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Regularities of fretting-corrosion wear of coatings formed by gas-thermal spraying methods

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The results of experimental studies of wear under fretting-corrosion conditions on a number of coatings formed by the methods of plasma-arc, pulse-plasma, and high-velocity gas-flame spraying are presented. Analytical studies of the regularities of the stress-strained state formation in the "GTS-coating-base" system and evaluation of the efficiency of various technological influences and methods of forming coatings on wear resistance were carried out.
Keywords: fretting-corrosion, wear, plasma spraying, gas-flame spraying, electric arc spraying

Закономірності фретинг-корозійного зношування покриттів, сформованих методами газотермічного напилення. *М.В. Кіндрачук, В.В. Харченко, В. Є. Марчук, І. А. Гуменюк, Н. М. Стебелецька, М. А. Гловин, І. В. Костецький*

Подано результати експериментальних досліджень закономірностей зношування в умовах фретинг-корозії ряду покриттів сформованих методами плазмового, імпульсно-плазмового та високошвидкісного газополуменевого напилення. Виконано аналітичні дослідження закономірностей формування напружено-деформованого стану в системі "ГТН-покриття-основа" та дослідження з оцінювання ефективності різних технологічних впливів і методів конструювання покриттів на зносостійкість.

1. Introduction

Among the current and actively developing methods of engineering wear-resistant surfaces, methods of gas-thermal spraying (GTS) of coatings are among the most versatile and productive. To date, a fairly wide range of materials, both simple and complex in terms of component content, has been developed and used for GTS, which allows obtaining coatings with various properties [1-5]. At the same time, the recommendations for their use in most cases indicate only the functional purpose of the coating, without taking into account the entire set of requirements for performance characteristics, which are put forward by operation conditions of parts. Establishing the relationships between the initial composition of the material, technological parameters of spraying and the tribotechnical properties of coatings will contribute to the improvement of efficiency and wider implementation of GTS technologies for solving tribotechnical problems.

Compared to the detonation method, methods of plasma and gas-flame spraying are characterized by higher productivity, but the coating have lower density and adhesive-cohesive strength. The development of plasma and gas-flame spraying technologies is aimed at ensuring a significant increase in the speed of particles of the sprayed material and makes it possible to control the temperature and gas-dynamic parameters of working jets.

Theoretical and experimental studies have established that the most significant increase in the adhesion strength of the GTS coating to the base material is achieved at supersonic speeds of the working jet and spray particles. Moreover, the density and cohesive strength of coatings increase as well [6-9]. This is due to an increase in the local pressure and temperature in the zone of collision of the sprayed particles with the base, which activates the processes of intermolecular and interatomic interactions in the base material.

2. Experimental

To increase the speed of sprayed particles and, accordingly, the operational characteristics of coatings, the Institute of Superhard Materials of the National Academy of Sciences of Ukraine has developed a method of pulse plasma spraying based on the use of pulse plasma jets generated by the discharge of a capacitive energy storage device between coaxially located electrodes. The velocity of the pulse plasma jet at atmospheric pressure can reach $1 \cdot 10^4 \ldots 2 \cdot 10^4$ m/s, and the speed of the spray particles is $1 \cdot 10^3 \ldots 2 \cdot 10^3$ m/s.

The so-called High Velocity Oxygen Fuel (HVOF) and High Velocity Air Fuel (HVAF) methods of gas flame atomization also belong to the advanced innovative technologies of GTS. In these methods, a gas jet is used for heating, spraying, and transporting the spray material, generated by a special burner with a jet-type acceleration chamber during the burning of combustible gas acetylene (propane, hydrogen, or propylene) mixed with oxygen fuel (HVOF method)\ or with compressed air (HVAF method) [10; 11]. When using the HVOF method, the velocity of the jet of combustion products reaches 1350 m/s to 2880 m/s, and the speed of the spray material particles – 700 m/s to 1000 m/s.

The purpose of this study was to establish the regularities of fretting-corrosion wear and the formation of the stress-strain state in the "coating-base" system during wear tests for various methods of spraying coatings.

The results of the wear tests under fretting-corrosion conditions of a number of coatings obtained from different materials using the plasma-arc, pulse-plasma, and high-velocity air flame HVAF spraying methods are presented in Table 1 in comparison with the structural titanium alloy VTZ-1. The technological parameters of spraying for each of the studied coating types were prior optimized to obtain the most uniform structure and achieve the highest adhesion strength for the coating tested. After spraying, the coatings were subjected to diamond grinding to a thickness of 0.2...0.3 mm and a surface roughness of Ra~0.2...0.3 mm.

The wear tests were performed in two amplitude-load modes of fretting: conditionally "moderate" (A = 125 μm; P = 20 MPa) and conditionally "hard" (A = 250 μm; P = 30 MPa). For the former, the test base was $N = 5 \cdot 10^5$ cycle and for the latter, $N = 2.10^5$ cycle. The counterbodies were samples made of steel 45, hardened and annealed to a hardness of HRC 50...52.

The linear wear H is determined by profiling the annular friction track formed on the friction surface of a fixed sample in eight directions. The wear intensity is determined by the formula:

$$I_N = \frac{\sum_1^8 h}{8},$$

where h is the distance on the friction track profilogram between the center lines of the profile of the initial and rubbing surfaces.

3. Results and discussion

The obtained data (Table 1) show that in both conditionally "moderate" and conditionally "hard" amplitude-load modes of fretting, the coatings of all types have higher wear resistance compared to the titanium alloy VTZ-1. It should be noted that, regardless of the spraying method, the coatings containing high-hard carbide phases (KHN-30, KTN-35, KTN-50, PS-12NVK-01 coatings) in the medium-amplitude fretting mode showed higher wear resistance than in the hard fretting mode compared to the less hard molybdenum coating.

Additional studies were carried out to determine the dependence of linear wear on the specific contact load for KKhN-30, KTN-35, KTN-50 coatings sprayed by the plasma-arc method, and Mo-coating sprayed by the HVGF method. The KKhN-30, KTN-35, and KTN-50 coatings were tested in pairs of the same material, the Mo coating – in a pair with hardened steel 45 (HRC 52...54).

The tests were carried out with stepwise-increase loads in the range of P = 9.8...49.0 MPa with a step of 4.9 MPa at relative displacement

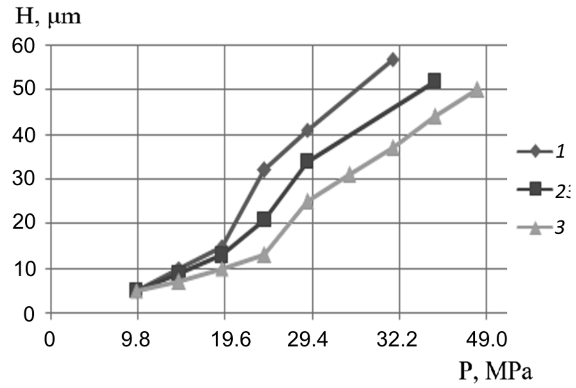


Fig. 1. Dependence of the average linear wear of KKhN-30 (1), KTN-35 (2), and KTN-50 (3) coatings on the specific contact load. Spraying by plasma-arc method. Test conditions: A=125 μm; v=30 Hz; T=293 K; N=5·10? cycles. Pairs from identical material.

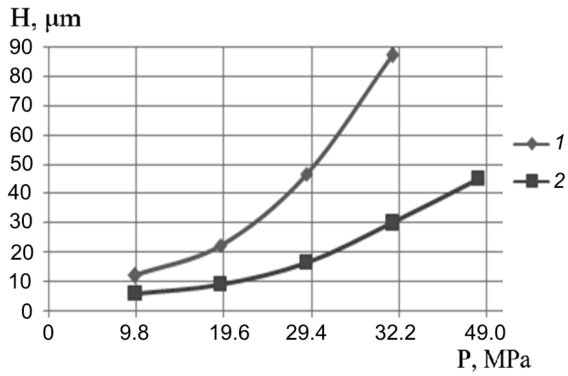


Fig. 2. Dependence of the average linear wear of the molybdenum coating on the specific contact load. Spraying by the HVAF method. Test conditions: (1) A=250 μm; P = 29.4 MPa; N = $2\cdot10^5$ cycles; (2) A=125 μm; P = 20.4 MPa; N=$5\cdot10^5$ cycles. v=30 Hz; T = 293 K. Counterbody material: steel 45 (HRC 50-52)

amplitudes of 125 μm and 250 μm on the basis of tests for $N = 5.10^5$ cycles and $N = 2.10^5$ cycles. The results of the study are presented in Figs. 1 and 2.

As shown in Fig. 1 for KKhN-30, KTN-35, and KTN-50 coatings, a non-monotonic jump-like increase in the wear is observed when the specific load in the contact increases above a certain critical value P_{cr}. Such a character of the $H = f(P)$ dependence indicates a change in the mechanism of frictional destruction.

Among the coatings of this group, the coating of the Cr_2C_3-Ni system (KKhN -30) has the lowest P_{cr} and the lowest wear resistance. Metallographic analysis showed that its structure consists of Cr_2C_3 carbide grains randomly distributed between the layers of the nickel binder. It was established [12, 13] that chromium carbide almost does not dissolve in Ni even at high temperatures, therefore, the binding of carbide and Ni particles in the KKhN-30 coating can occur primarily due to mechanical adhesion. When stresses exceed the cohesive strength of the material at the interface between the carbide and matrix phases, brittle local failure of the coating occurs; separation of free Cr_2C_3 particles and their movement in the contact zone under fretting conditions causes intense abrasive wear.

As shown in [14-17], the phase composition of coatings of the TiC-Ni system (KTN-35 and KTN-50), formed by plasma spraying, differs from the composition of the initial material. In addition to TiC and Ni, some other phases were found in the coatings such as a solid solution of TiC in Ni, double carbide $(TiNi)_6C$, and intermetallic compounds TiNi and $TiNi_3$. The presence

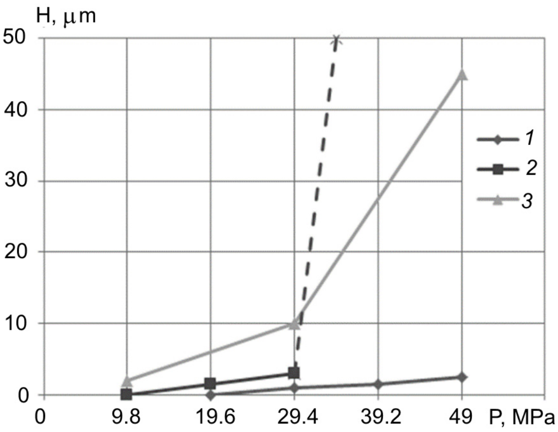


Fig. 3. Results of comparative tests on wear of coatings under fretting corrosion conditions with lubrication: (1) molybdenum, gas flame spraying; (2) 40Kh13, electric arc metallization; (3) hard electrolytic chromium. Test conditions: A=150 μm; v =30 Hz; T=293 K; N=$5\cdot10^5$ cycles. Counterbody material: steel 45 (HRC=50-52). Lubricating material: “Era”.

of these phases indicates solid-phase diffusion and chemical interaction of TiC and Ni during deposition with a high-temperature plasma jet. In this case, a higher cohesive strength of the coating and, accordingly, a higher value of P_{cr} should be expected.

Similar features of fretting-corrosion wear can be expected in other composite HTS coatings, the structural-phase composition of which is a system of “hard strengthening phase - soft matrix”; it is characterized by insufficiently high adhesion for this fretting amplitude mode. In this case, the difference in the dependence of the wear on fretting parameters will be associated mainly with the strength of cohesive bonds between individual structure-phase com-

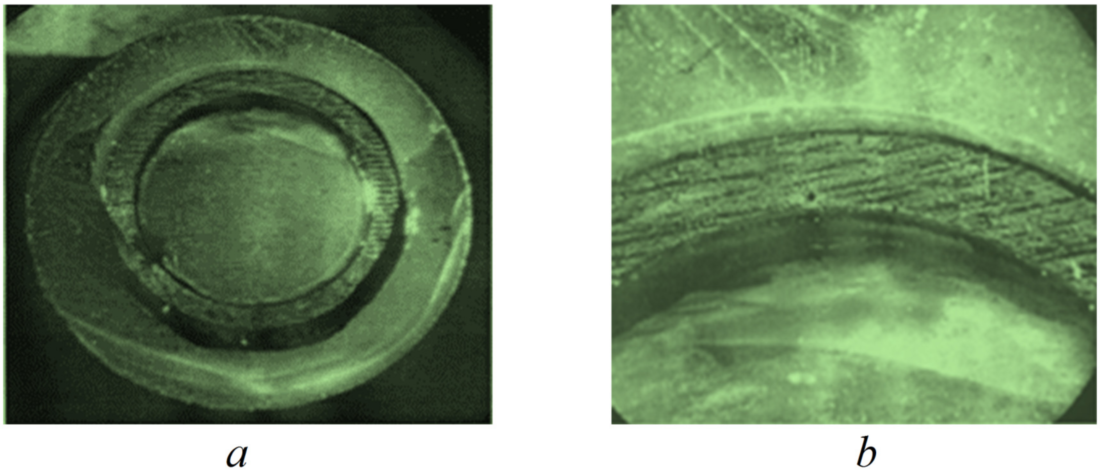


Fig. 4. Topography of the friction surfaces of the sample (*a*) and counterbody (*b*) after wear tests under fretting–corrosion conditions. Sample: molybdenum, HVAF method of spraying. Counterbody: steel 45 (HRC 52...54). Test conditions: A = 150 μm; P = 29.4 MPa; ν=30 Hz; T = 293 K; N = $5\cdot10^5$ cycles. Lubricating material: “Era”

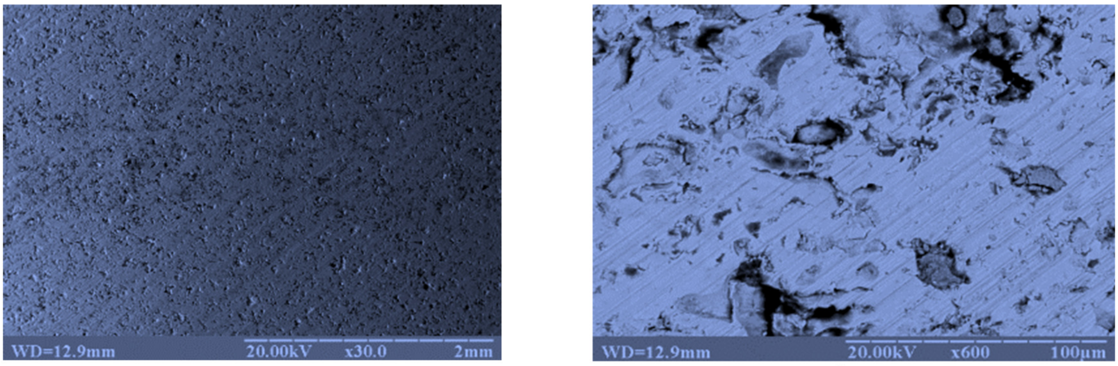
ponents of coating layers and the abrasiveness of its wear products.

The dependence $H = f(P)$ for the molybdenum coating increases monotonically with increasing specific contact load without a clearly expressed jump-like behavior of the degree of wear. This indicates that the evolution of frictional destruction in the molybdenum coating at given fretting parameters proceeds by the same leading mechanism; that is, the coating itself is characterized by a high level and high homogeneity of the strength of cohesive bonds.

It is worth noting that due to their porosity, gas-thermal coatings are considered promising for application to parts that work under conditions of friction with lubricant, in particular, as an alternative to the electrolytic chrome coatings, which are widely used so far. This is especially important for heavily loaded parts of conditionally fixed joints, where the wear life of electrolytic chromium coatings is limited due to unsatisfactory surface wettability with lubricants and the low ability of hard chromium coatings to be worn in. Recently, the use of electrolytic chromium plating has been limited in world practice due to the high toxicity of chromium compounds and the problems of their wastes. When searching for alternative

Table 1. Results of comparative wear tests under fretting-corrosion conditions of coatings formed by plasma-arc, pulse-plasma, and high-velocity gas-flame spraying methods

No	Coating	Composition of initial material	Method of spraying	Index of wear resistance I_N, cycle/μm, for amplitude-load mode of fretting	
				Moderate mode	Hard mode
1.	KKhN-30	70 mass% Cr_2C_3+ 30 mass% Ni	Plasma-arc	$3.6\cdot10^4$	$0.25\cdot10^4$
			Pulse-plasma	$5.0\cdot10^4$	-
2.	KTN-35	65 mass% TiC+35 mass %Ni	Pulse-plasma	$4.2\cdot10^4$	-
3.	KTN-50	50 mass% TiC +50 mass% Ni	Plasma-arc	$4.9\cdot10^4$	-
4.	PS-12NVK-01	65 mass% Ni-Cr-B-Si-Fe alloy +35 mass% WC	Plasma-arc	$4.8\cdot10^4$	$0.27\cdot10^4$
			Pulse-plasma	$5.9\cdot10^4$	-
5.	Molybdenum	Mo powder	Plasma-arc	$5.2\cdot10^4$	$0.5\cdot10^4$
			HVAF	$5.6\cdot10^4$	$0.91\cdot10^4$
6.	Alloy VTZ-1			$2.0\cdot10^4$	$0.22\cdot10^4$



a *b*

Fig. 5. General images of sample surfaces obtained in secondary electrons (*a*) molybdenum coating; (b) plasma spraying by HVAF method. Light areas are the Mo matrix; dark inclusions -— oxide phases

methods of applying protective coatings, the challenge is not only to ensure performance characteristics that are no worse than electrolytic chromium plating, but also to use less expensive and scarce materials. Fig. 3 presents the results of comparative wear tests during fretting under conditions of lubrication with consistent lubricant "Era" for the following coatings: electrolytic chrome coating, a molybdenum coating sprayed by the HVAF method, and a coating made of martensitic steel 40Kh13 obtained by the method of electric arc metallization by high-velocity spraying of combustion products of a hot propane–air gas mixture.

The analysis of the obtained H=f(P) dependences shows that, under the given fretting conditions, the molybdenum coating exhibits consistently higher wear resistance compared to electrolytic chromium in the entire studied range of specific contact loads. At the maximum specific contact load P = 49 MPa, the average linear wear of samples with molybdenum coating is almost 20 times lower than that of samples with an electrolytic chromium coating. At the same time, as seen from the images of the working surfaces of the samples after testing (Fig. 4), when paired with a molybdenum coating, no significant damage was detected due to fretting corrosion of the surface of the counterbody made of steel 45.

The high antifriction and antiwear efficiency of the lubricant on the surface of the molybdenum coating can be explained by both its high oil absorption capacity (due to porosity) and the complex of physical and mechanical properties of molybdenum, which provide destruction-resistant lubricant layers on the friction surface. These properties include high strength of interatomic bonds, a high level of internal amplitude-dependent friction, and a tendency

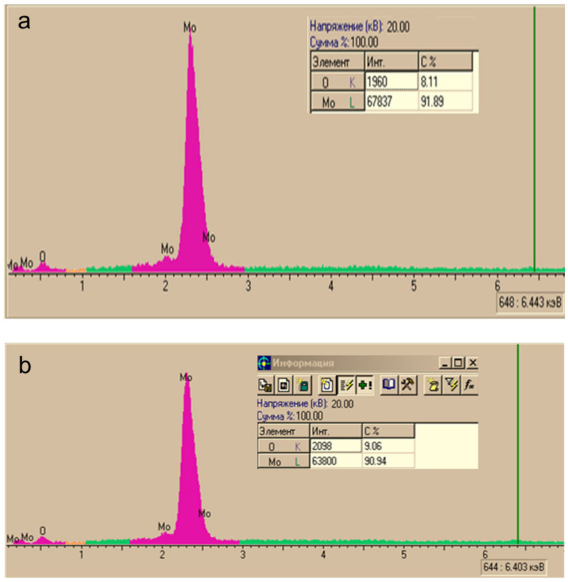


Fig. 6. Determination of the percentage of chemical elements on the surface of samples with molybdenum coating obtained using plasma spraying by the HVAT method: *a* – initial surface; *b* – electric arc spraying of coatings surface after fretting-wear tests

to strengthen under dynamic loads through the mechanism of dynamic strain aging while maintaining a sufficient supply of microplasticity [18].

It is known that steps and so-called "vincial faces" that are formed when dislocations emerge on the surface of crystals act as active centers of adsorption of polar molecules of the lubricating substance. Therefore, a sufficient resource of microplasticity (mobile dislocations under conditions of deformation below the yield point) in molybdenum can be considered as a factor promoting the formation and rapid regeneration of boundary lubricating layers on the friction surface. The high strength of interatomic bonds in combination with the effect of dynamic deformation aging and the presence of dispersed inclusions of solid oxide phases in the coating structure (Figs. 5 and 6) prevents excessive deformation of surface roughness protrusions; accordingly, the molecular structure of the mono- and multi-molecular lubricating layer is not destroyed at the points of actual contact.

It is obvious that at $P > 29.4$ MPa on the surface of chromium and the surface of the 40Kh13 coating of steel, the effectiveness of the protective action of the boundary lubricating film is lost, which manifests itself in a sharp increase in wear (see Fig. 3). At the same time, at specific contact loads of $P \leq 29.4$ MPa, the 40Kh13 coating, like the M_o-Mo coating, also exhibits consistently higher wear resistance compared to electrolytic chromium.

The patterns of changes in the resistance to fretting-corrosion wear of the 40Kh13 coating can be explained by the specificity of both the conditions of its formation and the structure-phase transformations that can occur in hardened steels under friction. During electric arc spraying of martensitic steel wire, as a result of high velocities of molten metal particles and high rate of cooling them, coatings are formed with a structure consisting predominantly of martensite, a small amount of residual austenite, and iron oxides FeO and Fe_3O_4 [19]. In the hardened state, structurally metastable martensite has increased hardness and strength along with slight resistance to small plastic deformations (high microplasticity) [20]. This combination of properties, on the one hand, ensures high relaxation ability and wear resistance of the coating itself, and on the other, the appearance of active centers on its surface for the formation of adsorption boundary lubricating layers. During external friction, with an increase in the intensity of temperature and force fields, the processes of decomposition of martensite and retained austenite are activated in the frictional contact zone. Under certain mechanical and thermal conditions, this process can develop according to the relaxation mechanism under stress or dynamic aging [21; 22]. In this case, in contrast to the usual tempering of hardened steel, martensite decomposes more completely, which is accompanied by an additional limitation of dislocation mobility, a decrease in microplasticity and the relaxation ability of the material. It is obvious that the blocking of dislocations will simultaneously cause a loss of adsorption activity and the ability of the coating material to form boundary lubricating layers resistant to destruction.

4. Conclusions

The influence of amplitude-force fretting parameters on the wear resistance of GTS coatings of the KKhN-30, KTN-35, KTN-50, Mo systems formed by plasma-arc, pulse-plasma and high-speed gas-flame spraying methods, has been studied. Regardless of the spraying method, coatings formed from heterogeneous composite materials, in contrast to Mo coatings, are characterized by a non-monotonic sharp increase in wear with increasing specific contact load above a certain critical value *P* for each of them.

The studies have shown the high efficiency of the anti-friction and anti-wear action of a lubricant on the surface of molybdenum coating, which can be explained both by its high oil-retaining ability (due to porosity) and resistance to the destruction of boundary lubricating layers. From the $H=f(P)$ dependences it is clear that, under the given fretting conditions, the molybdenum coating shows consistently higher wear resistance in the entire studied range of specific contact loads compared to electrolytic chromium coating. At the maximum value of the specific contact load $P = 49$ MPa, the average linear wear of samples with a molybdenum coating was almost 20 times lower than that of samples with an electrolytic chromium coating.

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