Molybdenum-carbide and tungsten-carbide CVD coatings obtained by *Avinit* vacuum-plasma technologies.

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Abstract.

The process of gas-phase deposition of Mo-C and W-C multilayer coatings by pyrolysis of molybdenum and tungsten hexacarbonyls on heat-treated technical steel X155CrVMo12-with high class of surface finish (>10) has been studied.

Metallographic research confirms the possibility of low-temperature deposition of high quality coatings with microhardness from ~ 11000 MPa to 20000 MPa at coating deposition rate of 40...170 mkm/h. This provides good adhesion to the substrate materials without reducing the strength characteristics of steel and without deteriorating the purity class of the original surface.

The conducted tribological tests reveal high tribological characteristics of the developed coatings and testify to the prospects of their use for increase of wear resistance and reduction of sliding friction coefficient of friction pairs (steel - coating and coating) of precision units in mechanical engineering.

Comparison of the properties of the developed coatings with the characteristics of electrolytic hard chromium coatings showed that molybdenum-carbide and tungsten-carbide CVD coatings, obtained by vacuum-plasma technology ***Avinit***, are not inferior to chromium coatings in friction values, can surpass them in hardness up to two times, and in resistance to abrasive wear up to 10 times.

According to the aggregate properties, molybdenum coatings can not only compete with electrolytic hard chromium coatings, as hardening and tribological coatings, but also be considered as an alternative to chromium coating in the environmental aspect.

On the basis of the conducted research the technological bases of the processes of applying metallic and metal-carbide CVD coatings on the basis of molybdenum and tungsten have been worked out, which are the base for the development of industrial technologies for precision parts of aggregate and engine construction and machine building.

Examples of application of the developed coatings in production conditions are given.

Keywords: Vacuum-plasma multicomponent multilayer coatings ***Avinit***, CVD, tribology.

Chemical vapor deposition (CVD) methods for coating have become quite widespread in modern technology [1-6]. Compared to other methods, they are distinguished by the relative technological simplicity of the process, the absence of high vacuum requirements (in many cases, the processes take place at atmospheric pressure). The high surface mobility of adsorbed metal-containing compounds allows in CVD processes to obtain a coating with a density close to the theoretical one at temperatures ~ 0.15-0.3 from the melting temperature of the material, which is unavailable for other coating methods.

Among the well-known methods of applying high-quality coatings, CVD methods are very effective in coating powders and other loose materials, as well as in impregnation (sealing) of porous structures.

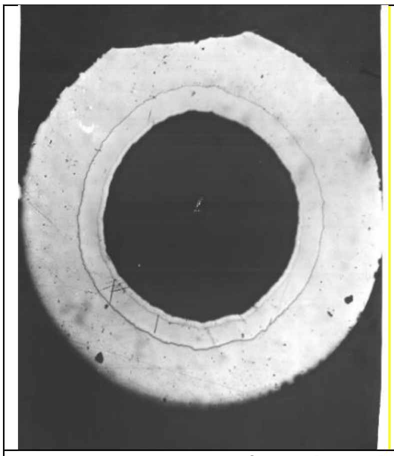
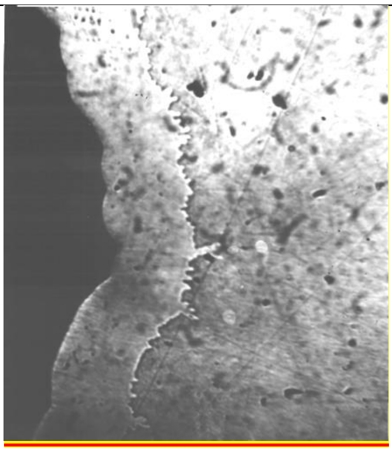
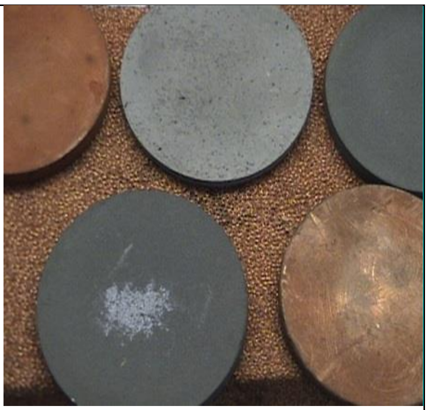
For many years, we have been carrying out scientific and technological work in the field of development and practical implementation of the latest nanomaterials and nanotechnologies of multicomponent coatings (mono- and multilayer, nanostructured, gradient) of various functional purposes to improve the operational characteristics of materials, assemblies and parts of machines and mechanisms using the method chemical deposition from the gas phase [7-12].

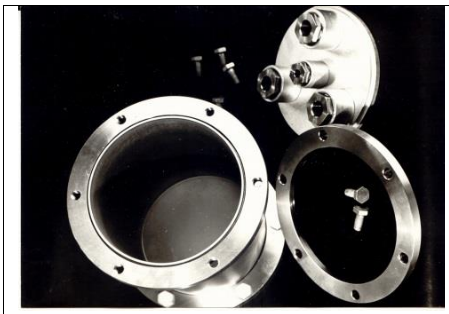
We have developed technological cycles of applying multi-layer coatings based on refractory materials that have high corrosion properties.

Composite materials with such coatings were tested for corrosion resistance in environments typical for pharmaceutical industries, which are hydrofluoric acid and its mixtures with hydrochloric and sulfuric acids, mixtures of organic and inorganic acids, alkalis and various salts with acidity in the range of $1 < pH < 14$, hydrogen-rich environments at temperatures of 20 -100 °C. As a result of the performed works and a set of tests of the corrosion resistance of materials, it was established [13] that composite materials with W, Mo coatings, obtained by the developed technologies, are practically resistant to the corrosive effects of all aggressive environments studied in the work, and their corrosion resistance is much higher than stainless steels.

Corrosion tests of titanium samples with a molybdenum coating with a thickness of 10...15 microns were also carried out in a hydrogen environment at a pressure of 600 mm Hg at a temperature of 60±2 ºC [14]. The results of the tests proved that the gas-phase method of forming such coatings ensures their necessary quality and can be recommended for practical use in the protection of materials actively interacting with hydrogen in hydrogen-rich environments.

The results of research on the corrosion resistance of metal coatings in drug synthesis environments showed the prospects of using coatings made of refractory metals to protect against corrosion the equipment of pharmaceutical and other industries exposed to aggressive environments. According to their mechanical and technological characteristics, composite materials with W and Mo coatings are superior to materials with enamel coatings. The corrosion resistance of such materials in conditions of elevated temperature and relative humidity is 10 -15 times higher than that of galvanic coatings [13]. The established resource of work in aggressive environments of capacitive equipment and technological equipment for the synthesis of drugs made of composite materials with W, Mo coatings, according to technical regulations, is at least 5 years with a coating thickness of at least 150-200 microns [15]. This makes it possible to replace expensive alloys with less scarce materials (including "black" steels that have good manufacturability) with highly corrosive protective coatings. In fig. 1 - 4 show photos of various samples with gas-phase coatings with W, Mo, obtained by the developed technologies.

		
Figer 1. Section of a channel (steel) with an internal coating of Mo (l/d = 300, d = 1 mm)	Figer 2. Penetration of the coating into the cavity of the substrate	Figer 3. Metal-ceramic filter elements obtained by the method of CVD impregnation of porous structures.

Figer 4. Elements of polyfunctional reactor made of structural materials 1.0038 and stainless 1.4541 with protective coatings W, Mo.

Recently, we have developed experimental and technological equipment for the application of functional multilayer composite coatings - the automated vacuum-plasma cluster ***Avinit***, which allows the implementation of complex coating methods (plasma-chemical CVD, vacuum-plasma PVD (vacuum-arc, magnetron), processes of ion saturation and ion surface treatment) [16-19]. A component of the Avinit vacuum-plasma cluster is the ***Avinit V*** unit for applying coatings to the external and internal surfaces of parts by thermal decomposition of organometallic compounds, mainly hexacarbonyls Mo, W, Re, Cr and their compounds with nitrogen, carbon, etc.

When applying CVD coatings using ***Avinit*** technologies, it becomes possible to carry out technological operations of ion-plasma cleaning of the surfaces of parts before applying coatings, if necessary, the creation of matching metal layers by PVD methods to increase adhesion, plasma support by methods of low-temperature unbalanced plasma in one technological cycle, which ensures obtaining high-quality tightly bonded coatings on the surface of parts.

The purpose of this work is to conduct research on the development of processes for applying multilayer, high-quality, tightly bonded Mo-C and W-C coatings by the gas-phase deposition method and conducting tribological tests to assess the prospects for use in friction pairs ("steel-coating" and "coating-coating") with increased wear resistance and a low coefficient of friction in precision engineering units.

Previously, in works [11, 12], we conducted studies of the process of gas-phase application of Mo - C coatings from molybdenum carbonyl.

The coating was applied to samples of heat-treated steels of technical purpose X155CrVMo12-1 and 24CrMoV55 with a high class of purity of surface treatment (> 10). These steels are widely used in aircraft construction, and the improvement of their structural properties in the future leads to a significant increase in the service life of aircraft units. Samples of 24CrMoV55 steel were polished according to factory technologies to a roughness of class 8 (Ra = 0,32 μm), and samples of steel X155CrVMo12-1 56...61HRC - to a roughness of class 10 (Ra = 0,063 μm).

Technological data of the coating process on steel 24CrMoV55 and X155CrVMo12-1 are presented in the table 1.

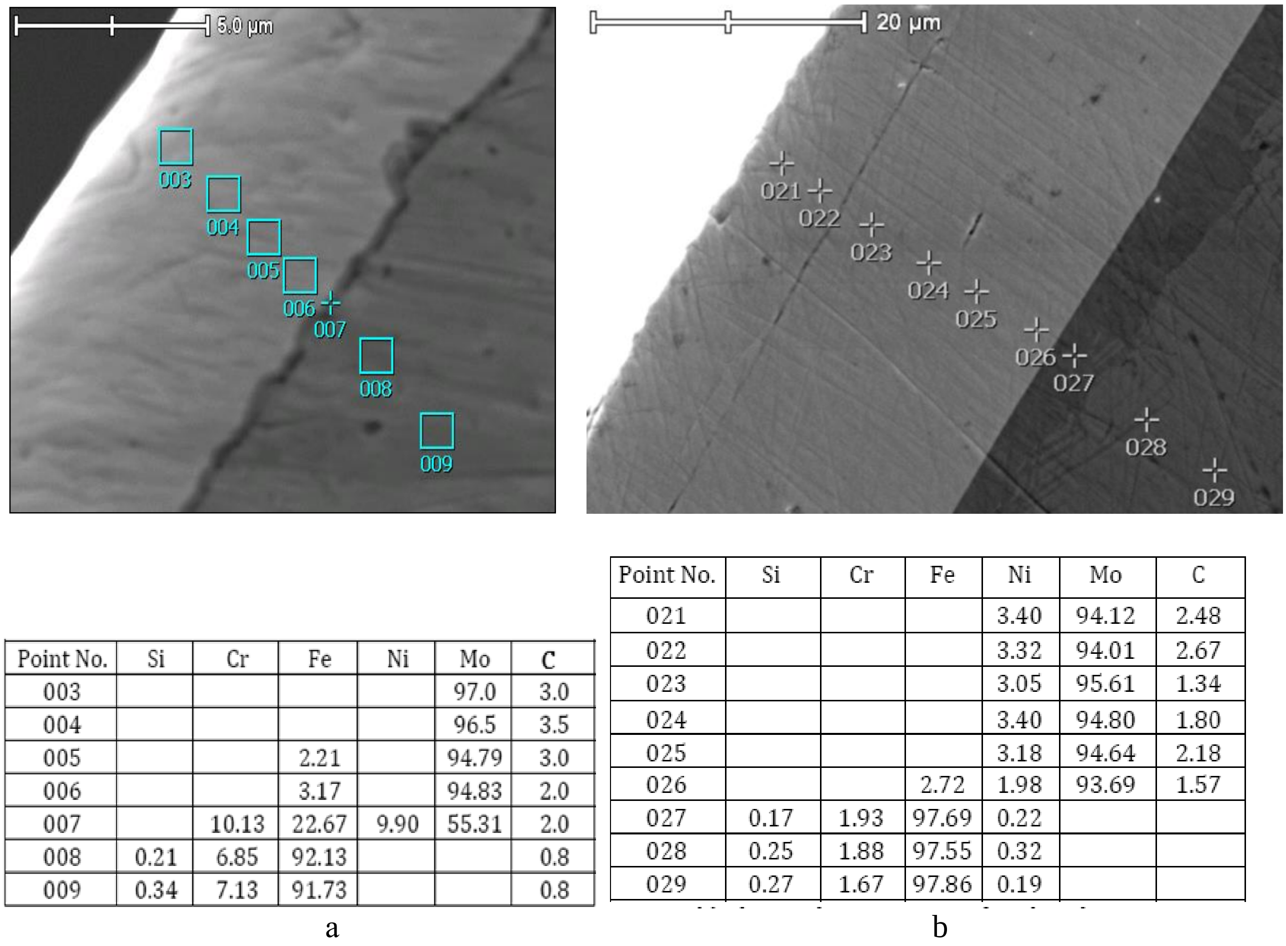
Table 1.

Technological data of the process of applying Mo coatings

T, °C	P, Pa	δ, μm	V, μm/ min	Adhesion
350	5,20	8	0,80	+++
	10,00	7	0,70	+++
	5,30	17	1,13	+++
	11,00	10	0,67	+++
	8,80	25	0,83	+++
	11,00	31	1,03	++
400	5,60	3	0,60	++
	5,40	8	0,80	+
	5,50	6	0,60	+
	6,10	8	0,80	+
	5,00	10	0,67	+
	5,40	12	0,80	+
450	7,60	6	1,20	+++
	5,30	17	1,13	+++
	7,20	20	1,33	+++
	5,10	12	0,40	+++

+++ - the coating is removed only by etching; ++ - minor cracks; + - many chips.

The microhardness of HB coatings increased from 16670 MPa at an application temperature of 450 °C to 21575 MPa when the temperature decreased to 350°C. At 450 °C, the coating had good adhesion to the base, at a lower temperature, a weakening of the adhesion to the original sample was observed. In fig. 5 shows a cross section of coatings on X155CrVMo12-1 and 24CrMoV55 steel samples obtained at different temperatures with marked analysis zones, and the chemical composition of the analysis zones.



Point No.	Si	Cr	Fe	Ni	Mo	C
003					97.0	3.0
004					96.5	3.5
005			2.21		94.79	3.0
006			3.17		94.83	2.0
007		10.13	22.67	9.90	55.31	2.0
008	0.21	6.85	92.13			0.8
009	0.34	7.13	91.73			0.8

a

Point No.	Si	Cr	Fe	Ni	Mo	C
021				3.40	94.12	2.48
022				3.32	94.01	2.67
023				3.05	95.61	1.34
024				3.40	94.80	1.80
025				3.18	94.64	2.18
026			2.72	1.98	93.69	1.57
027	0.17	1.93	97.69	0.22		
028	0.25	1.88	97.55	0.32		
029	0.27	1.67	97.86	0.19		

b

Figer 5. Appearance of Mo coating with marked analysis zones and chemical composition of the analyzed zones on steels: a) X155CrVMo12-1 (T = 350 °C, P = 8,8 Па); б) 24CrMoV55 (T = 450 °C, P = 7,6 Па).

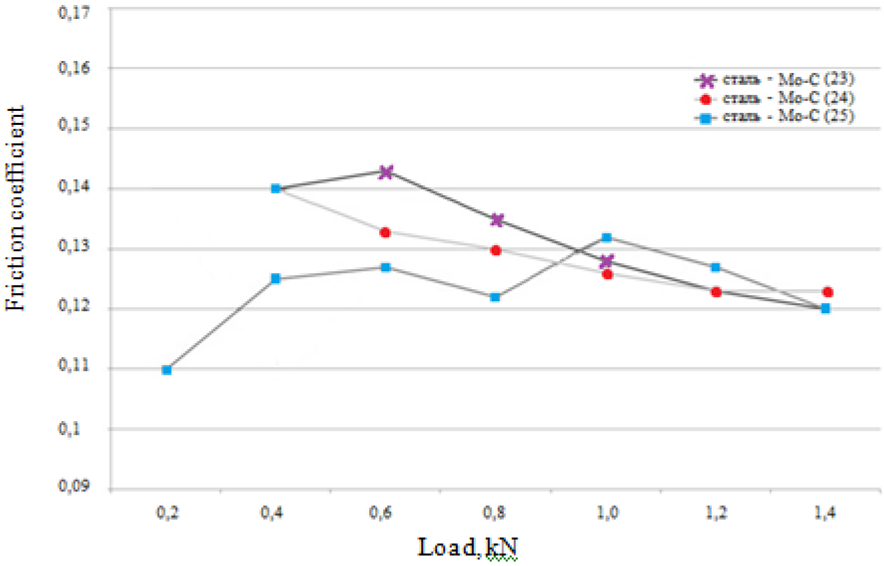
For comparative tribological tests, cubes (steel X155CrVMo12-1, 56...61HRC) were coated with CVD Mo-C. The parameters of the CVD coating process and their characteristics are given in table. 2.

Table 2.

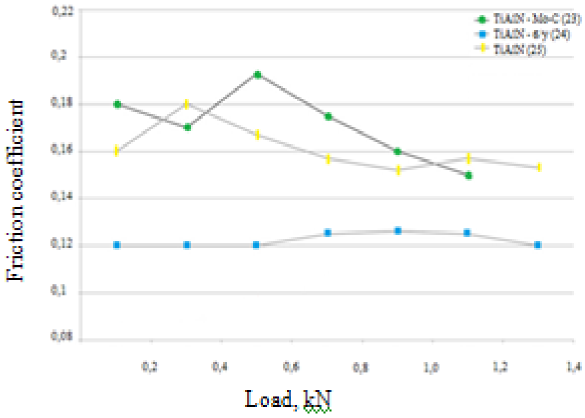
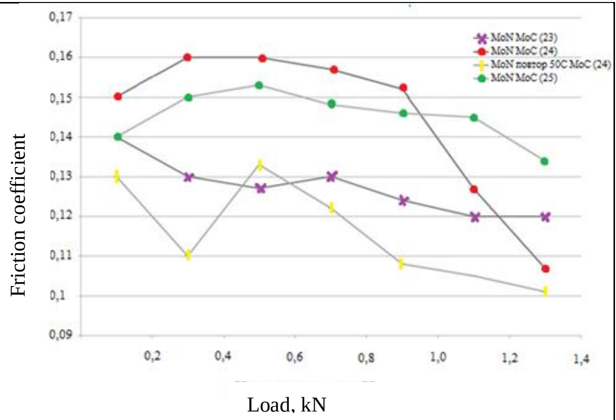
Parameters of the CVD coating process and their characteristics.

№	Cubes	CVD process parameters		Coating characteristics		Notes
		T, °C	*t*, min	Thickness h, µm	microhardness H_VMPa	
1	Cube № 23 - CVD Mo-C	410-440	10,00	15	24520	Finishing with ACM7/3 diamond paste with an allowance of 0.004-0.006 mm to restore flatness. After finishing - h=5...10 µm.
2	Cube № 24 – CVD Mo-C	360-370	10,00	10	176500	
3	Cube № 25 – CVD Mo-C	290,00	10,00	10	24520	

Tribological tests of samples with coatings were carried out with friction and wear machine 2070 SMT-1 under the scheme "cube" - "roller" test. The linear slip velocities - 1.3 m/s. Time of tests in each cycle – 150 seconds. Operating fluid was fuel TS-1, GOST 10227-86. Fig. 6 - 8 show the results of tribological tests of pairs "Mo-C coating/ steel 24CrMoV55" "Mo-C coating/ Avinit Mo-N and Avinit Ti-Al-N coating", which are widely used in the production of FED JSC.



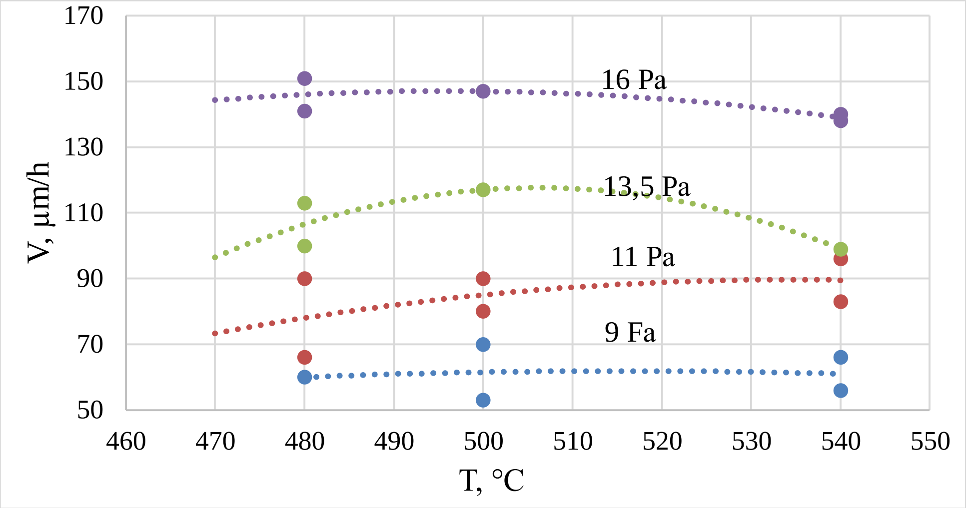
Fiiger 6. Dependence of the friction coefficient on the load for Mo-C/steel 24CrMoV55 friction pairs.

	
Figer 7. Dependence of the friction coefficient on the load for the Mo-C/Ti-Al-N friction pair.	Figer 8. Dependence of the friction coefficient on the load for Mo-C/Mo-N friction pairs.

Studies of the application process of Mo coatings and their properties showed the possibility of low-temperature application with sufficient adhesion to substrates made of 24CrMoV55, X155CrVMo12-1 steels of high-hardness Mo-C coatings, and also showed that such coatings may have the prospect of application for precision components of aircraft assembly construction. Therefore, in this work, the studies of the processes of applying molybdenum-carbide and tungsten-carbide coatings were continued at higher (≥ 480 °C) pyrolysis temperatures of molybdenum and tungsten hexacarbonyls. The experiments were performed on the ***Avinit V*** gas-phase unit, which is part of the ***Avinit*** vacuum-plasma cluster. The coating was applied to cubic substrates made of X155CrVMo12-1 steel. Samples of this shape made it possible to use them in tribological studies of the properties of the obtained coatings according to the "cube" - "roller" test scheme. The conditions for conducting such studies did not differ from those given above.

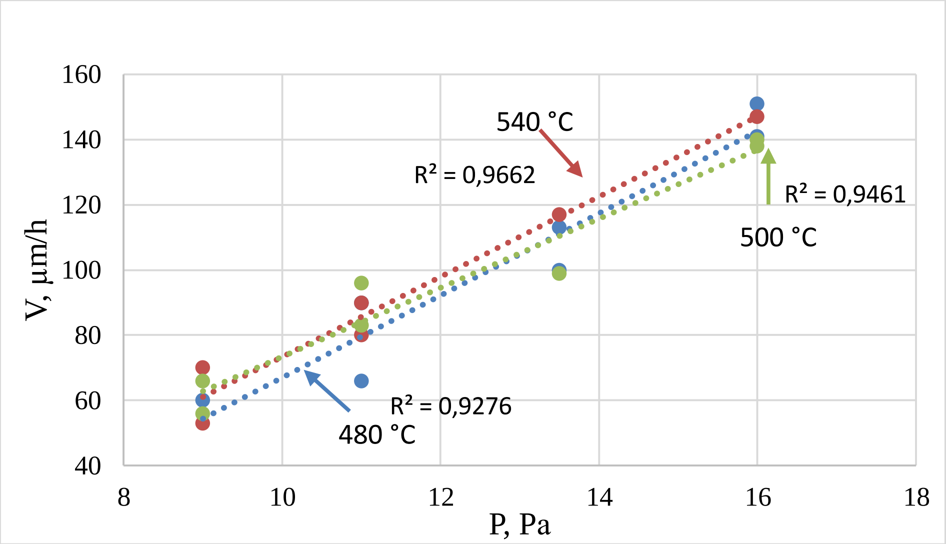
Methods of applying coatings, studying their metallographic and tribological properties are described in detail in works [16-19].

In fig. 9, 10 present graphs of the dependence of the growth rate of Mo coatings on temperature and pressure in the reaction volume.



Figer 9. Dependence of the growth rate of Mo coatings on the deposition temperature at different pressure values.

As can be seen on the curves of the dependence of the growth rate of the coating on the temperature at different pressure values (Fig. 9), there is a tendency for the growth rate to increase up to a certain temperature, and then its decrease. For different pressure values, the region of maximum deposition rate occurs in the temperature range of ≈ (500 – 530) °C. The presence of a maximum in the curves of the coating growth rate versus temperature is typical for CVD processes. This is due to the fact that upon reaching a certain temperature of the substrate, the decomposition reaction of the metal-containing compound begins to proceed not only on the surface of the substrate, but partly already in the gas phase near the substrate, i.e., a homogeneous process of thermal dissociation of $Mo(CO)_6$ becomes possible as a result of reaching temperature required for this in the near-surface layer of the gas medium with a substrate. This leads to a decrease in the concentration of molybdenum carbonyl directly above the substrate surface and, accordingly, the growth rate of the coating.

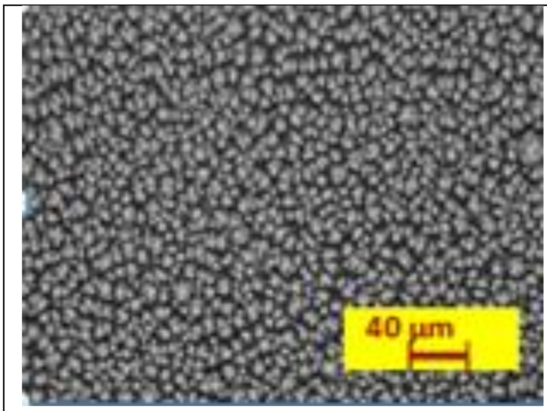


Figer 10. Dependence of the growth rate of Mo coatings on the pressure in the reaction volume at different temperature.

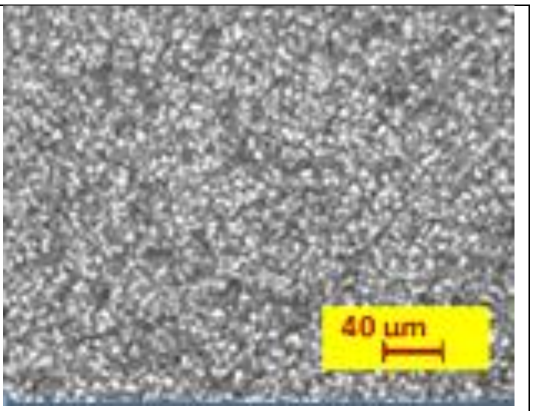
The growth rate of Mo coatings at different deposition temperatures (Fig. 10) is quite well approximated by a linear dependence on the pressure in the reaction volume. At the same time, the deposition curves lie within the range of experimental data for different temperatures. This indicates that the growth rate in the investigated temperature range is primarily controlled by the mass transfer processes of the gas phase components in the near-surface layer above the coating deposition surface, and not by the temperature of the substrate.

The study of the surface morphology of molybdenum coatings showed that depending on the temperature and pressure in the chamber during their deposition, it can differ significantly.

At a deposition temperature of 480 °C (fig. 11) it has a globular structure for all pressure values from 9 Pa to 16 Pa. At a temperature of 500 °C, the coating surface had a globular structure only for a pressure of 16 Pa. At lower pressure values and an increase in the deposition temperature to 540 °C, the structure of the surface of the coatings takes the form of a collection of crystallites of irregular shape and different sizes (Fig. 12).



Figer 11. Surface structure of molybdenum coating, T = 480°C, P =16 Pa.



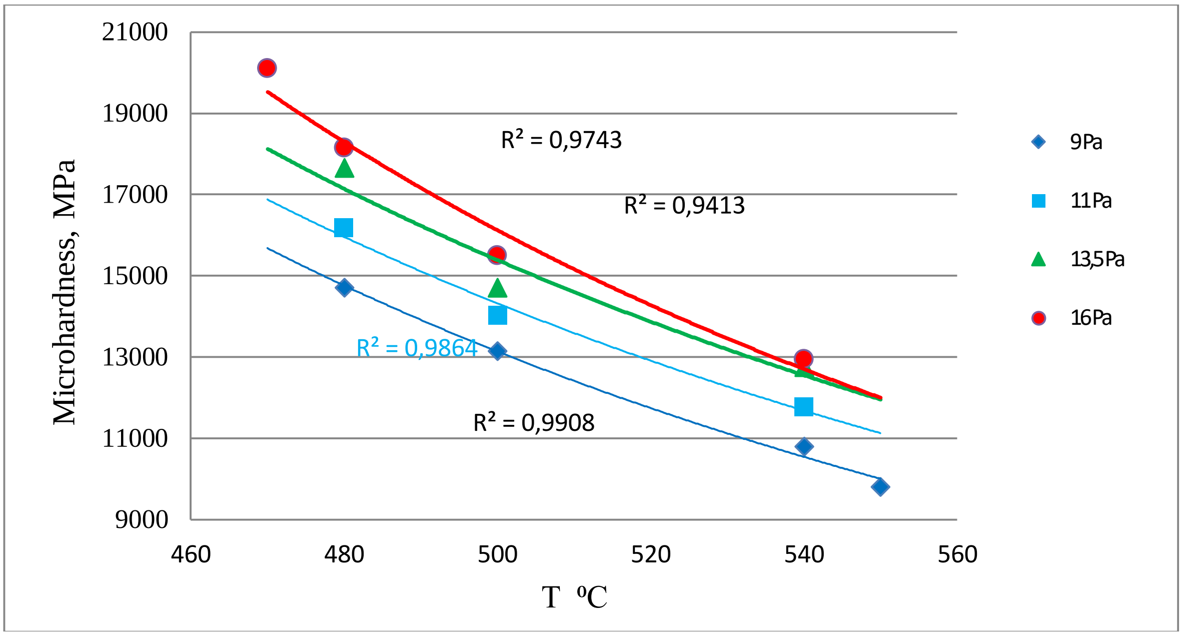
Figer 12. Surface structure of molybdenum coating, T = 540°C, P = 9 Pa.

The microstructure of the coatings obtained under different conditions had a columnar character and differed mainly only in the size of the crystallites, which to a certain extent adjusted to the sizes of the structural elements of the surface of the given coating. In fig. 13 shows a photo of a section of one of the samples with molybdenum coating.

Figer 13. The structure of the Mo coating obtained at a temperature of 500 °C and a pressure of 16 Pa.

Surface roughness Ra of samples with molybdenum coatings was in most cases in the range of 0.12 - 0.25 microns and did not exceed the value of 0.49 microns. Coatings can withstand filleting operations well. After the filleting operation, the roughness decreased to Ra = 0,11-0,15 μm, and in some cases even to 0,07-0,08 μm.

Studies of the microhardness of molybdenum coatings showed that it decreased with increasing temperature and increased with increasing pressure. Fig. 14 presents the results of these studies for different values of temperature and pressure with approximation by curves corresponding to the power law.



Figer 14. Graph of dependence of microhardness of Mo coatings on temperature at different values of pressure.

This character of the dependence of microhardness on the conditions of their deposition has an explanation related to the interaction of molybdenum carbonyl decomposition products with the growing coating and reactions in the gas phase described in works [2, 4]. Yes, in addition to the main reaction of thermal dissociation of molybdenum carbonyl:

$$Mo(CO)6 \rightarrow Mo+6CO \qquad (1)$$

other reactions also occur:

$$CO \leftrightarrow CO_2+C \qquad (2);$$

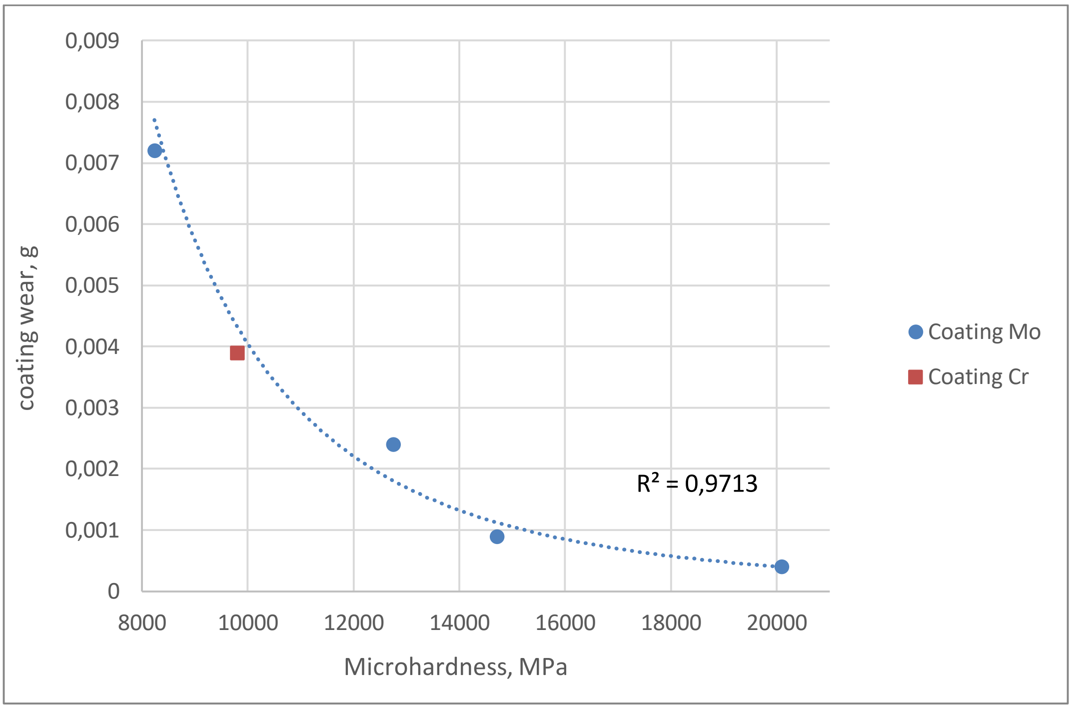
$$2Mo+CO \leftrightarrow MoO+MoC \qquad (3);$$

$$Mo+CO \leftrightarrow MoO+C \qquad (4);$$

$$Mo+2CO \leftrightarrow MoC+CO_2 \qquad (5)$$

The rate of flow of the main reaction of thermal dissociation of molybdenum carbonyl increases with increasing temperature, while the equilibrium of reaction (2) shifts to the left with increasing temperature, which leads to a decrease in the degree of CO conversion. Since the change in hardness within wide limits during the production of metal coatings is primarily associated with their contamination with various impurities, the decrease in hardness of molybdenum coatings with increasing temperature can be explained primarily by the decrease in contamination of the coating with products of incomplete decomposition of molybdenum hexacarbonyl according to reaction (1) and respectively, by carbon according to reaction (2). The consequence of increasing the pressure in the gas phase, according to Le Chatelier's principle, will be a shift in the equilibrium of reactions (1), (3-5) to the right, which will lead to an increase in contamination of the molybdenum coating and an increase in its hardness.

A study of the abrasive wear resistance of Mo coatings with different hardness was conducted. The test was carried out with the supply of abrasive to the contact zone according to the Brinell scheme (II) under a load of 0,05 kN along a friction path of 60 m at a sliding speed of 0,78 m/s. Quartz sand fraction 0,25-0,4 mm was used as an abrasive. The counterbody was a "disc" made of polytetrafluoroethylene (fluoroplastic-4) with a diameter of 50 mm. The amount of wear was determined by the weight method with an accuracy of $1x10^{-4}$ g. To compare the wear of different coatings, this study also used a sample with a galvanic coating of hard chromium, which is widely used as a strengthening and wear-resistant coating in friction pairs with different materials. In fig. 15 shows the graph of the dependence of wear of coatings depending on their hardness.



Figer 15. Dependence of wear of Mo coatings depending on their hardness.

The results of the study of the abrasive wear of Mo coatings depending on their hardness do not contradict the well-known fact that the wear resistance increases with the hardness of the coating. For this set of coatings, this dependence of wear on the value of microhardness can be fairly well approximated by the curve described by the equation $y = 4E+0.7x^{-3.321}$. The value of wear value for galvanic coating made of hard chrome, as can be seen from the graph, practically lies on the curve of dependence of wear of Mo coatings. If we take into account that the maximum hardness of galvanic hard chrome is at the level of 10790 MPa, then the wear resistance of Mo-C coatings under conditions of abrasive wear can be up to 10 times higher compared to hard chrome coatings.

The tribological properties of molybdenum coatings with a hardness of 17950 MPa and below were investigated in friction pairs with nitrided steel 20Cr3MoWV and with bronze VB-23NTS (Pd 18–22 %, Ni 3–4 %, Zn 3–4 %, Sb 3 –4 %, P 0.15–0.3).

To carry out tribological studies of gas-phase molybdenum coatings, samples were used that differed primarily in hardness and temperature of production (Table 3). The surface of the coatings after deposition and before conducting tribological studies was not subjected to any type of treatment.

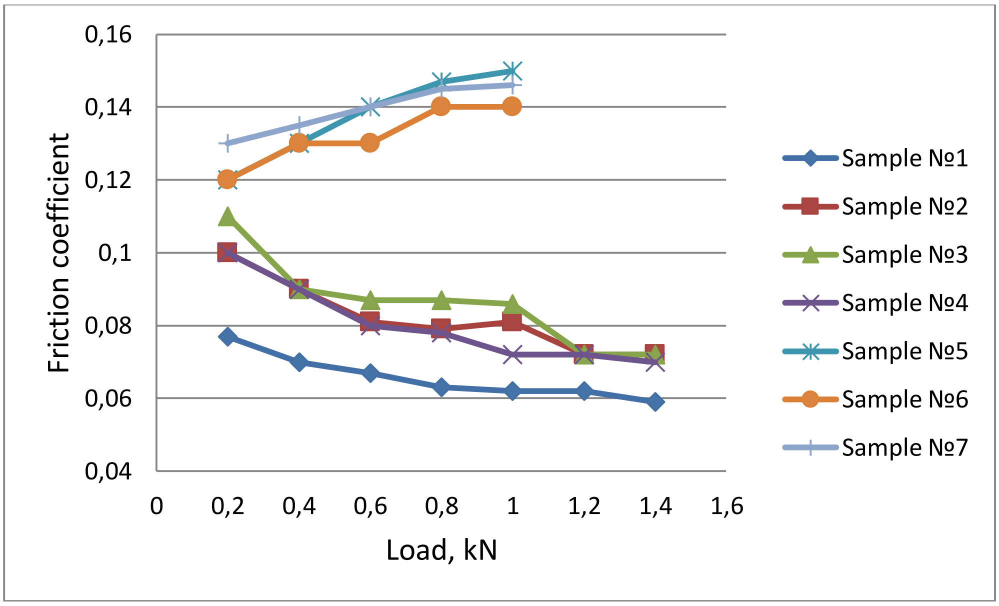
Table 3.

Characteristics of Mo coatings for tribological research.

№	Substrate temperature, °C	Pressure in the cell, Pa	$H\mu$, MPa	Notes
1	550	9	9810	Paired with bronze
2	540	13,5	12750	
3	480	13,5	17800	

4	Galvanic hard chrome		9810	
5	540	9	10790	Paired with steel
6	540	16	12950	
7	480	13,5	17950	

In fig. 16 presents the results of tribological studies of coatings under the numbers corresponding to the numbers in table 4.



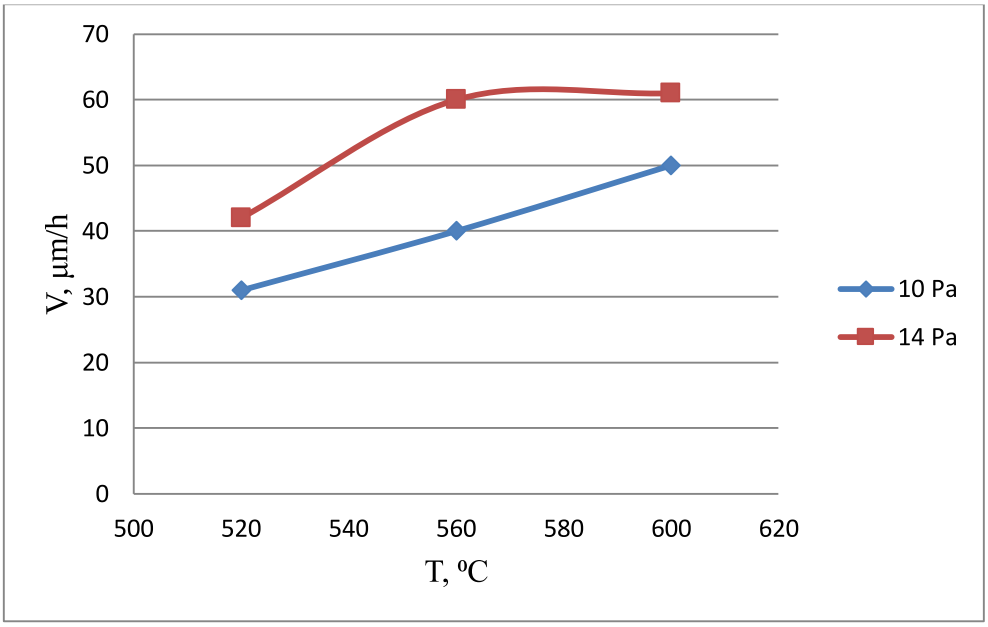
Figer 16. Dependence of the friction coefficient on the load for friction pairs Mo - bronze (samples No. 1 - No. 4) and Mo - nitrided steel 20Cr3MoWV (samples No. 5 - No. 7).

The conducted studies showed that the changes in the coefficients of friction Mo of coatings with nitrided steel 20Cr3MoWV and bronze VB - 23NTS with increasing load had the opposite character. Thus, if the friction coefficient of Mo with bronze decreased with increasing load, which usually occurs as a result of running-in of pairs in the process of testing to a certain stable value, then for the friction pair of Mo with steel, on the contrary, the coefficient of friction increased. In view of this, the maximum value of the load in the experiments for the Mo friction pair - nitrided steel 20Cr3MoWV was limited to 1 kN. The increase in the coefficient of friction of Mo with nitrided steel 20Cr3MoWV indicates insufficient time to reach a stationary mode of friction in these tests. This may be due to the use of samples with the original structure of the surface of the coatings without its preliminary treatment before the machining tests. The conducted studies did not reveal a certain dependence of the coefficients of friction of Mo coatings with nitrided steel 20Cr3MoWV on the hardness of the coating, and the value of the coefficients of friction itself was within the limits of the values indicated above for Mo coatings with higher hardness during tribological studies with other materials (Figs. 6-8).

The coefficients of friction in the friction pair of Mo with bronze for coatings with a hardness of 12750 MPa and 17800 MPa in the friction pair of Mo with bronze did not have a significant difference at a load of up to 1 kN, and at a higher load, they had the same value of 0.072. A noticeable decrease in the coefficient of friction in the entire range of loads was observed when testing a sample of Mo coating with a hardness of 9810 MPa, including, and compared to a chrome coating with the same hardness value.

The conducted experiments showed that in the studied range of conditions for applying molybdenum coatings, their hardness can vary from 9810 kgf/mm2 to 20100 MPa. For comparison, the hardness of hard chromium electrolytic coatings is 8825 -10890 MPa. A comparison of the properties of molybdenum coatings with the characteristics of electrolytic coatings made of solid chromium, obtained under similar test conditions, showed that molybdenum coatings are not inferior to chromium coatings in terms of the friction value, can exceed them in hardness up to two times, and in terms of resistance to abrasive wear up to 10 times. If we take into account that "hexavalent" chromium (CrVI)) is among the most toxic substances that affect nature and human health, and its use is already limited by the European Union directive (RoHS) in the production of a large list of industrial products, then, according to the set of properties, molybdenum coatings can not only compete with electrolytic coatings made of solid chromium, as strengthening and tribological coatings, but also be considered as an alternative to chrome coatings in the environmental aspect.

The processes of thermal dissociation of tungsten carbonyl have many features in common with the processes of thermal dissociation of molybdenum carbonyl, except that they occur at higher temperatures. In fig. 17 presents a graph of the dependence of the growth rate of the tungsten coating on the temperature at different pressure values in the reaction volume.

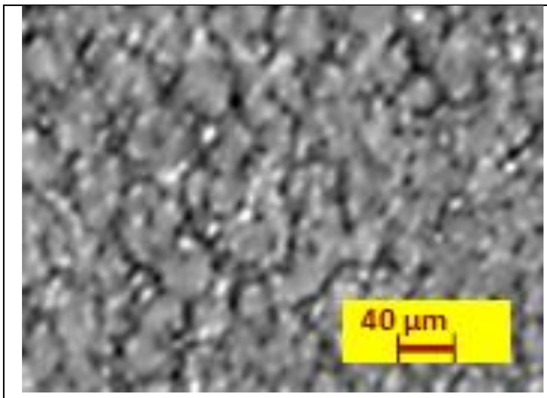
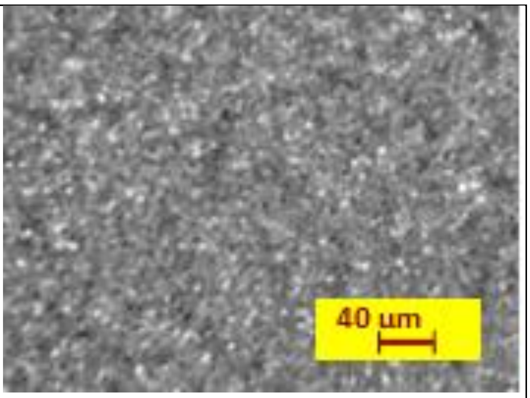


Figer 17. Dependence of the growth rate of W coatings on the deposition temperature at different pressure values.

As can be seen from the given graph, the growth rate of the coating in the studied range of parameter changes depends on both temperature and pressure in the reaction volume.

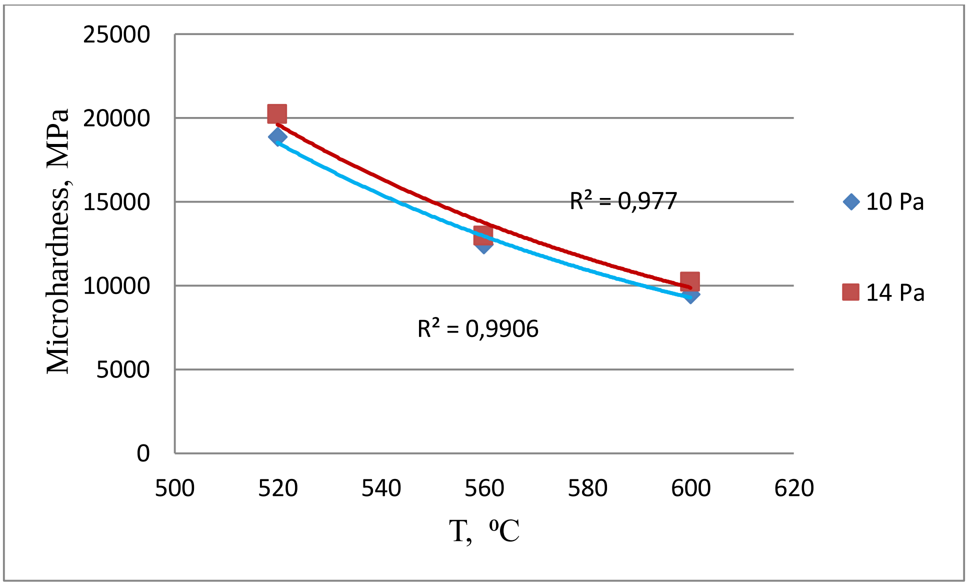
Studies of the surface morphology of CVD W coatings showed that in the studied range of process parameters at a deposition temperature of 520 ℃, the structure has the same regularities as for CVD Mo coatings.

The surface has a globular structure with a characteristic size of a single globule at the level of 1 - 4 microns, which form globular conglomerates with large sizes (Fig. 18). At higher temperatures (560-600 °C), the surface of the coatings also has a globular structure with dimensions at the level of 1 μm, but without the formation of large conglomerates (Fig. 19).

	
Figer 18. Surface structure of tungsten coating, T = 520°C	Figer 19. Surface structure of tungsten coating, T= 560°C.

At the coating growth temperature of 600 °C and 560 °C, the grains in the form of columns have dimensions in diameter of 1 µm throughout the thickness of the coating. At a temperature of 520 °C, grain boundaries are less visible, especially closer to the substrate.

In fig. 20 presents a graph of the dependence of the hardness of tungsten coatings obtained in different modes with approximation by curves corresponding to the power law.



Figer 20. Dependence of the hardness of tungsten coatings on temperature at different pressure values in the reaction volume.

The obtained dependences of the hardness on the process parameters show that its values practically do not depend from the pressure in the reaction volume, but depend, first of all, on the temperature of the coating growth.

As with studies of tribological properties of molybdenum coatings, samples that differed in hardness and temperature were used to conduct tribological studies of gas-phase tungsten coatings with nitrided steel 20Cr3MoWV and bronze VB-24 (Table 4).

Table 4.

Characteristics of W coatings for conducting tribological studies*.

№	Substrate temperature,°C	Pressure in the cell, Pa	$H\mu$, M*P*a	E, ГПа
1	520	10	18880	441
2	560	10	12945	486
3	560	14	13090	470
4	560	14	13240	463
5	600	14	10400	516

*The hardness and Young's modulus of the coatings were determined using the MST3 scratch tester.

Table 5.

Values of coefficients of friction of gas-phase tungsten coatings with bronze VB-24 and with nitrided steel 20Cr3MoWV (in parentheses - values of coefficients of friction with nitrided steel 20Cr3MoWV).

№	The value of coefficients of friction under load P, kN				
	0,2	0,4	0,6	0,8	1,0
1	0,120 (0,110)	0,120 (0,115)	0,113 (0,120)	0,112	0,116
2	0,120 (0,108)	0,120 (0,120)	0,113 (↑)	0,107	0,104
3	0,130 (0,110)	0,120 (0,120)	0,113 (0,123)	0,107	0,118
4	0,130 (0,108)	0,120 (0,123)	0,113 (0,127)	0,137	0,120
5	0,130 (0,110)	0,120 (0,112)	0,113 (0,120)	0,105	0,100

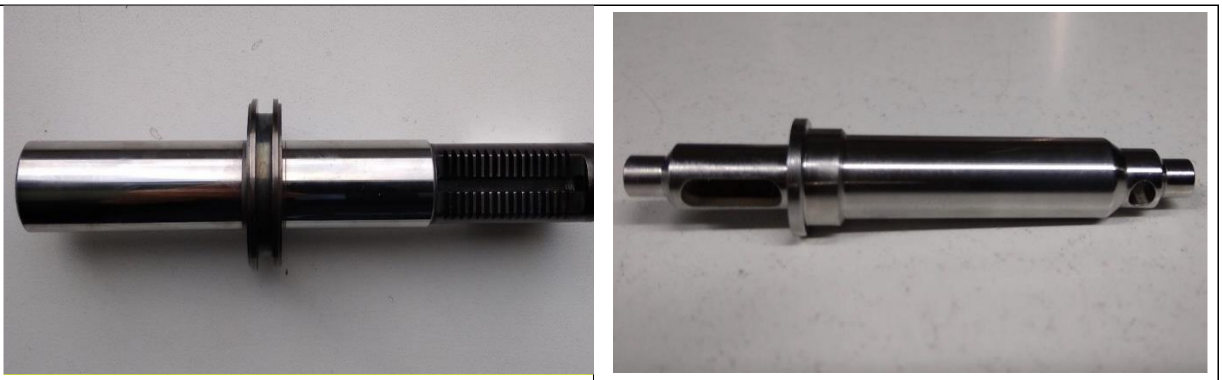
The conducted tribological tests of samples with tungsten coatings did not reveal certain dependences of the value of the coefficients of friction on the modes of obtaining the coatings, as well as the values of their hardness and modulus of elasticity. The friction pair "tungsten-nitrided steel" showed relatively low values of the coefficient of friction at the first load with a load of 0,2 kN. As the load increased, the friction coefficients increased, and the friction pair with sample No. 2 at a load of 0,6 kN developed a burr (↑).

The "tungsten-VB-24" friction pair showed a decrease in friction coefficients in the case of an increase in load up to 0,6 kN. At the same time, if the friction coefficients for different samples had small differences at the initial load of 0,2 kN, then at subsequent loads of 0,4 kN and 0,6 kN, the friction coefficients for different samples completely coincided. At a load of 0,8 kN, a further decrease in the coefficient of friction was observed for samples, except for sample No. 4, and at a load of 1,0 kN, this trend was preserved only for samples No. 2 and No. 5, although their values no longer coincided in magnitude. The results of these tests show that in the friction pair of the tested samples with VB-24 bronze there is wear of the rubbing surfaces in the range of loads up to 0,6 kN with a corresponding decrease in the coefficient of friction.

At higher loads, an increase in the coefficient of friction was observed for several tested samples, which, in the process of operation of such a pair, could lead to the formation of burrs. This may be due to the need for more time for the preliminary run-in of such pairs at lower loads and when working under conditions of higher loads.

The conducted studies confirmed the possibility of obtaining highly hard both Mo-C and W-C coatings at temperatures ≥ 480 °C, as well as obtaining new information about the tribological properties of such coatings in friction pairs with nitrided steel 20Cr3MoWV and bronzes VB 24, VB - 23NTS. The results of previously performed studies and studies in this work indicate the prospects of their use as reinforcements, to increase wear resistance and reduce the coefficient of sliding friction in friction pairs with different materials.

Elucidation of the possibility of practical application of such coatings as coatings of various functional purposes and in various conditions of their operation will require further research of a much larger volume and time to be carried out. Therefore, in order to speed up the obtaining of information about the possibility of practical application of such coatings in production, the process of applying Mo-C coatings to several types of parts of precision assemblies of JSC "Fed" products was carried out. In fig. 21 shows photos of details that were used during the development of the process of applying Mo-C coatings.



a

b

Figer 21. Details used in real designs of products of FED JSC: a – piston; b - stock .

The study of the characteristics of the Mo coatings obtained on the piston (Fig. 21a) in the optimized conditions of the process showed that the thickness of the coatings on the entire controlled surface did not exceed 10 % of the average value of 66 μm, and the microhardness was 15550 MPa with a deviation of about 5 %.

When molybdenum coatings were applied to the working surface of parts with a fairly simple geometry, such as a rod (Fig. 21b), even greater uniformity was achieved both in terms of thickness and microhardness. Thus, deviations in coating thickness did not exceed 2% of the average value of 40 μm, and the microhardness was 14810MPa with a deviation of up to 2.5% from this value.

The high uniformity of the coatings allows applying them with minimal tolerances and subsequent mechanical processing to size or grinding and polishing of the surface to a roughness of Ra < 0,08. Coatings have sufficient adhesion, withstand processing by felting and grinding without breaking the integrity or delamination, ensuring the necessary cleanliness of the processing of the coated surfaces.

The obtained parts with Mo-C coatings will allow testing them in accordance with the test program for these parts in force at the enterprise and determine the advantages or disadvantages of using such coatings, including the possibility and prospects of their use as an alternative to galvanic coatings made of hard chrome.

The results of the conducted research can be used in working out the technological foundations of the processes of applying metal and metal-carbide CVD coatings based on molybdenum and tungsten and serve as a basis for the development of industrial technologies for precision parts of aggregate and engine construction and mechanical engineering.

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