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Investigation of the Structure and Functional Properties of Diamond-Like Coatings Obtained by Physical Vapor Deposition

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Abstract—Diamond-like coatings with a total thickness of ~0.6 μm are obtained by physical vapor deposition with plasma separation and a pulsed carbon arc source with a cooled cathode and laser arc ignition; the substrates are titanium alloy (VT4), stainless steel (12Cr18N10T), and copper (M1). Scanning electron microscopy and profilometry are used to study the coatings surface and structure. The composition of the coatings and the fraction of sp^3 bonds are studied using Raman spectroscopy. A wide peak in the 1580 cm^{-1} region is observed characteristic of diamond-like coatings. The coatings have a dense, nonporous structure. The tribological properties of the coatings are evaluated by the ball-on-disk method using a friction pair with WC and technical diamond. The strength characteristics are determined using linear scratch testing and nanoindentation measurements. The strength characteristics of the coatings vary and depend on the substrate materials. The friction coefficient of a diamond-like coating on VT4 alloy is ~0.1 in a friction pair with WC and ~0.01 with technical diamond.

Keywords: antifriction coating, diamond-like coating, physical vapor deposition, surface structure, scanning electron microscopy, tribological tests, friction coefficient, Raman spectroscopy, nanoindentation

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INTRODUCTION

An important problem of rocket and space technology is ensuring the stability of operation and increasing the service life of friction units of spacecraft, for example, in devices used to open solar panels [1]. One of the methods for solving this problem is the application of antifriction coatings characterized by a low friction coefficient. At present, solid lubricant films based on MoS_2 and Teflon, as well as their combination with WC, are most widely used [2–5]. Diamond-like coatings are promising as antifriction coatings for friction units. They have a high hardness and abrasion resistance, low friction coefficient, and chemical inertness, and they are environmentally friendly [6–11]. Diamond-like coatings consist of carbon or its compounds with diamond and graphite-like bonds and are suitable for machines and mechanisms operating under conditions of high loading and wear, and moving, rotating parts and assemblies, and ball bearings. Vacuum methods for obtaining diamond-like coatings can be conditionally divided into thermal evaporation and plasma-chemical vapor deposition. Thermal methods are those in which the thermal effect plays the main role. Plasma-chemical methods are based on the generation of a gas phase and its activation and ionization in electrical discharges of vari-

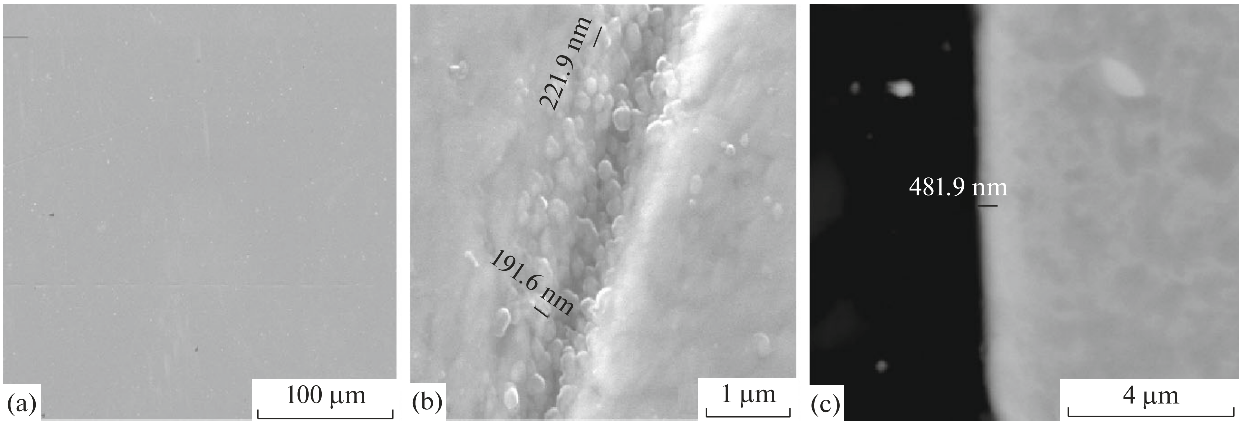

Fig. 1. SEM images of the surface structure of the diamond-like coatings: (a) general morphology of the surface, (b) structure of the coating in the region of a polishing defect on the substrate, and (c) structure on the cross section of the diamond-like coating on a titanium alloy substrate.

ous types. They are often used, and they yield coatings with the best physical and mechanical properties. The friction coefficient of diamond-like coatings depends on the deposition method, the content of sp^3 bonds, hydrogenation, roughness, coating thickness, and experimental conditions such as humidity, pressure, load, friction pair, and measurement circuit. For example, in the tests of a diamond-like coating formed by combining the methods of magnetron sputtering and Plasma-enhanced chemical vapor deposition, friction coefficients were obtained in a pair with a coating by the "pin-on-disk" scheme of ~0.01 in vacuum and ~0.1 at a humidity of 40–60% [2]. However, in [7], for coatings created by plasma-enhanced chemical vapor deposition, friction coefficients of 0.02–0.06 in vacuum and 0.1–0.3 at a humidity of 50% were obtained using the same measurement circuit. In a friction pair with steel, according to the ball-on-disk method, the friction coefficients are ~0.1 in dry air and ~0.12 at 50% humidity [9]. The dependence of the friction coefficient on the thickness of diamond-like coatings is also observed: the friction coefficient increases from 0.1 to 0.2 in a friction pair with chromium with an increase in thickness from 0.3 to 0.8 μm [11].

In [8, 10], the friction coefficients of these coatings were studied in friction pairs with sapphire and silicon carbide; their lowest values being ~0.07 and ~0.08. However, there are practically no publications devoted to studying the structure and tribological properties of diamond-like coatings on a substrate material.

The goals of this work are the formation and investigation of the structure and the mechanical and tribological properties of diamond-like coatings obtained by vacuum plasma spraying onto certain materials that can be used to fabricate dry friction units in rocket and space technology.

EXPERIMENTAL

Diamond-like coatings ~0.4 μm in thickness were obtained using a vacuum plasma setup (NPT, Russia) equipped with a plasma separation system and a carbon pulsed electric arc source with a cooled cathode and laser arc ignition. The coatings were deposited onto polished substrates of titanium alloy VT4, steel 12Cr18N10T, and copper M1. The operating temperature was 150°C. Prior to deposition, the surface was cleaned with Ar ions for 30 min. Then, an intermediate layer of titanium with a thickness of ~0.1 μm was formed, and the sample was cooled to a temperature of 24°C. The intermediate layer is necessary to increase adhesion and to decrease thermal stress in the coating–substrate system. Diamond-like coatings were deposited for 60 min at a laser-pulse frequency of 20 Hz and a power of 33 mJ. PGM8 graphite cathodes were used for deposition. The process was carried out at an operating pressure of 1×10^{-4} to 1×10^{-5} mbar and a temperature of 150°C.

The surface structure of the coatings was examined using an FEI Quanta 600 FEG scanning electron microscope (SEM). The surface roughness was determined by a profilometer of model 130 in accordance with *GOST* (State Standard) *19300–II*. The composition of the coatings and the fraction of sp^3 bonds were studied using a Horiba Jobin Yvon T64000 Raman spectrometer. The tribological properties of the coatings were investigated at a load of 1 N in the ball-on-disk geometry using a TRB-S-CE0000 CSM tribometer in a friction pair with WC and in the ball-on-plane geometry with reciprocating motion in a friction pair with technical diamond. The critical load was estimated by means of a linear scratch test with a diamond indentor under progressive load using a scratch tester with micromodules (MST) and nanomodules (NST) on the basis of an OPX open platform (CSM Instruments); the nanohardness was determined using an NHT2-TTX nanohardness tester.

RESULTS AND DISCUSSION

The surface relief of the coatings on the metal substrates of VT4, 12Cr18N10T, and M1 is rather uniform (Fig. 1a). In the regions of polishing imperfections of the substrates, a globular structure of the coatings is observed with a size of globules of 0.1–0.3 μm (Fig. 1b). It can be assumed that such a structure appeared because of a limited admission of deposited material in the crack region, and a thinner film was formed here. The total thickness of the diamond-like coating and the intermediate layer is ~0.6 μm (Fig. 1c). The coating is characterized by a dense, nonporous structure. The intermediate layer–substrate boundary is fairly homogeneous, without cracks or delamination, which suggests a high adhesion strength of the coating.

The following surface-roughness parameters were obtained for the coatings: R_a = 0.015 μm and R_z = 0.168 μm. Calculations were carried out using five tracks with a length of 12.5 mm. The profile measurement rate was 0.5 mm/s.

Analysis of the Raman spectrum of the coatings under study and comparison with the Raman & IR Research Lab database showed coincidence with the spectrum of a diamond-like coating (Fig. 2). The spectrum has a wide line in the region of 1580 cm^{-1}, which includes several bands, namely, the *D* and *G* peaks of graphite. The *D* peak is very wide and can consist of several peaks, including the diamond line. Similar results were obtained for coatings on other substrates.

A number of studies have shown that the intensity ratio of the *D* and *G* peaks is related to the fraction of carbon atoms in the sp^2 and sp^3 hybridization states [6, 10–12]. To calculate this ratio, the spectrum was decomposed into two Gaussian curves. The estimation results of the I_D/I_G ratio are given in Table 1. It is seen that the I_D/I_G ratio and, therefore, the fraction of carbon atoms with sp^2 and sp^3 bonds in the coating, do not depend on the type of substrate. At $I_D/I_G \approx 0.4$, according to [6], the fraction of carbon atoms in the sp^3 hybridization state ranges from 0.45 to 0.6.

Figure 3 shows the characteristic diagrams of the application–removal of nanoindentation load for the diamond-like coatings. The hardness of indentation and the modulus of elasticity of the coating for 12Cr18N10T steel at a maximum load of 1 mN are ~30 and ~360 GPa; for titanium, they are ~26 and ~239 GPa; and for copper, they are much lower, ~11.6 and ~151 GPa (Table 2). The Poisson's ratio ν_s is assumed to be 0.17. Despite the fact that the thickness and structure of coatings on different substrates is identical and the depth of indentation does not exceed 20% of the thickness of the coatings, the substrate material greatly affects the hardness. For a softer material, deeper penetration of the indenter into the coating was observed, which is associated with plastic deformation of the substrate material. Possible ways to lower this effect are the application of a thicker and harder intermediate layer or an increase in the thickness of the diamond-like coating itself.

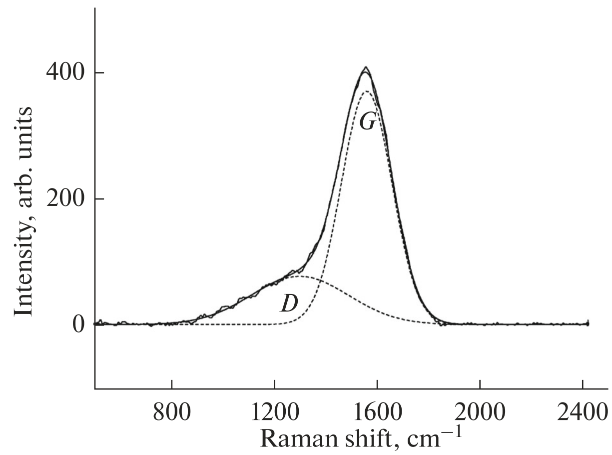

Fig. 2. Raman spectrum of the coating on a copper substrate.

The critical load of coating failure was determined by means of linear scratch testing using a diamond indenter with a curvature radius of 2 μm at a load of 2 to 102 mN at a loading rate of 100 mN/min. The scratch length was 0.4 mm. The dependences of the friction coefficient μ, the penetration depth R_d, and the friction force F_t on the indenter load along the

Table 1. Estimation of the fraction of carbon atoms in the sp^2- and sp^3-hybridization states in the coatings

Substrate	Peak position, cm^{-1}		I_D	I_G	I_D/I_G
	D peak	*G* peak			
12Cr18N10T	1312	1566	47322	109158	0.43
VT4	1305	1565	43402	105444	0.41
M1	1307	1567	36099	91069	0.40

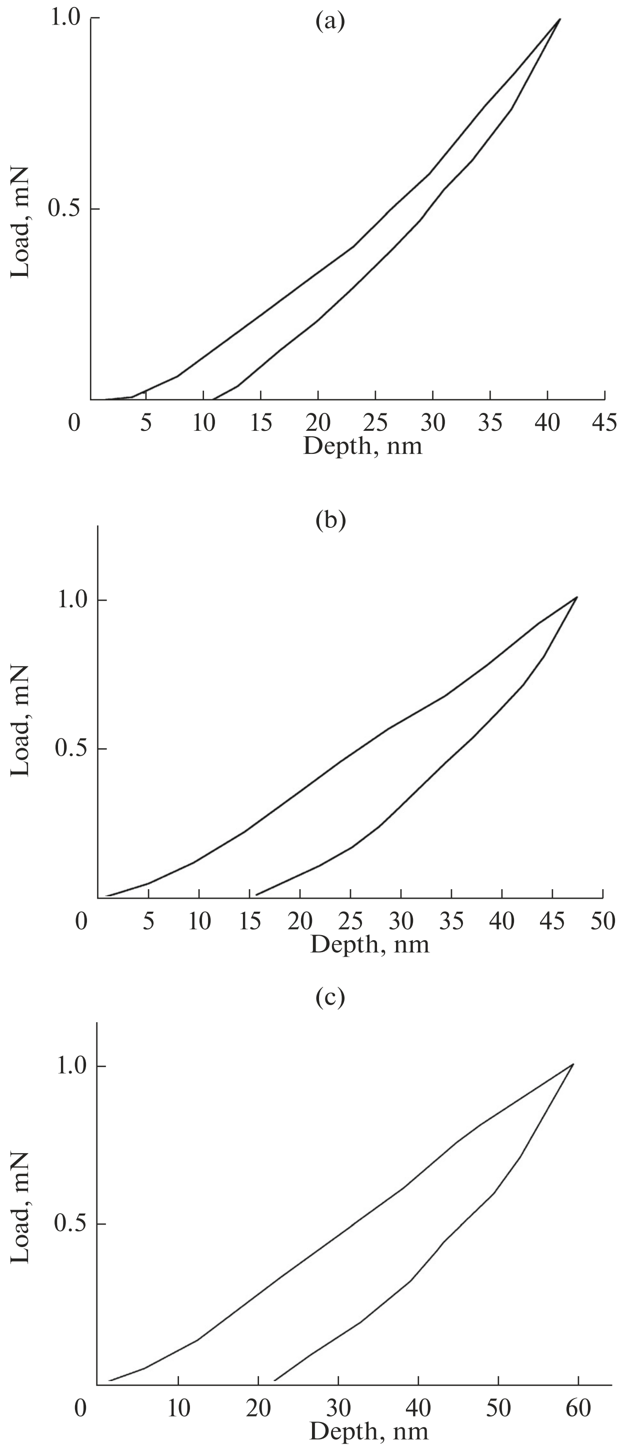

Fig. 3. Typical load-displacement diagrams recorded in the nanoindentation tests of the coatings on (a) 12Cr18N10T, (b) VT4, and (c) M1 substrates at a maximum load of 1 mN.

length of the scratch are presented in Fig. 4. The diagrams show a linear increase in the friction coefficient; then it reaches a constant value in the range 0.5–0.8, which corresponds to the materials of the substrates. Analysis of the dependences made it possible to determine that the critical load at which the coating is destroyed is ~30 mN for a diamond-like coating on 12Cr18N10T steel, ~28 mN for a coating on titanium, and much smaller, ~15 mN, for a coating on copper. In the latter case, penetration of the indenter into the

Table 2. Results of the nanoindentation of diamond-like coatings on substrates of various materials

No.	Parameter	Substrate		
		12Cr18N10T	VT4	M1
1	Maximum indentation depth h_{max}, nm	44	61	76
2	Indentation hardness H_{IT}, GPa	30 ± 4	25.6 ± 2.1	11.6 ± 1.3
3	Modulus of elasticity upon indenting E_{IT}, GPa	360 ± 90	239 ± 23	151 ± 14
4	Reduced modulus of elasticity E^*, GPa	380 ± 90	246 ± 24	156 ± 14
5	Proportion of elastic deformation work upon indenting η_{IT}, %	77 ± 4	67 ± 3	51 ± 3
6	Plasticity index (H/E)	0.08	0.11	0.08
7	Resistance to plastic deformation (H^3/E^2)	0.21	0.29	0.07

coating could lead to deformation of the substrate, which accelerated its destruction.

Tribological tests of the coatings in the ball-on-disk geometry under a load of 1 N in a friction pair with WC for coating on 12Cr18N10T steel showed a friction coefficient of ~0.1–0.4 (Fig. 5a). After "grinding" for 800–900 test cycles, a constant friction coefficient of ~0.1 was set at 500 cycles; after that, it increased to 0.3. Visual inspection and SEM studies showed that after 5000 test cycles performed over 60 min, the coating was not destroyed; its thickness decreased by approximately 0.02 μm. For the coating on titanium, a friction coefficient of ~0.1 was set after 1500 cycles, and it remained constant until the end of the tests (~5000 cycles). In the case of the coating on copper, a gradual increase in the friction coefficient to 0.3 over 3000 cycles, followed by reaching a constant value, was observed. The clearest signs of wear of the coating were also visible for the sample on M1 copper. The nature of the change in the friction coefficient for this sample can be explained by plastic deformation of the coated substrate and the gradual formation of a friction path, which increases the contact area of the friction pair, prevents leaving of the damaged material from the contact zone, and contributes to destruction of the coating.

The diamond-like coating on titanium demonstrated the smallest value of the friction coefficient (~0.1) and the highest stability of the tribological properties. For this sample, the friction coefficient of the technical diamond–coating pair was measured in the ball (OI-12-2)-on-plane (coating) geometry with reciprocating sliding of the samples relative to each other with an amplitude of 15 μm and a normal force of 1 N applied to the contact. The frequency of the reciprocating motion was 20 Hz. The experiments showed that the coating begins to be destroyed at a number of cycles of ~1000. The dependence of the friction coefficient versus the number of cycles is shown in Fig. 6. At the initial stage, the friction coefficient was less than 0.01; after reaching 1200 cycles, it began to increase and exceeded this value. The average value of the friction coefficient, set during subsequent cycles, was ~0.012. Visual inspection of the samples with the coatings showed its complete destruction at the point of contact after stopping the experiment at approximately the 30 000th cycle of tests.

Tribological testing of the coatings showed that they have good potential for applications requiring a low friction coefficient. The possible mechanisms for improving the functional properties and durability of coatings in the case of soft materials are increasing the ratio of sp^3/sp^2 bonds in the coating; forming a harder intermediate layer, for example, based on chromium, preventing plastic deformation of the coated substrate and the formation of a friction path; and increasing the thickness of the working layer of the coating.

CONCLUSIONS

Diamond-like coatings with a total thickness of ~0.6 μm are obtained by vacuum plasma spraying with

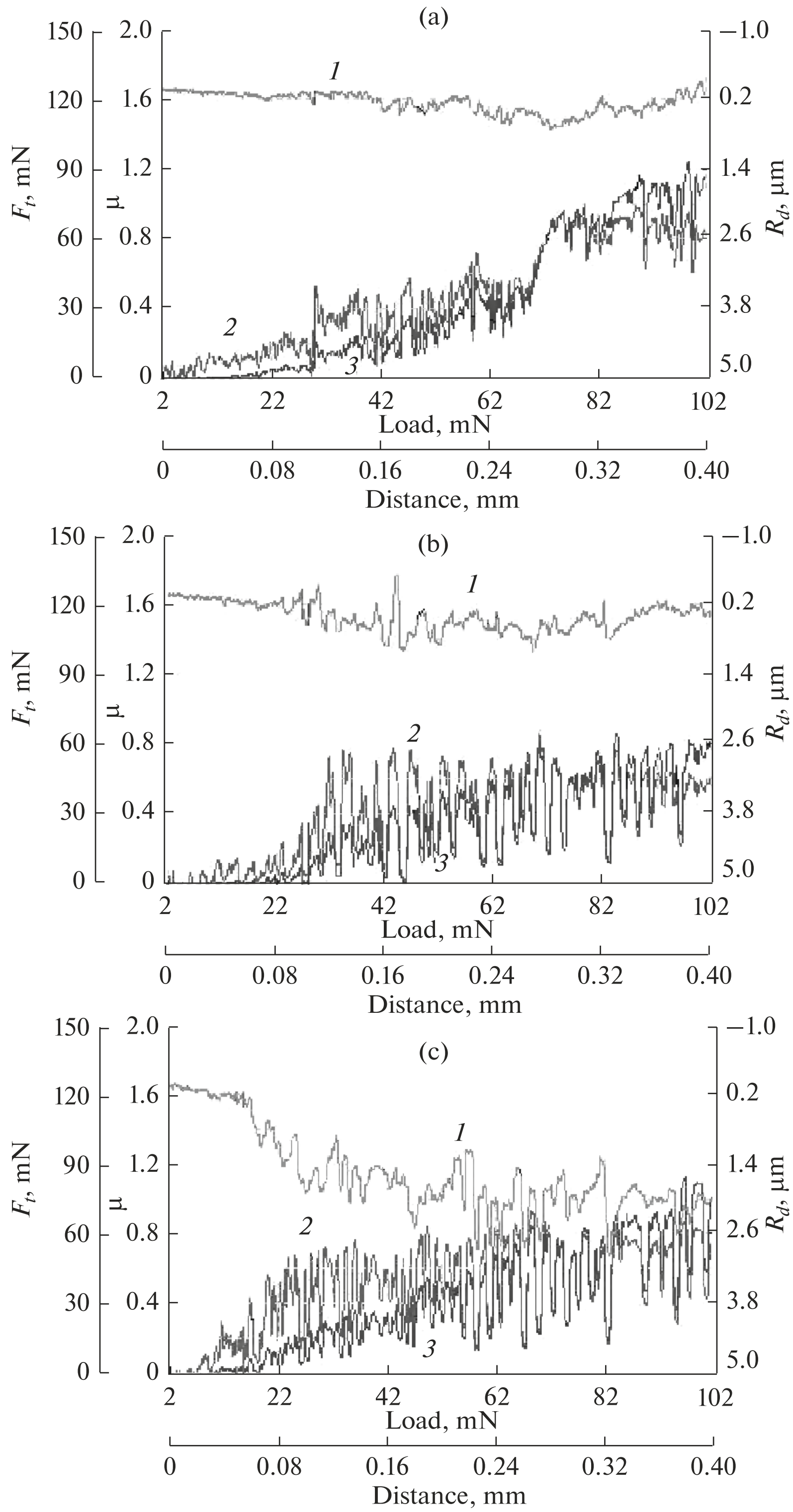

Fig. 4. Change in (*1*) the residual depth R_d, (*2*) the friction coefficient μ, and (*3*) the friction force F_t along the scratches for the coatings on (a) 12Cr18N10T, (b) VT4, and (c) M1 substrates.

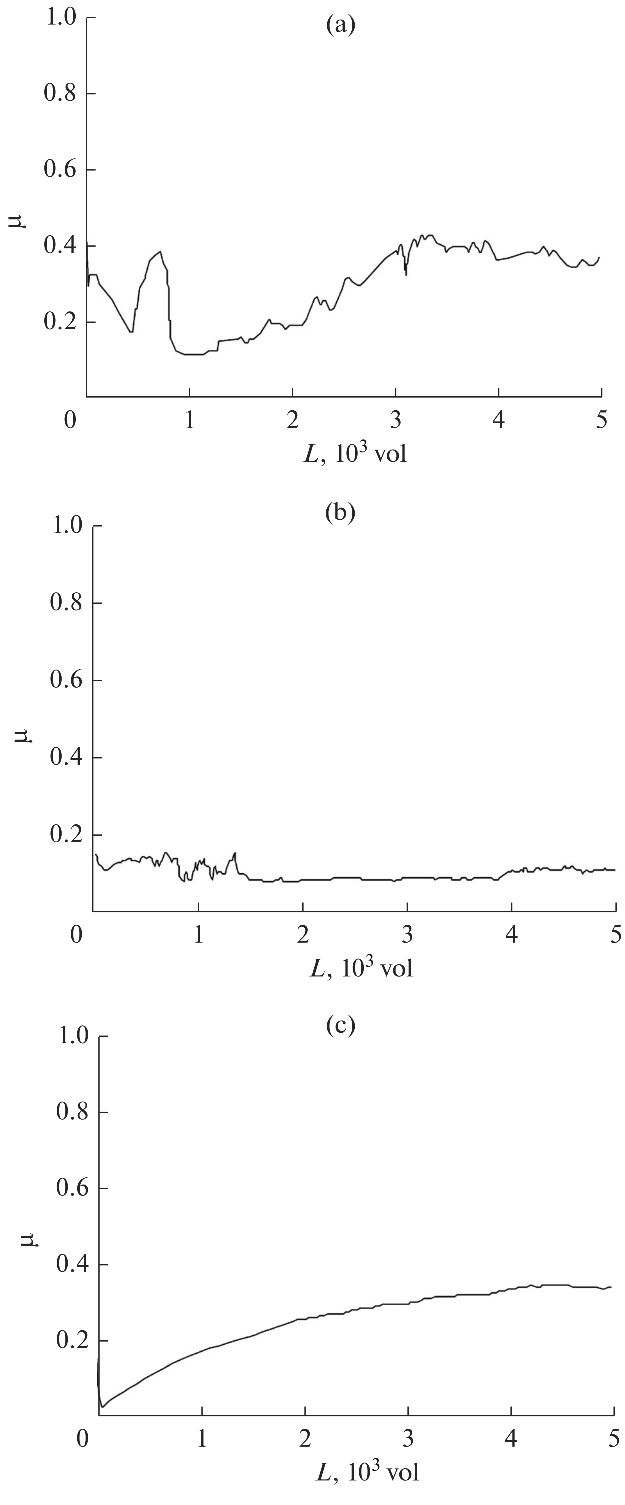

Fig. 5. Change in the friction coefficient μ along the path L for the coatings on (a) 12Cr18N10T, (b) VT4, and (c) M1 substrates.

plasma separation and a pulsed carbon arc source with a cooled cathode and laser arc ignition on substrates of VT4 titanium alloy, 12Cr18N10T stainless steel, and

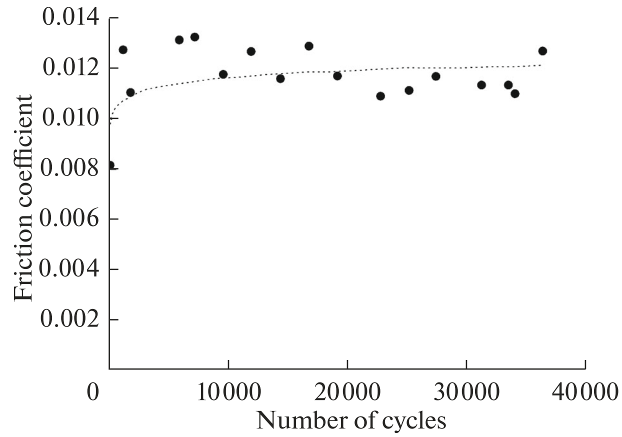

Fig. 6. Measurement of the friction coefficient in a technical diamond—diamond-like coating friction pair in the ball (OI-12-2)-on-plane (coating) geometry with reciprocating sliding.

M1 copper. The coatings are characterized by a dense, nonporous structure with a low surface roughness and a globular structure in the regions of polishing defects of the substrates.

In the Raman spectrum, a broad peak characteristic for diamond-like coatings is observed in the region of 1580 cm^{-1}. The fractions of carbon atoms in the sp^2 and sp^3 hybridization states in the coating do not depend on the type of substrate. At $I_D/I_G \approx 0.4$, the fraction of carbon atoms in the sp^3-hybridization state ranges from 0.45 to 0.60.

The strength characteristics of the coatings depend significantly on the substrate materials. The greatest hardness of indentation (~30 GPa), elastic modulus (~360 GPa), and critical fracture load (~30 mN) were obtained for the coating on 12Cr18N10T steel.

Tribological tests showed stable operation and the lowest friction coefficient (~0.1) for the diamond-like coating on VT4 alloy. The clearest signs of wear of the coating were observed on the sample of M1 copper, which can be explained by plastic deformation of the coated substrate and the gradual formation of a friction path.

The friction coefficient of a technical diamond—coating pair, measured in the ball-on-plane geometry with reciprocating sliding of the samples, is smaller than 0.01 at the beginning of coating failure at a number of cycles of ~1000 and at its complete destruction at approximately the 30000th cycle of tests.

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