Wear Resistance of Amorphous-Crystalline Coatings Under Boundary Friction

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Abstract: The results of tests under boundary friction conditions are present detonation coatings Zr-Al-B in a wide range of changes in friction conditions.

The obtained results were compared with the parallel tested coatings based on tungsten carbide type WK-15, also with samples of 30HGSNA steel and BrOCS6-6-3 bronze.

The qualitative and quantitative composition of surface layers participating in boundary friction conditions was assessed using modern physical methods of analysis. Profilograms and microphotographs of friction surfaces of amorphous-crystalline coatings are presented, showing that under boundary friction conditions, coating samples are smoothed, which leads to a decrease in roughness.

Installed the presence of the formation of solid solutions of oxygen interstitialization in zirconium, which corresponds to the formation of secondary structures of the first type on friction surfaces, the characteristic feature of which is their surface localization, ultra-dispersed structure, the ability to minimize destruction and screen unacceptable adhesive phenomena. Using Auger electron microscopy, it was confirmed that oxygen completely replaces sulfur in surface structures.

It is shown that the studied detonation coatings Zr-Al-B, developed for practice, have high tribotechnical characteristics in the entire range of tests under boundary friction conditions. At the same time, as a result of studies of the mechanism of tribochemical transformations of hydrocarbons and the properties of transformed surface films, it was established that they retain lubricating properties and provide high antifriction characteristics of the friction system in the entire wide range of changes in boundary friction conditions.

Keywords: Boundary friction, Detonation coating, Wear, Adsorption layer, Boundary lubrication, Surface activation.

INTRODUCTION

Tribological processes and phenomena are manifested in the overwhelming majority of machines and mechanisms. Reducing friction forces and reducing their wear is one of the main problems of technology.

Modern trends in minimizing wear of surfaces loaded with thorns also provide for the creation of lubricating films in the contact zone. In the presence of a lubricating medium, the performance of moving joints depends on the complex of oil properties and is determined by the friction mode.

Under operating conditions, the most unfavorable is friction under boundary lubrication conditions, which remains the least developed section of the physical problem of machine lubrication [1-3].

To date, theoretical and applied studies of lubricants under boundary lubrication conditions have not undergone a systematic and comprehensive generalization. Reliable methods for identifying the physicochemical mechanisms of action of lubricants have not been developed. In addition, information on wear resistance of amorphous coatings under boundary lubrication conditions is mainly illustrative; and there are no systematic studies in the literature. An attempt to isolate general wear patterns from particular dependencies, which are obtained on specific materials under given test conditions, indicates that the nature of changes in the chemical composition and organization of the structure in the presence of a boundary lubricant layer in the contact zone is much more diverse and complex than postulated in modern hypotheses, and existing theoretical concepts are unable to explain the diversity of experimental results without contradiction [4, 5].

At the same time, the analysis of the few scientific and technical sources and practical experience allows us to state that the task of minimizing wear and increasing the service life of machine parts remains relevant for modern technology and stimulates the development of achievements in modern surface engineering in the field of friction, lubrication and wear.

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THE AIM OF THE WORK

Is a generalization of the results of wear tests of the developed amorphous-crystalline coatings based on zirconium and a study of their friction mechanism in the boundary lubrication mode with MS-20 mineral oil.

The development of amorphous-crystalline coatings of the Zr-Al-B system [6] for the protection of friction units from wear is due, on the one hand, to the practical needs of creating materials with high operational tribocharacteristics based on the country's mineral-raw material potential that do not contain scarce and expensive components, and on the other hand, to the logic of developing the powder metallurgy field, namely, expanding the range of high-quality compositions for thermal spraying. The use of mineral oil of the MS-20 type as a lubricant is due to both the fleet of light aircraft that uses this lubricant and the wide capabilities of domestic oil refining for its production.

RESEARCH METHODOLOGY

Friction and wear tests were carried out in friction pairs with samples made of 30HGSNA steel (after high tempering, sorbitol structure) and tin bronze BrOCS6-6-3, which are widely used for parts operating under boundary lubrication conditions [7].

The tribological properties of the coatings were evaluated on the UMT-1 unit under boundary lubrication conditions with MS-20 oil on model samples according to the end friction scheme with a mutual overlap coefficient (K_{mo}) ≈ 0,5 in air conditions. The boundary friction mode was implemented using a designed lubrication system operating in a closed cycle, with the sliding speed monotonically changing to 4,0 m/s under a constantly acting load of 15,0 MPa.

The study of processes initiated by friction and wear of amorphous-crystalline coatings, their depth and reliability were determined by modern methods of physicochemical analysis taking into account the specifics of the tasks to be solved. X-ray structural studies were carried out on a Dron-3M diffractometer in $Fe_{k\alpha}$ radiation. The volume content of the amorphous phase was determined using the technique described in [8] and based on the separation of diffraction reflections from the amorphous and crystalline phases when comparing the areas under the X-ray scattering intensity curves [9]. Electron microscopic studies were carried out on a Camskan electron microscope. Studies using Auger electron spectroscopy of the surface were carried out on a JAMP-10S Auger scanning electron microscope.

Metallographic analysis of the sections was carried out using a MIM-8 optical microscope. The composition of the etchant and the etching modes of the polished samples were selected in accordance with the methodological recommendations [10]. Microhardness was measured using a PMT-3 device under a load of 0,49 N, and the adhesion strength of the coatings to the base was determined using the cone pin method [11].

For a comparative assessment of wear resistance of amorphous-crystalline coatings, coatings based on tungsten carbide of the WK-15 type were tested in parallel with samples of 30HGSNA steel and BrOCS6-6-3 bronze [12].

RESEARCH RESULTS

The study of the mechanism of action of the lubricating medium under boundary friction remains very relevant, as there are still no scientifically substantiated provisions developed to the extent that meets the requirements of the practice of production and operation of machines operating under boundary lubrication conditions. All this requires a differentiated approach to assess the influence of the lubricating medium on the performance of friction pair parts. However, the starting point for such an assessment is the results of fundamental developments in the field of lubrication theory, molecular physics of boundary friction and physicochemical mechanics of materials [13].

The main factor determining the nature of wear of coatings with boundary lubrication is the presence of physically adsorbed layers formed as a result of the activation of physical and chemical processes of interaction of the lubricating medium with the working surface. The adsorption layer in the friction system acts as a lubricant. In this case, the difference in the lubricating media used consists only in the degree of their effectiveness in forming strong quasi-crystalline boundary layers of adsorption origin.

The results of wear tests of amorphous-crystalline coatings in friction pairs with samples of structural and antifriction materials, as well as detonation tungsten-containing coating under boundary lubrication conditions are presented in Figure **1**.

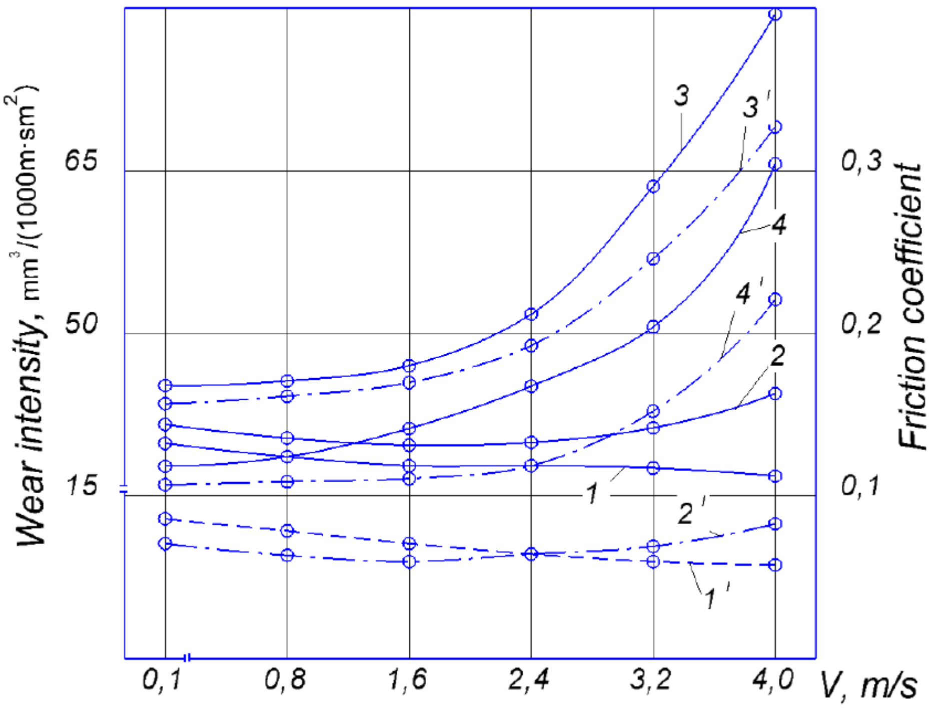


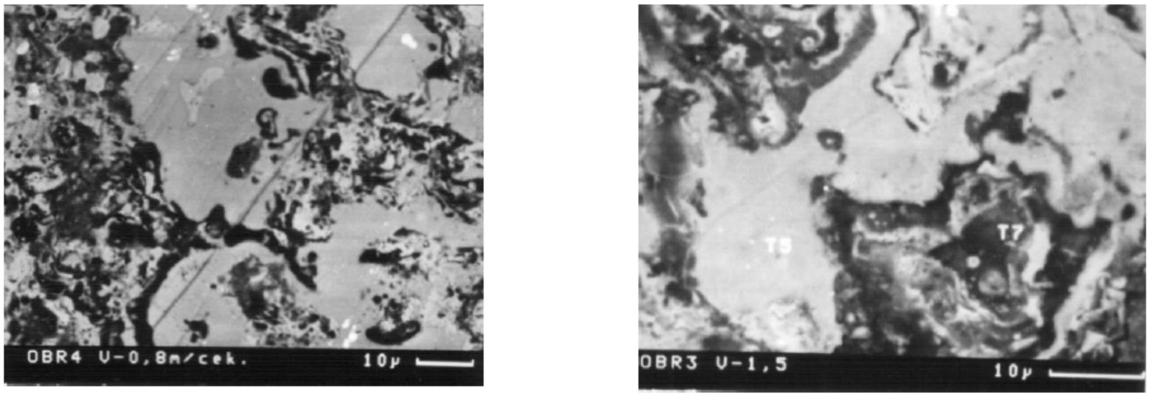
Figure 1: Dependence of wear intensity (1, 2, 3, 4) and friction coefficients (1^{I}, 2^{I}, 3^{I}, 4^{I}) on the sliding speed of amorphous-crystalline coatings in friction pairs with samples of 30HGSNA steel (1, 1^{I}) and BrOCS6-6-3 bronze (2, 2^{I}) and tungsten carbide-based coatings in pairs with samples of 30HGSNA steel (3, 3^{I}) and bronze (4, 4^{I}) at P=const=15,0 MPa.

The obtained research results allow us to clearly identify, under these test conditions, the high antifriction ability of amorphous-crystalline coatings, caused by stable and minimal values of both wear intensity and friction coefficients. According to the authors, under these test conditions, the values of the friction coefficient are determined not so much by the normal load function as by the dependence on tribophysical processes that occur due to the additive effect of both the load and sliding speed, as well as the temperature and the generalized vector of friction parameters (material, environment, conditions, etc.). At the same time, the nature of the friction coefficient values is consistent with the profile of the wear intensity curve, and its stability indicates the high performance of the studied amorphous-crystalline coatings.

It should be noted that the complexity of the composition of the oil used and the presence of foreign sulfur, nitrogen and other elements active on the working surface and initiating competing reactions complicates the study of the influence of hydrocarbon environments on the patterns of tribochemical processes that determine the lubricating effect.

Qualitative analysis of the chemical composition allowed us to establish that the surface of the amorphous-crystalline samples is covered with an oxide film, about 3-5 nm thick, and there is a reason to believe that the process of its formation is caused not by the entire tribosurface, but only by individual fragments, which are films of aluminum and zirconium oxides. This fully corresponds to the formation of secondary structures of the first type on the friction surfaces, which are supersaturated solid solutions of the active component of the medium in the metal. The characteristic feature of oxygen-type surface structures, which are the initial stage of chemical organization of elements in the solid state, is their surface localization, ultra-dispersed structure, the ability to minimize destruction and screen unacceptable adhesive phenomena.

Directly above the thin-film structure of zirconium, as a selectively oxidizing component, according to the data of analytical methods of surface research, an adsorption film is formed, the polar molecules of which, in particular long-chain hydrocarbons, are attached and retained relative to the friction surface mainly in a vertical orientation with a height of about 1.8 nm. The adsorption layer formed in this way is characterized by a number of specific properties, the most important of which are high compressive strength (more than 110 MPa) and significant ease of shear under the action of tangential forces, which in turn causes the minimization



a b

Figure 2: Microphotographs of the friction surfaces of amorphous-crystalline coatings under boundary friction conditions with MS-20 oil (P=15 MPa): **a** – at V=0,8 m/s; **b** – at V=1,5 m/s.

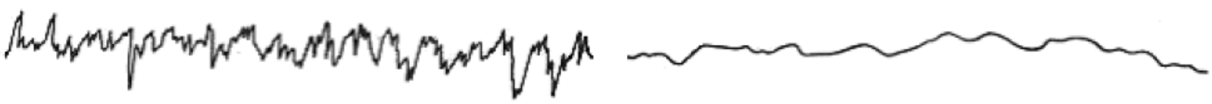


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Figure 3: Profilograms of the friction surface of amorphous-crystalline coatings under boundary lubrication conditions with MS-20 oil (P=15MPa): **a** – Ra=0,34μm (V=0,8 m/s); **b** – Ra=0,16 μm (V=1,5 m/s); (VUx1000, GUx40).

of friction coefficients during sliding of lubricated amorphous-crystalline surfaces. Figure **2** and Figure **3** show the friction surfaces of the investigated coatings and, accordingly, their profilograms.

The micro geometry of the working surface of amorphous-crystalline coatings together with their physical and mechanical characteristics determine their operational properties. The test results showed that during the running-in process the initial technological relief disappears, the chemical composition, structure of the surface layer and its geometry change significantly. It can be said that running-in is a manifestation of the self-organization process, during which the quasi-relaxation of the structure from the equilibrium passes to a stable state. At the same time, a new quality of the surface is formed, which is characterized by the formation of optimal roughness for specific friction conditions. At the same time, studies of the surface morphology showed that after long-term tests under boundary friction conditions with mineral oil MS-20, samples of amorphous-crystalline coatings are smoothed and acquire a mirror shine, which is due not only to a decrease in roughness, but also to a decrease in wear intensity. The results of scanning electron microscopy indicate the absence of significant deformations of the surface layer of the samples and the formation of a smoothed micro relief.

It should be noted that in friction modes from 0,2 m/s to 1,9 m/s and a load of 15,0 MPa, sulfur present in the lubricant diffuses from the volume of the lubricating medium to the surface and, chemically modifying it, forms films of zirconium and aluminum sulfides. The formation of surface structures occurs in extremely non-equilibrium conditions, which sharply changes the equilibrium constants of tribochemical reactions, and there are significant deviations from the classical laws of equilibrium solubility and the formation of chemical compounds. Sulfides Zr_2S_3, ZrS_2, ZrS, Al_2S_3 and metal oxides included in the coatings prevent adhesive interaction of the surface and reduce the friction force. At the same time, tribochemical aspects of the effect of oxygen on the development of the oxidation kinetics of surface structures activated during friction remain important. The amount of oxygen in detonation coatings formed in an air atmosphere significantly exceeds its content in compact materials obtained by traditional methods. There is almost always a sufficient amount of oxygen to ensure surface reactions, firstly, it is present in the composition of the environment, and secondly, it is dissolved in the lubricant.

Chemical compounds that make up the damping superficial layer, in particular sulfides, which are more stable than physically and chemically adsorbed molecules of the base lubricant, but less stable than oxides, and are displaced by a chemically active component such as oxygen. According to the authors, sulfides are consolidated at the initial stage of the reaction due to the excess of sulfur at the surface. Studies using Auger electron spectroscopy have experimentally confirmed that oxygen completely replaces sulfur in surface structures. It can be assumed that hydrocarbons, being carriers of a natural additive - molecular oxygen, actively participate in boundary lubrication processes, as the formation of oxide films that prevent direct contact of friction surfaces occurs, apparently, as a simultaneous act of oxidation of metal and hydrocarbon with subsequent replacement of sulfur in sulfur-containing compounds. The obtained results are confirmed by surface studies on a JAMP-10S Auger scanning electron microscope when studying the elementary composition of friction surfaces of amorphous-crystalline coatings (Figure **4**). The analysis of Auger spectra also illustrates the need for a comprehensive approach to studying the relationship between the chemical composition and lubricating action of the medium during friction, in addition, it confirms the effectiveness of using fine methods of physicochemical research to study the chemical transformations occurring in the lubricating contact.

Changes in structural and thermal activity initiated by mechanical effects (V≥2,4 m/s, P=15,0 MPa) have a direct influence on the structure and properties of lubricating layers. Active radicals formed as a result of internal tribochemical restructuring during the rupture of carbon bonds coagulate to form hydrocarbon molecules with a high molecular weight. The development of the process over time causes their deposition as a film on the friction surface. In this case, the filling of unsaturated bonds and the heterogeneity in the structure of hydrocarbon molecules of the surface film leads to the formation of high-molecular compounds close to the properties of solids, called friction polymers. For the first time, a detailed analysis of the formation of polymer films on the surfaces of solids was described in [14].

It should be emphasized that as a result of studies of the mechanism of tribochemical transformations of hydrocarbons and the properties of transformed surface films, carried out in a wide range of changes in friction conditions, it was established that they retain lubricating properties and provide high antifriction characteristics of the friction system amorphous-crystalline coating - steel 30KhGSNA, preventing the contact of their metal surfaces, adhesive interaction and reducing the friction force. Thus the smallest thickness of the boundary polymer-like film at the greatest convergence of surfaces fluctuates within 0,15-0,5 µm.

For the tested friction pairs based on carbide coatings of the WK-15 type with steel, the increase in load-speed parameters (V≥2,0 m/s, P=15,0 MPa)

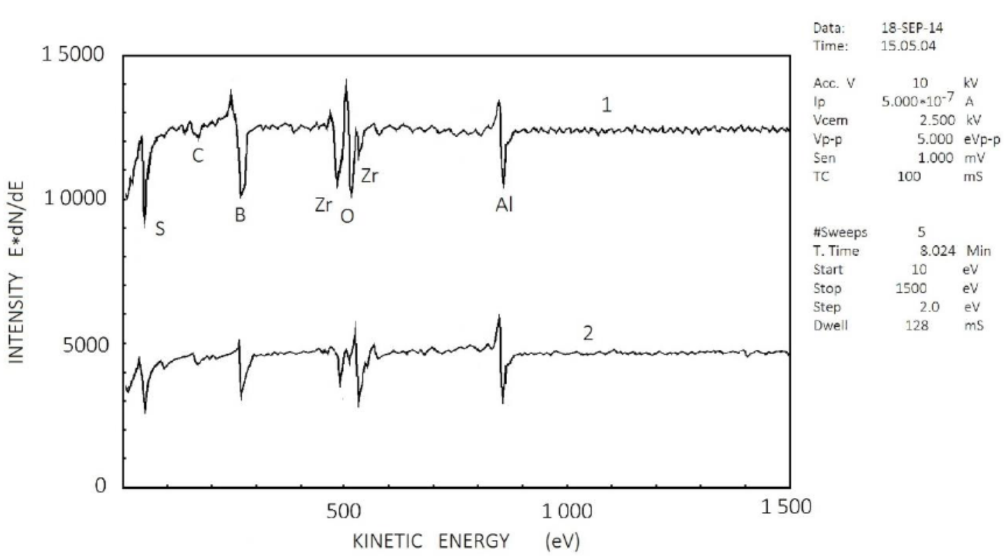

Figure 4: Auger spectra taken from the surface (**1**) and after etching (**2**).

causes a monotonous increase in the friction coefficient and a decrease in the protective functions of the lubricating film. A further increase in load stimulates the destruction of surfaces, while the surface strength of the coating is completely suppressed by the mechanical factor, which is characterized by a sharp increase in the friction coefficient and an increase in temperature in the contact zone and, as a consequence, intense adhesive processes leading to damage under test conditions.

It can be said that the study of tribotechnical properties of surfaces, in particular amorphous-crystalline ones, is inseparable from the study of the role of lubricants, while the study of the mechanism of lubricating action under boundary friction conditions is reduced to the tribochemical kinetics of the regeneration of ordered lubricating structures and their influence on adhesive and friction properties. At present, the areas of possible application of the tested amorphous-crystalline coatings that do not contain scarce and expensive components are being studied and the prospects for its use are obvious.

Thus, the development and creation of amorphous-crystalline coatings in combination with the use of not only mineral oil, but also with a variety of other lubricants allows us to significantly expand the arsenal of achievements in modern tribological materials science and put the tasks of predicting and managing machine wear on a scientific basis accessible to engineering practice.

CONCLUSIONS

1. During friction of amorphous-crystalline coatings, both the composition of lubricating oils and the content of dissolved oxygen and oxygen-containing compounds in them, as well as their oxidizing activity, are essential. It is noted that in unalloyed lubricating oils, the main active element-passivator is oxygen. Therefore, during friction in MS-20 oil, surface structures of the oxygen type are formed, representing the initial stage of chemical organization of the substance in the solid state.

2. High antifriction properties of amorphous-crystalline Zr-Al-B coatings were established under boundary lubrication conditions with MS-20 oil in wide load-speed friction modes. It was noted that the friction coefficient reaches a stable value in the initial period of testing and does not change over time. With increasing load, the nature of the change in the friction coefficient is maintained up to the seizing load.

3. In hydrocarbon lubricating environments that do not contain natural or synthetic additives, the nature of the adhesive interaction process and the friction parameters at which it occurs are determined by the intensity of oxidative tribochemical reactions in the contact zone. It can be assumed that in the absence of oxygen (or oxidation products), hydrocarbons are ineffective as lubricating environments.

CONFLICTS OF INTEREST

The author declared no conflicts of interest.

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