Self-Organization of Surface Structures during Friction Coatings Based on Forsterite

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Abstract: In the work, the patterns of friction and wear of forsterite-based coatings were studied, and their structural-phase composition, conditions of formation and self-regulation of surface structures were determined from the standpoint of the structural-energy theory of friction. Detonation coatings developed on the basis of forsterite are characterized by high anti-friction properties. The conducted studies showed that the most appropriate application of the investigated coatings is to increase the reliability of operation of friction nodes during strengthening and restoration, for example, for moving pairs of control mechanisms, hinges of guide surfaces, cams, sliding supports, pairs with reciprocating movement, bearings, sliding guides, etc. in which the use of traditional lubricants is undesirable. Compounds of complex oxides of magnesium orthosilicate were used as the basis of composite coatings. The structural and phase composition of the coatings, the peculiarities of the formation of complex alloyed secondary structures, taking into account both the properties of the alloying elements and the structures formed by them, were established. The physical mechanism was determined and the main factors determining the level of thermodynamic graphitization were clarified. The studied self-lubricating compositions can be used both for strengthening and for high-quality restoration of worn triboelements by any technological methods using powder materials.

Keywords: Detonation coating, Wear intensity, Structural-phase composition, Graphitization.

INTRODUCTION

The performance of machines and mechanisms mainly depends on the trouble-free functioning of moving connections, which are different in design and purpose. Overcoming the forces of friction and reducing wear is primarily related to the use of lubricant.

The use of resource coatings without adding additives to reduce wear is very limited. In modern technical systems, the contact interaction of moving joints in the absence of lubricants is practically not carried out [1, 2]. Among the applied friction units, which are operated in the presence of lubricants, the most innovative are self-lubricating designs [3, 4]. At the same time, the use of self-lubricating coatings, which include solid lubricants with a layered structure, becomes more and more necessary to ensure the long-term operation of movable couplings.

The purpose of the work is the study from the standpoint of the structural-energy theory of friction of the patterns of friction and wear of forsterite-based coatings and the determination of their structural-phase composition and the conditions for the formation and self-regulation of surface structures that have self-lubricating ability.

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The creation of anti-friction self-lubricating coatings for tribotechnical purposes is determined, on the one hand, by the needs of practice in creating materials with high operational tribological characteristics, which do not contain scarce and expensive components, on the basis of the mineral resource potential of the country, on the other hand, by the logic of the development of the powder metallurgy industry, namely, expansion of the assortment of high-quality compositions for gas-thermal spraying.

RESEARCH MATERIALS AND METHODS

Compounds of complex oxides based on periclase are of significant theoretical and applied interest in the field of tribotechnical materials science. One of these compounds is forsterite (magnesium orthosilicate), which is used as the base material of the investigated self-lubricating coatings, it does not undergo polymorphic transformations, it is resistant to high temperatures, it is characterized by increased mechanical properties and chemical inertness. Coatings based on forsterite (Mg_2SiO_4), in turn, were alloyed with chromium, zirconium, nickel, titanium, aluminum, silicon, and carbon. The initial composition of crystalline powders with a complex chemical composition for spraying was obtained by the proven technology of mechano-chemical synthesis (MCS). Structurally free magnesium carbide (MgC_2) was added to the thus obtained mixture in the appropriate proportion and the resulting mechanical mixture was stirred until complete and uniform distribution.

Forsterite-based coating for the study of physicochemical properties and patterns of friction and wear was applied by the detonation-gas method using an oxygen-acetylene mixture on prepared samples of high-strength steel type 30ХГСНА. The tests were carried out according to the end scheme under conditions of distributed contact at normal temperature in the mode of continuous sliding with a constant load of 13.5 MPa. At the same time, the research program included a comparative analysis of the friction parameters of forsterite-based coatings with similar values of coatings of the WC-Co15 type and coatings made of alloyed nichrome. The adhesion strength was determined by the pin method [5], which for forsterite coatings was more than 90 MPa with a porosity of almost 0.5%, besides this, after preliminary fine grinding, their initial roughness was Ra 0.32-0.63.

Both the intensity of wear and the coefficient of friction, as well as the condition of the working surfaces, were used as criteria for the performance of forsterite-based coatings.

When studying the laws of friction and wear to explain the technology-structure and structure-properties relationships, a complex of modern physico-chemical methods of structural-phase analysis was used, including consideration of surface layers at the macro- and microscopic levels.

At the same time, the complex research methodology included metallography (optical microscope "Neofot-32" with an attachment);durometric analysis (hardness meter M-400 of the LECO company); raster electron microscopy (scanning electron microscope JSM-840); X-ray structure phase analyzer (DRON-UM1 diffractometer)

RESEARCH RESULTS AND THEIR DISCUSSION

The level of activation of the contact surfaces of the tested coatings is determined by the joint action of mutually determined external influences and determining internal factors, among which the degree and gradients of deformations, displacements, thermomechanical conditions, the value of the environment, and the nature of conjugated materials, the kinetics of surface phenomena, the action of chemical reactions, the level of activation, the combined effect of which ultimately determines the normal level of mechano-chemical friction and the conductive type wear and tear

The test results of the investigated coatings (Figure **1**) are presented in the form of graphs of functional average values of wear intensities and friction coefficients, obtained in the field of monotonically increasing sliding speeds under a constant load corresponding to 13.5 MPa.

The results show that in the working range, the values of the controlled parameters of wear intensities and friction coefficients for forsterite coatings compared to control coatings are minimal and stable (curves 1 and 2, respectively), which causes normal mechanochemical wear.

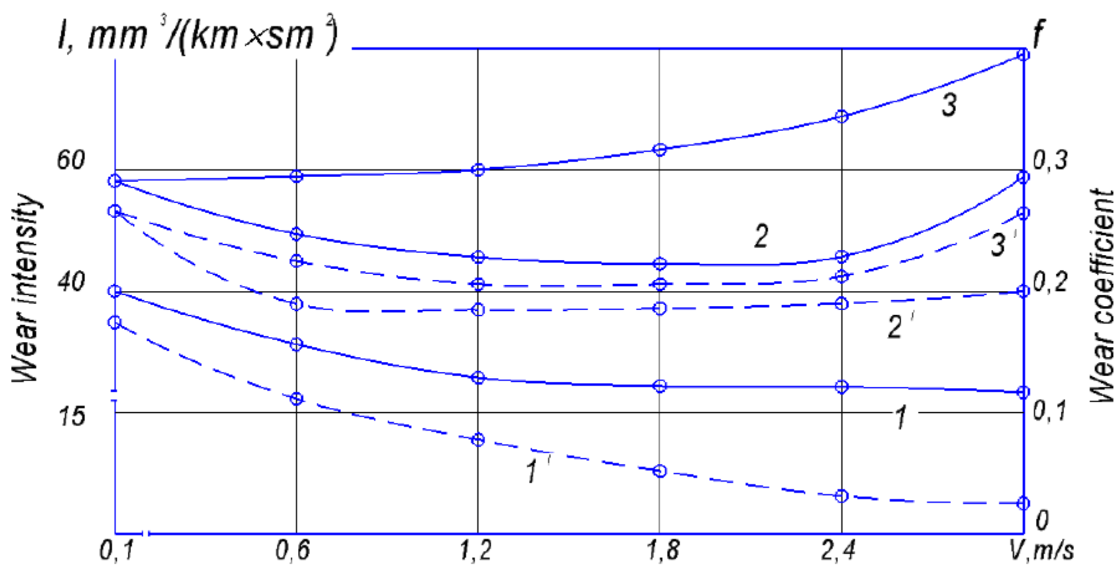


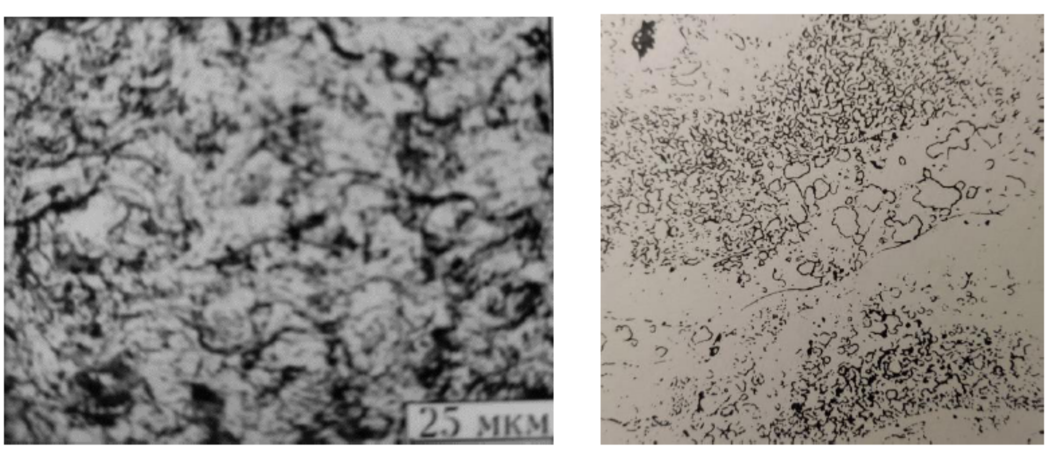
Figure 1: Dependencies of wear intensities (1, 2, 3) and friction coefficients (1', 2', 3') on the sliding speed of coatings based on forsterite (1, 1'), WC15 (2, 2') and alloyed nichrome (3, 3') at P=const=13.5 MPa.

The microgeometry of the working plane of the coatings in combination with the physical and mechanical properties of the surface layer determines their operational condition. The results of the research showed that during the run-in process, the initial technological relief disappears, the chemical composition, structure of the surface layer and its geometry fundamentally change. It is possible to determine that run-in is one of the manifestations of the process of self-organization of friction, in which the quasi-relaxation of the surface structure moves from an equilibrium state to a steady state. At the same time, a new surface quality is formed, characterized by the formation of a balanced roughness, which is not only optimal for specific friction conditions, but also ensures stable wear in the entire range of tests. Thus, the original technological roughness is transformed into the optimal operational roughness, which for forsterite coatings corresponds to ~ Ra 2.5-1.5. At the same time (Figure **2**), the sprayed layer has a quasi-ordered lamella-like appearance, closely adheres to the base and copies the surface relief, at the same time, accumulation of oxide films, slag inclusions and other impurities, as well as defects in the form of micropores and microcracks, were not detected.

From the results of quantitative X-ray phase analysis of composite forsterite coatings, it was established that they have a multi-component fine-grained aggregate, the main of which consists of homogeneous hexagonal magnesium orthosilicate, which is a double oxide with the general chemical formula $2MgO\text{-}SiO_2$, and a significant number of finely dispersed inclusions of aluminomagnesian spinel distributed in it ($MgAl_2O_4$) and thin a conglomerate of high-temperature strengthening chemical compounds of chromium, zirconium, titanium, which are Cr_2Si_3, $CrSi_2$, Zr_3Si_2, $ZrSi_2$, TiSi, $TiSi_2$, $ZrAl_3$, $CrAl_4$, $TiAl_3$, TiAl, as well as significant colonies of metal carbides that are part of the coatings, and heat-resistant intermetallic formations of the type $ZrCr_2$, ZrV_2, NiAl, NiTi, in addition, ternary compounds of transition metals with carbon Cr_2SiC, Ti_3AlC, TiZrC, SiZrC were found, as well as, most likely, the presence of titanium carbosilicide Ti_3SiC_2, in addition, on the background of solid solutions of the TiSi-CrSi type, the presence of lower melting intermetallics of the Mg_2Al_3, Mg_5Al_8 and nickel silicidesNiSi, however, their total content is relative small, but along with more strengthening phases, they also affect the quality of the coating.

Practically all structural components of forsterite-based coatings, which form solid solutions, chemical compounds and mechanical mixtures, have increased thermodynamic properties, significant hardness and strength, corrosion resistance, which ensures their high wear resistance and operational reliability.

The problem of coating quality is inextricably linked to the assessment of reproducibility and optimization of the sputtering technological process. A change in technological regimes leads to a change in the properties of coatings. In order to obtain high-quality coatings by optimizing the technological process, the processing of technological parameters is implemented, including particle size composition, loading depth, the degree of barrel filling, the ratio of working gases and the spraying distance [6]. Thus, by managing the technological process of forming forsterite coatings, it was possible to realize not only



a) x240 б) x5000

Figure 2: Cross-sectional microstructure of the coating formulated with composite powders based on forsterite.

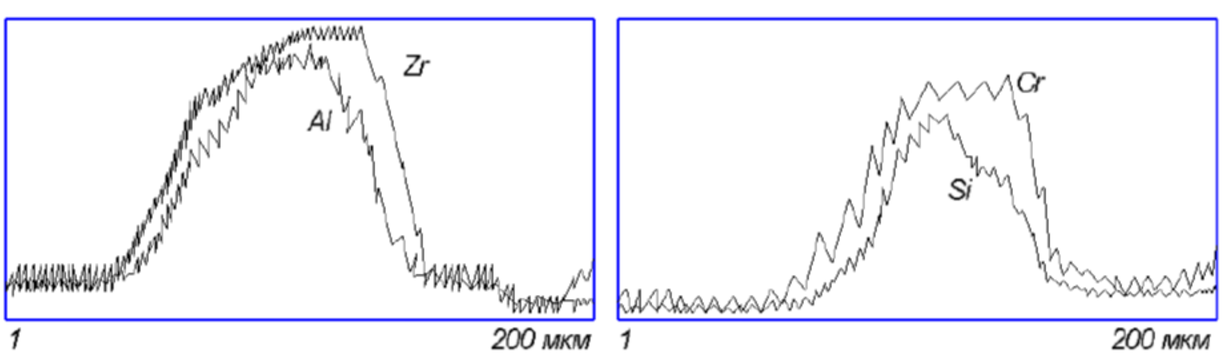
the desired chemical composition, but also to obtain the predicted stable structure during sputtering, which optimizes the complex of properties that determine the stability of structural adaptability. At the same time, the possibility of obtaining constant quality was achieved, namely, the variation of strength and plastic properties in the samples of one batch that was sprayed was stable at about 5-10%.

The study of the physical mechanisms of the formation and evolution of the structural and phase states of secondary layers under the conditions of mechanochemical activation is one of the important tasks of managing the surface strength of coatings and regulating their tribotechnical properties.

For comprehensive and reliable information in the study of thin surface layers in which the processes of structural and thermal activation take place, the method of secondaryion-ion mass spectroscopy (IMS), which analyzed the change in the microstructure and established the nature of the phases, their crystal structure, and the parameters of elementary cells, which are necessary for identification and composition within the regions of their homogeneity.

The obtained results made it possible to generalize that the initiation of physical and chemical transformations as a resultelastic-plastic deformation is primarily manifested in the process of inversion of the interaction with air oxygen and, as a result, the reformation of secondary surface oxide films through additional formations that are formed within the structure of the forsterite composition and, according to the stoichiometric composition, represents a complex complex in the form of oxides Al_2O, SiO_2, ZrO_2, TiO_2, Cr_2O_3, MgO, which, interacting, form as solid solutions of the type Cr_2O_3-SiO_2, ZrO_2-Al_2O_3, as evidenced by the coincidence of concentration maxima (Figure **3**), as well as spinel phases $NiCrO_4$, Zr_2SiO_4, Al_2SiO_5, Cr_2TiO_5, in addition, the presence of double compounds of the type TiO-ZrO_2, MgO-TiO_2, MgO was identified -ZrO_2, the possibility of presence is also not excluded ternary compounds such as Mg-ZrO_2-TiO_2, MgO-Al_2O_3-TiO_2. It should be noted that the secondary oxide structures found are characterized by significant strength, hardness, thermal stability and chemical inertness. At the same time, the processes of formation and destruction of oxide structures are in dynamic equilibrium and automatically self-regulate, which determines the stability of the phenomenon of structural adjustment. However, due to statistical regularities, the processes of disintegration of ultradispersed secondary structures on different parts of the working surface as a result of contact discreteness do not coincide in stages. At the same time, there is an opportunity to believe that the process of their formation does not take place on the entire tribosurface, but only on individual uneven fragments of the working area, but their additive distribution is stable structural and temporary states.

In order to study the state of the oxide surface layer, in which activation processes occur during friction, an electronographic analysis was used, performed on the ERM-100 installation (reflection recording at U=5kV). Figure **4** shows an electronogram from the surface of the forsterite-based coating, which records the change in fine structure, which indicates the presence of intensity maxima on diffusion haloes. The studied thin film layer represents an ultradispersed oriented structure. At the same time, the microhardness of the surface layer is 21.0–23.0 GPa (at the initial level of about 16.0 GPa). Thus, low and stable values of both friction coefficients and wear intensities of forsterite-based coatings are ensured by the formation of an integral dynamically stable conglomerate of oxide structures that shield the adhesive-molecular



(**a**) (**b**)

Figure 3: Distribution of elements in the oxide film on the surface area of the forsterite coating.

interaction during friction and have a finely dispersed structure and, under conditions of local contact pressures and temperatures, form dense heterogeneous heat-resistant and fairly plastic surface structures without cracks and chips, which contribute not only reduce the rate of oxidation and increase heat resistance, but also perform the role of solid lubricants.

Figure 4: Electrongram from the surface of the contact layer zirconium-based coating at V=1.5 m/s and P=13.5 MPa.

When the sliding speed increases to 0.15 m/s, the specific work of wear reaches approximately 10^4 kJ/mm^3, which corresponds to the necessary and sufficient condition for the thermal decomposition of magnesium carbide and, as a result, fragments of structurally free α-graphite appear on the friction surface (Figure **5**). The shape of the particles of the graphite structure is close to scaly, consisting of polydisperse crystallites oriented in the direction of friction. It should be noted that the strength of graphite as an antifriction material is its weak interaction between layers. Thus, running-in, in a certain sense, can be considered as a specific type of heat treatment accompanied by graphitization.

The physical phenomenon that determines the mechanism of magnesium carbide decomposition is based on the process of structural transformation in the solid phase, which develops as a result of thermal exposure. The main factors that determine the limit values of thermodynamic processes of graphitization are the level of dispersion of structural components, specific pressure, operating temperature, the surrounding environment, the presence of initiating elements (carbon, silicon, nickel, aluminum), in addition, internal factors determined by the composition, structure, the presence of defects, etc.

Figure 5: Topography of the surface during the formation of a graphite film (v=0.17 m/s).

The elementary act of a high-temperature reaction in a unit volume of local contact, accompanied by the formation of carbide graphite, due to the exotic effect causes the next elementary act, thus determining the ability to self-propagation.

The self-lubrication of the forsterite-based composition depends on the formation of a self-lubricating graphite film. At test speeds of more than 0.21 m/s, the frictional self-lubricating graphite surface film already covers more than half of the friction area and, at the same time, is a layer of an ordered set of polydisperse graphite particles, the dynamic equilibrium of which is maintained due to their active formation as a result of low-temperature pyrolysis. At the same time, the higher the temperature, the more carbon is transformed into a graphite-forming antifriction film, and the longer the areas of contact conjugates interact, the more graphite is formed.

Thus, a means of regulating wear and ensuring the antifriction of coatings is the use of magnesium carbide, which through its structure affects the process of adaptation during friction due to the modification of surface layers with carbide graphite, which, in the case of cooperative self-organization with oxide structures, ensures the realization of a complex of stable surface structures, this prevents direct contact surfaces that effectively reduce the force of friction, the intensity of wear, withstand high loads, facilitate running-in and prevent unacceptable hardening processes.

From the point of view of structural thermodynamics, the systematic ordering of self-adapting surface films due to changes in composition and structure can be considered as adequate elementary physicochemical processes and mechanisms of adaptation in the process of structural adaptability [7].

In Figure **1** also presents the test results of coatings of the WC15 type (curves 2, 2'), sprayed with tungsten-cobalt powder. This type of coating, as a classic wear-resistant material, is widely used to protect against wear a significant range of important parts of different design and purpose. As it was established, at sliding speeds greater than 1.9 m/s, the temperature factor, which ultimately turns out to be decisive in the development of destructive processes during friction, has a tendency to decrease their speed against wear.

For coatings based on nichrome (Figure **1**, curves 3, 3') doped with aluminum and boron, a monotonous increase in wear intensity with increasing speed is characteristic. The study of the phase composition showed the presence in the coating composition of both a nickel-based solid solution and dispersed compounds of nickel aluminides (NiAl, Ni_3Al), chromium borides (Cr_2B, Cr_5B_3), as well as the presence of complex borides of the type (Cr,Ni). The passive capabilities of secondary structures with an increase in the test speed are suppressed by the development of plastic deformation and, as a result, the dynamic equilibrium shifts towards an increase in the activation energy, and the type of wear changes qualitatively. According to the data of metallographic analysis, their friction surfaces at speeds of 1.8 m/s have random local tears, scratches, characteristic of the initial development of setting processes.

Thus, detonation coatings developed on the basis of forsterite, capable of self-lubrication, are characterized by high anti-friction properties and, in terms of operational capabilities, have the prospect of being used in the production of competitive tribotechnical purpose systems. The conducted research also confirms the expediency of continuing their tests for use in order to increase the antifriction of friction pairs in real operating conditions, but it can already be noted that their use will increase operational reliability, the resource of products and reduce repair costs during restoration. It is most appropriate to use the investigated coatings to increase the reliability of operation of friction nodes during strengthening and restoration, for example, for moving pairs of control mechanisms, hinges of guide surfaces, cams, sliding supports, pairs with reciprocating movement, bearings, sliding guides, lever parts of high-speed and difficult loaded nodes, in which the use of traditional lubricants is undesirable.

It should be noted that the developed composite powder based on forsterite for the formation of protective coatings can be used for any technological methods using powder materials.

The presented work continues the cycle of research on the development of promising coatings to minimize friction coefficients and wear intensities due to the use of materials containing magnesium compounds.

CONCLUSIONS

1. Components for self-lubricating antifriction coatings were obtained for the first time on the basis of targeted studies of magnesium orthosilicate compounds, which have improved physical and mechanical properties, long-term phase stability and wear resistance.

Their structural and phase composition, features of formation under friction load of complex alloyed surface oxide structures, which act as solid lubricants and shield working surfaces, have been determined.

2. Powder mixtures based on forsterite were obtained on the basis of the tested technology, cause-and-effect relationships between technological and operational factors of the formation of self-lubricating coatings were established.

3. The optimal mode of detonation-gas sputtering of composite powders based on forsterite was worked out, while it was possible to improve the technological process of detonation-gas sputtering of composite powders. At the same time, it was possible to reproduce not only the planned chemical composition, but also to obtain at the same time the predicted structure, which modernizes the friction surface with an anti-friction film, which minimizes tribotechnical properties and contributes to the localization of plastic deformations and shielding of unwanted setting processes.

4. The physical mechanism and main factors determining the level of thermodynamic graphitization are defined. The nature and regularities that determine the susceptibility of coatings to passivation have been studied. It is noted that its implementation is carried out both due to solid-phase tribochemical reactions and diffusion processes in the formation of quasi-layered polydisperse surface films that have self-lubricating ability and are synthesized on the basis of carbide α-graphite and finely dispersed oxide compounds.

5. Developed self-lubricating coatings based on forsterite, which are obtained by detonation-gas technology, expand the achievements of modern tribotechnical material science. Research self-lubricating compositions can be used both for strengthening and for high-quality restoration of worn triboelements by any technological methods using powder materials.

CONFLICTS OF INTEREST

The author declared no conflicts of interest.

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