, which changes the condensate deposition rate, the energy of carbon ions, as well as the thermal load on the substrate and the growing coating properties [1].

Polished silicon monocrystal wafers (100) were used as substrates. Before sputtering, the wafers were cleaned in an ultrasonic bath in acetone and then in alcohol. The substrates were placed in the vacuum chamber, which was evacuated to a residual pressure of 10^{-3} Pa. Then, argon was injected into the chamber to a pressure of $3 \cdot 10^{-2}$ Pa. After that, the cleaning was performed using an ion source for 15 minutes.

The coating thickness was determined by the step size using a profilograph-profilometer (Syrtronic 25 (Taylor Hobson, UK)). The measurements showed that the coating thickness was 180±10 nm.

The coating microstructure was studied by Raman spectroscopy (Senterra, Bruker). The Raman spectrum was excited by laser radiation with a power of 20 mW and a wavelength of 532 nm from the area of 1 μm in diameter. The resulting spectra were mathematically processed using a Gaussian function.

The coating surface morphology was evaluated by atomic force microscopy (Solver Pro, NT-MDT) in the semi-contact mode: the scanning field size was 40×40 μm, the scanning speed was 1.0 μm/s.

Microhardness testers DM-8 (Knoop) were used to measure microhardness in the studies. The load on the diamond pyramid was 25 mN.

For tribological tests, a sphere-plane friction pair was used. The counterbody diameter was 5 mm, which provided a Hertz contact pressure of 478 MPa. After conducting tribotechnical tests, the volume wear coefficient of the counterbody j ($m^3/(N \cdot m)$) was calculated.

The internal stress (σ, GPa) in the coatings was determined from the change in the curvature radius of the silicon substrate before and after coating deposition, and the internal stresses were calculated in accordance with the Stoney formula [1, 6].

3. Result and discussion

The determination of the coating thickness showed that increasing the pulse discharge duration allows increasing the coating deposition rate. However, the evaporation efficiency, defined as the ratio of deposition rate to pulse energy, depends on the pulse shape. When using a pulse discharge with the energy decreasing during its combustion, the evaporation efficiency increases by 32%. Apparently, more equilibrium conditions of evaporation are realized in this mode, which can affect the composition and energy of the generated carbon plasma flows and the coating phase composition. Changes in the ratio of sp^3 and sp^2 hybridized carbon atoms were evaluated based on the analysis of Raman spectra of the deposited carbon coatings (Fig.2). The spectrum represents a broad peak with a maximum localized in the region of 1600 cm^{-1}. At the same time, there is a peak symmetry violation and manifestation of a low-intensity arm in the spectral region from 1200 to 1400 cm^{-1}. According to the data given in [1–3], the shape of the resulting spectra corresponds to the Raman spectra for amorphous carbon coatings with high content of carbon atoms with sp^3-hybridized bonds. Comparing the spectra, one can notice a slight difference both in the shape of the spectrum envelope and in their intensities.

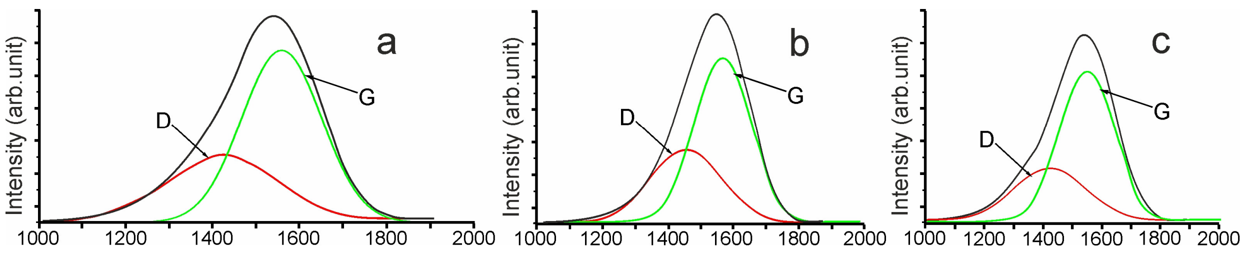

Fig.2. Raman spectra of the a-C coatings: a – single-pulse with an amplitude of 350 V; b – composite pulse with amplitudes of 350 V, 350 V, 350 V; c – composite pulse with amplitudes of 350 V, 250 V, 150 V.

The spectra can be represented by the sum of two Gaussian functions centered at 1565 cm^{-1} (peak G) and at 1380 cm^{-1} (peak D). Both peaks are determined by vibrations of sp^2 bonded carbon atoms.

In Raman spectroscopy, the structural features of carbon materials are related to such Raman spectral parameters as the position of G and D peaks, the full width at half maximum (FWHM) of the G peak, and the I_D/I_G ratio of peak intensities. Therefore, these parameters are widely used to determine the degree of disorder in carbon materials. Table 2 presents the results of mathematical processing of the Raman spectra.

Table 2. Raman spectra parameters and AFM results

Carbon coating	**G peak position, cm^{-1}**	**FWHM(G), cm^{-1}**	**I_D/I_G ratio**	**Roughness *Ra*, nm**	**D_{grain}, nm**
a-C_I	1553.1	213	0.6	6.9	131.1
a-C_{II}	1557.6	217	0.7	6.4	211.6
a-C_{III}	1565.6	221	0.4	3.9	70.0

FWHM(G) is a key parameter for observing structural disorder in carbon materials, which occurs due to bond angle and bond length distortions. An increase in FWHM(G) indicates an increase in structural disorder determined by a higher bond length and a higher bond angle in the material. An increase in the degree of disorder, according to high values of the FWHM(G) parameter, is associated with an increase in the content of atoms with sp^3-bond hybridization. The analysis of the Raman spectra parameters leads to a conclusion that an increase in the pulse energy, as well as its distribution, presented in Fig.1d, causes an increase in the number of carbon atoms in the state with sp^3-hybridized bonds, while there is an increase in the Csp^2 cluster size [1].

The results of studying the surface of carbon coatings formed with various shapes of the combined pulse of the cathode-arc discharge are shown in Fig.3.

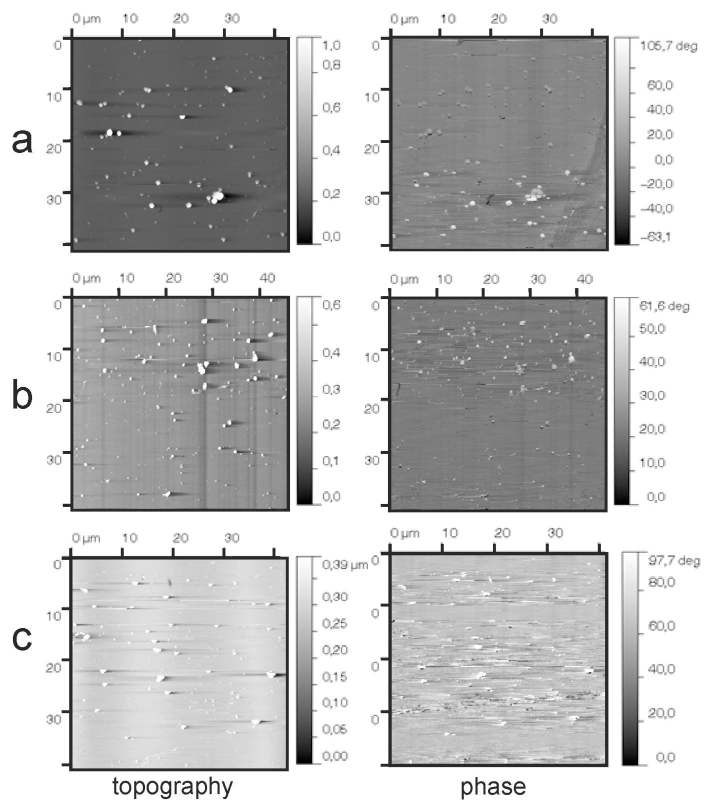

Fig.3. AFM image of the surface of a-C coatings: a – a-C_I, b – a-C_{II}, c – a-C_{III}.

It is clear that particles are observed on the coating surface regardless of the discharge pulse structure. The occurrence of the particles on the coating surface is typical for arc methods of coating formation. Typically, such particles are fragments of a graphite cathode. It should be mentioned that the number of such particles slightly decreases, and the formation of a surface with a lower roughness and grain size occurs when using a complex pulse (Table 2). The coating surface morphology is formed due to the contact with the graphite microdroplets and fragments from the plasma flow. The ratio between these phases (ionic and droplet) depends on the evaporation thermal mode, as well as on the condensation conditions and, chiefly, on the energy distribution in the pulse.

The microhardness (Table 3) of the coatings depends on the ratio of Csp^2/Csp^3 phases in the coating, and is in line with the results of determining the phase composition.

Carbon coatings are characterized by the presence of significant internal mechanical stresses [7], the magnitude and nature of which affect the performance properties of the thin-film system (Table 3).

Table 3. Mechanical properties of a-C coatings

Carbon coating	***Hv*, GPa**	**σ, GPa**	***f***	***j*, ×10^{-15} m^3/(N·m)**
a-C_I	13.8	0.98	0.18	189
a-C_{II}	14.5	1.54	0.15	262
a-C_{III}	15.9	1.1	0.12	147

The occurrence of high σ for the a-C_{II} coating is explained by two reasons: the difference in the thermal expansion coefficients of the deposited coating and the substrate, as well as the high temperature of the substrate during coating deposition. In our case, the a-C_{II} coatings were deposited in a high-energy evaporation mode, which led to an increase in the substrate temperature and, hence, an increase in the level of internal stresses due to a significant increase in the internal stress component caused by thermal processes [8].

The conducted tribological tests showed high wear resistance of the deposited coatings and the counterbody, as well as low values of the friction coefficient for the friction pairs under study. It has been shown that the friction kinetics is influenced by differences in surface morphology and hardness, which depend on the time and energy parameters of the pulse, as well as the distribution of energy in the pulse.

4. Conclusion

The effect of the energy and time parameters of the pulsed discharge, which is used to create carbon plasma flows, on the phase composition, morphology, and mechanical properties of the resulting coatings has been determined. The use of pulses with energy parameters changing during combustion has been shown to be an effective method for controlling the deposition rate of carbon layers, their morphology, and mechanical properties. It has been found that the highest evaporation efficiency, an increase in the content of sp^3-hybridized atoms and, accordingly, the coating hardness, a decrease in the friction coefficient and the wear rate of the counterbody, internal stresses and roughness are achieved when using pulses with a lower energy on the falling edge.

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5. References

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