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RESEARCH

Mo-C Multilayered CVD Coatings

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A B S T R A C T

Production processes of multi-layered Mo-C coatings by the method of chemical vapor deposition (CVD) with the use of organometallic compounds were developed. Coatings are applied on technical purpose steel DIN 1.2379 *(Х12Ф1) and DIN 1.7709 (25Х2МФ (ЭИ10) heat-treated ball with the high class of surface roughness (> 10). The average deposition rate was 50 μm/h. The optimal conditions of coatings deposition for different technological schemas were defined.*
Metallographic investigations of the obtained coatings were carried out.
Tribological studies of the friction and wear characteristics of sliding friction in conditions of boundary lubrication of Mo-C multilayered CVD *coatings shows, that coatings have low friction coefficients (0.075 - 0.095) at loads up to 2.0 kN, showed high resistance to wear and are effective in increasing the stability of the pair for precision friction pairs of hydraulical units.*

1. INTRODUCTION

Ever-increasing requirements to raise durability and efficiency of various newly created parts and mechanisms working in friction conditions lead to sharp increase in demands to search new materials working in the conditions of frictional contact and their tribotechnical characteristics. Complexity and integrated nature of these demands boost constant search of new materials and techniques of their production. Especially acute problem of making new highly effective wear resistant materials is for advanced industries of machine building – aircraft engineering, aggregate building, shipbuilding, rocket and space engineering [13].

Raise of the functional properties of parts by use of protective coatings is very widespread technological tool for today. Hardsurfacing, wear resistant, corrosion resistant, etc. functional coatings are widely applied in the industry.

Among coating deposition methods are chemical vapor deposition methods (CVD) based on the pyrolysis of gaseous metal containing compounds [1]. The relative simplicity of realization of processes, absence of high demands to vacuum (in many cases processes take place at atmospheric pressure), high coating deposition rates (up to a few millimeters per hour), and possibility of deposition of the even qualitative coatings on figurine-shaped (including internal) surfaces with great value of relationship L/d, make these methods rather perspective for deposition of the functional coatings [1-3].

Wei and Lo [4] carried out examination of deposition of Mo and Cr coatings at temperatures 170-450 °C and pressure ~ 1 torr using a mixture of carbonyl with hydrogen. Upon that, they used specially prepared carriers made of SiC and SS304. The main emphasis in the work is placed on studying of structure of obtained coatings.

In the work [5] molybdenum was deposited on a porous ceramic carrier at atmospheric pressure. Chromium was deposited from carbonyl at atmospheric pressure also, but already on the polished carriers in the work [6].

It should be pointed out that application of CVD methods to receive hardsurfacing wear- and corrosion resistant coatings was limited yet. From the point of view of practical application, development of processes of obtaining of chemical vapor deposited functional coatings on geometrically complex precision surfaces of high surface finish class (above 10 grade) is of interest. The purpose of this study is development of process of deposition of multilayered Mo-C coatings by a chemical vapor deposition method with use organometallic compounds, studying multilayered and tribological properties of the obtained coatings and an estimate of possibility of their application in the capacity of candidate materials for precision friction pairs.

2. EQUIPMENT, TECHNIQUES, AND USED PROCEDURES

Making Mo-C coatings was carried out by a thermal decomposition of metal-containing compound – molybdenum hexacarbonyl $Mo(CO)_6$. Process development was carried out using gas-phase unit of *Avinit* installation intended for deposition of the multilayered functional coatings by means of complex methods (plasma-chemical CVD, vacuum-plasma PVD (vacuum-arc, magnetron), and processes of ion saturation, and treatment of surfaces by ions) united in one technological cycle), presented in [7].

Process of coating application was controlled by means of temperature of the sample, working pressure in the chamber, and a method of evaporation of molybdenum hexacarbonyl.

For heating of the sample, high-frequency heater was applied with working frequency of 3 MHz and effective power ~ 0.2 kW. Pressure was controlled by dynamical changing of velocity of a pumping-out of vacuum system within 2.6 … 13 Pa (0.02 … 0.1 torr).

Carbonyl evaporation was carried out under two process flow charts:

- The process flow chart of excessive evaporation when a considerable quantity of carbonyl was evaporated within a container volume. Then, along the heated up steam pipeline through the adjustable valve, the gas mixture immediately supplied to the sample. It allowed obtaining major streams of carbonyl and, accordingly, high concentration of molybdenum in a reaction layer. In this case the carbonyl stream depended on temperature of the carbonyl.
- Under other process flow chart (the residual atmosphere) evaporation of a small amount of carbonyl was made immediately inside chamber volume. Thus, the uniform concentration of the reaction gas consisting of carbonyl and carbonic oxide vapors was obtained. At that, molybdenum volume concentration in a chamber atmosphere decreased with the course of process.

3. PROCEDURES OF EXAMINATION

During metallographic analysis the multilayered and microlayer coatings on the basis of system Mo-C were deposited on samples.

Samples were made of structural steel DIN 1.2379 (Х12Ф1) and heat steel DIN 1.7709 (25Х2МФ (ЭИ10) which are the materials commonly used in the industry.

Samples made of steel DIN 1.7709 (25Х2МФ (ЭИ10) with a size of 20 x 10 x 5 mm were polished according to factory production method up to 8 grade surface roughness (R_a=0.32 μm). Microhardness was HB~900.

Samples made of steel DIN 1.2379 (Х12Ф1), 56... 61 HRC, with a size of 10 x 10 x 10 mm were polished to surface roughness of 10 grade (R_a=0.063 μm) to demanded geometrical parameters (nonflatness ≤ 0.001 mm, surface roughness – R_a 0.08 μm).

Tribological tests of antifriction and wear properties and seizure of samples with coatings were carried out with friction and wear machine 2070 SMT-1 under the "cube" - "roller" test pattern at an incremental loading (with increments of 200N) in 1-20 MPa loading range according to the procedures presented in [8,9].

The linear slip velocities - 1.3 m/s. Time of tests in each cycle – 150 seconds. Operating fluid is fuel TS-1, GOST 10227-86.

For reproducibility of results of wearing tests, mating of face surfaces by size of the contact area was controlled: not less than 90 % of a working area of each sample.

During tribological tests there were registered:

- Values of frictional force F_{tr}, normal loading N, contact pressure P, by which value mechanical losses in tribosystems were estimated;
- Temperature of devices was continuously recorded in real time during the tests in immediate proximity (1 mm) from a friction zone, with application of the sliding thermocouple. Friction coefficients were determined as $f = F_{tr}/N$.

4. RESULTS

4.1 Deposition of coatings

Technological information for process of coating deposition on steel DIN 1.7709 (25Х2МФ (ЭИ10) is presented in Tables 1.1, 1.2 and 2.

Table 1.1 Mo/Mo-C coatings obtained at puffing of carbonyl from the container.

Temperature, °C	Pressure, Pa	Exposition τ, min.	Thickness δ, μm	Deposition rate V, μm/min.	Adhesion
350	5.20	10	8	0.80	+++
	10.00	10	7	0.70	+++
	5.30	15	17	1.13	+++
	11.00	15	10	0.67	+++
	8.80	30	25	0.83	+++
	11.00	30	31	1.03	++
400	5.60	5	3	0.60	++
	5.40	10	8	0.80	+
	5.50	10	6	0.60	+
	6.10	10	8	0.80	+
	5.00	15	10	0.67	-
	5.40	15	12	0.80	-
450	7.60	5	6	1.20	+++
	5.30	15	17	1.13	+++
	7.20	15	20	1.33	+++
	5.10	30	12	0.40	+++

+++ - the coating is deleted only by pickling
++ - insignificant chipping
+ - a lot of chipping

Table 1.2 Coatings Mo/Mo-C obtained in an atmosphere of the residual gases.

Temperature, °C	Pressure, Pa	Exposition τ, min.	Thickness δ, μm	Deposition rate V, μm/min.	Adhesion
350	3.90	15	4	0.27	+++
	10.0	15	4	0.27	++
	12.0	30	10	0.33	+
	11.0	60	16	0.27	-
400	2.80	15	0.5	0.03	-
	3.20	30	1	0.03	-
	3.80	60	5	0.08	-
450	4.00	15	2	0.13	++
	30	3.70	4	0.13	+

Table 2. Parameters of CVD process of coating application.

Sample No.	Sample temperature, ° C	Exposition, min.	Microhardness H_v, kg / μm ²	Thickness δ, μm
23	430	10	2500	15
25	360	10	1800	10
25	290	10	2500	10

Properties of coatings sharply differ in the set temperature interval. At 350 °C and 450 °C stable uniform deposition of coating with high value of microhardness is observed: HB=2200 at 350 °C, HB=1700 at 450 °C. The thickness of a coating depends linearly on cure time. The lower temperature, the lower adhesion to the initial sample is observed, while at 450 °C the coating has the good adhesion with a carrier.

Deposition rate of the coatings obtained in an atmosphere of the residual vapors at temperature 350 °C is even during long enough time intervals; however, quality of a coating deteriorates in process of magnification of coating thickness that is obviously related with accumulation of sufficient internal stresses in a film.

Parameters of CVD-process of coating application on samples made of steel DIN 1.2379 (X12Ф1) are shown in Table 2. After deposition of CVD coating samples were polished with diamond paste ASM7/3 with removal of 0.004-0.006 mm stock up to recovery of flat surface accuracy.

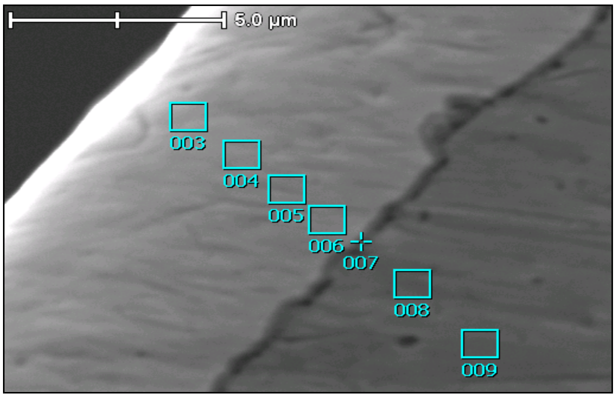
Change of working pressure within 0.01 ... 0.1 torr affects Mo/Mo-C composition and leads to inappreciable decrease in adhesion which becomes more appreciable at magnification of a thickness of a coating.

4.2 Metallographic examination

Metallophysics measurements of the obtained samples are carried out on raster-type electronic microscope JSM T-300. Appearance of Mo-C coating on samples made of steel DIN 1.2379 (X12Ф1) (a traversal metallographic sample) with marked zones of analysis (a) and an approximate chemical composition of analyzed zones (b) is shown in Fig. 1.

Appearance of Mo/Mo-C coating on the sample made of steel DIN 1.2379 (X12Ф1) in a mapping mode is shown in Fig. 2.

Appearance of Mo-C coating on samples made of steel DIN 1.7709 (25X2MФ (ЭИ10)) (a traversal metallographic sample) with marked zones of the analysis (a) and an approximate chemical composition of analyzed zones (b) is shown in Fig. 3.

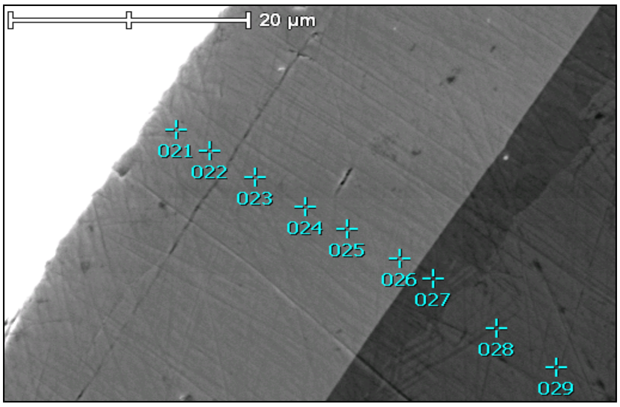


a) DIN 1.2379 (X12Ф1)

Point No.	Si	Cr	Fe	Ni	Mo	P
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

b) Chemical composition of analyzed zones

Fig. 1. Appearance of Mo-C coating on samples made of steel DIN 1.2379 (X12Ф1) with marked zones of analysis (a), and the chemical composition of analyzed zones (b).



a) DIN 1.7709 (25X2 MФ (ЭИ 10)

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) Chemical composition of analyzed zones.

Fig. 3. Appearance of Mo-C coating on samples made of steel DIN 1.7709 (25X2MФ (ЭИ10)) with marked zones of the analysis (a) and the chemical composition of analyzed zones (b).

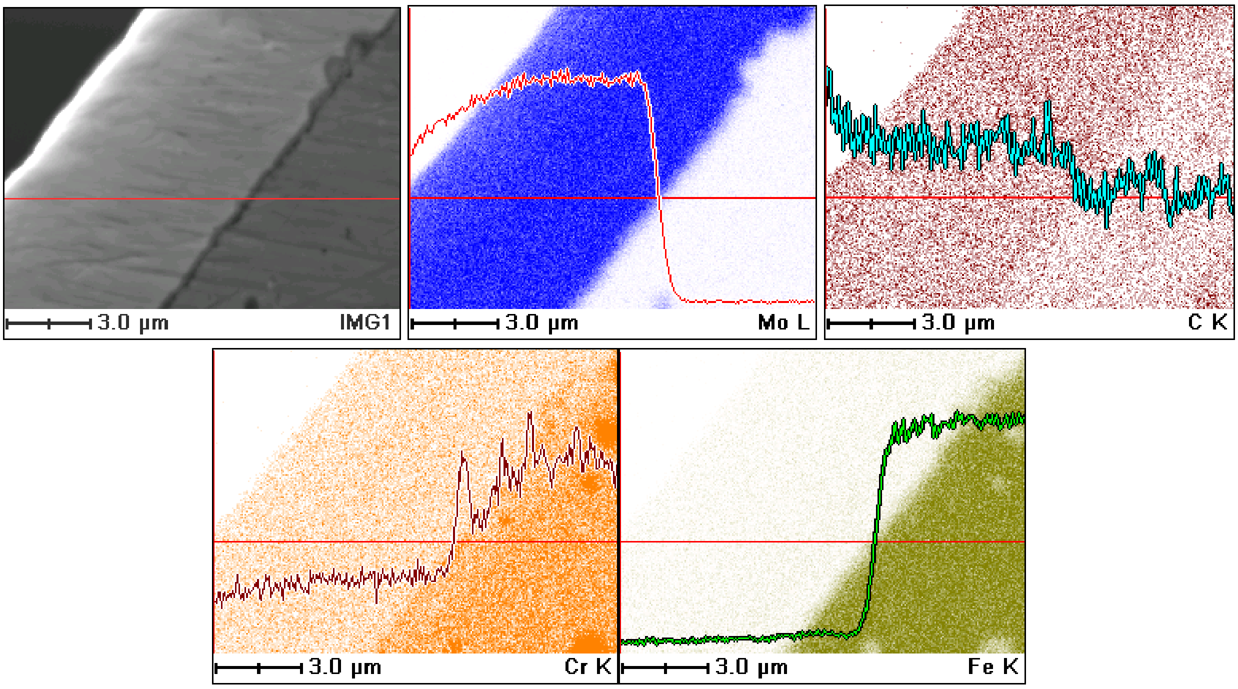


Fig. 2. Appearance of Mo/Mo-C coating on the sample made of steel DIN 1.2379 (X12Ф1) in a mapping mode. More content of the element there matches to more saturated color.

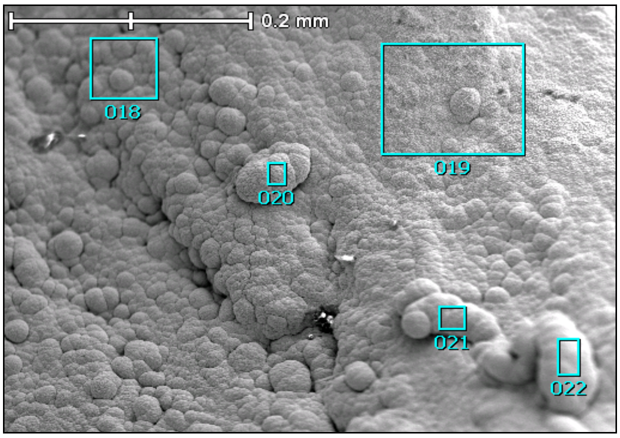


Fig. 4. A microrelief of a surface of the sample (steel DIN 1.7709 (25X2MФ (ЭИ10)).

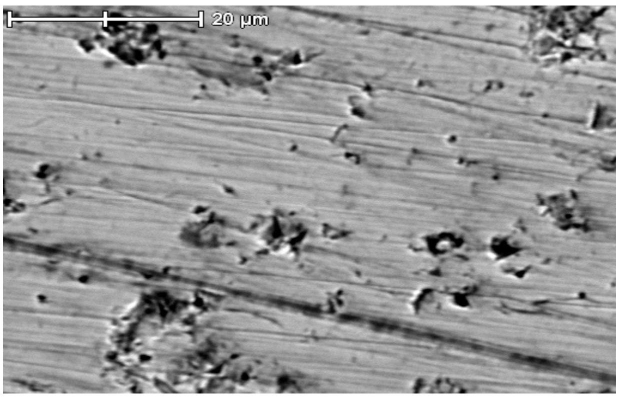


Fig. 5. A microrelief of a surface of the sample (steel DIN 1.2379 (X12Ф1)) after its polishing.

Metallophysics measurements have shown high enough extent of coincidence of phase composition of a carrier material - steels DIN 1.2379 (X12Ф1) and DIN 1.7709 (25X2MФ (ЭИ10)) (zones 009 and 029, accordingly).

Photos of a microrelief of coating surfaces are shown in Figs. 4 and 5.

4.3 Results of tribological tests

Multilayered and microlayer coatings on the basis of Mo-C system are deposited on basic samples - cubes made of steel DIN 1.2379 (X12Ф1) with hardness 56 ... 61HRC (HB~900) with the working planes polished by diamond paste to reach required geometrical parameters (nonflatness - ≤ 0,001mm, surface roughness - R_a 0,08 µm) for carrying out of tribological tests. Parameters of CVD-process of coating application on examined samples and properties of the obtained CVD-coatings are shown in tab. 2. After deposition of CVD coatings samples were polished by diamond paste ASM7/3 with with removal of 0.004-0.006 mm stock up to recovery of flat surface accuracy.

Results of tribological tests are presented in Figs. 6-8 and in Tab. 3.

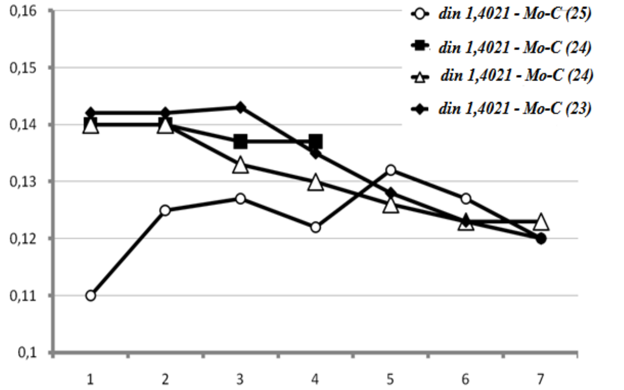


Fig. 6. Dependence of friction coefficient on loads for a friction pair Mo-C/steel DIN 1.4021 20Х3МВФ (ЭИ 415).

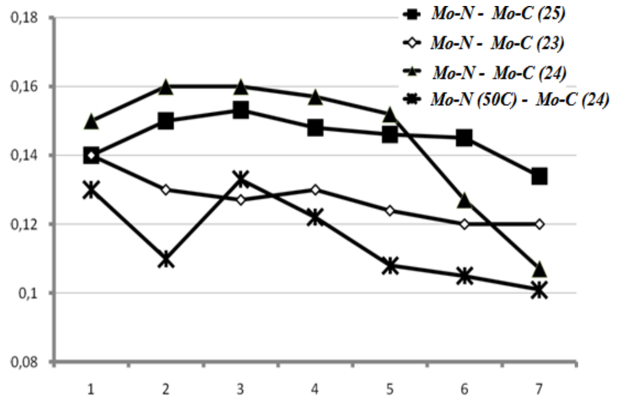


Fig. 7. Dependence of friction coefficient on a loading for a friction pair Mo-C / Avinit coating (on the basis of Mo-N).

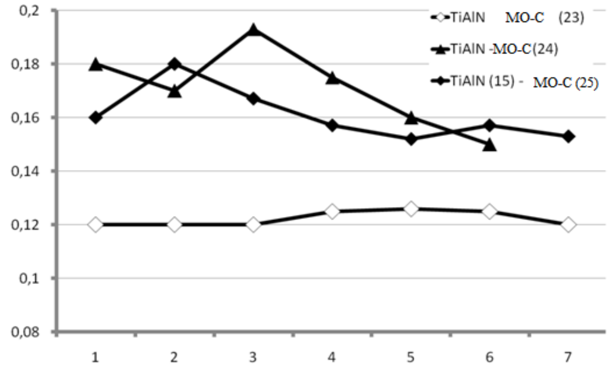


Fig. 8. Dependence of friction coefficient on a loading for a pair of a friction Mo-C / Avinit coating (on the basis of Ti-Al-N).

When carrying out tribological tests, the special priority has been given to studying of behaviour of the developed coatings in tribological matings with steels.

As is clear from the obtained data, and also by results of carried out earlier tribological studying [10,11], the best tribological parameters in contact pair with steel are determined for Mo-C coatings. Good tribological properties are exhibited by Mo-C coatings in case of friction in pairs with hard and extremely hard coatings which have been already used in friction pairs of precision units in aircraft aggregate building [10-12].

Table 3. Friction coefficients of samples during tribological tests.

Roller (coating)	Cube (coating)	Applied loading, kN						
		0.2	0.4	0.6	0.8	1	1.2	1.4
Avinit coating (on the basis of Mo-N) δ =1.5 μm, 2200HV	Mo-C (23)	0.14	0.13	0.127	0.13	0.124	0.12	0.12
	Mo-C (24)	0.15	0.16	0.16	0.157	0.152	0.127	0.107
	Mo-C (24)	0.13	0.11	0.133	0.122	0.108	0.105	0.101
	Mo-C (25)	0.14	0.15	0.153	0.148	0.146	0.145	0.134
Avinit coating (on the basis of Ti-Al-N) δ =1.5 μm, 3500HV	Mo-C (23)	scoring						
	Mo-C (24)	0.18	0.17	0.193	0.175	0.16	0.15	
	Mo-C (25)	scoring						
The same *Run in separately*	Mo-C (25)	0.16	0.18	0.167	0.157	0.152	0.157	0.153
The same *Run in separately*	Mo-C (23)	0.12	0.12	0.12	0.125	0.126	0.125	0.12
DIN 1.4021 20Х3МВФ (ЭИ 415), cementation, 88HRC	Mo-C (23)	0.14	0.14	0.143	0.135	0.128	0.123	0.12
	Mo-C (24)	0.14	0.14	0.137	0.137			
	Mo-C (25)	0.11	0.125	0.127	0.122	0.132	0.127	0.12
DIN 1.4021 20Х3МВФ (ЭИ 415), *run in separately*	MoC (24)	0.14	0.14	0.133	0.13	0.126	0.123	0.123

Table 4. Estimate of aging traces on samples after tribological tests.

Mo-C cube (No. 23) $\delta \approx 15$ μm, 2500HV; After a lapped finishing with diamond paste $\delta \approx 10$ μm.		
No.	Roller (coating)	Test results
1	DIN 1.4021 20Х3МВФ (ЭИ 415), cementation, ≥88HRC	The cube has aging traces with parameters (determined using the profilogram): - depth - ≈0.4 μm; - width - 0.6 mm. The roller has a normal aging trace; signs of wear are visually absent.
2	Avinit coating (based on Mo-N) δ =1.5 μm, 2200HV	The cube has aging traces with parameters (determined using the profilogram): - depth - ≈0.5 μm; - width - 0.8 mm. The roller has a normal aging trace, signs of wear are visually absent
3	Avinit coating (based on Ti-Al-N) δ =1.5 μm, 3500HV	The cube has 2 seizure sites which are placed near to ribs of a cube, the main aging trace has following parameters (determined using the profilogram): - Depth - ≈3.4 μm; - width - 1 mm. The roller has two ring furrows which are reciprocal to the seizure sites on the cube
3 a	Avinit coating (on the basis of Ti-Al-N) δ =1.5 μm, 3500HV *Run in separately*	The cube has aging traces with parameters (determined using the profilogram): - depth - ≈1.2 μm; - width - 0.8 mm. The roller has a normal aging trace; signs of wear are visually absent.
Mo-C Cube (No. 24) $\delta \approx$ 10мкм, 1800HV; after a lapped finishing diamond paste $\delta \approx 5$ μm.		
No.	Roller (coating)	Test results
4	DIN 1.4021 20Х3МВФ (ЭИ 415), cementation, ≥88HRC	The cube has large fretting in width of ≈7 mm The roller has ring traces of cube material transport
5	Avinit coating (based on Mo-N) δ =1.5 μm, 2200HV	The cube has aging traces The roller has a normal aging trace; signs of wear are visually absent.
5a		The cube has aging traces with parameters (determined using the profilogram): - depth - ≈18 μm; - width - 1.8 mm. The roller has a normal aging trace; signs of wear are visually absent.
6	Avinit coating (based on Ti-Al-N) δ =1.5 μm, 3500HV	The cube has aging traces with parameters (determined using the profilogram): - depth - ≈19μm; - width - 1.9mm. The roller has a normal aging trace; signs of wear are visually absent.
6a	DIN 1.4021 20Х3МВФ (ЭИ 415), cementation, ≥88HRC, *run in separately*	The cube has aging traces with parameters (determined using the profilogram): - depth - 0.4 μm; - width - 0.5 mm. The roller has a normal aging trace; signs of wear are visually absent.
Mo-C Cube (No. 25) $\delta \approx 10$μm, 2000 ... 2500HV; after a lapped finishing diamond paste $\delta \approx 5$ μm.		
No.	Roller (coating)	Test results
7	DIN 1.4021 20Х3МВФ (ЭИ 415), cementation, ≥88HRC	The cube has aging traces with parameters (determined using the profilogram): - depth - ≈0.3 μm; - width - ≈0.5 mm. The roller has a normal aging trace; signs of wear are visually absent.
8	Avinit coating (based on Mo-N) δ =1.5 μm, 2200HV	The coating on a cube inside the trace is visually worn to the carrier. The cube has aging traces with parameters (determined using the profilogram): - depth - ≈4.4 μm; - width - 1 mm. The roller has a normal aging trace; signs of wear are visually absent.
9	Avinit coating (based on Ti-Al-N) δ =1.5 μm, 3500HV	The cube has 2 seizure sites which are placed near to ribs of a cube; flaws on a coating were formed on the same plane of a cube. The roller has two ring furrows which are reciprocal to the seizure sites on the cube.
9a	Avinit coating (based on Ti-Al-N) δ =1.5 μm, 3500HV *run in separately*	Exfoliation of the coating on the given plane of a cube, along aging traces from both its sides, is available, parameters of aging traces (determined using the profilogram): - depth - 19 μm; - width - 2 mm. The roller has a normal aging trace; signs of wear are visually absent.

When friction of cubes with Mo-C coatings over rollers with Avinit coating (on the basis of Mo-N), low enough antifrictional parameters are also observed.

Rollers with extremely hard *Avinit* coatings (on the basis of Ti-Al-N) exhibit higher friction coefficients, and there are cases of a scoring of Mo-C coating.

Results of an estimate of aging traces in tested friction pairs after tribological tests are shown in Table 4.

It is noted, that in case of use of already run-in rollers, minimum friction coefficients are obtained, thus cases of a scoring of Mo-C coating are not available.

Carried out tribological tests of Mo-C coatings testify to efficiency of the developed coatings for precision friction pairs («steel/coating» and «coating/coating») with the raised wear hardness and low friction coefficient.

5. CONCLUSIONS

1. Process of application of multilayered Mo-C coatings by a chemical vapor deposition method with use of organometallic compounds is developed. The multilayered composite coatings on the basis of Mo-C system are obtained. Optimization of processes of deposition of qualitative tightly interconnected coatings is carried out.
2. The kinetics of coating deposition process is studied. Coating deposition rate up to 100 μm/hour is obtained.
3. Metallographic examination confirm possibility of the low-temperature deposition of qualitative very hard Mo-C coatings in developed *CVD* process, good adhesion to carrier materials (to steels DIN 1.2379 (Х12Ф1), DIN 1.7709 (25Х2МФ (ЭИ10)) without decrease in strength properties of a steel and without a deterioration of an initial surface finish class is thus provided.
4. Multilayered and nanolayer coatings on samples for tribological tests are obtained and tribological tests of samples with coatings are carried out.
5. Possibility of postoperative machining of coatings by industrial methods without losses of the functional properties of coatings is proven.
6. Tribological tests exhibit high tribological properties of Mo-C coatings and testify to perspectivity of the developed coatings for selection of optimum constructions of coatings for raise of stability of precision friction pairs.

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