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PHYSICS OF RADIATION AND ION-PLASMA TECHNOLOGIES

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OPTIMIZATION OF DIAMOND-LIKE CARBON COATINGS FOR MECHANICAL AND TRIBOLOGICAL APPLICATIONS. REVIEW

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Diamond-like carbon (DLC) coatings are used to improve the quality of industrial products due to a wide range of exceptional physical, mechanical and tribological properties. Problems that limit the scope of application of hard non-hydrogenated DLC coatings with properties closest to those of diamond are considered. The scientific literature is reviewed devoted to improving the characteristics of DLC-based wear-resistant coatings. The approaches currently used to reduce internal compressive stresses, improve adhesion to the substrate, and increase the strength of coatings are analyzed. Aspects of optimization of deposition parameters, doping, constructing the gradient and multilayer structure are considered. Based on the generalization of the results of the reviewed publications, a conclusion is made about the advantages of using coatings with a multilayer structure. A promising design undoped multilayer DLC coatings with high protective properties is discussed.

INTRODUCTION

Among the various types of diamond-like carbon (DLC), an attractive material for protective and functional coatings is tetrahedral amorphous carbon (ta-C), which exhibits unique physical and mechanical properties similar to diamond. High hardness, excellent wear resistance, low coefficient of friction, corrosion resistance, biocompatibility make such coatings an indispensable material for various applications in metalworking, mechanical engineering, aerospace industry, medicine, micromechanics and other fields. The continuous increase in requirements for the properties of materials used in increasingly harsh conditions, such as high loads and temperatures, requires the development of new types of coatings with improved characteristics.

One of the important restraining factors on the way to expand the areas of use DLC is the problem of insufficient adhesion of thick ($\geq 0.5 \mu\text{m}$) coatings. The low adhesion of hard coatings is associated with a high level of internal mechanical stresses, which do not allow to build up their thickness more than a few hundred nanometers, which is too small for many technical needs. In addition, hard surfaces may be too brittle to provide sufficient strength. Currently, various methods have been developed that allow obtaining thick DLC-based coatings with an optimal combination of hardness, strength, wear resistance and tribological characteristics: application of transitional and gradient layers; alloying of coating material; formation of nanoscale multilayer and composite structures.

This review presents the results of research on ways to improve the performance of mainly undoped DLC coatings for mechanical and tribological applications at high loads. In the presented material, attention is mainly focused on information about the synthesis and properties of coatings based on DLC, which are obtained by methods of magnetron sputtering and vacuum-arc deposition.

1. CURRENT TRENDS IN THE CREATION OF HARD WEAR-RESISTANT COATINGS

An important problem of modern materials science is obtaining materials with increased strength characteristics, that is, high ability to resist destruction and irreversible change of shape under the action of external loads. Most materials work under conditions of wear, cavitation, cyclic loads, corrosion at cryogenic or high temperatures, in which the maximum loads occur in the surface layers, where the main stress concentrators are located. The condition and properties of the surface layer largely determine the operational characteristics of the products as a whole. Therefore, applying protective, strengthening and wear-resistant coatings to cutting tools, parts, technological equipment units, machine-building and instrument-building products is an effective way to improve their physical and mechanical characteristics, performance and service life. Protective coatings with a thickness of several to tens of microns are widely used in various industries. The most common among hard materials for them are ceramics based on nitrides, carbides, borides, oxides, silicides of transition metals, as well as DLC. Traditional methods of applying such coatings are varieties of Chemical Vapor Deposition (CVD) and Physical Vapor Deposition (PVD) [1–3].

Every year, the requirements for protective properties become stricter, which requires the search for new types of coatings and the improvement of their application methods. In traditional ceramic systems, the most common approach to the creation of new hard coatings in the last decade is related to reduction of crystal grain sizes and formation of nanocomposites and nanolayered structures. Among nanostructured coatings for surface strengthening, considerable attention is paid to multicomponent coatings, which combine compounds with metallic and covalent types of bonds. A nanocomposite structure can consist of nanocrystalline

(*nc*-) grains of hard nitrides, carbides, borides or silicides of transition metals surrounded by an amorphous matrix (a typical and well-studied representative is the *nc*-TiN/Si₃N₄ coating). The limited solubility of components in such systems makes it possible to form coatings under non-equilibrium deposition conditions that not only possess increased hardness, but also demonstrate high temporal and thermal stability of structure and properties [4–7]. Another trend in the development of new protective coatings is attempts to combine the best properties of various systems by further increasing the number of components. It should be noted that amorphous carbon is also used for the synthesis of numerous hard coatings, including as a component of multicomponent nanocomposite and nanolayered structures. The research results indicate the possibility of obtaining multi-component protective coatings with radically improved functional properties due to the formation of a nanostructured state.

Usually, to characterize the material's ability to resist wear, the value of hardness (H) is involved, and to characterize the resistance to elastic deformations without destruction, the value of Young's modulus (E) should be taken into account. As a rule, materials with high hardness and rigidity possess high wear resistance. Diamond, whose properties are due to an electronic structure that ensures strong covalent interatomic bonding, is a prime example, with its highest known hardness and exceptional wear resistance [8, 9]. Many researchers have been trying to obtain nanostructured coatings with maximum hardness for a number of years, however, it has now become especially clear that high-quality wear-resistant coatings require a combination of strength, hardness and the ability to recover. Hardness and elasticity are of equal importance for increasing wear resistance, especially in complex processes associated with shock loading and erosion. An important feature of hard coatings is that materials with

high hardness can significantly differ in values of the modulus of elasticity [4, 7, 10]. The development of nanoindentation devices and techniques currently allows for fairly accurate measurement of these characteristics even for thin coatings, minimizing the effect of the substrate on the results [11–13]. The combination of high hardness and low modulus of elasticity is considered optimal [4, 10].

Recently, the H/E plasticity index has been considered as a quantitative characteristic of the mechanical properties of nanostructured coatings. The H/E ratio is used to characterize the material's resistance to elastic fracture deformation (resistance to brittle fracture). It is believed that the higher the H/E ratio, the better the strength and wear resistance of the coating. Coarse-crystalline materials are characterized by values of H/E < 0.04. For nanostructured coatings, the H/E values are in the range of 0.06...0.1, which indicates their better stability. A hard coating with a low modulus buckles under load and then recovers, instead of fracturing [4, 10].

In this sense, DLC coatings exhibit unique characteristics. Differences in the DLC structure of different types lead to a significant difference in hardness and modulus of elasticity [14–20]. The plasticity index H/E for DLC is extremely high (0.08...0.21) compared to steels and ceramics. This means that DLC possess a relatively high deformation tolerance. The variety of values can be seen in Table. In more detail, the types of DLC coatings will be considered in section 2.1.

Another factor important for high wear resistance of coatings is the coefficient of friction. A low coefficient of friction can effectively reduce the contact temperature during dry sliding and thus has a huge potential to reduce the thermal load on the coating and substrate material. In addition, components with such a coating ensure high energy efficiency by reducing frictional losses.

Classification of DLC coatings and their characteristics [14–17]

Type of coating	DLC coating				Graphite	Diamond
	a-C	a-C:H	ta-C	ta-C:H		
Method of deposition	PVD	CVD, PVD + CVD	PVD	PVD, CVD, PVD + CVD	–	–
Deposition temperature, °C	RT–200	RT–500	RT–300	RT–500	–	–
sp ³ , %	5...50	10...60	50...90	40...70	0	100
Hydrogen, at.%	<5%	5...60	<5%	5...50	0	0
Density, g/cm ³	1.4...2.2	1.2...2.0	2.5...3.2	2.0...2.6	2.267	3.515
Hardness H, GPa	9...25	5...25	25...90	9...60	0.2...2	100
Young's modulus E, GPa	100...400	100...300	200...900	120...300	10	1000
H/E	0.08...0.1	0.1...0.16	0.1...0.2	0.16...0.21	–	–
Coefficient of friction (low humidity <5%)	0.3...0.8	0.003...0.3	0.4...0.8	0.08...0.2	0.01	0.1
Coefficient of friction (high humidity >5%)	0.1...0.2	0.02...0.5	0.08...0.12	–	–	–
Coefficient of friction (in water)	0.04...0.1	0.01...0.7	0.03...0.07	–	–	–
Wear resistance relative to steel (low humidity)	C	B÷A	A	B–A	–	–
Corrosion resistance	x–C	B	B–A	C–B	–	–

A – Excellent; B – Good; C – Somewhat poor; x – Poor.

Much effort has been devoted to the development of protective layers with a low coefficient of friction capable of acting as solid lubricants in order to replace the commonly used expensive and dangerous cooling lubricants, or in conditions where the use of lubricants is not possible. The application of coatings is especially important for high-speed and dry cutting, processing of non-ferrous metals, hard materials and wood, as well as in friction pairs operating at high loads [21, 22].

In Fig. 1. the classification of various hard coatings according to their hardness and friction characteristics is given, from which it follows that most carbon films are able to provide not only high hardness, but also low friction. In particular, DLC films appear to provide the widest range of hardness and friction values, while some of the more recently developed nanocomposite coatings (based on ceramics) are ultrahard but unable to provide lubrication or low friction [23].

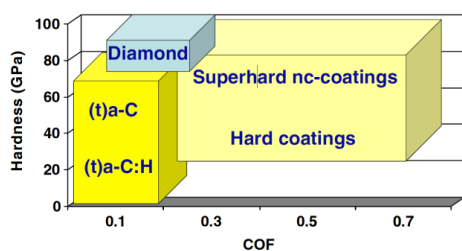


Fig. 1. A schematic representation of hardness and coefficients of friction (COF) of carbon-based and other hard coatings [23]

Thus, amorphous carbon remains a relevant material for creating wear-resistant coatings, as it allows to adapt them to a wide range of applications, including in heavy and difficult operating conditions. Hard DLC coatings are suitable for improving the performance of many types of products. However, achieving this improvement requires choosing the appropriate type of carbon coating and optimizing its characteristics.

2. STRUCTURE, SYNTHESIS AND MECHANICAL PROPERTIES OF DLC COATINGS

2.1. STRUCTURE AND CLASSIFICATION

Carbon is a unique material due to the variety of allotropic modifications, which are characterized by different types and spatial orientation of chemical bonds (sp^3 , sp^2 , sp^1 types of hybridization). In addition to the well-known crystalline diamond (sp^3), graphite (sp^2), and carbene (sp^1), there are also various amorphous forms with a predominant amount of one or another type of hybridization [8, 9, 14, 15]. In graphite, carbon atoms have hybridization of the sp^2 type, in which three of the four valence electrons are involved. This type of hybridization leads to trigonal coordination of atoms, which form a flat hexagonal grid with strong covalent bonds – a graphene sheet. The electrons of the carbon atoms that remained unhybridized connect the graphene sheets together. Thus, graphite crystals consist of graphene layers connected only by weak van der Waals bonds. Graphite is a soft material. The layered structure is the reason for its ability to wear layer by layer. Weak interlayer connections can be destroyed by small

external mechanical forces, so graphite is often used as a dry lubricant for friction units [8, 9].

Unlike graphite, for a wear-resistant coating, diamond has more desirable mechanical properties, such as high values of atomic density, hardness and Young's modulus. This is due to the four covalent bonds that connect each carbon atom to its nearest neighbor, forming a tetrahedral coordination that has high bond energy in all directions. The tetrahedral environment of carbon atoms in diamond is arranged due to hybridization of the sp^3 type, in which all four valence electrons are involved [8, 9].

DLC is a collective term for a wide range of amorphous carbon coatings, including those containing bonded hydrogen (hydrogenated). The term “diamond-like” emphasizes a set of properties similar to diamond and, at the same time, implies the lack of order of crystalline diamond [14, 15]. According to the two-phase model, films of amorphous carbon consist of two phases embedded in each other. The first phase is diamond-like, having sp^3 -hybridization of carbon atoms. The second phase is graphite-like, consisting of fragments of graphite planes and distorted fragments like fullerenes. The last phase is characterized by sp^2 -hybridization of carbon. The characteristic size of the clusters of each of the phases is several nanometers [24, 25].

Hydrogenated DLCs are formed during deposition in a hydrogen-enriched atmosphere. A hydrogen atom has only one valence electron and preferentially binds to sp^2 sites, turning them into sp^3 sites. The limitation is that hydrogen can only bond to one carbon atom, unlike carbon, which can bond to four other atoms in this hybridization. As a result, the structure of hydrogenated DLC will have fewer strong carbon bonds than if the structure were free of hydrogen [14–16].

Thus, due to the two-phase structure, DLC combines the properties of diamond and graphite, while hydrogenated areas do not contribute to diamond-like properties. The sp^3/sp^2 -bond ratio and hydrogen content are key parameters that determine the physical characteristics of coatings. The ternary phase diagram of amorphous carbon is shown in Fig. 2 [15]. This classification is an updated version of the one summarized by J. Robertson [14]. It shows how hydrogen-free and hydrogenated DLCs are formed, depending on the amount of sp^2 , sp^3 , and hydrogen.

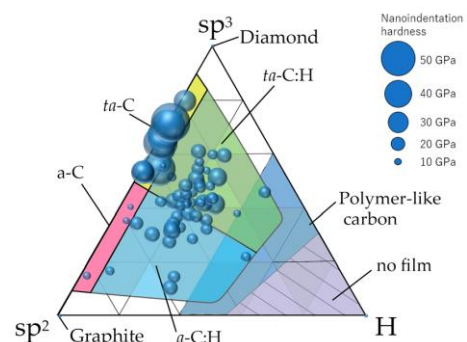


Fig. 2. Ternary phase diagram of carbon materials as a function of hybridization type and hydrogen content [15]

The forms of amorphous carbon with a graphitic structure, such as carbon black, coal, glassy carbon, and graphitic films of amorphous carbon are placed in the lower left corner of the diagram. The area of carbohydrate polymers frames the right lower corner. At the zone near the corner, the coating is not formed. Different technological methods of deposition make it possible to form the coatings of amorphous carbon with a different amount of sp^3 -bonds, as well as the coatings of hydrogenated amorphous carbon, placed in the middle of the phase diagram. In order to distinguish amorphous carbon with a large number of sp^3 -bonds from amorphous carbon with a large number of sp^2 -bonds, the designations ta-C (tetrahedral amorphous carbon) and a-C (amorphous carbon) were introduced, respectively. Variations of the plasma chemical gas phase deposition method allow obtaining hydrogenated amorphous carbon both with a low content of sp^3 -bonds (a-C:H) and with a large content of sp^3 -bonds (ta-C:H). However, the name a-C and a-C:H is often used for amorphous carbon in general, without specifying the amount sp^3 .

Introduction of hydrogen into the coating makes it possible to vary widely the optical, electrical, and

mechanical properties of amorphous carbon films. In addition, doping with other chemical elements also leads to changes in existing properties or even to appearance of new ones. All this leads to a great variety of existing options. The classification of DLC coatings is shown in Fig. 3. All coatings are divided into three large groups according to their chemical composition: unalloyed, alloyed and hybrid.

In undoped DLCs, the carbon atoms are bonded to hydrogen or another carbon atom, and the structure contains no other elements. Unalloyed coatings can be divided into subclasses based on hydrogen content: hydrogenated and hydrogen-free. Further division of each of these subclasses is based on the content of tetrahedral sp^3 -bonds: amorphous DLC (a-C:H, a-C) and tetrahedral amorphous DLC (ta-C:H, ta-C). In doped DLCs, metal or non-metal atoms can be added to the coating. With coatings alloyed with metals, chromium, titanium, molybdenum or tungsten are usually used. As for non-metals, nitrogen, silicon or fluorine are used. By hybrid, we mean DLC coating with a combination of alloyed and non-alloyed layers [26, 27].

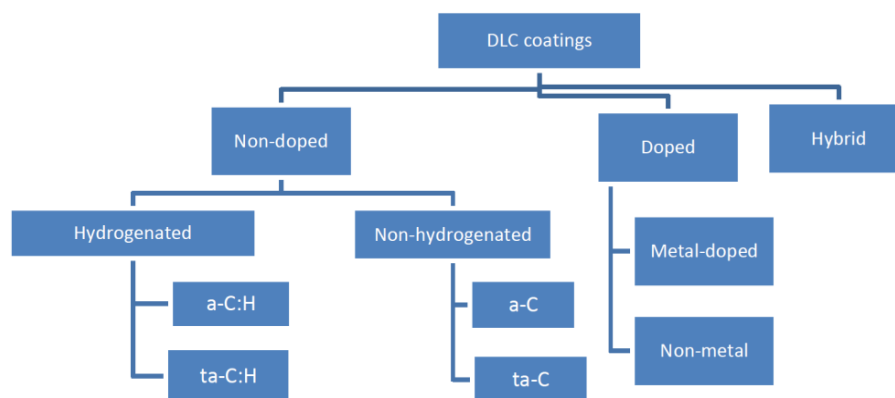


Fig. 3. General classification of types of DLC coatings [26, 27]

2.2. METHODS OF DEPOSITION AND MECHANISM OF FORMATION

A wide range of CVD and PVD thin film deposition methods are suitable for obtaining DLC coatings [14]. Some are suitable for laboratory research, while others are better for industrial production. Plasma Enhanced Chemical Vapor Deposition (PECVD) [28] is mainly used to deposit hydrogenated DLCs. In the PECVD process, the coating on the substrate is formed during chemical reactions activated by an electric discharge in the environment of hydrocarbons (acetylene, methane, benzene, and others). A significant advantage of the method is the possibility of depositing a-C:H on fairly large areas and on objects of complex shape. Filtered vacuum-arc deposition (FCVAD) [29], magnetron sputtering (MS) [30], and to a large extent pulsed laser deposition (PLD) [31] can be attributed to the most common methods of deposition of hydrogen-free DLC coatings. In these methods of physical deposition, a graphite cathode (target) is used as a source of carbon particles.

Different DLC deposition methods share three important characteristics: (i) plasma is used as a source

of active substances, (ii) the substrate is usually at room temperature (at least there is no need to maintain a high temperature of the substrate during the process, as in classical CVD processes), (iii) energetic particles (ions and/or neutrals) participate in the deposition process [32]. The latter is due to the fact that the formation of sp^3 -bonds is effective in the field of thermodynamic stability of diamond (high pressure and temperature), which is ensured due to radiation-stimulated processes associated with ion bombardment of the growth surface of the coating [33, 34]. C^+ ion energies of about 100 eV are required to achieve the highest sp^3/sp^2 ratio. Initially, the main factor increasing the sp^3 content was considered to be the preferential sputtering of sp^2 sites during DLC film growth [35]. Later, they discovered the formation of DLC under the surface of the film. The so-called subplantation model considers the progressive densification of DLC in the subsurface layer, which is associated with the formation of sp^3 metastable regions due to the penetration of energetic ions [36, 37]. Incoming neutrals and low-energy ions do not penetrate the surface of the coating, but form an outer layer saturated with sp^2 . Thus, the properties of the

synthesized diamond-like material are primarily determined by the ion energy, which is controlled by a negative bias potential on the substrate. The higher the degree of ionization of carbon plasma, the greater is the part of carbon ions with increased energy that are deposited on the substrate and form a coating with the maximum content of sp^3 -bonds. In this regard, the use of filtered cathode vacuum-arc plasma, the degree of ionization of which is almost 100%, is one of the most common industrial methods of deposition of hydrogen-free ta-C thin films, which have the best characteristics [29, 38]. In addition to being able to generate a stream of highly ionized carbon plasma efficiently enough, the vacuum-arc method has advantages over other methods in terms of the deposition rate of ta-C condensate, its adhesion to the substrate, and hardness. The use of modern high-performance plasma filters allows you to avoid the problem of the presence of coarse defects in the form of graphite macroparticles, products of graphite cathode erosion in the arc discharge process, in vacuum-arc coatings. The principle of operation of the filters is based on the separation of charged (ions, electrons) and neutral (droplets, macroparticles, atoms) components of the plasma generated by the cathode in the plasma-optical system [39].

The method of MS is free from the problem of macroparticles, however, the degree of ionization of the carbon flow is much lower than that of vacuum-arc plasma, even when using high-power impulse magnetron sputtering (HIPIMS) [40]. In addition, during MS, bombardment of the surface of the growing carbon film with inert working gas ions, which not only affect the sp^3 content, but can also be implanted into the film [41, 42], which worsens its characteristics, has a significant impact.

Magnetolectric filters are the most radical means of eliminating the droplet fraction in vacuum-arc coatings, but the higher the desired degree of purification, the smaller the output ion current of the filter, and therefore the lower the deposition rate. At the same time, in many practical cases, there is no need for ultrapurification of plasma. Creating conditions that limit the size of the macroparticles in the plasma flow may be sufficient to make the film suitable for practical use. For example, in wear-resistant anti-friction coatings on the working parts of friction surfaces and tools, the presence of particles with a size of no more than 1 μm is quite acceptable. In this regard, alternative methods of limiting the size of macroparticles are of considerable practical interest, which, although they do not provide ideal plasma cleaning, but are simpler and cheaper compared to methods that require the use of filters. One of the ways to reduce the emission of macroparticles of increased size is to reduce the time the cathode spot stays in one place, which is achieved in a pulsed arc [43, 44]. The DC vacuum arc method with superimposed high current pulses also gives good results [45, 46].

The mechanism that contributes to the formation of sp^3 -bonds is related to the shallow implantation of low-energy carbon ions (25...500 eV) [14]. Fig. 4 shows the dependence of the sp^3 fraction on the ion energy for ta-C. With increasing ion energy, the sp^3 content first sharply increases, reaching a maximum in the range of

100...140 eV, and then gradually decreases [47]. Such a course of dependence was qualitatively explained in terms of the balance between implantation and relaxation, which is described by the model of thermal peaks. The same model is used to describe the formation of compressive stresses in coatings [48...50]. Ion bombardment is a non-equilibrium process that is not identical to conventional heating, because the kinetic energy of the bombarding ions is transferred to a local region and is accompanied by excessively fast cooling at a rate of about 10^{13} ... 10^{14} K/s. Near the trajectory of the ion in the substance, a region of high thermal energy density is formed, a thermal peak, that exists for a short period of time ($\sim 10^{-13}$... 10^{-12} s). This provides conditions for atomic rearrangement in the superheated collision zone, resulting in changes in the structure and internal stresses in the coatings. Estimates show that with instantaneous heating to 3000...4000 K, the pressure in the zone can reach 10 GPa, which exceeds the static pressure required for diamond synthesis. It is the presence of high compressive stresses that makes it energetically advantageous to rearrange sp^2 -bonds into sp^3 , which leads to the formation of dense ta-C. When the average energy of the ions increases above 100 eV, in the thermal peaks conditions arise capable of ensuring the relaxation of the compacted region to a more stable sp^2 state, which determines the non-monotonic dependence of the content of the sp^3 fraction on the energy of the ions. Similarly, the hardness, density and level of residual compressive stresses in the coatings change, as there is a linear correlation between these parameters and the sp^3 fraction [14].

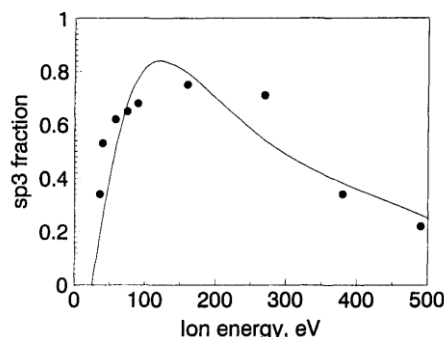


Fig. 4. Dependence of the sp^3 fraction on energy of carbon ions for DLC films [47]

2.3. MECHANICAL PROPERTIES

A feature of the properties of diamond-like coating is a strong dependence on the deposition method and conditions. As an illustration, Table shows the typical mechanical characteristics of different categories of DLC coatings summarized according to the data of review works [14–17], as well as data for diamond and graphite. Characteristic values of the percentage of sp^3 -bonded carbon, hydrogen content, approximate density, hardness and Young's modulus, coefficients of friction in wet and dry atmospheres, the degree of wear resistance relative to steel and corrosion resistance are shown for the coatings. Hydrogen-free ta-C coatings have properties closest to diamond. At the content of sp^3 -bonds of 80...90%, the coatings possess density close to that of diamond, 3.1...3.2 g/cm^3 , and their

hardness can reach 90 GPa. They are characterized by high resistance to corrosion and wear. The coefficient of friction of such coatings at humidity >5% is in the range of 0.08...0.12, however, in dry conditions it increases several times [15, 17]. Hydrogenated coatings are softer and less dense, and their advantage is lower values of friction coefficients compared to hydrogen-free ones, in particular in vacuum, dry air and inert gases [16].

The frictional behavior of DLC is controlled by a number of factors, both internal (composition, structure, roughness, configuration of carbon atoms) and external (environment, sliding speed, type of movement, applied load, counterbody material). J. Fontaine and others [51] consider coating friction as a result of a combination of adhesion, abrasive and shear mechanisms. The strongest adhesive interactions for DLC coatings result from the covalent bonds that form between the contacting surfaces. The abrasive contribution is caused by the mechanical interaction of surface irregularities. The shear component of friction is associated with the formation of an interphase transfer layer during sliding. A transition layer with low shear strength is responsible for low friction coefficients. Each of these mechanisms is sensitive to the hydrogen content in the coating, and depending on the test conditions becomes decisive.

DLC differs from graphite, which is used as a solid lubricant, by the mechanism of displacement during friction. Because DLC is amorphous, it cannot undergo the same type of volumetric shear as graphite, whose lubricity is provided by the shear deformation of the slip planes. Instead of shear planes, DLC films shear across the interface between the opposing surface material and the coating. Under the effect of friction in DLC graphitization occurs in the contact zone, localized in so-called hot spots with a high contact temperature, which leads to low friction due to the formation of a thin tribolayer [16].

The increase in the coefficient of friction in a vacuum or dry environment for hydrogen-free coatings is due to the increase in the contribution of the adhesion mechanism. Absence of hydrogen in the structure makes it impossible to passivate the surface of the coating, which is characteristic of hydrogenated coatings. In the event that hydrogen is present in the structure or in the external environment, hydrogen atoms bind to carbon atoms in the film, which limits the number of areas where covalent bonds can be formed between the contacting surfaces, that is, adhesion between the mating surface and the tested sample is low. This leads to very low values of the coefficient of friction. However, the further expansion of the areas of practical use of hydrogenated coatings is mainly hindered by their relatively low hardness (not more than 40 GPa) and low thermal stability (not higher than 400 °C). The transformation of DLC to its more stable graphite structure can begin at a temperature of about 250 °C, which leads to a decrease in the hardness of the coating. The formation of graphite is facilitated by the loss of hydrogen, which is responsible for the stabilization of sp^3 -bonds [16].

As for protective and wear-resistant coating, structural stability, hardness and wear resistance may be more important factors than a low coefficient of friction.

High wear resistance is ensured both by the formation of nano-sized tribolayers on the contacted surfaces, which dampen external stresses, prevent degradation of the base material and provide a minimum coefficient of friction, and by increasing the stability and hardness of the surface layer itself [16]. Such requirements under significant loads in mechanical and tribological applications are best met by solid hydrogen-free ta-C coatings, especially in active environments or in lubrication conditions.

Let us consider in more detail the influence of deposition parameters on the characteristics of ta-C coatings. For the synthesis of films with properties close to diamond, it is necessary to maximize the sp^3 content, which is a function of the bias potential and substrate temperature. Many works show that the accelerating potential of the substrate is the most important factor that determines the sp^3/sp^2 ratio, as well as the mechanical, electrical, and optical properties of ta-C films [14, 52–65]. Fig. 5,a shows the dependences of the sp^3 content and compressive stresses of ta-C films on the substrate potential obtained in [65]. The coatings were deposited by the FCVAD method at room temperature using an S-shaped magnetic filter. With increase in the potential from 20 to 350 V, the sp^3 content varied non-monotonically from 84 to 88%, and the stress level from 6 to 11 GPa. The curves with maxima near 90 V have a general appearance similar to the dependence of the sp^3 content on the ion energy shown in Fig. 4.

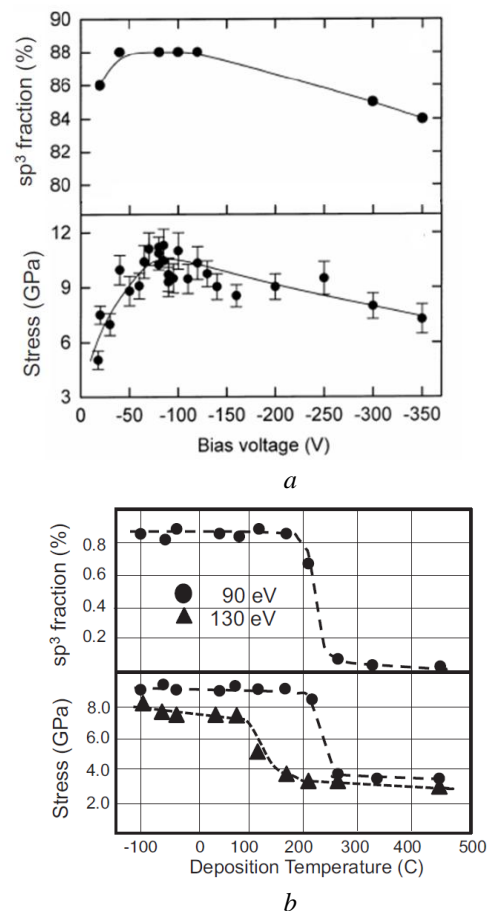


Fig. 5. Dependence of the sp^3 content and compressive stresses of the ta-C coatings obtained by the FVAD method as a function of the substrate bias potential (a) and temperature (b) of the substrate [57, 65]

Indeed, vacuum-arc carbon plasma contains mainly singly charged ions with the most likely energy of about 25 eV, which are then accelerated to the substrate surface in the field of a bias potential. However, it should be taken into account that the use of filters leads to a change in the characteristics of the plasma flows from which coating is formed on the substrate, in particular, to a shift in the energy distribution function of ions [38, 39]. That is why the value of the substrate potential corresponding to the maximum content of sp^3 -hybridized bonds and their quantity are parameters that have certain values not only for each deposition method, but also depend on the features of the equipment, in particular, they differ for different filtration systems. Similar non-monotonic dependences on the substrate potential were obtained when using curvilinear filters of different designs [54–59], however, the positions of the maxima were slightly different. The maximum sp^3 content could be achieved at DC potential values from 50 to 200 V, depending on the features of the equipment. The authors of [53] did not observe the maximum, as it was outside the scope of the research – the sp^3 content monotonically decreased from 60 to 36% when the potential increased from 50 to 350 V. For DLC magnetron films, the effect of the potential is not so significant, which is quite expected. In work [30], for the MS method, different sp^3/sp^2 ratios were obtained by changing the bias potential from 175 to 300 V. As the potential increased, the sp^3/sp^2 ratio increased in the range from 0.74 to 0.98, which corresponds to an increase in the sp^3 content from 40 to 50%.

As already mentioned, there is another important factor affecting the sp^3 content – growth temperature. It is known that it is necessary to ensure a deposition temperature below 120 °C in order to obtain energy dependences with a maximum like in Fig. 5,a [66]. Fig. 5,b shows the sp^3 content and residual stress level for carbon FCVAD coatings as a function of substrate temperature during deposition at certain ion energy. It can be seen that when a certain temperature is reached in the coating, the diamond-like bonds suddenly disappear and the stresses decrease. The transition temperature in these experiments is about 140 °C with an average energy of carbon ions of 130 eV, and 200 °C for ions with a lower energy of 90 eV [57]. However, the effective ion energy and substrate temperature are often not precisely known. In addition, when choosing the optimal deposition parameters, the effect on the temperature of the deposition rate, ion current, and the angle of incidence of the flow should be taken into account [66, 67]. Thus, the optimum ion energy for maximum sp^3 content discussed above is often not directly applicable to industrial coating equipment, especially when using rotary part mounting systems. In addition, the optimal sets of deposition parameters must be adapted not only to obtain the highest sp^3 content and corresponding hardness, but also to achieve other desired coating properties (adhesion, stress, coefficient of friction, etc.) that are determined by the geometry of the products and their application.

Unfortunately, the correlation between sp^3 content and other mechanical characteristics of coatings is not unambiguous. The hardest coatings are the most

stressed, which can negatively affect their adhesion to the substrate [14]. In addition, the sp^3 content can affect the coating roughness, another surface property that is related to the coefficient of friction and determines the suitability of DLC for tribological applications. It is known that when using highly ionized carbon plasma, the increase in ion energy significantly contributes to the preferential removal of protruding areas due to sputtering, which makes it possible to achieve values of rms surface roughness at the level of 0.05 nm, i.e., almost atomic smoothness of the surface [68].

Sometimes coatings containing more diamond-like bonds show an optimal set of properties. Thus, in [52], an electromagnetic filter of the “blind” type was used to obtain DLC coatings by the FCVAD method. It is shown that the dependence of the content of the sp^3 fraction with an increase in the DC potential from 25 to 200 V has a maximum. The highest content of sp^3 -bonds, about 63%, was measured in the coating deposited at a substrate bias potential of 100 V, which also possess maximum hardness and Young's Modulus of 50 and 371 GPa, respectively, in combination with minimal surface roughness. In addition, the coating synthesized at this bias potential had excellent adhesion-complete peeling of the film occurred at a load of 41 N. On the contrary, in [30] the authors who deposited films by MS method showed that with an increase in the sp^3/sp^2 ratio from 0.74 to 0.98, the adhesion worsened and the critical load decreased from 31 to 18 N. As the sp^3 content increased, the coefficient of friction varied depending on the material of the counterbody due to various mechanisms. In contact with Si_3N_4 , the friction coefficient increased from 0.12 to 0.16 due to the reduction of the effect of the graphite tribolayer on the friction boundary, and in contact with the Ti6Al4V alloy it decreased from 0.32 to 0.13 due to the inhibition of the formation of hard abrasive oxides. However, the wear rate of the DLC films in both cases showed a linearly decreasing correlation with the bias potential on the substrate and not with the sp^3/sp^2 ratio.

As a rule, the analysis of literature data makes it possible to make a fairly reliable comparison of DLC films created by different methods only by some mechanical characteristics, which are determined using the same standardized methods. These include the stress level in DLC coatings, which is usually measured by the degree of curvature of a thin silicon substrate, and the calculations are based on Stoney's formula [69]. With the advent and development of nanoindentation methods, it is quite correct to compare the hardness and Young's modulus of coatings, which are determined based on the Oliver and Pharr method [11].

As for brittleness, fragility of DLC films, one of the methods of their assessment consists in visual observations of the appearance of the coating surface around the place of indentation of a Rockwell spherical indenter or a Vickers or Berkovich pyramid. This method is only partially standardized, that is, it allows only a relative comparison of coatings. Adhesion of hard coatings is measured by scratch testers [70]. In a standard surface scratch test, a spherical Rockwell indenter with a radius of 200 μm is drawn along the surface under a load of 0...100 N, which gradually

increases [71]. The measure of adhesion is the value of the critical load L_c , from which the peeling of the coating within the limits of the scratch track and the destruction of its edges begins. Currently, microscratch testers are also used, in which the Rockwell indenter radius is 25...100 μm , and the load is from units of mN to 30 N, and nanoscratch testers, in which the indenter radius is 1...25 μm , and the load is from 10 μN to several mN [72]. Such a wide range of testing conditions makes it difficult to compare the adhesion of DLC coatings [73], given the dependence of the L_c measurement results on the indenter tip radius [74].

The coefficient of friction and the rate of wear are determined by the results of tests on friction machines of various types, while in fact it is difficult to find at least two publications by independent authors in which the kinematic parameters of the tests, the material of the counter-body and its geometric parameters completely match. In addition, the results of studies of mechanical characteristics are significantly influenced by the thickness of the coatings, as well as the type and method of preparation of the surface of the substrate before their application. The only thing that can be relied on more or less precisely is the comparison of the measurement results within each specific study, which allows to determine the general trends in the change of the deposition parameters, which can ensure the improvement of the mechanical properties of the coatings.

3. PROBLEMS OF USING sp^3 -RICH DLC COATINGS AND GENERAL WAYS TO SOLVE THEM

Thin hard DLC coatings have a wide range of applications in industry. In the automotive industry, DLC is used due to its excellent tribological properties that reduce wear and friction losses [23, 27, 29, 75–77]. The high wear resistance of DLC coatings opens up wide possibilities for their use in the production of measuring instruments, templates, tips of active control, probes, as well as for significantly improving the tribotechnical characteristics of units operating in dry friction conditions, in particular for protection against fretting wear in read and write heads for hard drives. DLC is actively used to strengthen the surface of cutting instruments – from high-speed cutting tools to kitchen knives and razor blades. In some cutting applications, only one surface of the cutting edge is coated. As a result, the blade self-sharpenes as one side wears faster than the other. Positive results were obtained when using tools with DLC coatings for polishing copper, brass, aluminum, steel, hard alloys and superhard materials based on cubic boron nitride. Being chemically inert and biocompatible, DLC has broad potential for biomedical applications, including cardiovascular valves, orthopedic implants, joint endoprostheses, and surgical instruments. In most existing applications, it is sufficient to apply fairly thin coatings from a few to hundreds of nanometers to achieve a positive effect. In all these areas, the search for better technical solutions is ongoing, which are often associated with the need to reduce production and operating costs. Despite the significant progress made

over the past decade in hard coating technology, the many different deposition systems and processes that have been developed introduce additional challenges in terms of coating uniformity, deposition rate, process cost.

A restraining factor on the way to expanding the scope of use of ta-C coatings is the problem of insufficient adhesion of thick ($\geq 0.5 \mu\text{m}$) layers. Low adhesion is largely due to a high level of internal mechanical stresses. As the coating becomes thicker, the deformation energy as a result of residual stresses increases, and the adhesion energy remains unchanged, which inevitably leads to delamination when a certain thickness is reached. This fact does not allow to increase the thickness of coatings more than a few hundred nanometers, which is too small for many technical needs. The main types of damage of DLC coatings include surface deformation, development of cracks, chipping of individual areas, peeling off the coating from the substrate. Critical factors for this can be insufficient strength of the coating itself, insufficient adhesion to the substrate, high internal compressive stresses, mismatch of mechanical properties between the coating and the substrate. This complex situation explains why the number of applications of hard carbon films is still more limited than originally anticipated [23, 27, 29, 75–77].

Searching for opportunities to expand the application of coatings in various areas makes sense to start with the analysis of test results. Optimized wear resistance, for example, is not necessarily achieved using the hardest coating materials, but also depends on the modulus of elasticity, adhesion, chemical and thermal resistance, coefficient of friction and other mechanical properties [77]. The stability of the coating properties during service is important, as the coefficient of friction, hardness and adhesion can deteriorate with temperature. The number of sp^3 -bonds is not the only criterion for the quality of “diamond-like” properties. The best coating material is useless if the coating has insufficient adhesion. However, it is obvious that a better material with strong adhesion will provide better results.

Various techniques can be used to overcome the above-mentioned problems and ensure the synthesis of thick, high-quality DLC coatings. According to the classification given in work [75], such methods can be divided into three large groups: alloying of coatings, creation of multilayer structures, application of transition layers. All techniques commented above and typical structures obtained in this way are presented in Fig. 6. Stress relaxation is possible by alloying (Si, N, P, Cr, Ti, Mo, W, etc.), as well as by annealing or introducing nanometer particles (creation of DLC nanocomposites). But these operations usually reduce the hardness and modulus of elasticity of the coatings. Low stress values are also achieved by alternating hard and soft DLC coating layers. The resulting multilayered structure can provide a reduction in overall stresses with less significant changes in hardness. Multilayer coatings, in which DLC layers alternate with metal, nitride or carbide layers, can also contribute to improving properties.

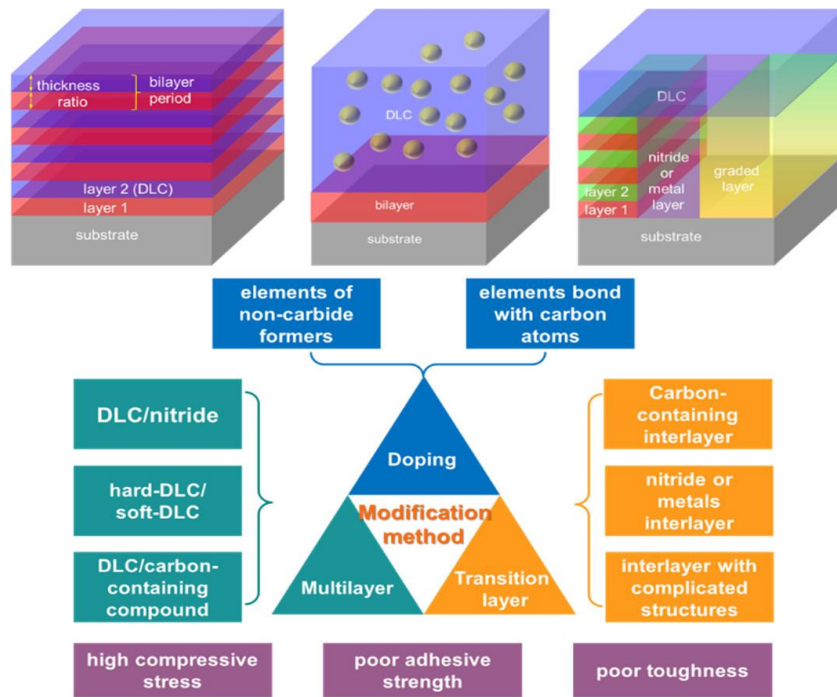


Fig. 6. Schematic representation of the main methods of modification of DLC coatings to solve problems arising from their application [75]

Deposition of gradient DLC coatings with good tribological performance is possible due to the high sp^3/sp^2 ratio in the surface, which gradually decreases from the surface to the substrate to enhance adhesion. A traditional way to improve coating adhesion is to use a transition layer (Ti, Cr) between the base and the DLC. Also, carbides or nitrides can be used in transition layers [29, 75].

The concept of multilayer structures appears most promising for thick diamond-like coatings, in terms of overcoming some of the limitations of single-layer films associated with insufficient ta-C adhesion. In addition, this approach allows you to create coatings with additional functional properties. Various options for forming a multilayer structure of the coating allow solving a complex of problems [29]:

- reduce compressive stress in the coating;
- adapt mechanical behavior (hardness, development of cracks, etc);
- adjust the tribological behavior of the surface;
- optimize the adhesion between the substrate and the DLC coating by using adhesive layers such as carbide-forming metals or by structural cross-linking;
- increase the ability to withstand mechanical loads due to the buffer layer;
- regulate interaction with the external environment, including bioreaction;
- tune other physical properties such as electrical resistance etc.

It is clear that the simplest multilayer type is a two-layer system, for example, a homogeneous functional diamond-like coating with an adhesive sublayer, however, to achieve a certain coating thickness of several micrometers, it is better to use a package of at least two separate monolayers of different composition or structure, alternating. To achieve the desired

properties, individual layers in a multi-layer coating package may contain:

- layers with different sp^3/sp^2 ratios;
- a-C:Me and a-C:X layers with different doping elements;
- metal layers;
- nitride, carbide or carbonitride layers.

Additional degrees of freedom associated with the thickness of individual layers are added to the considerable variety of possible combinations.

From the point of view of ease of practical implementation, the option of forming a multilayer structure in a coating that is formed exclusively from carbon atoms and does not contain additional alloying elements appears to be the most economical and promising for industrial implementation. Traditional existing equipment and graphite cathodes can be used for the synthesis of such coatings, and synthesis processes can be based on previously developed processes for single-layer coatings. In the following sections of the review, the main ways of modifying DLCs consisting of carbon and containing no alloying elements are considered in more detail.

4. IMPROVEMENT OF THE MECHANICAL PROPERTIES OF NON-ALLOYED DLC COATINGS

According to the conclusions of works on the development of thick hard ta-C coatings, the first requirement for the synthesis process is to ensure a high level of adhesion, for which it is necessary to increase the coupling of the coating material and the base, as well as to reduce the level of internal stresses. At the same time, they try not to reduce significantly the hardness, but to improve the strength of the coating by reducing the modulus of elasticity. In addition, in new developments, as a result of the modification, they try

not to increase the coefficient of friction and the rate of wear, the low values of which are the advantage of DLC coatings. A wide range of forms and varieties of amorphous carbon allows combining carbon layers with different physical and mechanical properties in the coating. In this way, variants of pure carbon (unalloyed) spatial structures of coatings with improved characteristics are realized. The most efficient creation of such coatings is achieved by changing the energy of deposited ions by changing the value of the substrate potential. Different approaches are used here. First, stress relief, which is necessary for the synthesis of thick coatings, is achieved thanks to ion-induced thermal annealing when high-voltage pulses are applied to the substrate [77–87]. On the other hand, a similar effect can be achieved by alternating more stressed hard and less stressed soft layers. Coating layers enriched with the sp^3 phase and sp^2 one are called “hard” and “soft” respectively, which corresponds to their relative hardness. If the value of the potential is switched stepwise during the deposition, a layered structure is formed in the coating. When the hardness of each subsequent layer is greater than the previous one, we speak of a quasi-gradient structure of the coating. If the potential of the substrate is changed smoothly, the properties of the coating material also change smoothly, and a gradient structure is created. In this way, it is possible to form a coating structure with a hardness gradient from the base to the surface [88–93]. Designs with periodic alternation of hard and soft layers with different modulation coefficients are more common [94–117].

4.1. APPLICATION OF HIGH-VOLTAGE PULSED SUBSTRATE BIAS POTENTIAL TO REDUCE THE LEVEL OF RESIDUAL STRESSES IN COATINGS

Application of technologies that combine deposition and implantation processes is quite promising for improving methods of synthesis of protective coatings. The main feature of such technologies is intensive ion bombardment of the surface during coating deposition. Deposition of coatings by the method of Plasma immersion ion implantation and deposition (PIII&D) is carried out by applying to the substrate microsecond pulses of negative bias potential with an amplitude of several hundred to several thousand volts. In contrast to the high DC bias potential, in such conditions it is possible to minimize the effects associated with sputtering of the coating surface, and at a low substrate temperature form metastable high-temperature structures with a reduced stress level. The coating thickness increases mainly between potential pulses, and during the pulse the processes of ion implantation, sputtering, and radiation-stimulated annealing of already formed coating layers prevail. Pulse parameters (f – repetition frequency, t_p – duration, V – amplitude) are key characteristics that allow you to control the structure of the coating, the level of residual stresses in them, and therefore their properties. The amplitude of the potential must be of sufficient magnitude to accelerate the ions to an energy that ensures their penetration deep into the substrate [77–79].

The details of the use of the PIII&D method in the formation of DLC coatings depend on the method of creating the carbon plasma from which the deposition is carried out. Supply modes and high-voltage potential parameters are slightly different for different methods (PECVD, FCVAD, MS, HIPIMS, PLD). The energy of the ions generated in most sources of carbon plasma does not exceed a few tens of electron volts, however, the degree of ionization of the plasma flow varies considerably. Highly ionized streams of filtered vacuum-arc plasma allow to change the conditions of deposition by the PIII&D method in the widest possible range [78].

Initially, this approach was used in order to reduce the level of high compressive stresses, which are characteristic of ion-plasma coatings and can be the cause of low operational properties and even their destruction [80, 81]. In [81], it was shown that during the deposition of carbon vacuum-arc coatings, the supply of pulses with a duration of 20 μ s to the substrate leads to decrease in stresses at ion energies above 500 eV, however, the decrease can be achieved both by changing the displacement potential and the pulse frequency. It is substantiated that stress relief is achieved due to ion-induced annealing in thermal peaks. Fig. 7 illustrates that the residual compressive stresses decrease exponentially by an order of magnitude with the growth of a parameter equal to the product of the amplitude by the pulse frequency ($V \cdot f$). A wide range of pulse frequencies from 100 to 1200 Hz and amplitudes in the range of 0.5...20 kV were used in study. In these ranges the value of stress remains the same if reduce the amplitude V and simultaneously increase the pulses repetition frequency f by the same number of times. In industrial applications lower voltage processing is favoured over high voltage both because of cost of equipment and safety issues. The stress reduction allows the PIII&D method to deposit thicker DLC coatings compared to DC potential [78].

It was later shown that the impulse potential significantly affects not only the stress level, but also the coating structure. In [82] compared hydrogen-free a-C and hydrogenated a-C:H coatings deposited by the FCVAD and PECVD methods, respectively, which were deposited under PIII&D conditions. Measurements of internal stresses also showed that for both types of coatings with increasing pulse amplitude, the stress level first increased and then decreased, with a peak of 8 GPa at approximately 150 V. The parameters of the pulses during the deposition of a-C coatings were: amplitude 0...20 kV, duration 20 μ s, repetition rate 200 Hz, and during deposition of a-C:H coatings: amplitude 0...30 kV, duration 400 μ s, repetition rate 60 Hz. It was found that the change in amplitude affects the ratio of sp^3/sp^2 -bonds in the coating. In the case of hydrogen-free a-C, hard coatings with the maximum percentage of sp^3 -bonds of carbon atoms and a hardness of 40...60 GPa were deposited at bias potentials in the range of 80...150 V. Outside this range, sp^2 -bonds of carbon atoms prevailed in the coating material, and coatings were deposited, the hardness of which is much lower, 20...30 GPa, but the level of mechanical stress is also much lower.

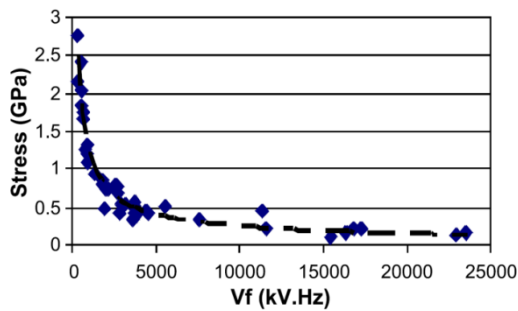


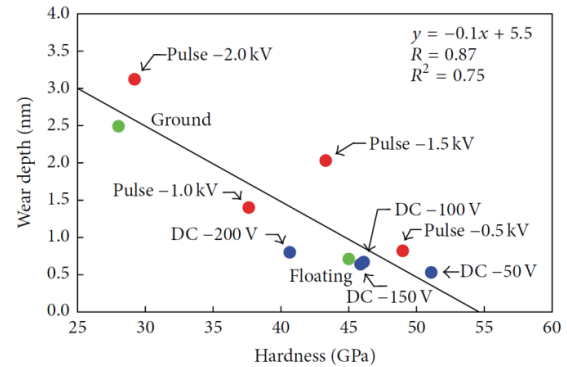
Fig. 7. Stress in a-C coating as a function of voltage–frequency product for a range of voltages between 1.7 and 20 kV and frequencies from 200 to 1200 Hz [81]

Thus, the non-monotonic nature of the dependence of the sp^3 content and the hardness of DLC coatings on the amplitude of the pulsed potential is similar to such dependence for a DC one, only the position of the maximum is shifted towards higher values of the potential [82, 83]. Since the use of high-voltage pulses significantly changes the sp^3/sp^2 ratio, the properties based on this ratio may change.

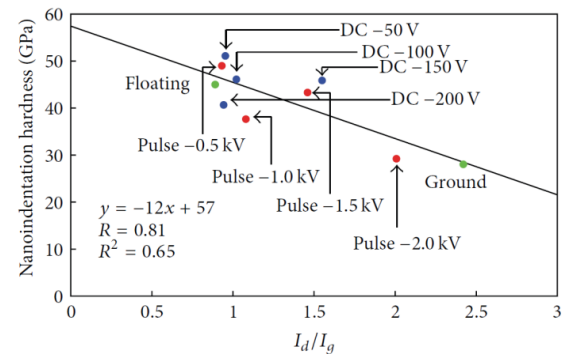
In work [84], the change in the characteristics of FCVAD ta-C coatings depending on the amplitude of the high-voltage pulse potential of the substrate in the range of 3...7 kV (pulse frequency 600 Hz, duration 25 μ s) was studied in comparison with a low DC potential of 85 V. Morphological and mechanical characteristics were measured, as well as adhesion and tribological properties of DLC films. The level of mechanical stresses at potential of 85 V is 10 GPa, and at pulsed voltage it decreases to 1 GPa and is practically unchanged in the studied range of amplitudes. Nanohardness at DC potential of 85 V is 52 GPa, and at pulsed potential it decreases from 36 to 26 GPa. In deposition regimes with increased potential amplitude, an improvement in adhesion is observed, which is associated with the formation of a thicker transitional mixed layer of the coating material and the substrate, and the surface of the film tends to be rougher. All coatings show a very low coefficient of friction (from 0.07 to 0.09) regardless of the amplitude. The rate of wear, on the contrary, increases with an increase in the amplitude of the substrate bias potential by approximately 35 times from $0.2 \cdot 10^{-7}$ to $7 \cdot 10^{-7}$ mm³/Nm.

The results of [83] show that high hardness is an important requirement to ensure wear resistance if the coatings adhesion is sufficient. This conclusion is confirmed by the authors of [84], who studied ta-C coatings deposited by the FCVAD method at DC 50...200 V and pulsed 0.5...2.0 kV substrate bias potential, as well as at floating potential and grounded substrate. They found a clear correlation between the hardness of the coatings and their wear resistance (Fig. 8,a). The hardness, in turn, was determined by the content of sp^3 -bonds, which was evidenced by a negative correlation with the ratio of I_d/I_g Raman scattering peaks (see Fig. 8,b) [19, 85]. The coefficient of friction of the coatings, obtained when applying both DC and pulsed substrate potential, changed slightly and was within 0.20...0.27 for dry test conditions and 0.09...0.12 under lubrication conditions. However, it should be noted that sufficiently thin films with a

thickness of 200 nm were studied, while the advantages of the pulse mode are manifested in thicker coatings, where good adhesion is more important. The use of high-voltage impulse potential contributes to a significant increase in the adhesion of diamond-like coatings, both due to the formation of transition layers when mixing the coating material and the substrate, and due to the reduction of residual stresses [78].



a



b

Fig. 8. Correlation diagrams between hardness and wear depth (a) and the ratio of Raman scattering peaks (b) for ta-C coatings obtained by the FCVAD method at different values of DC and pulse substrate bias potentials [84]

Currently, there is no clear understanding regarding the optimal values of the pulse potential parameters (amplitude, frequency, duration of pulses) which promote reaching the best desired properties of DLC. Theoretical studies of radiation-stimulated processes of their formation can be of great benefit in determining the optimal deposition regimes of diamond-like coatings, in particular, the concept of nonlocal thermoelastic peaks (NTP) [49, 50, 86, 87], which, by means of mathematical modeling, effectively allows one to estimate the level of residual stresses in coatings and determine the parameters of the deposition process, which ensure the formation of sp^3 - or sp^2 -bonds, based on the analysis of the trajectories of the ions thermoelastic peaks on the carbon P,T phase diagram. Theoretically, it is shown that the internal stresses in the DLC in the pulse substrate bias mode of FCVAD deposition can be reduced several times without a significant decrease in the concentration of sp^3 -bonded carbon, compared to the coating obtained in the DC bias mode, however, there are certain limitations. For example, with an amplitude of 1000 V pulses with a

duration of 5 μs , increasing the frequency from 0 to 200 kHz leads to a linear decrease in the stresses in the coatings from 8.5 to 0.5 GPa, but at frequencies above 130 kHz, the trajectory of the ion peaks on the phase P,T diagram go beyond the stability region of diamond, which evidences the graphitization of the coating [86]. In addition, the important role of the deposition temperature in controlling the internal stresses in the deposited coating is noted [87].

4.2. GRADIENT COATINGS

Gradient DLC coatings are characterized by the feature that the content of the sp^3 fraction and, accordingly, the hardness of the deposited amorphous carbon increases monotonically from the substrate to the surface. To form a gradient structure, the substrate bias potential changes monotonically throughout the deposition time [88–90]. If the potential is changed stepwise, a quasi-gradient structure is synthesized [91–93]. The range of potential change, as well as the direction (increase or decrease) depend on the features of the DLC manufacturing method. So, gradient ta-C coating was deposited on a hard alloy base from a magnetron source of carbon plasma [88]. The potential of the substrate during deposition was increased linearly from 0 to 300 V. At the same time, the microhardness of the coating in the direction from the base to the surface increased from 1800 to 4100 HV. The gradient design made it possible to reduce the stress level in the coating to 3.8 GPa and to apply an ultrahard coating 1 μm thick with adhesion up to 50 N on a hard alloy base. Similar results were obtained for magnetron quasi-gradient coatings up to 1.6 μm thick that were deposited on stainless steel with a stepwise increase potential from 20 to 150 V in steps of 2 V every 100 s. Internal stresses in such a coating of 1.5 GPa turned out to be 2.5 times lower than in a coating deposited at a DC potential of 140 V [91].

During fabrication the gradient ta-C coatings by FCVA method, as a rule, value of substrate potential is decreased. Micron-thick coatings deposited under gradually decreasing the amplitude of the pulsed substrate bias potential from 3 kV to 0 V (pulse duration 25 μm , frequency 600 Hz) demonstrate hardness and wear properties close to ta-C and a stress level of 1.5 GPa, which is 6 times less than in the coating deposited at DC substrate potential 100 V [89]. Quasi-gradient (graded) coating deposited on rotated silicon substrate under stepwise decreased negative DC substrate potential (1500, 1000, 500, 80 V) have low stress level without significant reduction in hardness and Young's modulus, due to the fact that the average content of sp^3 -bonds remains high. Scratch testing demonstrates favorable scratch resistance and improved adhesive strength [90].

Thus, deposition of gradient ta-C coatings with good protective properties is achieved due to the high sp^3/sp^2 ratio at the surface, which gradually decreases towards the substrate to enhance adhesion. The surface of the coating is hard, which provides a low coefficient of friction and a low rate of wear, however, to achieve a significant thickness of coatings, this method is less effective than the formation of a multilayer structure.

4.3. FORMATION OF MULTILAYER CARBON STRUCTURES

Creation of multilayer DLC coatings with alternating hard and soft amorphous carbon layers with different sp^3 content is achieved by changing the energy of the deposited ions by changing the bias potential of the substrate. The parameters of the potential depend on the method of manufacturing the multilayer coating: FCVAD [53, 94–104], MS [105–112] or PECVD [113–117]. A change in the DC potential [53, 102–107, 111–115] or the pulse amplitude [94–97] is applied. Alternation of layers leads to a significant reduction of residual stresses in comparison with single-layer ta-C coatings, which makes it possible to obtain carbon coatings with a total thickness of several to 10 μm [29, 78, 94, 97, 104, 117]. A less common way to implement this alternation is to periodically interrupt the coating process followed by Ar ion bombardment to create an sp^2 -bonds on the surface before restarting the coating process [104].

In the case of the synthesis of hydrogen-free multilayer DLC, hard layers with a high percentage of sp^3 bonds and a hardness of 50...80 GPa are usually deposited at bias potential in the range 80...150 V. Beyond this range, the content of sp^2 -bonds of carbon atoms in the coating material increases, these are conditionally soft coatings, the hardness of which is much lower (20...30 GPa), but most importantly, the level of mechanical stress is much lower. Thus, the non-monotonic course of the dependence of the carbon coating properties on the substrate bias potential opens up two ways of synthesizing soft layers. In one of them, during the deposition of the soft layer, the forced bias potential is not applied, or it has rather low values (<40 V), in the other, the potential is hundreds of volts or even several kilovolts. Each of these ways leads to a significant improvement in adhesion, however, it should be taken into account that at too low particle energies, less dense, more defective and rough layers can be formed [82].

Fig. 9 shows typical electron microscopic images of the cross-section of a nanoscale multilayer coating at different magnifications. The microscopic image (see Fig. 9,a) clearly shows alternating soft (light) and hard (dark) layers about 30 nm thick. The difference in contrast is the result of different densities between the layers deposited by MS at a bias of 40 and 120 V. The image of the boundary between the soft and hard layers in Fig. 9,b, obtained at a higher magnification, indicates that both layers have an amorphous structure [112].

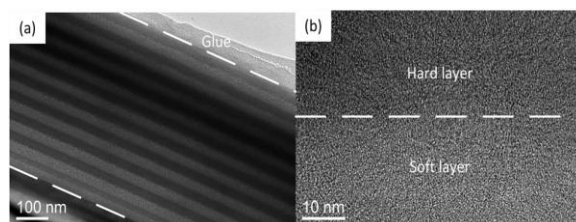


Fig. 9. Electron microscopic images of the cross section of a multilayer DLC coating with alternating hard and soft layers (1/1) at different magnifications [112]

Multilayer DLC coating designs with alternating soft and hard layers have been mentioned in publications since 1994 [94]. Coatings consisting of four carbon bilayers were deposited from filtered vacuum-arc plasma in a PIIID mode with pulse duration of 2 μ s and repetition rate of 120 kHz. The pulse amplitude during the deposition of a hard layer with sp^3 content of 85% and a hardness of 60 GPa was 100 V, and of a soft layer with sp^3 content of 40% was 2 kV. Three variants of multilayer constructions were produced with different ratios of the duration of the hard/soft layer deposition: 10/90, 50/50 or 90/10. It turned out that the hard layers are noticeably thinner than the soft ones. For the 50/50 variant, measurements give values of 7 nm for the hard layer and 22 nm for the soft layer. The use of high-energy 2 kV ions to deposit the soft layers limits the thickness of the individual layers to about 20 nm, since the hard layer of less thickness is destroyed by the subsequent deposition of the soft layer. Nanoindentation showed that the hardness of the investigated multi-layer coatings decreases with increasing content of soft layers and is in the range of 33...23 GPa. Thanks to the multi-layer structure, the overall compressive stresses in the coatings were reduced compared to a hard single-layer coating, and the wear resistance was significantly increased, especially at high loads [95, 96].

In other experiments, the deposition parameters were tried to be chosen in such a way that during the deposition of the soft layer, the effects of implantation and partial destruction (transformation) of the part of the hard layer located below were avoided. For example, during the application of the PIIID method on the OPDB-FCVAD industrial equipment, coatings with a total thickness of 1 μ m with equal thicknesses (of 12.5 nm and more) of soft and hard layers were deposited. A soft DLC layer with 60% sp^3 fraction and a hardness of 25 GPa was deposited under a pulse bias potential of 3 kV, 600 Hz, 25 μ s, and a hard layer with 80% sp^3 fraction and a hardness of 52 GPa was deposited in the absence of pulses [97, 98]. Also, nanoscale layers with a thickness of 15 nm were obtained by changing the DC bias potential. In FCVAD multilayer coatings – when switching the potential between 50 V (hard layer, 60% sp^3) and 150, 250 or 350 V (soft layer, 51, 44 or 36% sp^3 , respectively) [53]. In MS coatings – between 120 (hard layer, 39 GPa) and 40 V (soft layer, 14 GPa) [112].

Many works were aimed at studying the influence of the internal architecture of multilayer coatings on their mechanical characteristics. It was found that the properties of the coating are determined both by the ratio of the layers thickness and by the modulation period in the composition [53, 87–100, 105, 109–112, 114, 116, 117]. In most studies on the synthesis of unalloyed diamond-like coatings, the greatest positive effect is achieved if the modulation period is within 50...100 nm, i.e., a nanostructure is formed in the coatings. The hardness value of the nanolayer structure is usually close to the weighted average of the hardness of the constituent layers, the H/E ratio is sometimes higher, and the total residual compressive stresses are much smaller than would be expected based on the

proportions of the layer components. Compared to a single-layer film, changing the thickness or the ratio of layer thicknesses has little effect on the roughness and friction coefficient, however, the wear rate of multilayer diamond-like films is effectively limited. The lowest wear rate is recorded in films with alternating hard and soft layers of approximately the same thickness, mainly due to the balance between hardness and residual stresses. Thus, the modulation factor appears to be optimal 1/1.

As an example, Fig. 10 shows the results of tests of multilayer DLC coatings produced by MS [111]. The wear rate and characteristic curves of the coefficient of friction for single-layer coatings and multilayer coatings with different percentages of the thickness of the hard layer and different thickness of the bilayer depending on the load are shown. Among them, the coating with 50% hard layer and 61 nm period has better wear resistance and lower friction coefficient, especially at high contact load of 3.65 GPa (80 N). It is noted that under high load, strength is critical in influencing wear resistance, while under low load wear rate is strongly dependent on hardness. The lowest rate of wear is more often demonstrated by coatings characterized by the highest H/E ratio. Adding layers with lower sp^3 content in a multilayer structure promotes plastic deformation by reducing high compressive stresses. More ductile coatings may exhibit better adhesion. For example, the authors note a correlation between the high adhesion strength of multilayer diamond-like coatings and higher values of H^3/E^2 compared to single-layer coatings. In addition, the interfaces between the soft and hard layer in the multilayer architecture create barriers to limit the nucleation and propagation of cracks [53, 102, 108, 111].

In a number of works, the importance of the formation of a strong adhesive sublayer between the substrate and the coating is noted. It is advisable to start the deposition of the coating by applying a high-voltage pulsed bias potential to the substrate to ensure the implantation of carbon ions. In deposition regimes with a high potential, an improvement in adhesion is observed due to the formation of a transitional mixed layer with an increased thickness of up to several tens of nm. If the substrates consist of carbide-forming elements (Si, Ti, Fe, etc.) or are covered with them, a carbide zone is created, which increases the adhesion strength of DLC coatings. In addition, it is advisable to use a soft coating layer in contact with the substrate to ensure a smoother transition from the soft base to the hard coating [53, 94, 95, 97, 103, 112].

It should be noted that in most studies of the tribological characteristics of multilayer DLC coatings, wear resistance was measured under conditions of low loads (1...10 N) [83, 96, 100, 103, 107, 116]. In the few works containing tribological characteristics at high contact loads (up to 80 N) [111, 112], the significant influence of the additional surface layer is noted. In [112], it was shown that a soft top layer with a thickness of 50 nm significantly improved the wear resistance of magnetron multilayer films with a period of 60 nm.

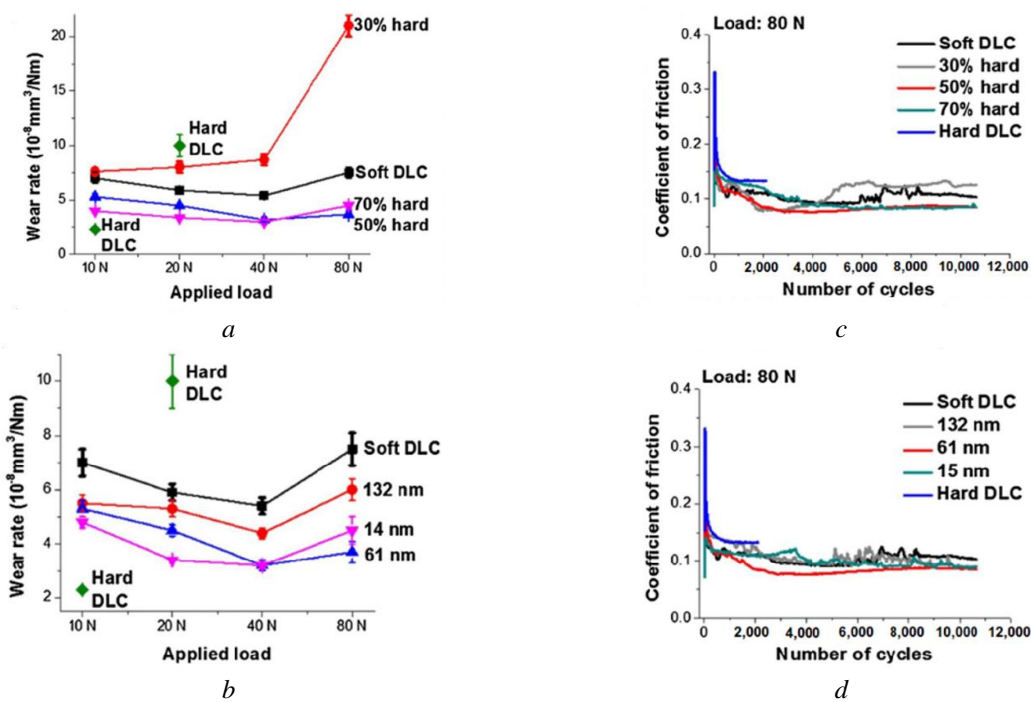


Fig. 10. Wear rate (a, b) and friction coefficient curves (c, d) for multilayer DLC coatings with different percentages of hard-layer thickness (a, c) and with different bilayer thicknesses (b, d) [111]

Fig. 11 shows the results of tribological tests of such coatings with different percentages of the thickness of the hard layer, which had an additional soft top layer, as well as without it. The tests were carried out according to the ball-on-disc scheme under dry sliding conditions under loads of 20 and 80 N, corresponding to initial Hertzian contact stresses of 2.5 and 4 GPa. It can be seen that with a load of 20 N (see Fig. 11,a), the

presence of an additional layer reduces the wear of all coatings by 2–3 times. Fig. 11,b shows the wear volume of DLC coatings with an additional top layer under an extreme applied load of 80 N. Tests lasting 2000 s did not withstand a single-layer hard (36 GPa) coating and a multilayer coating with a low content of a hard layer of 30% (15 GPa). Very small wear was shown by a coating with a 50% hard layer, which had a hardness of 18 GPa.

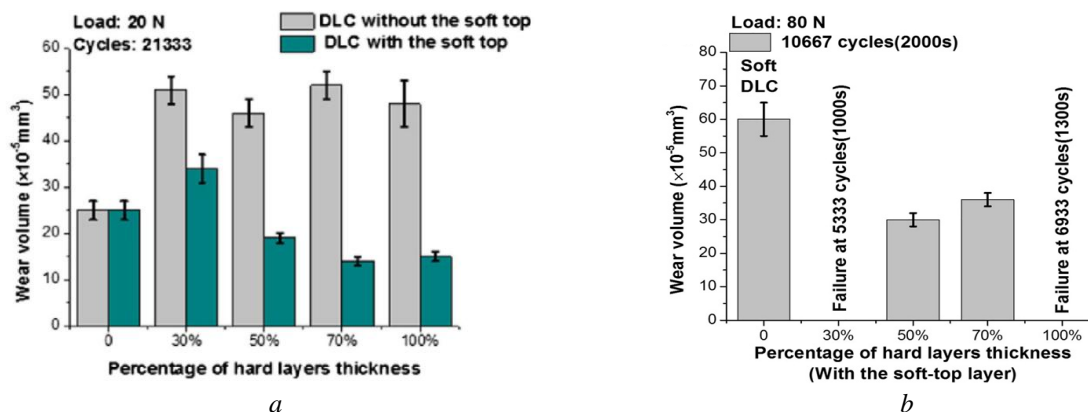


Fig. 11. Volume of wear of DLC coatings with different percentages of hard layers content: a – comparison of wear of coatings with and without an additional soft top layer under a load of 20 N; b – wear of coatings with an additional top layer at 80 N [112]

The dependences of the coating friction coefficients on the number of test cycles, which are shown in Fig. 12, show that the presence of a soft top layer reduces the time required for the formation of the transfer layer, ensuring a low coefficient of friction and reducing wear.

Various fields of application are affected not only by mechanical stress, but also by high temperature, which can create a problem for the ta-C protective coating. In [103], the effect of applying a soft or hard additional layer with thickness of 120 nm on the surface of multilayer ta-C coatings with a period of about 60 nm

and a modulation factor of 1/1 was compared from the point of view of friction processes at high temperature (400...600 °C). The hardness of the hard and soft top layer measured by nanoindentation tests was 55.2 and 36.7 GPa. The results showed that the upper layer of the multilayer structure had a decisive influence on the process of high-temperature friction of the coating as a whole. In Fig. 13,a shows the design of the multilayer structure of DLC coatings with an additional soft and hard layer and the schematic diagrams of their wear mechanisms.

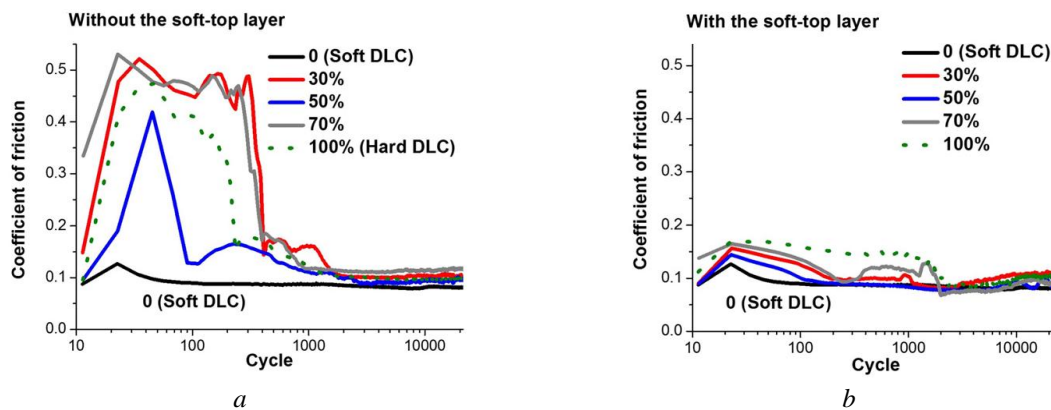


Fig. 12. Curves of the dependence of the coefficient of friction at a load of 20 N on the number of test cycles for multilayer DLC coatings without an additional soft top layer (a) and with it (b) [112]

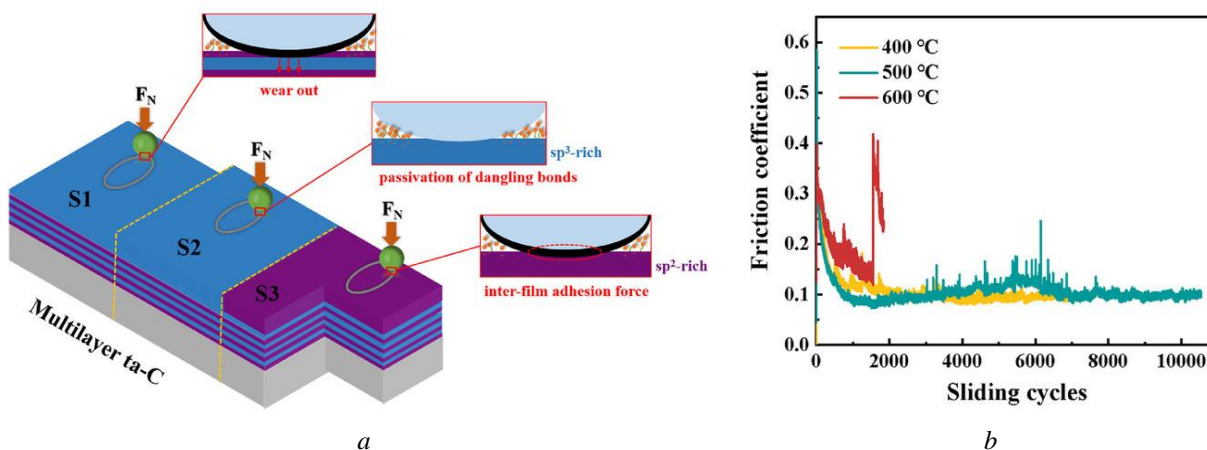


Fig. 13. Diagrams of the multilayer construction of DLC coatings with an additional soft and hard layer and their wear mechanisms at elevated temperature (a) and the dependence curve of the friction coefficient on the number of test cycles at different temperatures for a coating with a hard top layer (b) [103]

The hard top layer contributes to an excellent lubrication effect and a negligible wear rate ($4.0 \cdot 10^{-7} \text{ mm}^3/\text{Nm}$) at 400 °C due to sufficient load-bearing capacity and reduced wear residue formation. In addition, the strong sp^3 -bonded carbon restricted the formation of a graphitized tribolayer, which weakened the adhesion force at the sliding interface. Unpaired bonds on the sp^3 -enriched surface of ta-C were effectively passivated by active compounds in the atmosphere. The soft top layer worsened the frictional properties because it had limited mechanical properties and insufficient ability to withstand the load, which led to an increase in the contact area and strong friction. The low wear resistance of the sp^2 -rich upper layer contributed to the formation of wear debris and a graphitized transfer layer. The sp^2 -rich surface layer strongly interacts with the graphitic transfer layer, which sticks to the counterpart at high temperature, resulting in severe adhesive interaction and undesirable friction behavior.

The ta-C multilayer coating with a hard top layer maintains a low coefficient of friction (0.11...0.12) at 500 °C as can be seen from Fig. 13,b, while at 600 °C the coefficient of friction increases rapidly, indicating wear of the coating, which is explained by the oxidation and evaporation of carbon atoms. Thus, the addition of a

hard top layer contributes to a low coefficient of friction and high wear resistance, which are maintained at temperatures up to 500 °C [103].

It should be noted that in most studies of the mechanical properties of coatings, the total thickness of multilayer compositions was relatively small ($<0.5 \mu\text{m}$), which may not be sufficient for some mechanical and tribological applications. In addition, the effect of the upper layer on the tribological characteristics of multilayer DLC coatings is not clear enough, as evidenced by the conflicting results of papers [103] and [112]. The data presented in the literature are not complete enough, so the practical application of this approach requires further comprehensive research.

Summarizing the results of the reviewed works, it is possible to propose a generalized structure of the developed multi-layer carbon coatings in the form of a perspective design, scheme of which is presented in Fig. 14. The structure includes three basic zones. Each of them implements certain function, can be flexibly configured for specific tasks and is important for the final promotion of high protective properties of the coating. The first zone is formed on the surface of the substrate, it plays the role of binder, which is used to optimize adhesive properties by mixing carbon with the substrate material, generating carbide phases and

smoothly transitioning from a softer base to a hard coating. The second one is a buffer zone that has a multilayer structure with alternating hard (with a higher sp^3 content) and soft (with a lower sp^3 content) layers with a period of 50...100 nm and a modulation factor of 1/1, which allows you to provide the required coating thickness of several μm . The third one is a functional zone with a thickness of 100...300 nm, the properties of which are chosen depending on the conditions of use of the coated product. In the case of high loads, it is advisable to use a hard layer with a high content of sp^3 -bonds as a functional one.

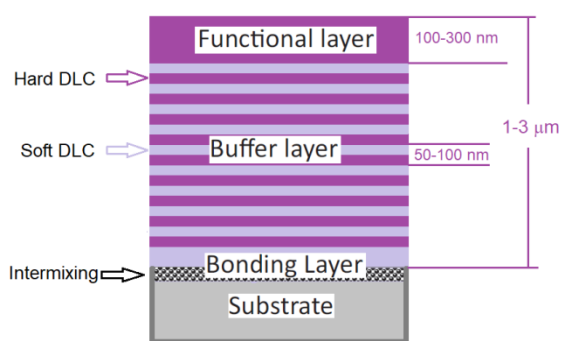


Fig. 14. A promising design of a multilayer structure of DLC with high protective properties

CONCLUSIONS

DLC coatings offer excellent opportunities to improve wear resistance and reduce friction, making them useful for many industrial applications from cutting tools and friction units to biomedical devices.

The decisive factor determining the properties of hydrogen-free (a-C or ta-C) DLC coatings is the ratio of the content of diamond-like sp^3 and graphite-like sp^2 -bonds. Hardness and wear resistance correlate with sp^3 content. A key parameter in the synthesis affecting the sp^3/sp^2 ratio is the energy of carbon ions coming to the surface of the growth, which is controlled by the bias potential on the substrate.

A restraining factor on the way to expanding the spheres of use of hydrogen-free ta-C coatings with properties closest to diamond is the problem of unsatisfactory adhesion of thick ($\geq 0.5 \mu\text{m}$) layers, high stress level and insufficient strength. When modifying coatings, they try to maintain high hardness, low coefficient of friction, stability and at the same time improve strength and wear resistance due to reducing level of stress and fragility.

The concept of multilayer structures looks most promising for thick diamond-like coatings. From the point of view of ease of industrial implementation, the option of multilayer structure that is formed exclusively from carbon atoms and does not contain additional alloying elements appears to be the most economical and promising. For deposition of thick multilayer hydrogen-free films based on ta-C, which have the best diamond-like characteristics, the most promising in industrial production is the use of highly ionized filtered cathode vacuum-arc plasma. For the synthesis of such multilayer coatings, it is possible to use the equipment available in the production and traditional graphite cathodes, and the synthesis processes are based on the

previously developed processes for single-layer coatings.

In the multi-layer design of the coating based on unalloyed DLC, which is promising for mechanical and tribological applications at high loads, it is advisable to combine three basic zones, each of which performs a certain function and is important for the final promotion of high protective properties. The first – bonding zone is used to optimize adhesion properties by mixing carbon with the substrate material, generating carbide phases and ensuring a smooth transition from a softer base to a hard coating.

The second is a buffer zone with alternating hard/soft layers (high/low sp^3 content), which allows you to provide the necessary coating thickness of several microns. The parameters of the buffer zone are chosen based on the fact that the greatest positive effect is achieved if the modulation period is within 50-100 nm, that is, a nanostructure is formed in the coatings. The hardness of the nanolayer structure is usually close to the weighted average of the hardness of the constituent layers, the H/E ratio is higher, and the total residual compressive stresses are much lower than would be expected based on the proportions of the layer components. Compared to a single-layer film, changing the thickness or modulation period of the layers has little effect on the roughness and coefficient of friction, however, the wear rate is effectively limited. The lowest rate of wear is achieved by coatings with a modulation coefficient 1:1.

The third is a functional zone with a thickness of 100...300 nm, the properties of which are chosen depending on the conditions of use of the coated product. In the case of high loads, it is advisable to use a hard layer with a high content of sp^3 -bonds as a functional layer. The hard top layer contributes to a low coefficient of friction and a negligible rate of wear.

Hard and soft layers can be deposited both at DC substrate bias potentials or in high-voltage pulse mode. Applying high-voltage pulses to the substrate allows to additionally reduce the stress in individual layers of the coating due to ion-induced thermal annealing, as well as to increase the thickness of the bonding zone.

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ОПТИМІЗАЦІЯ АЛМАЗОПОДІБНИХ ВУГЛЕЦЕВИХ ПОКРИТТІВ ДЛЯ МЕХАНІЧНИХ ТА ТРИБОЛОГІЧНИХ ЗАСТОСУВАНЬ. ОГЛЯД

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Алмазоподібні вуглецеві покриття використовуються для підвищення якості промислових виробів завдяки широкому спектру виняткових фізичних, механічних і трибологічних властивостей. Розглянуто проблеми, що обмежують сферу застосування твердих негідрогенованих алмазоподібних покриттів із властивостями, які найбільш близькі до алмазу. Проведено огляд наукової літератури, що присвячена покращенню характеристик зносостійких покриттів на основі алмазоподібного вуглецю. Проаналізовано сучасні підходи до зниження внутрішніх напружень стиску, покращення адгезії до основи та підвищення міцності покриттів. Розглянуто аспекти оптимізації параметрів осадження, легування, побудови градієнтної та багатшарової структури. На основі узагальнення результатів розглянутих публікацій зроблено висновок про переваги використання покриттів із багатшаровою структурою. Розглядається перспективна конструкція нелегованих багатшарових DLC-покриттів з високими захисними властивостями.