

THE TRIBOTECHNICAL CHARACTERISTICS OF DIAMOND-LIKE COATINGS FORMED BY HYBRID TECHNOLOGY

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Abstract

The use of low temperatures to improve the performance of steel products is a widely used technology in mechanical engineering. Another direction of increasing the efficiency of machine parts and mechanisms is the creation of thin-layer systems using vacuum technologies. The combination of these technological approaches made it possible to obtain antifriction vacuum superhard coatings with increased tribotechnical characteristics. The effect of increasing the wear resistance of hybrid coatings is the formation of nanodisperse structures in the steel substrate and coating, the decay of residual austenite, which leads to an increase in martensite in the structure of steel subjected to cold treatment, a significant change in the values of internal stresses in superhard coatings.

Keywords: diamond-like coating, cryogenic treatment, coefficient of friction, steel, wear resistance.

ТРИБОТЕХНИЧЕСКИЕ ХАРАКТЕРИСТИКИ АЛМАЗОПОДОБНЫХ ПОКРЫТИЙ, СФОРМИРОВАННЫХ ПО ГИБРИДНОЙ ТЕХНОЛОГИИ

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Реферат

Применение низких температур для повышения эксплуатационных характеристик стальных изделий является широко применяемой технологией в машиностроении. Другим направлением увеличения работоспособности деталей машин и механизмов является создание тонкослойных систем с применением вакуумных технологий. Сочетание данных технологических подходов позволило получить антифрикционные вакуумные сверхтвердые покрытия с повышенными триботехническими характеристиками. Эффект увеличения износостойкости гибридных покрытий заключается в образовании нанодисперсных структур в стальной подложке и покрытии, распад остаточного аустенита, что приводит к увеличению мартенсита в структуре стали, подвергнутой обработке холодом, существенному изменению значений внутренних напряжений в сверхтвердых покрытиях.

Ключевые слова: алмазоподобное покрытие, криогенная обработка, коэффициент трения, сталь, износостойкость.

Introduction

There are various ways to impart surface strength. The most famous is the thermal hardening with high-speed heating and cooling of the laser beam or electron beam, treatment with plasma compression flows, leading to stirring of surface layers and administration of alloying additives [1–5]. However, from the point of view of vacuum methods of engineering of the surface, the surface treatment with bunches of nitrogen ions is the most profitable. Almost all modern sets of physical precipitation of coatings from the steam phase are equipped with sources of argon ions for pre-cleaning and activating the surface before applying coatings. This means that there is already a necessary toolkit for the implementation of ion-beam nitriding. In this case, the single vacuum technological cycle of applying solid coatings is not disturbed. This is the great advantage of the method being developed.

Simple and effective way is the modification of the structure of materials by cryogenic processing. The sharp cooling of the surface layers leads to significant temperature gradients, which in turn causes the appearance of high compressive stresses. Such treatment is important for structural steels, which temperature of the end of martensitic transformations is significantly lower than room temperature. Transformation of residual austenite in martensite, as well as the appearance of a significant amount of dislocations leads in some cases to crushing the grain and a significant increase in surface hardness. In this case, the depth of

the modified layer is several hundred micrometers [2]. As a result of cryogenic effects, nanodisperse phases are formed in the modifiable material.

The hardness of vacuum coatings increases by the formation of an ultrafine structure characteristic of thin-layer vacuum coatings. In the process of creating low-dimensional structural formations, it is necessary to consider the change in the thermodynamic properties of coatings, which, ultimately, can change phase fields on the status diagrams. One of the main tasks in the formation of thin-layer coatings in the field of mechanical engineering is to increase their physical and mechanical properties, which makes it possible to increase the operational resource of the processing tool. This is achieved by studying the peculiarities of the transformation of the coating structure of refractory compounds at high temperatures. The study of crystallization processes, recrystallization of carbonitrides, nitrides, carbides, including in thin-layer systems, is a priority in the field of surface engineering.

The aim of the present work was to study the influence of the processes of the hybrid technology of hardening metal surfaces on the tribotechnical characteristics of obtained nanocomposition coatings.

The technique of experiment

The application of composite coatings based on titanium nitride was carried out on a vacuum installation UVNIPA-1-001, equipped with a cathode-arc evaporator with a plasma electromagnetic filtering system,

as well as an ion source II-4-0.15. H11steel was used as a substrate. The surface of the substrates from steels was hardened and grinding to cleanliness not lower than grade 11. Before applying of the coatings the surface of the sample was cleaned and heated by titanium ions under such conditions: the evaporator current 105–110 A; the potential on the sample 1,0 kV. The coating precipitation was carried out at a current of the stabilizing coil of 1,7 A, the current of the control coil 2,0 A and the current of the arc 90 A. The pressure of the reaction gas (nitrogen) was within $(0,87-5) \times 10^{-2}$ Pa. During the deposition of the coating on the substrate, the displacement voltage was supplied from -50 V to -100 V. Pre-processing of metal substrates in liquid nitrogen was carried out at a boiling point of liquid nitrogen (-195,6 °C), processing time was 30 minutes – 72 hours. Coatings formed on activated substrates were exposed by cryogenic liquids at a temperature of -195,6 °C in the time range from 30 minutes to 72 hours.

Tribotechnical studies were carried out on the friction machine FT-2 (Microtestmachines Co.), which operates according to the "Finger-Disk" scheme by dry friction of three spherical samples $D = 1,5$ mm on a flat surface of the disk (counter body), made of steel and polished on a flat surfaces using abrasive paper or grinding paste to the average arithmetic deviation of the surface profile $Ra = 0,1-0,3$ μm. The tests were carried out at a normal load from 20 H to 100 H and a linear slide speed of 0,1-0,5 m/s. The tribotechnical characteristics for a "diamond-coating" pair were determined on the device J&L TEX.

Research results

The requirement of increased strength of mechanical components, which are used in heavily-grooved conditions and at high slip velocity led to the creation of materials for coatings with high hardness to ensure greater wear resistance of modified bodies [3]. Due to the high tribotechnical characteristics of carbon-based coating, widespread use for modifying products used in mechanical engineering: bearings, gears, sleeves and other components of transmissions, machines, automotive units [4]. According to classical representations, there are two main types of carbon coating: diamond-like carbon [5] and ceramic coatings [6]. Ceramic materials with high hardness and Jung modules as coatings for steel parts are widely used to ensure resistance to abrasive wear. Coatings on the basis of diamond-like carbon (DLC), on the other hand, provide low coefficients of friction, as well as high wear resistance by friction in a pair with steel counter bodies [7]. Typically, the friction coefficient values of DLC are in the range from 0,01 to 0,5, depending on the type of coating and conditions of testing conditions [8].

DLC are usually amorphous, consisting of different phases with sp^2 and sp^3 -hybridized C-C and C-H bonds. In the process of friction, in particular, in the process of sliding, local or general heating of the rubbing body with a coating occurs, as a result of which sp^2 -hybridized carbon bonds can form a graphite-like tribolayer, which can reduce and/or stabilize the process of friction of the contacting bodies. In case of inobservance of technological regimes of the DLC coatings precipitation in the coating structure the formation of cracks and delamination of coatings from the substrate can be observed due to the presence of high internal stresses in the coating [9].

Diamond-like coatings (DLC) containing hydrogen in their structure are thermally unstable and can be transformed into graphite when heated over 300°C. This process of the complete transition of the DLC to graphite in air occurs at a temperature of 450–600°C [9].

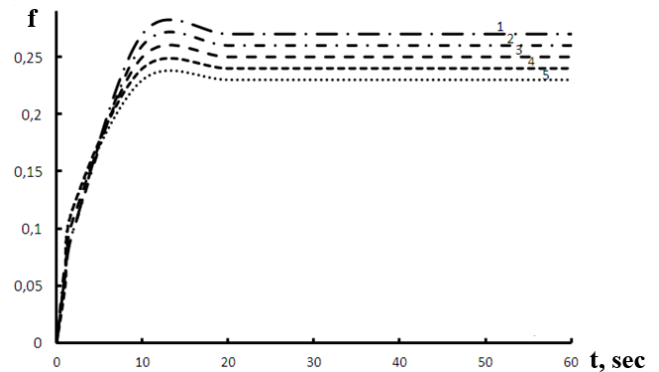
To increase the thermal, tribotechnical characteristics, various non-metallic materials such as: silicon (Si), fluorine (F), nitrogen (N), as well as metals chrome (Cr), titanium (Ti) and tungsten (W) are introduced into the DLC. The introduction of non-metallic materials improves the mechanical properties of the coating (N, Si). Thus, the introduction of fluorine into the structure of the coating allows to change the surface energy [10].

The introduction of metals in the DLC leads to the formation of nanocrystals, usually carbides of metal. These formations are statistically distributed over the volume of the coating matrix. Uniform distribution over the volume of the coating and low-dimensional geometric characteristics of the formations significantly reduces the internal residual stresses in the coating.

Conducted research show that a perspective direction for modifying diamond-like coatings may be a hybrid technology consisting in the preliminary modification of the steel substrate in a cryogenic medium, the

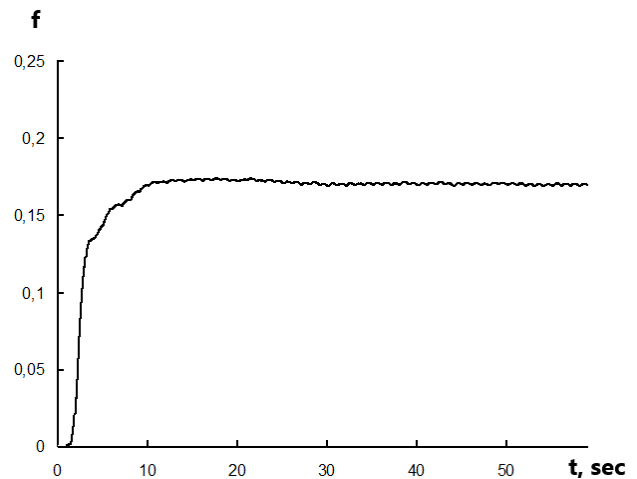
formation of a diamond-like coating and the subsequent processing of this system at a low temperature.

The studies show the change in the tribological characteristics of the DLC of coatings formed according to this technology (Figures 1–5).



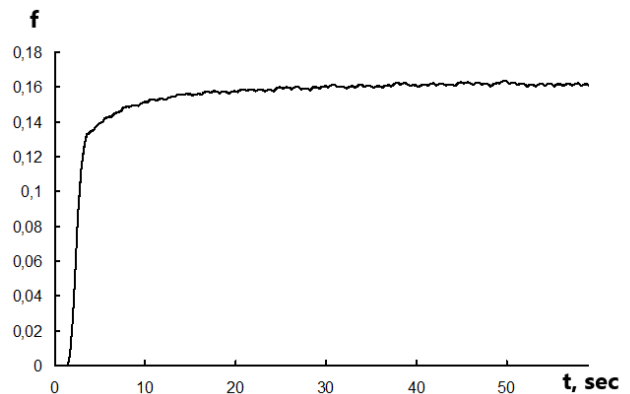
The substrate of steel H11 was subjected to pretreatment in liquid nitrogen: 1 – source substrate; 2 – during 60 min; 3 – during 180 min; 4 – during 1440 min; 5 – during 4320 min. $V = 0.1$ m/s, load 30 H, counterbody – steel 52100

Figure 1 – Dependence of the coefficient of friction of the diamond-like coating formed on steel H11 (1–5)



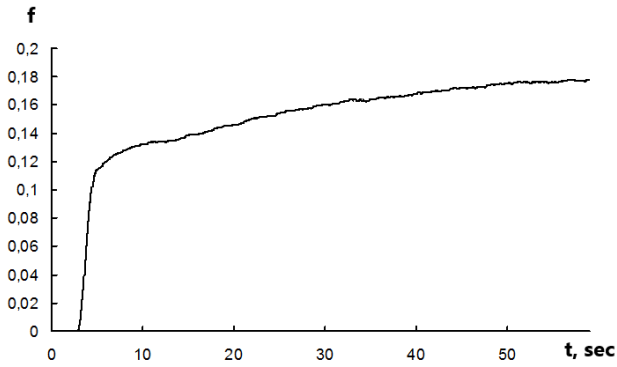
$V = 0,1$ m/s, load 30 H, counterbody – steel 52100

Figure 2 – Dependence of the coefficient of friction of a diamond-like coating formed on steel H11 and subjected to cryogenic processing for 30 minutes



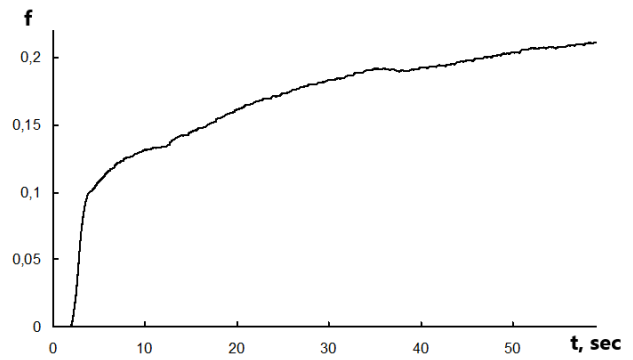
$V = 0,1$ m/s, load 30 H, counterbody – steel 52100. The substrate was subjected to pre-processing in liquid nitrogen for 60 minutes

Figure 3 – Dependence of the coefficient of friction of a diamond-like coating formed on steel H11 and subjected to cryogenic processing for 30 minutes



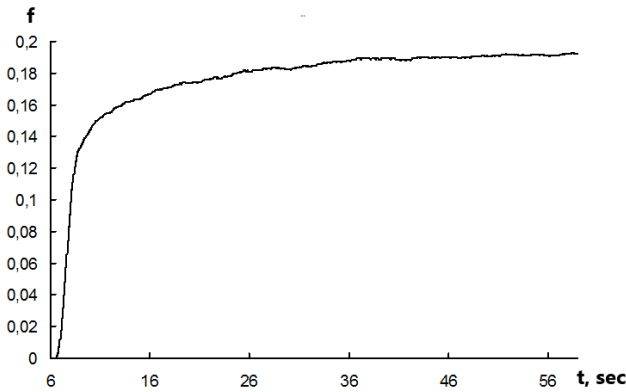
$V = 0,1 \text{ m/s}$, load 30 H, counterbody- steel 52100. The substrate was subjected to pre-processing in liquid nitrogen for 4320 min

Figure 4 – Dependence of the friction coefficient of a diamond-like coating formed on steel H11 and subjected to cryogenic processing for 30 minutes



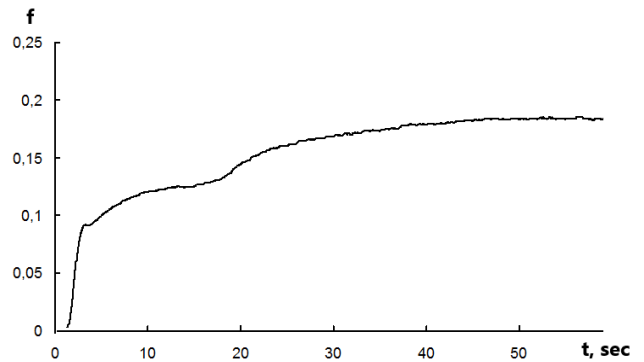
$V = 0,1 \text{ m/s}$, load 30 H, counterbody – Steel H11. The substrate was subjected to pre-treatment in liquid nitrogen for 180 minutes

Figure 7 – Dependence of the coefficient of friction of a diamond-like coating formed on steel 52100 and subjected to cryogenic processing for 60 minutes



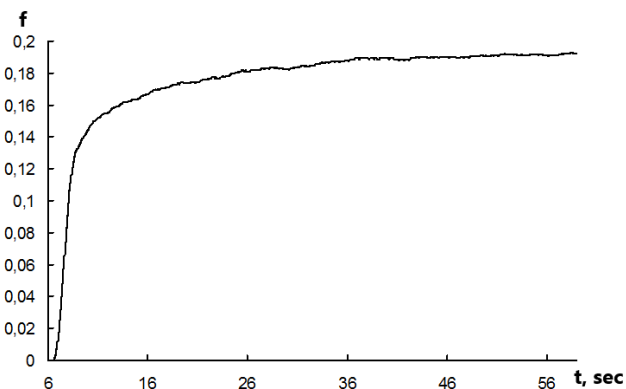
$V = 0,1 \text{ m/s}$, load 30 H, counterbody – steel 52100

Figure 5 – Dependence of the coefficient of friction of the diamond-like coating formed on the steel H11 and subjected to cryogenic processing to 60 minutes



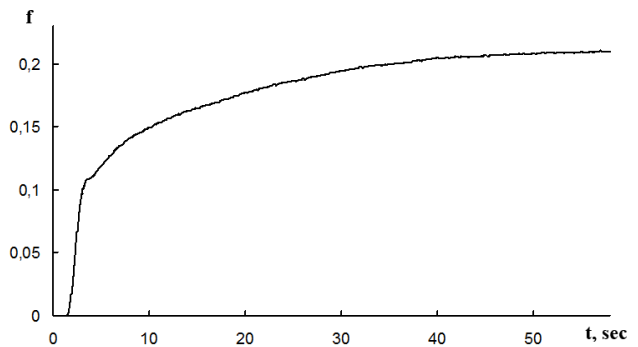
$V = 0,1 \text{ m/s}$, load 30 H, counterbody – Steel 52100. The substrate was subjected to pretreatment in liquid nitrogen for 1440 minutes

Figure 8 – Dependence of the coefficient of friction of the diamond-like coating formed on steel H11 and subjected to cryogenic processing to 60 minutes



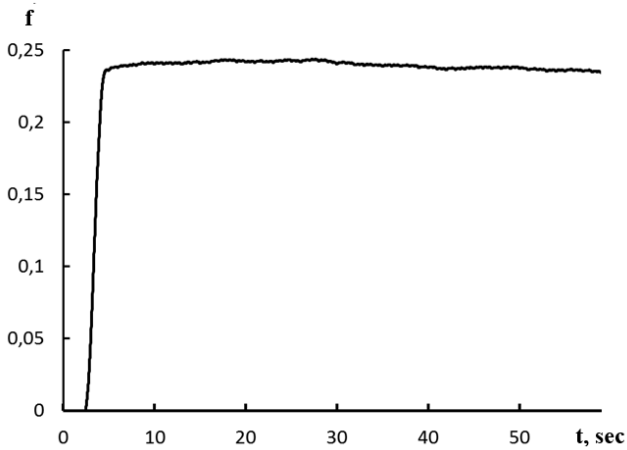
$V = 0,1 \text{ m/s}$, load 30 H, counterbody – Steel 52100. The substrate was subjected to pre-processing in liquid nitrogen for 60 minutes

Figure 6 – Dependence of the coefficient of friction of a diamond-like coating formed on steel H11 and subjected to cryogenic processing for 60 minutes



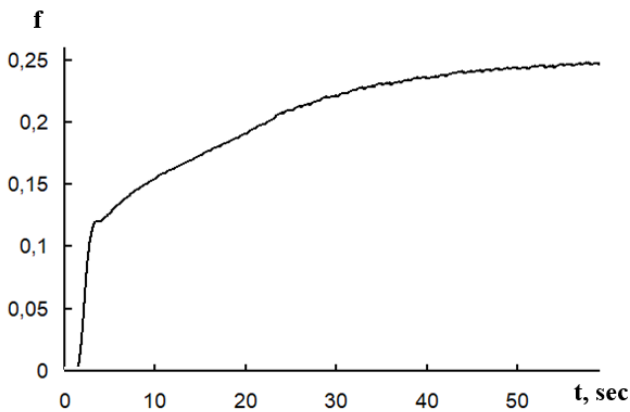
$V = 0,1 \text{ m/s}$, load 30 H, counterbody – Steel 52100. The substrate was subjected to pre-processing in liquid nitrogen for 4320 min

Figure 9 – Dependence of the coefficient of friction of a diamond-like coating formed on steel H11 and subjected to cryogenic processing for 60 minutes



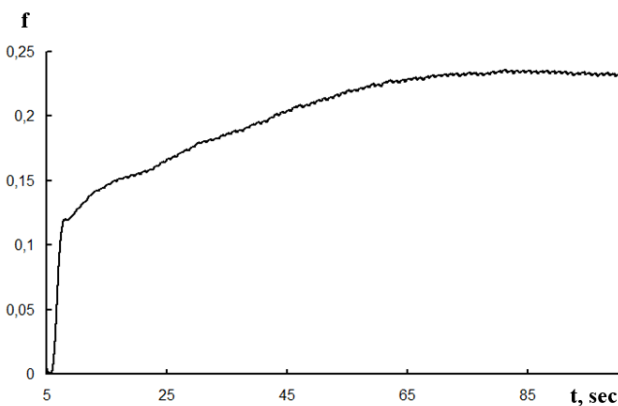
$V = 0,1$ m/s, load 30 H, counterbody – Steel 52100. The substrate was subjected to pre-treatment in liquid nitrogen for 180 minutes

Figure 10 – Dependence of the coefficient of friction of the diamond-like coating formed on steel H11 and subjected to cryogenic processing for 180 minutes



$V = 0,1$ m/s, load 30 H, counterbody – Steel 52100. The substrate was subjected to pretreatment in liquid nitrogen for 1440 minutes

Figure 11 – Dependence of the coefficient of friction of a diamond-like coating formed on steel H11 and subjected to cryogenic processing for 180 minutes



$V = 0,1$ m/s, load 30 H, counterbody – Steel 52100. The substrate was subjected to pre-processing in liquid nitrogen for 4320 min

Figure 12 – Dependence of the coefficient of friction of a diamond-like coating formed on steel H11 and subjected to cryogenic processing for 180 minutes

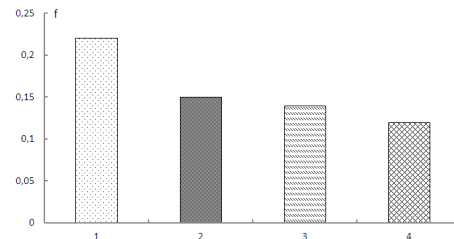
A general tendency associated with the tribotechnical characteristics of diamond-like coatings is the increase in the friction coefficient in hybrid processing for the friction pair "modified diamond-like coating -

Steel 52100". This effect can be explained on the basis of an increase in the SP^3 -hybridization phase, which leads to an increase of the coating hardness and, as a result, increase the friction coefficient for the studied friction pair.

Based on the data obtained, it can be seen that the pretreatment of the steel substrate in the cryogenic medium leads to a certain decrease in the coefficient of friction of the pair "diamond-like coating-steel 52100". The value of reducing the values of the friction coefficient depends on the exposure time in the cryogenic liquid. It is possible to assume the next mechanism of the friction process flowing in the system "diamond-like coating - solid". At the initial stages of contacting the DLC surfaces and solid body, the wear of nanoirregularities of a softer solid body (SS) occurs due to the penetration of nano- and microroughnesses of the diamond-like coating into the surface layers of the SS, as a result of which plastic deformation of the mating surfaces occurs in the low-dimensional range and is accompanied by local plastic deformation, plastic flow of the material occurs in the contact zone. This process leads to an increase in the physicomachanical characteristics of rubbing surfaces. The formation of wear products of solid leads to the closure of microirregularities in surface layers of the counterbody and the beginning of the abrasive wear. This process is intensified as the temperature and friction force increases in the contact zone. At the same time, carbon diffusion occurs in the near-surface metal layers, there is an alignment of the source relief of the substrate and the formation of nano- and microcracks on it. Diffusion of carbon in the counterbody, the formation of carbon-containing friction products in the contact area leads to a decrease in the friction coefficient.

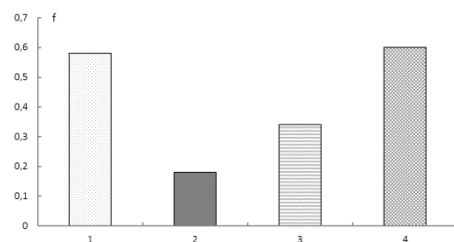
Pre-treatment of substrate at low temperatures and then the subsequent treatment at cryogenic temperatures leads to an increase in the microhardness of diamond-like coatings, and then, as a result, to the intensification of the above-described processes occurring during the friction of the modified DLC, which ultimately affects the increase in the wear resistance of coatings and reducing the friction coefficient. However, tribotechnical characteristics depend on the processing technology. An increase in carbon diffusion in the steel substrate leads to stabilization of friction force, smoothing the surface layers of both the DLC and the counterbody, which leads to a significant reduction in wear intensity. The lowest coefficient of friction is possessed by diamond-like coatings formed on a steel substrate pretreated in a cryogenic medium for 60 min, followed by treatment of the formed DLC in liquid nitrogen for 30 min.

The similar nature of the friction of the DLC, formed on a hybrid technology, is characteristic of the friction pair of "DLC-diamond" (Figures 13–18).



1 – initial steel; Steel is treated in a cryogenic medium for 60 min (2), 180 min (3), 4320 min (4). The friction coefficient was determined at the time of complete destruction of the diamond-like coating

Figure 13 – Dependence of the coefficient of friction of diamond-like coatings (a pair of friction "DLC-diamond") formed on the H11 steel substrate on the time of activation of the substrate in the cryogenic medium



1 – initial steel; Steel is treated in a cryogenic medium for 60 min (2), 180 min (3), 4320 min (4). The friction coefficient was determined with the load on the indenter 20 H

Figure 14 – The dependence of the coefficient of friction of diamond-like coatings (the pair of friction "DLC -diamond") formed on the H11 steel substrate on the activation time of the substrate in the cryogenic medium

Conclusions

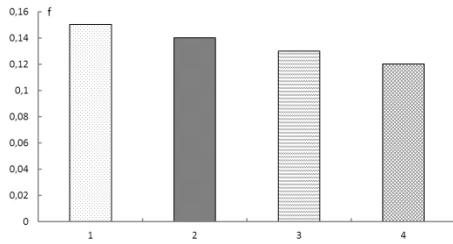
Conducting additional cryogenic processing of the "DLC- activated substrate" system affects the internal stresses in the coating structure. Taking into account the fact that the diamond-like coatings themselves are metastable systems with high internal stresses in the region 1–2 GPa, additional increase in the internal voltages values of the order of 80–500 MPa in the system "DLC – activated substrate" should result in further increase in the dispersion of structural components diamond-like coating and, as a result, to an increase in the physicomechanical characteristics of coatings (microhardness, adhesion strength).

Conducting hybrid treatment of diamond-like coatings leads to a decrease in the values of the friction coefficient and a decrease in the intensity of wear in the friction pairs "DLC – steel", "DLC-modified steel substrate".

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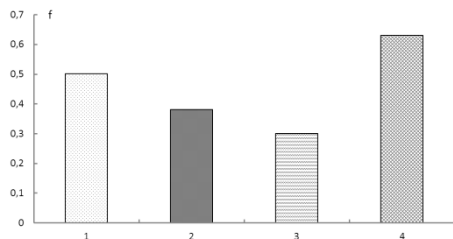
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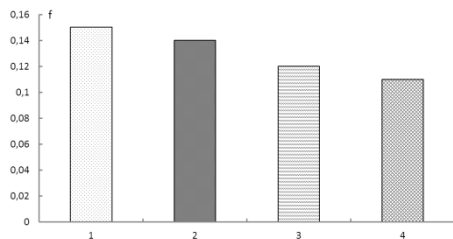
The coating was formed on the H11 steel substrate, which was activated in the cryogenic medium. 1 – initial steel; Steel is treated in a cryogenic medium for 60 min (2), 180 min (3), 4320 min (4). The friction coefficient was determined at the time of complete destruction of the diamond-like coating

Figure 15 – Dependence of the coefficient of friction of a diamond-like coating formed on H11 steel and cryogenic processing for 30 minutes, counterbody-diamond



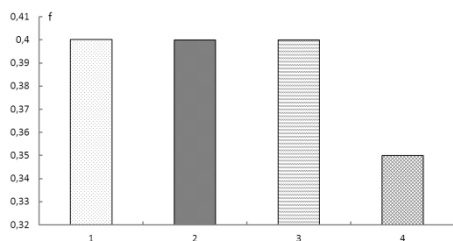
The coating was formed on the 4x5mfs steel substrate, which was activated in the cryogenic medium. 1 – initial steel; Steel is treated in a cryogenic medium for 60 min (2), 180 min (3), 4320 min (4). The friction coefficient was determined with the load on the indenter 20

Figure 16 – The dependence of the coefficient of friction of a diamond-like coating formed on H11 steel and cryogenic processing for 30 minutes, counterbody-diamond



The coating was formed on the H11 steel substrate, which was activated in the cryogenic medium. 1 – initial steel; Steel is treated in a cryogenic medium for 60 min (2), 180 min (3), 1440 min (4). The friction coefficient was determined at the time of complete destruction of the diamond-like coating

Figure 17 – Dependence of the coefficient of friction of a diamond-like coating formed on H11 steel and cryogenic processing for 60 minutes, counterbody-diamond



The coating was formed on the H11 steel substrate, which was activated in the cryogenic medium. 1 – initial steel; Steel is treated in a cryogenic medium for 60 min (2), 180 min (3), 1440 min (4). The friction coefficient was determined with the load on the indenter 20 H

Figure 18 – Dependence of the coefficient of friction of a diamond-like coating formed on steel H11 and cryogenic processing for 30 minutes, counter body-diamond