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Cryogenic treatment of diamond-like vacuum coatings

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The article considers the cryogenic treatment of diamond-like coatings formed on tool die steel. It studies the morphology, physical-mechanical, adhesive, and tribological characteristics of carbon coatings treated by hybrid technology, which consists of the complex effect of cryogenic liquid on both the metal substrate and the system „modified steel substrate−diamond-like coating". It also studies structural transformations occurring in vacuum coatings formed on steel substrates with subsequent treatment at low temperatures. The change in the tribological characteristics of diamond-like coatings during hybrid treatment in cryogenic liquid is shown.

Keywords: cryogenic treatment, structure, properties, carbon, coatings, metals.

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Introduction

Application of coatings formed using various process approaches makes it possible to change significantly the strength properties of surface layers of the modified products [1–3]. Vacuum coating processes are widely used to produce protective surface layers. Such process approaches include physical vapor deposition (PVD), chemical vapor deposition (CVD) and combination thereof in fabrication of thin-layer coatings. Vacuum techniques are used to fabricate coatings with pre-defined stress-strain properties that are quite well predicted on the basis of numerous existing experimental and theoretical studies in this field. Thus, there is a particular strength limit for coatings made using vacuum processes. Modification of material structure by means of cryogenic treatment is a simple and effective method. Sudden cooling of vacuum coated products to cryogenic liquid boiling point gives rise to large temperature gradients, which in turn causes significant compressive stresses. Such treatment causes various structural transformations and variation of dispersity of particles and phases contained in the coating and substrate matrix [4,5]. Several studies emphasize the formation of nanodispersion phases in a modified material. A modern surface engineering trend in the vacuum coating area includes the formation of low-dimensional structures in material volume and fabrication of nanodispersion materials. Several studies show that the change in geometrical parameters of structural components affects considerably the stress-strain properties of the boundary layers of various types of materials [6–9]. Such properties are displayed when the dimension of crystalline formations is in the region below 40 nm. This type of substances, the dimension of structural components of which is in the range below 100 nm, are usually classified as nanocrystalline substances. Structure, physical and chemical composition of grain boundaries in a nanocrystalline coating are the governing factors that influence the vacuum coating performance. This phenomenon is observed in most cases for coatings whose grain boundaries, that form a protective layer, are in metastable state (multicomponent chemical compounds). The observed non-equilibrium processes at the grain boundary cause self relaxation of the boundaries at low operating temperatures. Nanocrystallite interface in terms of its structure contains various defects: dislocations, vacancies, combination of the defect structures listed above. Note that the distribution and number of defective structures at the interface differ from their distribution in the material volume. The trend of the past decade is the increase in performance of products and tooling used for metal working through the use of coatings based on diamond-like compounds formed by various vacuum processes. Diamond-like vacuum coatings formed in the pre-defined conditions and after a proper preparation have increased strength properties, in particular, hardness reaches $HV = 30-40$ GPa, which is 2 to 3 times as high as that of other vacuum metallic coatings. Generally, higher temperatures and friction coefficient are achieved in the contact zone, and adhesive interaction in the tribocontact decreases after formation of these protective layers.

Diamond-like coatings (DLC) having high strength, adhesive and antifriction properties have been used widely in mechanical engineering to increase the service life of metal-working tools. Nanocomposite DLC for surface reinforcement of various materials is one of the widely used surface engineering method [6–9]. This is associated with their unique stress-strain properties. DLC generally means a finely-dispersed carbon material whose structure corresponds to diamond that has high hardness, strength and wear resistance and which is usually produced by the PVD, CVD or PCVD methods. This class of coatings is used in the optical-mechanical industry as protective and antireflection coatings, biocompatible coatings in medicine, antifriction coatings in chemical industry due to their high inertness to aggressive media, in electronic industry for creation of thin-layer systems designed for data storage [10,11]. Possible formation of nanoobjects in the DLC matrix is shown in [10,11]. Formation of these low-dimensional systems causes additional increase in the DLC hardness and adhesive strength. According to the existing data, the properties of DLC are close to those of a natural diamond. However, by varying vacuum process conditions for DLC deposition, stress-strain properties of these superhard carbon layers may be modified, in particular, conductivity and antifriction properties of DLC may be controlled. Nanocomposite carbon coatings are widely used as antifriction layers that combine a low friction coefficient, biocompatibility and high wear resistance [9–11]. Compared with other methods, the main advantage of DLC formed through the use of vacuum processes is low roughness of surface layers. However, the concentration of sp^2/sp^3-hybridizations in DLC films may be changed significantly during formation of a coating and, consequently, the size of phases in the coating structure, grain boundary properties, etc., will be changed.

The purpose of this study is to examine the morphology and stress-strain properties of diamond-like vacuum coatings formed on metals depending on the history of substrate preparation process and post-process low-temperature treatment.

1. Experiment

1.1. DLC synthesis

DLCs were used as test objects. These coatings were deposited on steel substrates. 4Kh5MFS steel was used for metal substrates. To achieve high quality coatings, preliminary substrate preparation was used that included specialized heat treatment to achieve hardness of about Rockwell C 50. Then the steel substrate were polished to 10 degrees of finish. Nanocomposite coatings were formed by the cathodic arc deposition method using the UVNIPA-1-001 vacuum unit equipped with a stationary metal plasma source with a zirconium cathode, and the Radikal ring-anode ion source through which N_2+C_2H_2 gas mixture is supplied to form $1-1.5\,\mu$m DLC. DLC was deposited both of the initial steel and on the cryogenically treated metal substrate. Cryogenic treatment time for the steel substrate was from 30 min to 4320 min. After the formation of vacuum coatings on steel substrates, the coating–substrate system also underwent liquid nitrogen treatment during 30 to 200 min. Stress-strain property variables were determined using standard procedures as specified in the applicable standards.

1.2. Characterization of coatings

Structural gradient was determined by measuring hardness and microhardness using standard equipment. Microhardness was determined using the HWMMT-X7 (Japan) hardness tester and PMT-3 diamond-pyramid tester. Morphology of the studied DLC, distribution of various phases in coating, topography of sample surface friction were examined by the scanning backscattered electron microscopy (SEM) method using the MIRA3 TESCAN (Czech Republic) microscope, reflection optical microscopy using the metallographic system made by Spectroscopic Systems and by contactless probe atomic force microscopy (AFM) using the NT-206 system. AFM images were recorded in various scanning fields followed by visualization in original Windows software packages using a procedure developed by Mikrotestmashiny company. Coating and friction surface roughness was measured using the Surftest SJ-210 profilometer. Tribotechnical test was carried out on the FT-2 multipurpose friction machine interfaced with a high performance multiprocessor unit capable of processing the collected experimental data in Windows environment using Mikrotestmashiny's software. A steel ShKh-15 spherical indenter was used as a counterbody. Indenter loading varied from 1 N to 30 N. Indenter sliding velocity on the sample surface was 0.1 m/s. A scratch test method was used to determine adhesive properties of vacuum coatings. Gradually increased loads from 1 N to 30 N were applied to the indenter. The scratch length was 10 mm.

2. Findings and discussion

There are various process approaches to increasing stress-strain properties of DLC. One of the superhard carbon nanocomposite coating fabrication areas includes formation of these diamond-like layers on cryogenically hardened metal substrates followed by cryogenic modification.

DLC morphology is one of the aspects that define coating performance. Morphology of DLC formed on hardened steel substrates depends considerably on both the metal substrate history and cryogenic post-treatment of the cryogenically hardened steel — DLC system.

Figure 1 shows the optical microscopy images of steel sample surfaces after cryogenic treatment.

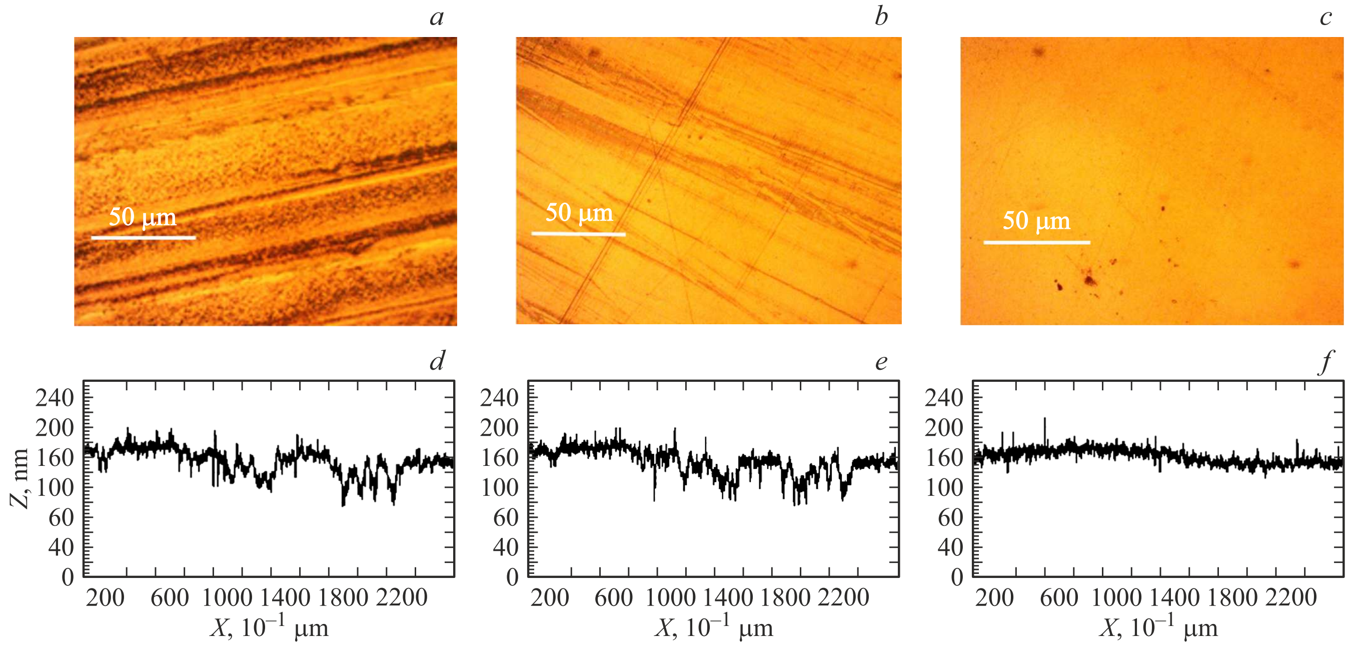

Figure 1. Morphology (*a–c*) and topography (*d–f*) of steel product surfaces after pre-hardening in cryogenic liquid, where *a* — initial sample; *b, c* — cryogenic liquid treatment during 60 min and 1440 min, respectively; *d* — initial sample, *e–f* — cryogenic liquid treatment during 60 min and 1440 min, respectively.

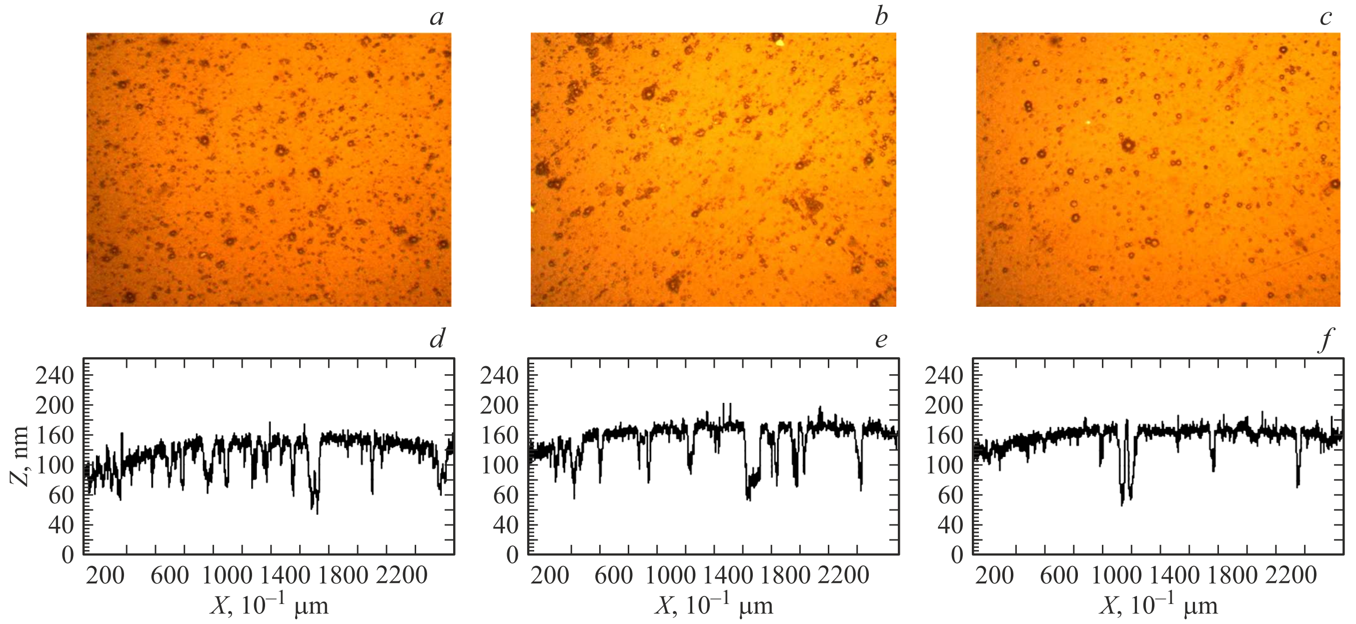

Figure 2. Morphology (*a–c*) and topography (*d–f*) of nancomposite DLC surfaces formed on pre-hardened steel substrates, where *a* — initial sample; *b, c* — cryogenic liquid treatment during 60 min and 1440 min, respectively; *d* — initial sample, *e–f* — cryogenic liquid treatment during 60 min and 1440 min, respectively.

According to the obtained data, it can be seen that cryogenic liquid pre-treatment of 4Kh5MFS steel causes some kind of texture smoothing. This effect is confirmed by the steel substrate surface roughness examination data obtained using Autoscan software package (Figure 1). During low temperature exposure, dispersion hardening of surface layers probably takes place and is followed by the improvement of strength properties and dispersion of DLC constituents.

Morphology and topography of nanocomposite DLC formed on hardened steel substrates are shown in Figure 2.

Surface roughness examination of nanocomposite DLC formed on hardened steel substrates was carried out in Autoscan and the results are shown in Figure 2, *d–f*.

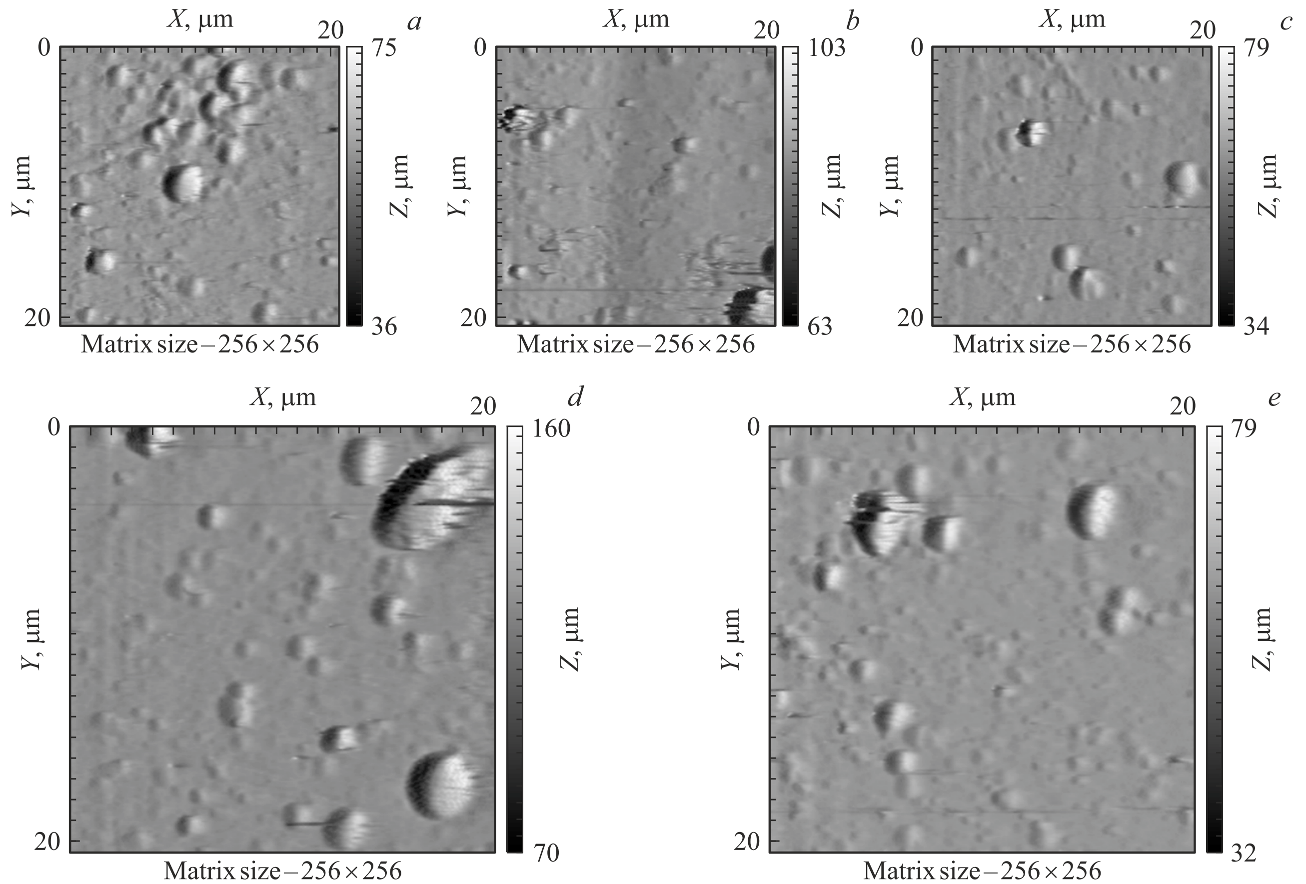

Figure 3. Morphology of DLC exposed to cryogenic environment during 60 min. Coatings were formed on steel substrates (4Kh5MFS steel) after cryogenic liquid pre-hardening: *a* — initial sample; *b* — 60, *c* — 1800, *d* — 1440, *e* — 4320 min. The image was obtained by the AFM method, scanning area (25 × 25 μm).

According to the obtained data, cryogenic liquid treatment of initial metal substrates and coatings formed on them gives rise to partial smoothing of the initial coating texture, which may indicate restructuring of diamond-like coatings during cryogenic treatment.

According to the existing literature data [12], FTIR (frustrated total internal reflection) IR spectra of DLC on steel substrate have absorption bands at 520–630 cm^{-1}; 950–1300 cm^{-1}; 2200–3000 cm^{-1}. Absorption bands at 950–1300 cm^{-1} may be assigned to C–H group stretching. Absorption bands at 2200–3000 cm^{-1} contain stretching peaks of carbonyl groups, single C–C- and double C=C bonds and deformation vibration peaks of C–H groups. Peaks were observed at 2100, 1000 cm^{-1} and corresponded to C–C bond stretching [12].

Atomic-force microscopy was used to examine the morphology of cryogenically treated DLC formed on 4Kh5MFS steel (Figure 3)

Variation of stress-strain properties of ceramic coatings formed in vacuum after liquid nitrogen treatment was found in [12–14]. To study the strength property variation in steel samples during cryogenic treatment, microhardness of 4Kh5MFS steel was measured depending on the cryogenic

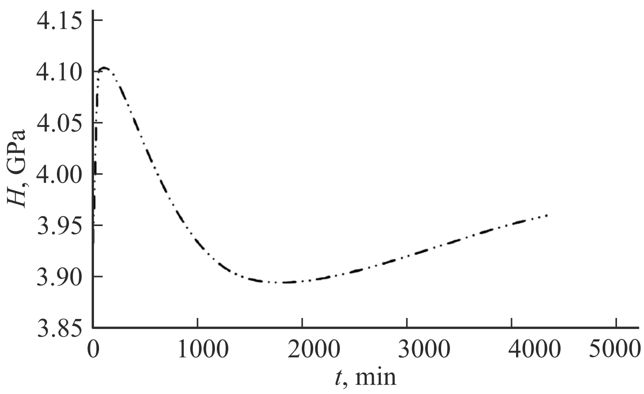

Figure 4. Dependence of steel 4Kh5MFS microhardness on cryogenic holding time.

liquid holding time (Figure 4). According to the obtained data, increase in the microhardness of cryogenically modified steel is observed in the liquid nitrogen treatment tame range from 30 h to 72 h. A decrease in the microhardness of modified steel samples is observed in the treatment time range from 60 min to 2000 min, then an increase in the mi-

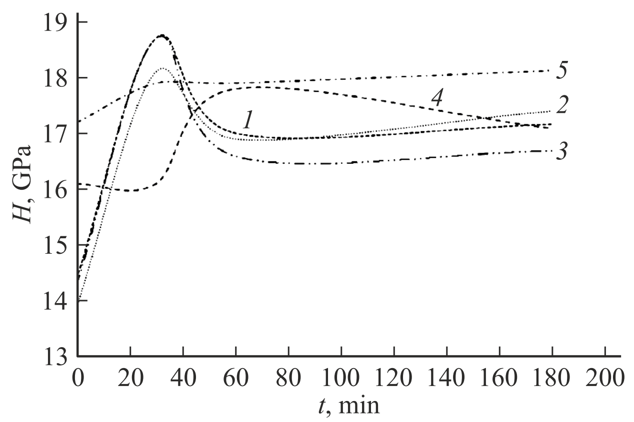

Figure 5. Dependence of DLC microhardness on cryogenic holding time. Coatings were formed on steel substrates (4Kh5MFS steel) after cryogenic liquid pre-hardening: *a* — initial sample; *2–5* — cryogenic liquid treatment during 60 min, 1440 min, 1800 min and 4320 min, respectively.

crohardness of 4KhMFS steel is observed in the cryogenic treatment time range from 2000 min to 4000 min. Note that these microhardness variations in cryogenically modified samples are higher than the microhardness measured for the initial 4Kh5MFS steel (Figure 4).

The microhardness studies of DLC formed on the pre-activated 4Kh5MFS steel (Figure 5) induce strength property variations. Thus, cryogenic pre-treatment of 4Kh5MFS steel substrates causes the increase in microhardness of the DLC to be formed, when the treatment time is longer than 30 min (Figure 5). Variations of DLC coating microhardness may be caused by significant variations of charge center concentration on the metal surface after cryogenic liquid treatment. Charge mosaic occurs on the polycrystalline metal surface as a result of a contact between crystallites and various crystallographic surfaces, which defines the Fermi level difference. Low temperature exposure may cause particle dispersion variation both in the coating structure and substrate structure. This gives rise to a change of lattice planes, which affects the Fermi level difference and concentration of active charge centers on the metal substrate surface. Increase in the number of charge centers on the substrate surface causes the increase in the number of DLC formation centers and therefore to the increase in dispersity of DLC structural formations. Dimensions of structural formations may vary both in the substrate and coating due to high stresses that occur during cryogenic treatment. According to classical concepts, stresses that occur in a substance at differential temperatures are directly proportional to the substance's linear expansion temperature coefficient, modulus of elasticity and temperature gradient, and are described by the following equation:

$$\Sigma = \alpha E \Delta T, \qquad (4)$$

where α is the linear expansion temperature coefficient, E is the modulus of elasticity, ΔT is the temperature difference.

Calculation of stresses that occur in steels and diamond-like coatings gives approximate values of ~ 500 MPa for steel and ~ 80 MPa for DLC after treatment at the liquid nitrogen boiling temperature (-195.8°C). These stresses that occur in the studied material structures may cause restructuring of both the substrate and coating. The hybrid treatment of DLC influences significantly on the adhesive properties of the studied coatings (Figure 6, 7). The type of adhesive interaction depends on the nature of both bodies and also on the interaction environment. According to the classical concepts, the shape of both contacting bodies, ambient conditions, temperature and force have a significant influence on the body convergence and disconnection processes. Adhesive interaction is usually considered from one side and understood as a process that causes a contact and force interaction with the establishment of interatomic or intermolecular bonds between two contacting bodies. To break this interaction, the contacting bodies shall move relative to each other. The second aspect is associated with the failure or damage of the established bonds between the contacting bodies. To describe this process, energy (force) required to break the interaction is used as a quantitative parameter. Thus, for the former case, convergence conditions and kinetics are of interest, in the later case — adhesive bond disruption process is of interest. The latter case is generally typical when adhesion of dispersed particles to semiconductors, metals and dielectrics in various gas media is studied because in this case there are no factors preventing from interaction between bodies and intermolecular interaction establishment. The degree of adhesive interaction depends considerably not only on the interacting body spacing, but also on the molecular interaction in the direct contact area. Then the adhesive interaction process is of interest in terms of contact failure resistance, i.e. is a quantitative measure of „adhesion“. However, the first adhesive interaction process cannot be studied without the second process. Therefore, development of methods that can evaluate the second process (adhesive contact failure) is one of the paramount tasks of surface engineering.

According to the obtained data, hybrid treatment, that includes cryogenic pre-treatment of the steel substrate followed by the formation of DLC and finishing liquid nitrogen treatment of the formed coating, gives rise to the increase in adhesive interaction between the DLC and steel substrate.

The studies have shown that a promising DLC modification area may involve a hybrid technique of cryogenic pre-modification of a steel substrate, formation of DLC and low-temperature post-treatment of this system.

The studies have shown variation of tribological properties of DLC coatings formed using this technique (Figure 8, 9).

Steel substrate pre-treatment causes the decrease in the friction coefficient for the DLC-ShKh15 pair from 0.27 to 0.22. These results agree well with the friction

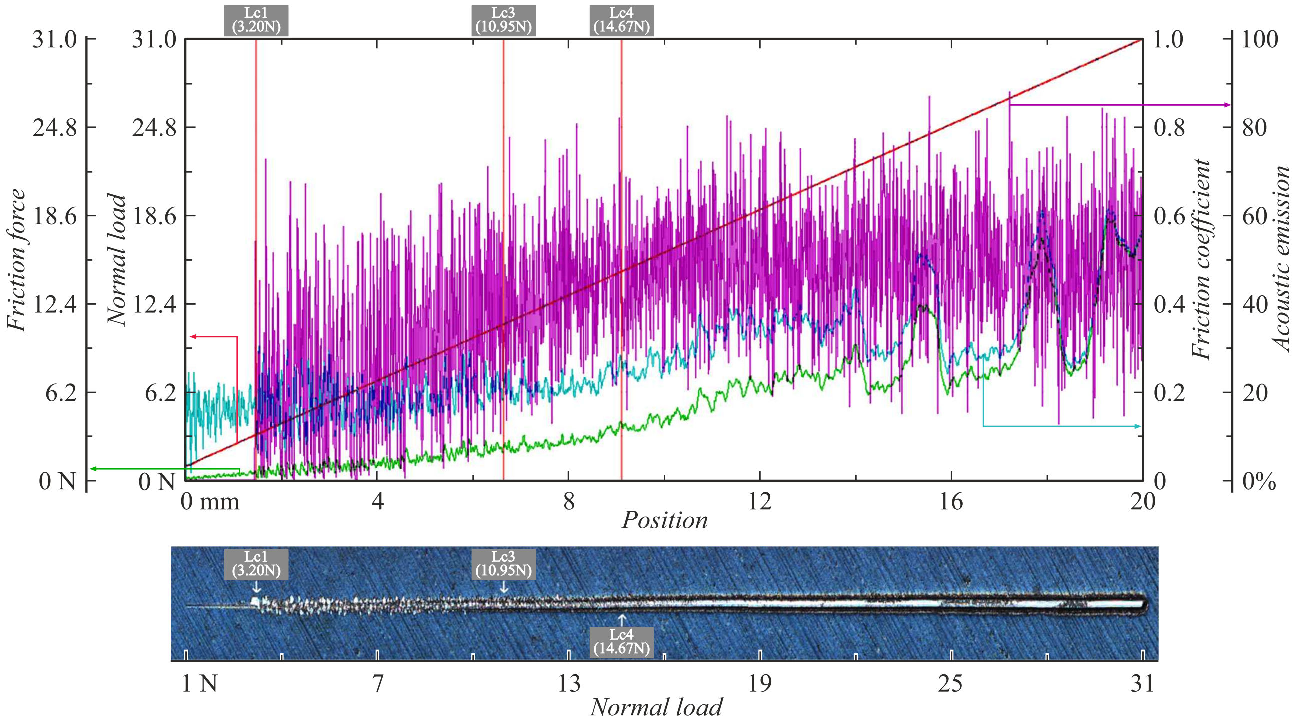

Figure 6. Scratch test data of DLC formed on 4Kh5MFS steel.

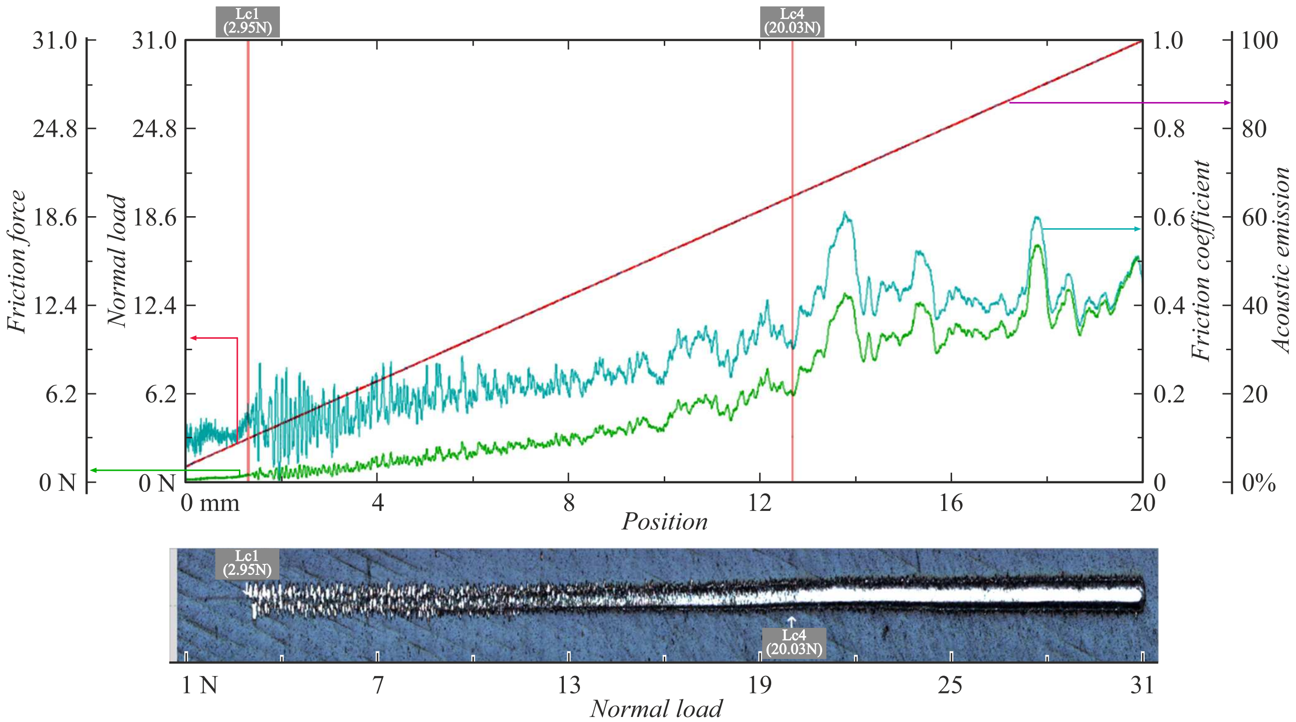

Figure 7. Scratch test data for DLC formed on 4Kh5MFS steel and subjected to cryogenic treatment during 60 min. The steel substrate was subjected to cryogenic pre-treatment during 4320 min.

coefficient data obtained for the diamond indenter–DLC pair (Figure 9).

Decrease in the friction coefficient during cryogenic post-treatment of DLC is a general trend associated with the tribotechnical properties o DLC (Figure 9, *b*).

Variation of the friction coefficient of DLC formed on the steel substrate pre-modified in liquid nitrogen causes the decrease in the friction coefficient of the „DLC–diamond“ pair. However, as the cryogenic treatment time of the metal substrate increases, the friction coefficient of the

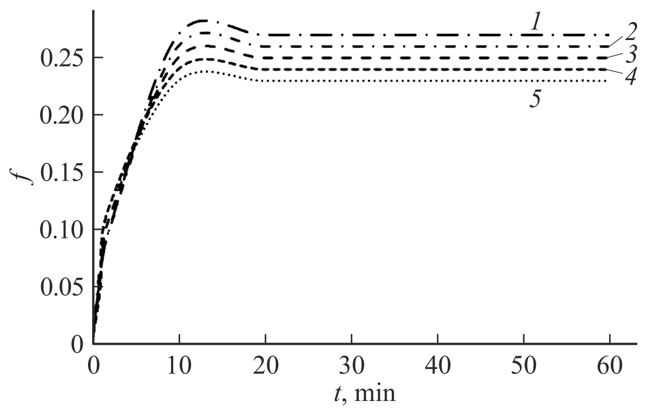

Figure 8. Dependence of the friction coefficient of DLC formed on 4Kh5FMS steel. The 4Kh5FMS steel substrate was pre-treated in liquid nitrogen during: *1* — initial substrate, *2* — 60 min, *3* — 180 min, *4* — 1440 min, *5* — 4320 min. $V = 0.1$ m/s, load 30 N, counterbody —ShKh15 steel.

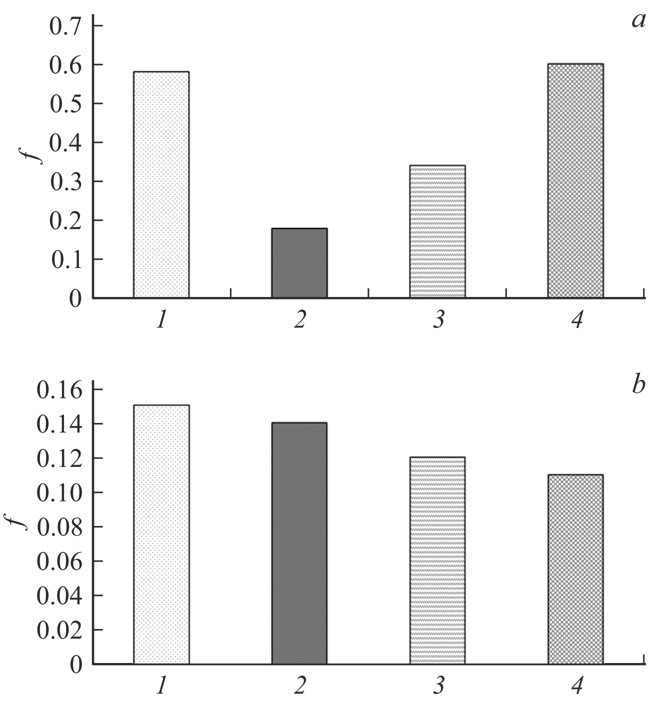

Figure 9. Dependence of the friction coefficient of DLC („DLC–diamond“ friction pair) formed using the hybrid technique: *a* — dependence of the friction coefficient of DLC („DLC–diamond“ friction pair) formed in the 4Kh5MFS substrate on the cryogenic substrate activation time: *1* — initial steel; steel was cryogenically treated during: *2* — 60 min, *3* —- 180 min, *4* — 4320 min. The friction coefficient was measured with the indenter load of 20 N; *b* — dependence of the friction coefficient of DLC („DLC–diamond“ friction pair) formed on 4Kh5FMS steel and cryogenically treated during 60 min: *1* — initial steel, steel was cryogenically treated during: *2* — 60 min, *3* — 180 min, *4* — 1440 min.

„DLC–diamond“ pair increases. An optimum cryogenic modification region is observed on the steel substrate in the 60 min treatment region where the friction coefficient values are minimum (Figure 9, *a*). The degree of reduction of the friction coefficient depends on the cryogenic holding time. The following friction mechanism is suggested in the „DLC–solid body“ system. At the initial stages of contact between DLC and solid body (SB), wear of nanoirregularities occurs on the softer SB due to DLC microroughness penetration into the SB surface layers that gives rise to the plastic deformation of the mating surfaces in a low-dimensional range that is followed by local plastic deformation, and plastic yield takes place in the contact zone. This process causes the increase in stress-strain properties of the friction surfaces. Formation of SB wear products gives rise to the closure of microirregularities in the counterbody surface layers and start of abrasive wear. This process is intensified as the contact zone temperature and friction force increase. At the same time, carbon diffusion into the metal near-surface layers takes place, smoothing of the initial substrate texture and formation of a nano- and microfracture network are observed. Carbon diffusion into the counterbody, formation of carbon-containing friction products in the contact zone lead to the friction coefficient reduction.

Conclusion

Cryogenic liquid pre-treatment of steel substrates leads to the increase in strength properties of vacuum coatings. Additional liquid nitrogen treatment of coatings formed on the activated steel substrates causes further growth of strength properties. It is shown that the cryogenic pre-treatment of 4Kh5FMS steel substrates gives rise to the increase in microhardness. This effect is induced by the formation of nanodispersion structures in the steel substrate as well as by residual austenite disintegration, which causes the increase in martensite in the low-temperature treated steel structure. Steel substrates (4Kh5MS steel) treated during 30 min (4.1 GPa) and 72 h (3.95 GPa) have the highest microhardness. Formation of DLC on a cryogenically hardened steel substrate gives rise to the increase in the DLC microhardness compared with the initial carbon coatings. This effect may be explained by the growth of the number of active charge centers on the substrate surface due to cryogenic treatment. Increase in the concentration of active charge centers leads to the increase in dispersion of phases contained in the DLC structure, which affects the strength properties of carbon coatings. Additional cryogenic treatment of the „DLC–activated substrate“ system affects the internal stresses in the coating structure. Taking into account the fact that DLCs themselves are metastable systems with high internal stresses in the range of 1–2 GPa, additional growth of the internal stresses of about 80–500 GPa may cause dispersion hardening of DLC affecting the stress-strain properties of the modified DLC.

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Conflict of interest

The authors declare no conflict of interest.

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