

Досліджено процес газозфазного осадження Mo і $Mo-C$ покриттів шляхом термічного розкладання гексакарбоніла молибдену. Вивчена кінетика росту покриттів в діапазоні $480-540$ °C та тиску в реакційному об'ємі від 9 Па до 16 Па. Встановлені залежності швидкості росту покриттів, величини їх мікротвердості від параметрів отримання, а також зміни морфології поверхні покриттів, шорсткості та структури. Досліджені трибологічні властивості отриманих покриттів в парі з бронзою $Br.CuZn3C20\Phi0,2$ на машині тертя 2070 СМТ-1 за схемою «кубик – ролик» в інтервалі навантажень $0,2-1,4$ кН. Змашування при визначенні коефіцієнтів тертя здійснювалося методом занурення рухомого контртіла в ванночку з паливом $ТС-1$, ГОСТ 10227-86. Проведення таких досліджень було обумовлено недостатністю даних з прив'язкою до конкретного обладнання та особливостей об'єкта, на який наноситься покриття.

При розробці процесу нанесення покриттів на конкретні деталі відпрацьовані прийоми та засоби, що забезпечують рівномірність нагріву деталей та подачу прекурсору до їх поверхні. В результаті проведених досліджень визначено області параметрів отримання покриттів з різною структурою, швидкістю, твердістю, а також закономірності зміни цих характеристик при зміні основних параметрів процесу отримання таких покриттів. В залежності від умов нанесення покриття можуть мати твердість від ~ 11000 МПа до 18000 МПа при швидкості росту від 50 мкм/год до 170 мкм/год. Усереднені значення коефіцієнта тертя покриттів з різною мікроструктурою і мікротвердістю становили $0,101$ при навантаженні $0,2$ кН і $0,077$ при навантаженні $1,4$ кН.

На базі проведених досліджень відпрацьований процес нанесення металевих і метал-карбідних CVD покриттів на основі молибдену стосовно деталей агрегатів і двигунобудування, який може служити основою для розробки промислових технологій

Ключові слова: CVD процеси, молибденові, молибден-карбідні покриття, властивості покриттів, трибологічні характеристики, розробка технологій

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DEVELOPMENT OF THE CHEMICAL VAPOR DEPOSITION PROCESS FOR APPLYING MOLYBDENUM COATINGS ON THE COMPONENTS IN ASSEMBLY AND ENGINE CONSTRUCTION

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1. Introduction

The development of technology and its high-tech directions, such as aviation, put forward increasing requirements for products and coatings materials, which often cannot be realized within the application of any single method and demand the combined use of various methods. This approach to the solution of the problems of development of new materials and coatings served as the basis for the creation of multifunctional cluster Avinit at the joint-stock company "FED" (JSC "FED").

The cluster includes:

– the Avinit C unit to apply hard and superhard multilayer and nanolayer functional coatings by the method of modernized vacuum-arc deposition;

– the Avinit M unit to apply a coating using magnetron spraying method;

– the Avinit N unit for ion-plasma treatment;

– the Avinit E unit for the processes of ion etching and cleaning;

– the Avinit V unit to apply coatings using the chemical vapor deposition (CVD) and plasma chemical vapor deposition (PECVD) methods.

The first four positions implement the group of plasma vacuum physical methods of surface treatment and coating application (PVD-methods), which are widely used in machine building and other industries. Based on these methods, more than 30 modern plasma vacuum technologies were developed and put into mass production at the JSV "FED"

to enhance reliability and operation resource friction couples in the assembly production.

The Chemical Vapor Deposition (CVD) methods have been widely used in microelectronics in the production of high-purity materials, toolmaking, and some other areas [1–3]. In machine building, these methods have not yet acquired such widespread use. This is due, partly, to the fact that the period of development of the chemical vapor method of obtaining materials and coatings coincided with no less rapid period of development of plasma-vacuum physical vapor deposition methods (PVD-methods). Due to various causes, the PVD-methods of coating application saw a more dynamic spread at that time. However, CVD-methods have great opportunities in obtaining materials with a variety of properties: from superhard, such as diamond, cubic boron pyronitride, to supersoft, they make it possible to obtain on complex-profile surfaces with blind holes, canals, carvings, etc. the porous surfaces of the thickness from unities of nanometers to several mm from different metals and compounds, including dielectrics [2, 4]. Therefore, the existence of the unit of coating application by the chemical vapor deposition method as part of the Avinit cluster makes it possible to use to the full the advantages and capabilities of each of the methods when creating new coatings and technologies for their obtaining.

In paper [5], it is noted that the limited use of the chemical vapor deposition methods in engineering is mainly associated with the lack of affordable specialized equipment for the implementation of these methods. The existence of such equipment at the JSC “FED” makes it possible to work in the direction of the creation of new technologies of chemical vapor coating application with regard to components of the assembly and engine construction. Despite a large amount of research in the field of chemical vapor deposition of coatings of different composition, the development of specific technologies requires additional studies, taking into consideration both the features of the equipment and covered products. The relevance of this kind of work is beyond doubt.

2. Literature review and problem statement

Review of the publications on the use of chemical vapor coating methods for the last decade proves that, as before, these methods in most cases are used in microelectronics, tool making, and tool producing industry [6–10]. Thus, paper [6] explores the issue of the properties and the use of TiN/TiCN/Al₂O₃ coatings. Such coatings are applied using the chemical vapor deposition method from chlorides of corresponding metals at temperatures of ~800 °C. This limits the range of materials, on which coatings can be applied at such temperature, only with the use of hard-alloy tools. Paper [7] explores obtaining the coatings based on molybdenum and tungsten from various precursors with regard to microelectronics using the chemical vapor deposition method. The emphasis is placed on the formation of thin and ultra-thin coatings of different compositions, which have special properties from the standpoint of application in quantum electronics systems. The formation of such coatings requires the simultaneous use of several precursors, which have different temperatures of sublimation and chemical interaction. This creates difficulties for obtaining coatings from compounds with the necessary properties. The issue of deposition of thin films and nanostructures is also considered in article [8]. The complexity and insufficient

exploration of the physical-chemical processes occurring during deposition from the gas phase lead to the fact that the development of new technological processes of chemical vapor deposition faces significant practical difficulties. Most of them concern the optimization of the technology for obtaining coatings with assigned physical and chemical properties. The authors of this article offer their approach to solve these problems based on the application of technology of micro-reactor deposition from the gas phase. Paper [9] is devoted to the plasma-activated synthesis of carbon-based coatings for biomedical products. This is an example of a fairly new area of application of gas-phase methods with specific requirements for coating properties. They primarily concern the need to have biocompatibility, high elasticity, and other properties, which differ significantly from the requirements for the coatings that are applied in mechanical engineering.

The use of chemical vapor deposition methods of coating is examined in review [10]. In it, the authors reach the conclusion that technologies based on the use of the methods of activated plasma chemical vapor deposition (APCVD) are economically reasonable for use in the manufacture of lithium batteries and supercapacitors. Some separate papers are devoted to the development of chemical vapor deposition methods to be used in other industries. Paper [11] deals with the process of manufacturing with the use of the chemical vapor method of a molybdenum pipe for the use as a nuclear fuel shell by means of hydrogen reduction of molybdenum pentachloride at the temperature 750 °C. In addition, in article [12], the process of manufacturing a pipe from SiC at the temperature of 1,100–1,200 °C was developed to be used as a nuclear fuel shell. Compound CH₃SiHCl₂ was used as a precursor. The results of technological developments in these recent papers cannot be used to apply coatings on the parts of components and mechanisms in mechanical engineering because of excessively high temperatures. It should be noted that there are many papers focusing on obtaining molybdenum disulfide coatings with the use of the chemical vapor deposition method, but they have not yet reached the level of possible practical application in the industry [13, 14]. There are very few references to the use of chemical vapor deposition methods for coating application directly in the field of mechanical engineering.

A successful example of the development of industrial technology and equipment is the coating application using the chemical vapor deposition method based on the W-C system for various functional purposes (Hardide-T coating) [15]. Their thickness can reach 100 μm and can be used as wear-resistant, protective coatings or the coatings for other purposes on both internal and complex-profile surfaces (a pump cavity, a turbine rotor). However, the paper does not contain either the data on the specific method and conditions of coating application, or the references to the conduction of such works before. A whole range of papers of the group of authors [5, 16, 17] focuses on the development of equipment and technologies for applying chromium gas-phase coatings to restore and strengthen agricultural machinery parts. In this paper, chromium carbonyl is used as a precursor for obtaining chromium coatings. The results of research into the development of gas-phase chromium-carbide coatings for the use in aircraft construction are given in papers [18, 19]. In these papers, the metalorganic substance “Barhos” is used as a precursor for coating application. However, the application of chromium and its compounds in production is undesirable from environmental considerations. The common thing for

the above papers is that the motivation for the use of chemical vapor deposition methods in technologies is their ability to provide high-quality coating both on complex external and internal surfaces.

Research [20, 21] revealed that the Mo coatings, obtained from molybdenum hexacarbonyl $\text{Mo}(\text{CO})_6$ by means of chemical vapor deposition, have good tribological properties in the couples with hard and very hard coatings. The conducted studies have shown that gas-phase coatings based on Mo with high wear resistance and low friction coefficient have prospects for being used in precision nodes of aviation assembly construction.

When choosing a particular method of coating application, the properties of coatings and conditions of their application, taking into consideration the features of the object, on which the coating is applied, are essential. Expansion of both nomenclature of materials of coatings, and the methods of their application, are natural for the development of coating application technologies and spheres of their use. That is why the studies of the chemical vapor deposition method of Mo coating application are appropriate in terms of obtaining additional information that is necessary for the development of new industrial technologies and a more detailed clarification of the properties of coatings and the possible area of their application.

3. The aim and objectives of the study

The aim of this study is to develop the chemical vapor deposition process of obtaining molybdenum and molybdenum-carbide coatings for the parts of aviation assembly and engine construction of a complex shape.

To achieve the aim, the following tasks were set:

- to determine the dependence of the growth rate, structure, hardness, tribotechnical characteristics of coatings on conditions of their obtaining;
- to develop the process of application of Mo-MoC coatings and techniques that ensure obtaining the coatings with high thickness and hardness uniformity on the parts of assembly construction of a complex shape.

4. Equipment, materials, and procedure for studying the obtaining of molybdenum coatings and their properties

The Avinit V unit (Fig. 1) is a separate element of the cluster, which was designed and manufactured to implement the processes of chemical vapor deposition of coatings from carbonyls of the group of metals, including Cr, Mo, W.

Main features of the Avinit V unit are:

- dimensions of the vacuum chamber (reaction volume) – $\varnothing 300$ mm, $L=600$ mm;
- previous dilution in reaction volume is not less than $1.3 \cdot 10^{-2}$ Pa;
- operating pressure is 2–20 Pa;
- method of heating is the inductive method by an HF generator with the capacity of 20 kW;
- coating application rate is 10–170 $\mu\text{m}/\text{h}$ depending on the area of the surface of the covered products;
- the highest electrical power consumed by the plant, kW, is not more than 25.

The plant has a closed system of heating and cooling of a vacuum chamber, the system of maintaining at the specified

level of the temperature of an evaporator with the metal-containing connection and steam pipeline to transport it to the reaction volume. Feeding of precursor and working gases to the reaction volume is controlled and maintained at an assigned level by the controller.



Fig. 1. The Avinit V unit (JSC “FED”)

The operation of the systems, registration, and management of the basic parameters of the process are controlled by the automatic control system. Fig. 2 shows the photograph of the board of the system of the process parameters control and recording.

Molybdenum carbonyl $\text{Mo}(\text{CO})_6$ is used as a precursor when applying molybdenum coatings. Molybdenum coatings were applied to the samples in the temperature range of 480–540 °C and pressure in the chamber from 9 Pa to 16 Pa. The samples' temperature was determined using the pyrometer of the spectral ratio of DPR-1 with the precision of ± 5 °C. The pressure in the chamber was changed by changing the temperature of the container with molybdenum carbonyl, on which the amount of precursor, which entered the reaction volume, depended. The time of coating application was chosen so that the coating thickness should be in the range from ~ 40 μm to ~ 60 μm . The cubes of $10 \times 10 \times 10$ mm^3 made of steel X12F1 with a hardness of 56...61 HRC and roughness of $Ra=0.05 \div 0.063$ μm were used as the samples for coating application. The experimental processes of coating application were tested using actual details applied in designs of assemblies of the JSC “FED”.

The properties of the coatings were studied with the use of the methods of metallographic and X-ray structural analysis. The structure and the morphology of the surface of coatings were studied using an optical microscope Altami MET-1C with a digital camera (manufactured in Russia). The roughness of coatings was determined by means of a profilometer-profilograph JENOPTIK JENOPTIK nanoscan 855, (produced in Germany); microhardness was determined with the help of the hardness meter QNESS Q60M (produced in Austria) with the load of 0.2 kg. The X-ray structural studies were conducted on the diffractometer DRON-2.0 (manufactured in Russia) in filtered radiation $\text{Cu-K}\alpha$. Diffractograms for phase analysis were made in the scanning scheme $\theta-2\theta$ with focusing by Bragg-Brentano in the angles interval from 10 to 110 degrees. After diffractograms were processed, the angular position of the diffraction maxima was determined and phases were identified using the Wolf-Bragg formula, the interplane distance d_{hkl} for crystallographic planes (hkl) was calculated. The value of lattice parameter a was determined from the ratio:

$$a = d_{hkl} \sqrt{h^2 + k^2 + l^2}.$$

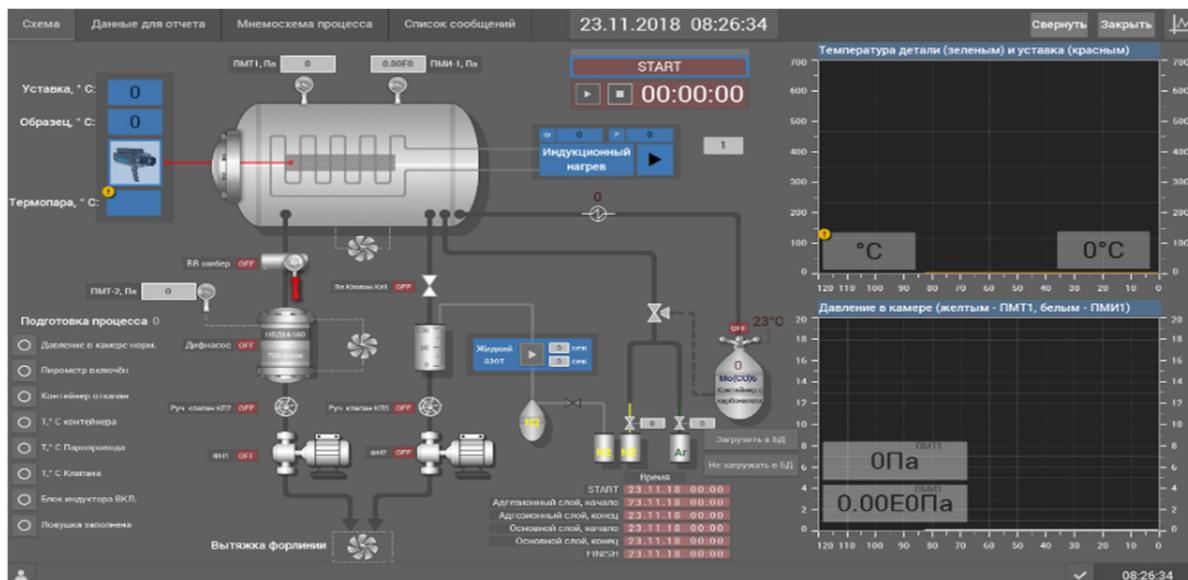


Fig. 2. The board of the automatic system of control and recording of process parameters with the mnemo-scheme of the plant

The tribological properties of coatings were determined on the friction machine 2070 SMT-1 by the “cube – roller” scheme, which is similar to the “unit-on-ring” scheme in accordance with standard ASTM G77-17. Testing took place in the interval of loads of 0.2–1.4 kN at the step load by 0.2 kN according to the procedures described in [5, 6]. The testing time at each stage of loading was 120 seconds. The counter body during testing was the samples of bronze Br.Su3N3C20F0.2 (BB23HTs) in the form of rollers of 50 mm in diameter. The lubrication during determining the friction coefficients was carried out by immersion of the movable counter body into a bath with fuel TC-1, GOST 10227-86. The sliding speed during testing was 1.3 m/s. In the process of tribological tests, the value of friction force $F_{тр}$, normal load N , contact pressure P were recorded, by the magnitudes of which we judged about mechanical losses in a tribosystem. Friction coefficients were determined as $f = F_{тр}/N$.

Before conducting tribological studies, the samples with Mo coating were subjected to tumbling in a tumbling plant OTEC CF 2×18 in the mode of rough treatment with ceramics DZS 6×6 for 60 min and in the mode of finishing treatment with ceramics ZSP 2/2+DZP2 for the same period of time. This treatment in case of unsatisfactory adhesion of coatings led to their peeling and rejecting such samples; it also made it possible to smoothen the surface microrelief, which contributed to the reduction of time of alignment of friction surfaces.

To determine the wear resistance of the coatings, we conducted the testing by feeding an abrasive to the contact area. Quartz sand of Starovirivsky deposit of the fraction of 0.25–0.4 mm was used as an abrasive. The tests were performed according to the Brinell-Howard scheme at the load of 0.05 kN on the friction path of 60 m at a slipping speed of 0.78 m/s. A “disk” from polytetrafluoroethylene (Fluoroplast-4) with a diameter of 50 mm served as a counter body. The magnitude of wear resistance was determined using the weight method with a precision of 1×10^{-4} degrees. The friction path and the material of the “disk” were chosen on condition that the influence of the substrate on wear resistance of the coating should be prevented.

The experimental processes of the application of molybdenum and molybdenum-carbide coatings were tested on the

parts of the nomenclature, which is applied in the assemblies made by JSC “FED”.

5. Results of studying the process of application of molybdenum coatings in relation to the parts of assembly and engine construction

5.1. Dependence of growth rate, structure, hardness, tribotechnical characteristics of chemical vapor deposition Mo-MoC coatings on conditions of their obtaining

The studies of the process of chemical vapor deposition of molybdenum coatings in the range of temperatures of 350–450 °C and of the pressure of 5–11 Pa were carried out in research [20]. In this paper, the range of temperatures and pressures during the study was expanded into the area of higher values of these parameters. The selected range of conditions of molybdenum coating deposition, according to the data in the literature, corresponds to the so-called diffusion region, in which the coating growth rate is controlled by diffusion processes of transferring the reagent to the reaction surface and withdrawal of products of its decomposition [22]. Implementation of the processes of decomposition of molybdenum carbonyl in this region makes it possible to obtain the coating with maximum density and growth rate. Fig. 3 shows the results of research into the dependence of the growth rate of molybdenum coatings on the temperature at different values of pressure in the reaction volume.

The absolute values of growth rate in each specific case depend not only on the temperature of the substrate and the pressure of the reagents in the reaction volume. Its magnitude is influenced by several other factors, such as geometry, dimensions of the chamber and samples, the rate of gas pumping from the chamber and other features of the apparatus-based process of coating deposition.

In this case, it is possible to state that the growth rate of the molybdenum coating had rather high absolute values and could vary widely from ~40 $\mu\text{m}/\text{h}$ to ~170 $\mu\text{m}/\text{hour}$, depending on the conditions of conducting the experiment.

One of the important characteristics of coatings in assessing their use in various spheres, in particular, in friction couples, is their hardness. Fig. 4 shows the results of deter-

mining the microhardness of the coatings obtained under different modes. The hardness of coatings has a fairly explicit character of a change, depending on deposition temperature and pressure in reaction volume, specifically, the hardness of molybdenum coating increases at an increase in pressure in the reaction volume and a decrease in the temperature of its obtaining. Accordingly, the coatings, obtained at the temperature of 480 °C and pressure of 16 Pa had the maximum values of microhardness HV 0.2 at the level of 17,950 MPa, and the coatings, obtained at the temperature of 540 °C and the pressure of 9 Pa, had the minimum values at the level of 10,850 MPa.

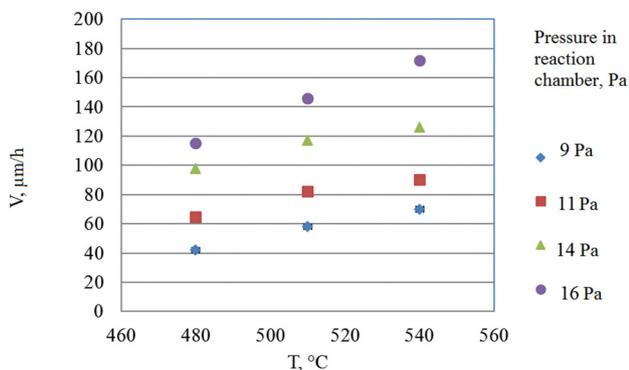


Fig. 3. Dependence of growth rate of Mo coating on substrate temperature at different values of pressure in the reaction volume

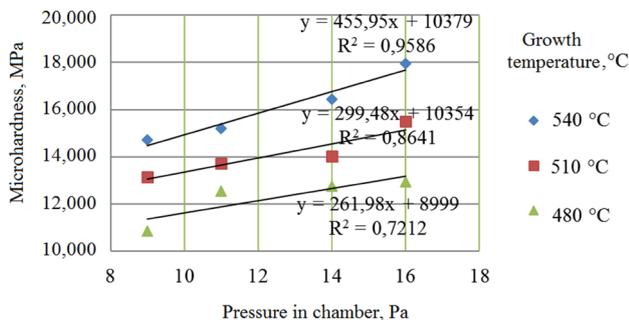


Fig. 4. Dependence of microhardness of coatings on pressure in the chamber at different temperatures of growth

The study of the morphology of the surface of molybdenum coatings showed that depending on the temperature and pressure in the chamber can vary significantly during their deposition. At deposition temperature of 480 °C, it had a globular structure for all values of pressure from 9 Pa to 16 Pa. At the temperature of 510 °C, the coating surface had a globular structure only at the pressure of 16 Pa. At other values of pressure and deposition temperatures, the structure of the coating surface looked like a totality of crystallites of the irregular shape of different sizes. Fig. 5 presented the types of surface of the structure of coatings, obtained under different conditions.

Similar structures of the coating surface at a change in their deposition conditions are typical for the CVD method, including the case of deposition of molybdenum coatings from molybdenum hexacarbonyl [23].

The range of temperature and pressure, in which various structures of molybdenum coatings are observed, may have different values, depending on the reactor design, mass flow of molybdenum carbonyl, and other factors.

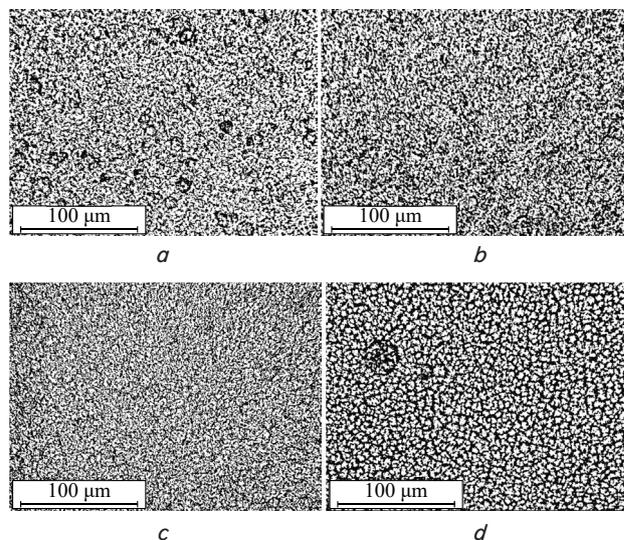


Fig. 5. Morphology of the surface of Mo coatings obtained at a deposition temperature of 510 °C and different pressures in the chamber: a – 9 Pa; b – 11 Pa; c – 14 Pa; d – 16 Pa

The structure of coatings, except for the coatings with the globular morphology, had a columnar character and differed mainly in the dimensions of crystallites, which correlated with the dimensions of the structural elements of the surface of this coating. The coating with the globular morphology of the surface had a layered structure with the cones of growth, representing a totality of micro crystallites within each layer.

Measurement of the roughness of the coatings revealed that its magnitude Ra depended on the temperature and pressure in the chamber and was within the range from $Ra 0.12 \div 0.13$ to $Ra 0.63 \div 0.65$. With a decrease in deposition temperature and an increase in pressure, the roughness of coatings decreased, while it increased at the reverse change in these parameters.

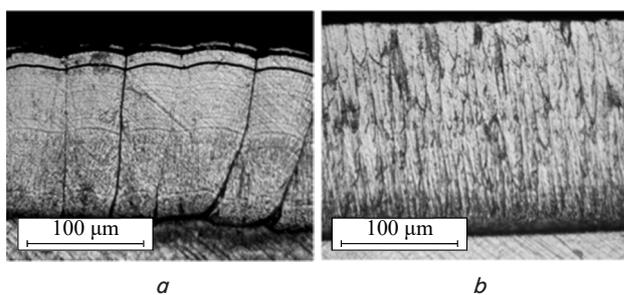


Fig. 6. Characteristic structures of coatings with a different type of surface morphology: a – globular; b – microcrystalline

The tumbling of coatings led to a noticeable reduction in the roughness of the coatings. The magnitude of roughness after tumbling changed most of all for the coatings with minimum values of hardness. Fig. 7 shows the micropictures of the surface of coatings with different structures and Ra values before and after tumbling.

The studies of surface morphology, coating structure in the explored range of conditions of their obtaining revealed that it is possible to separate the coatings that are qualitatively different by these characteristics, specifically: the coating with the layered structure and globular surface

morphology and the coatings with the columnar structure and microcrystalline surface structure. If we compare these coatings by the magnitude of microhardness, the former from the above group of coatings had the highest values of microhardness. In this regard, for more additional information about the features of such coatings, they were studied with the involvement of the X-ray structural methods.

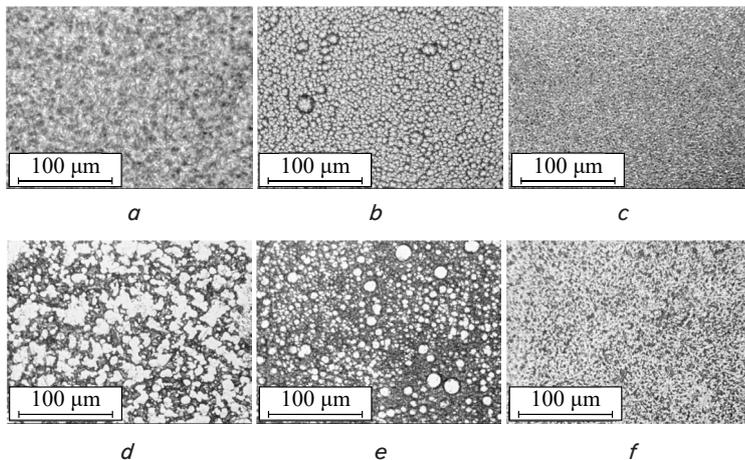


Fig. 7. Microphotographs of the surface of coatings and their roughness *Ra*: *a* – *Ra* 0.63; *b* – *Ra* 0.17; *c* – *Ra* 0.13 before tumbling; *d* – *Ra* 0.37; *e* – *Ra* 0.12; *f* – *Ra* 0.07 after tumbling

The samples that had the coatings with various structures and microhardness were studied. The coatings of sample 1, which were obtained at the temperature of 480 °C and the pressure of 16 Pa, had a globular morphology and microhardness of 18,220 MPa. The coatings of sample 2, obtained at the temperature of 540 °C and pressure of 16 Pa had the microcrystalline surface structure and microhardness of 12,770 MPa.

The diffractograms of the samples contained the displays of Mo with the body centered structure. There were no other lines or sections in the form of blurred maxima from the carbide or other phases. Information about the existence of a certain texture is given by the calculation of textural coefficients. The results of calculating the textural coefficients are shown in Table 1. It is seen that orientation (200) prevails in sample 1 and orientation (211) prevails in sample 2.

Table 1

Textural coefficients for displays of Mo

	T ₁₁₀	T ₂₀₀	T ₂₁₁	T ₂₂₀	T ₃₁₀
Sample 1	0.1	2.7	0.4	0.3	1.5
Sample 2	0.6	0.6	2.3	0.9	0.6

Table 2 shows the results of the numerical processing of diffractograms: angular position, interplane (interplanar) distance, integral intensity, and semi-width for the first five diffraction lines, existing in the diffractograms. It follows from the data shown in Table 2 that the crystalline lattice parameter for sample 1 is 3.1604 Å, and for sample 2 – 3.1563 Å, which in both cases is noticeably above the tabular value of 3.1472 Å. An increase in the crystalline lattice parameter can be associated with the existence of implementation impurities in the coating and, above all, with a carbon impurity.

It is known that the content of carbon impurity decreases at an increase in temperature of decomposition of molybdenum carbonyl and a decrease in pressure in the reaction volume [22, 23]. Higher values of the lattice parameter for sample 1, in this case, can be attributed to the high content of carbon impurity due to the lower temperature of its obtaining in comparison with sample 2. The difference in temperature of coatings deposition for samples 1 and 2 explains the difference in the magnitude of the DKR of these coatings, which, respectively, was 22 μm and 25 μm.

It is possible to explain the course of dependences of the hardness of molybdenum coatings on temperature and pressure in the reactive volume, shown in Fig. 4, in the same way, namely, by different content of carbon impurity.

To determine the tribological properties of molybdenum coatings coupled with bronze BB23HTs, the samples, obtained under different modes, with microhardness from 11,000 MPa to 18,000 MPa and a different structure were selected.

The performed tests revealed that at an increase in load, the friction coefficient of all the samples without exception decreased up to the maximum load. This indicates the ability of the tested friction couples to operate without forming any burseries on tangent surfaces up to the load of 1.4 kN. A comparison of the obtained values of friction coefficients for molybdenum coatings with such characteristics as hardness, structure (surface morphology), and roughness did not reveal any particular relationship. The values of the friction coefficient averaged for six samples at the load of 0.2 kN made the magnitude of 0.101 at a minimum value of 0.077 and a maximum value of 0.11. At the load of 1.4 kN, the mean value of the friction coefficient was the magnitude of 0.0698 at a minimum value of 0.056 and a maximum value of 0.074.

Table 2

Results of numerical processing of diffractograms

<i>hkl</i>	2θ _{max} , degree	<i>d</i> , 10 ⁻¹ μm	<i>I</i> _{int} , cond. unit	<i>B</i> _{1/2} , degree	<i>a</i> , 10 ⁻¹ μm	Coherent scattering regions, μm
Sample 1						
110	40.22	2.2400	24	0.50	3.1604	22
200	58.33	1.5807	91	1.02		
211	73.15	1.2927	23	1.17		
220	86.96	1.1194	2	1.20		
310	100.84	0.9994	45	1.76		
Sample 2						
110	40.35	2.2333	64	0.40	3.1563	25
200	58.49	1.5765	10	0.71		
211	73.31	1.2902	74	0.95		
220	87.15	1.1174	9	0.97		
310	101.02	0.9981	15	1.34		

Tests for wear resistance showed that molybdenum coating with a layered structure, which were characterized by the highest values of microhardness, had the wear of 0.4–0.9 mg. The coatings with mean values of microhardness at the level of 13,000–16,000 MPa and a columnar microcrystalline structure had the wear from 2.4 mg to 5.3 mg.

The coatings with lower hardness and larger columnar structure had the largest wear up to 9 mg.

In abrasive wear of fragile materials, along with normal mechanical wear of the contact surfaces, surface microcracks, followed by brittle destruction of local areas of the surface layer, can be formed. In layered structures, crack propagation from the surface can be localized within the same layer or be inhibited during further spreading inside the coating, thereby reducing the magnitude and the number of microchips on the friction surface. For columnar structures, cracks within the grains can freely reach the substrate, leading to chipping of large fragments of the coating up to chipping of separate grains. This can explain how big the difference between the magnitude of wear of the studied coatings with a layered and a columnar structure is.

To compare with the results of tribological studies of molybdenum coatings, the tribological characteristics of the friction couples of bronze BB23HTs with solid chromium coating, which is widely used in mechanical engineering, were determined in the same way. The chromium coating was applied by the electrolytic method according to the plant technology and had microhardness of 10,020 MPa and surface roughness after machining Ra 0.11÷0.2. The testing of the coating from solid chromium showed that the friction coefficient at the load of 0.2 kN was equal to 0.1. At an increase in load, as in the case of tests of molybdenum coatings, friction coefficient decreased and at the load of 1.4 kN was equal to 0.07. The wear of chromium coating during the wear resistance tests was 3.9 mg. A comparison of the results obtained for molybdenum and chromium coatings showed that molybdenum coatings are not inferior to chromium coatings by the coefficient of friction with bronze WB23NC and may have even lower values. As for wear resistance, they may surpass chromium coatings by up to 10 times.

5. 2. Testing the chemical vapor deposition process of obtaining molybdenum and molybdenum-carbide coatings for parts of aviation assembly and engine construction of complex shape

In the development of the process of applying molybdenum by means of deposition from the gas phase on a particular product, it would be ideal to ensure the uniformity of the temperature of the product surfaces to be covered and the adequate delivery conditions and the precursor mass exchange conditions along with the entire covered surface, which is required to achieve uniformity on coating thickness and its properties on the surface of the product. The solution to these issues has a complex nature and in most cases requires finding a compromise in searching for a solution between the ideal and really possible way of meeting the above conditions for specific products, taking into consideration their shape, geometric dimensions, and other possible features. This requires appropriate testing of the design of the inductor structure, the mode of heating to assigned temperature, and the development of the necessary equipment.

As a result of the conducted studies, the geometry and dimensions of inductors for different experimental parts, which ensured uniform heating of the covered surfaces, were worked out.

It was most difficult to solve the problem of meeting the necessary delivery conditions and precursor mass exchange

conditions along the entire surface of the piston (Fig. 8) to obtain a homogeneous coating thickness on the product surface.



Fig. 8. Photograph of the piston

This problem was solved by developing the structure of the gas-distributing tract with the possibility of using various types of nozzles and various precursor flow resistance, as well as the possibility of moving the nozzles along the surface of the product. The position of the nozzles, their configuration, and cross-section of nozzle openings, which ensured obtaining sufficiently uniform thickness of coatings on pistons, were selected experimentally. Fig. 9 shows the photograph of the gas-distributing tract, used during the application of the coating on the piston, and Fig. 10 shows a schematic representation of the reaction chamber with a steam pipeline and gas-distributing nozzles to feed vapors of molybdenum carbonyl to the surface of the product.



Fig. 9. Photograph of the gas-distributing tract used for the application of the coating on the piston

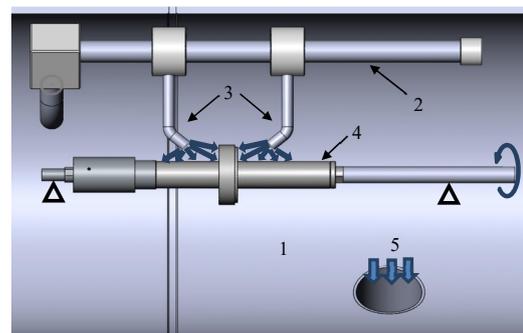


Fig. 10. Schematic representation of the reaction chamber with steam pipeline and gas-distributing nozzles to feed molybdenum carbonyl on the surface of the product to be covered: 1 – reaction chamber; 2 – steam pipeline; 3 – gas-distributing nozzles; 4 – product to be covered (piston); 5 – opening for withdrawal of products of decomposition of molybdenum carbonyl from the reaction chamber

When choosing the conditions for coating application and their optimizing, we followed the requirements for

the characteristics of the coating on the studied parts. According to these requirements, the uniformity of coating thickness and microhardness should not exceed 10 %. In terms of the magnitude of microhardness, it should ensure wear resistance, comparable to wear resistance of coating from solid chromium. The magnitude of microhardness of molybdenum coatings, in this case, should correspond to the value within the 13,000–16,000 MPa. The studies of the characteristics of the Mo coating, obtained on the piston in the optimized conditions of the process, showed that the coating thickness on the entire controlled surface did not go beyond 10 % of the mean value of 66 μm , and microhardness was 15,545 MPa with a deviation of around 5 %.

When applying molybdenum coatings on the working surface of a part with simple enough geometry, such as a rod (Fig. 11), even more uniformity was achieved of both the thickness and magnitude of microhardness. Thus, the deviation from the mean value of 40 μm of the coating thickness did not exceed 2 %, and microhardness was 14,810 MPa with a deviation of up to 2.5 % from this value.



Fig. 11. Photograph of the rod

High uniformity of coatings makes it possible to apply them with minimum tolerances for further machining in size or surface grinding and polishing to the roughness of $Ra=0.08$. The coatings have sufficient adhesion and can withstand the tumbling and grinding treatment without violating the integrity or peeling, ensuring the necessary purity of treatment of coated surfaces. The obtained results on the development of the process of the Mo-C coating application are fundamental for the development of experimental-industrial technological processes of application of such coatings on specific products for aviation technical purposes.

6. Discussion of results of studying the process of obtaining molybdenum coatings on the components of assembly and engine construction

The obtained dependences of the growth rate of Mo coatings on temperature and pressure in the reaction volume is typical for the processes of thermal decomposition of molybdenum carbonyl under conditions when the growth rate of coatings is controlled by diffusion processes (Fig. 3). This distinguishes the results of this paper from the results presented in research [20], in which the growth rate of coatings depended primarily on temperature. The difference in the temperature range of coatings, which in paper [21] was 350–450 $^{\circ}\text{C}$, affected structural and other characteristics of the coatings obtained in this research. The studies of microhardness of the samples (Fig. 4) showed a very clear dependence of this magnitude on the conditions of deposition of coatings, which makes it possible to obtain the coating with pre-assigned values of hardness. Depending on the conditions of coatings growth, it

could have the values from ~11,000 MPa to ~18,000 MPa. For comparison, the hardness of coatings Hardide-T based on W [15] does not exceed 16,000 MPa, the chromium-carbide coatings from “Barhos” have the same level of hardness, according to the data of research [18, 19]. Hardness is a very important magnitude for coatings when considered from the position of their application as strengthening or wear-resistant coatings. It can be proved by the results of testing of molybdenum coatings for wear resistance, which by 10 times exceeded the wear resistance of electrolytic coatings from solid chromium that are widespread in the industry, the hardness of which does not exceed 11,000 MPa. In this respect, molybdenum gas-phase coatings cannot only compete with the electrolytic coatings from solid chromium but also be considered as an alternative to chromium coatings in the environmental aspect. It is known that “six-valence” chromium (CrVI) is among the most hazardous toxic substances and its use in manufacturing a wide range of industrial products is limited by the European Union directive (RoHS) [24]. On the same basis, the method for obtaining gas-phase molybdenum coatings has application advantages over the gas-phase methods for obtaining chromium-based coatings.

The results of the study of the process of applying molybdenum coatings and their properties served as the basis during working out of the process of the application of coatings on the components, which are used in the assemblies of the JSV “FED” production. This refers to both specific values during the choice of parameters of the process of coating, and consideration of the established patterns of the influence of parameters on the kinetics and properties of coatings. Technology development also requires taking into account the peculiarities of the equipment and components, on which coatings are applied with corresponding requirements to their characteristics. In the case of coating application on the components with complex geometry, as noted in paper [4], the most complicated task is to ensure the uniformity of coating thickness. This task was solved successfully on the example of one of the components.

The obtained research results, methods, and means, which were used during the process of working out of the process of coatings application on specific details, can serve as the basis for the development of industrial technologies in aviation construction and other spheres.

The specific requirements for the characteristics of coatings on the components will determine the range of issues, which may be necessary to solve in the process of development of the technology of Mo-MoC coatings application using the chemical vapor deposition method. First of all, this may concern the behavior of coating in various tribocouples and conditions of their operation to determine the optimal conditions for obtaining the necessary tribotechnical characteristics of the coating. Equipment for the application of coatings with the use of the chemical vapor deposition method may use the methods for heating components, precursor feeding and other features affecting the kinetics of growth and coating properties, which are different from those used in this research. Further research in these areas will make it possible to outline more fully the possibilities and the benefits of using the method of chemical vapor deposition method for Mo-MoC coating application on the components in aviation and other fields of machine building.

7. Conclusions

1. The conducted studies revealed that it is possible to obtain the coatings with hardness from ~11,000 MPa to 18,000 MPa using the chemical vapor deposition method in the chosen range of conditions of molybdenum coatings from molybdenum hexacarbonyl. The ranges of parameters of obtaining coatings with different structure, speed, hardness, as well as the patterns of changes in these characteristics at the change of basic parameters of the process of obtaining such coatings, were determined. The tests of the friction couple “molybdenum coating – bronze BB23HTs” in the medium of fuel TC-1 in the range of loads from 0.2 kN to the maximum load of 1.4 kN demonstrated the operation efficiency of the experimental friction couples without forming bursaries. The magnitude of friction coefficient for the tested molybdenum coatings with different structure and hardness did not significantly differ and on average was 0.101 at the load of 0.2 kN and 0.07 at the load of 1.4 kN. The tests for abrasive wear showed that molybdenum coatings with the layered structure, which have the highest hardness values, are superior to the coatings with a columnar structure in terms of stability. Comparison of the properties of molybdenum coatings with the characteristics of electrolytic coatings from solid chromium, obtained under similar

testing conditions, showed that molybdenum coatings are not inferior to chromium coatings by the value of friction magnitude, they can surpass them by 2 times in terms of hardness, and by up to 10 times when it comes to resistance to abrasive wear.

2. When developing the process of coating application on specific components used in the assemblies of JSC “FED”, the methods, and tools to ensure uniformity of heating components and precursor feeding to their surface were worked out. This ensures obtaining the coatings that are uniform in thickness and properties with different surface configurations. Thus, on the piston, which had the highest non-uniformity of the surface geometry, the deviations in thickness of the coating did not go beyond the limit of 10 % of the mean value of 66 µm. Microhardness was 15,545 MPa with a deviation of about 5 %. For a part with a simpler surface geometry, the deviations from the mean value of 40 µm on the coating thickness did not exceed 2 %. The microhardness deviation from the mean value of 14,810 MPa was not more than 2.5 %. The developed process, methods, and means, which were used in coating application on the components, can be used as the basis for the development of technologies of molybdenum coating application regarding the components of the assembly and engine construction using the chemical vapor deposition method.

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