Triboresistance of Composite Nanocoatings Based on Magnesium Compounds at Elevated Temperatures

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Abstract: The results of the study of the wear characteristics of detonation composite nanocoatings based on magnesium orthosilicate under conditions of high-temperature friction under constant load in the field of sliding speeds, on the surface of which stable antifriction structures are formed under conditions of elevated temperatures, are presented. The structural-phase composition of the coatings was determined by methods of modern physical analysis and the complex of high-temperature compounds of the surface layers was determined. The developed and studied coatings have high and stable antifriction properties. It was determined that the antifriction property under friction loading is due to the self-ordering of surface high-temperature oxide and oxygen-free structures, which are characterized by low shear resistance and work as solid lubricants that modify the contact surfaces and prevent damage to moving joints.

Keywords: Composite coatings, Wear intensity, Structural-phase composition, Oxide structures, Solid lubricants.

INTRODUCTION

Wear of friction pairs reduces the resource, at the same time, the use of lubricants in friction units increases the duration of their operation. At the same time, whatever modern materials are used as friction pairs, the most effective and reliable minimization of wear parameters is due to the use of lubricating and technical components in the form of liquid oils or solid lubricants. At the same time, the prerequisites for ensuring wear resistance in extreme operating conditions, which include both high loads and speeds of movement, and increased operating temperatures, remain relevant.

As a rule, the use of polymer lubricants is effective from room temperature to 300°C, solid laminar lubricants extend the operating range to 400°C; graphite, being a layered solid material, is an exception, as it provides lubricating ability at temperatures exceeding 450°C. At the same time, stable fluorides and metal oxides can be used as lubricants at temperatures above 1000°C [1-4].

One of the directions of increasing thermal resistance is connected with the search for regularities of structure formation of a complex of high-temperature surface oxide and oxygen-free magnesium compounds, which have high thermo mechanical properties and have low shear strength under friction. These studies are based on tribotechnical tests of composite coatings containing magnesium compounds, in particular, orthosilicate. Development and application of powder compositions containing magnesium orthosilicate as a basis for detonation-gas spraying of antifriction coatings operating in extreme conditions is one of the priority directions of modern tribotechnical materials science and an urgent task of increasing operational reliability and extending the production life of parts.

The Purpose of the Presented Work is to study the wear sequence under high-temperature friction conditions of coatings based on magnesium compounds, to study their structural and phase composition, and to analyze the structure formation of heat-resistant surface oxide and oxygen-free components with low shear resistance, which play the role of a solid lubricant during friction.

Materials and Research Methods As a powder base for spraying high-temperature coatings, a heat-resistant oxide compound was used, namely, magnesium orthosilicate with the chemical formula $2MgO{\cdot}SiO_2$, which has significant mechanical and thermal properties and is widely used as a refractory. For the purpose of hetero genization, nanosized impurities of chromium, zirconium, nickel, titanium, aluminum, silicon and carbon were added to the initial powder base material. Further step-by-step development involved the use of mechano chemical synthesis (MCS) technology, as a result of which a multi component mixture was obtained, individual granulometric particles of which, as a result of selective interaction, which is due to thermodynamic and diffusion characteristics, consisted of micro volumes of several nanocomponents. Thus, a mixture of micron-sized base particles and nanosized doped phases was obtained. Subsequently, the mechanical mixture was mixed until complete and uniform distribution of structural components and a state of suitability for spraying was achieved.

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The nanosized powder conglomerate obtained in this way was sprayed by the detonation-gas method onto ring samples of the HN78T alloy. The physical and mechanical properties and patterns of friction and wear of the coatings at elevated temperatures were tested according to the end-face scheme on universal friction machine M-22PV at a sliding speed of 1.5 m/s and a load of 7.5 MPa. The temperature was measured with a thermoelectric thermometer of the KTHA type at a distance of 1-2 mm from the friction surface according to the standard method [9]. The adhesion strength was determined by the pin method, which for coatings based on orthosilicate was over 89 MPa with a residual porosity of 0.5-1.0%, along with this, after preliminary finishing grinding their roughness parameter was equal to Ra 0.32-0.63. At the same time, the research program provided for a comparative analysis of the friction parameters of the developed coatings with the values of control coatings based on both tungsten carbide type WK-15 and alloyed nichrome.

The wear intensity, friction coefficient, and condition of working surfaces were determined as criteria for the performance of coatings [10].

When studying the patterns of wear and structural transformations under friction conditions and establishing the technology-structure and structure-property relationships, a complex of modern physicochemical methods of structural-phase analysis was applied, capable of studying surface layers at the macro- and microscopic levels. The comprehensive research methodology included metallography (optical microscope "Neophot-32" with an attachment); durometric analysis (hardness tester M-40 from LECO); scanning electron microscopy (scanning electron microscope JSM-840); X-ray structural phase analyzer (diffractometer DRON-UM1).

Research Results and their Discussion. The contact interaction of surfaces under friction conditions is a complex sequence of cooperative influence of both external and internal factors, on which the regularities that determine the course of friction and wear processes depend; they determine the degree and gradients of elastic-plastic deformation, temperature, activation level and a number of associated phenomena and ultimately determine the leading type of wear.

The results of high-temperature friction wear tests of magnesium orthosilicate-based coatings and control coatings are presented in Figure **1**. The studies were conducted in a field of monotonically increasing temperatures at a constant load corresponding to 7.5 MPa.

The obtained results allow us to clearly distinguish, under the given experimental conditions, the satisfactory antifriction properties of coatings based on magnesium orthosilicate, which are due to the long-term and minimum values of both the wear intensity and the friction coefficients. According to the authors, under the given test conditions, the value of the friction coefficients is determined not so much by the function of the normal load, but by the dependence on the tribophysical processes that are formed as a result of the additive action of the load, sliding speed, temperature and the generalized vector of friction parameters (material, environment, conditions, etc.). At the same time, the nature of the values of the friction coefficients on the sliding speed under the test conditions is consistent with the profile of the dependence of the wear intensity, and its stability indicates the high workability of the studied coatings based on orthosilicate.

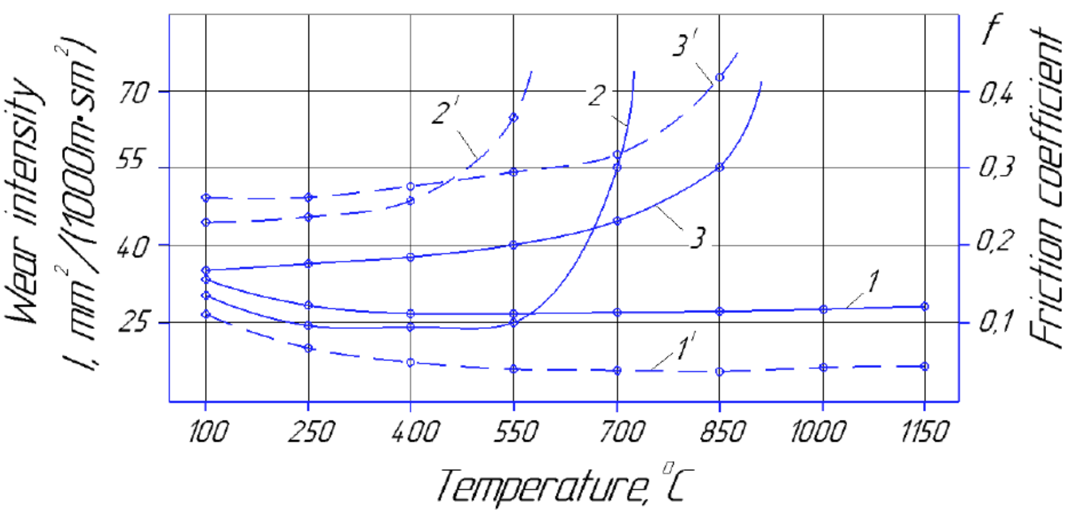


Figure 1: Dependence of wear intensity (1, 2, 3) and friction coefficients (1^I, 2^I, 3^I) on the temperature of coatings based on magnesium orthosilicate (1, 1^I), WK-15 (2, 2^I), alloyed nichrome (3, 3^I) at P=7.5 MPa.

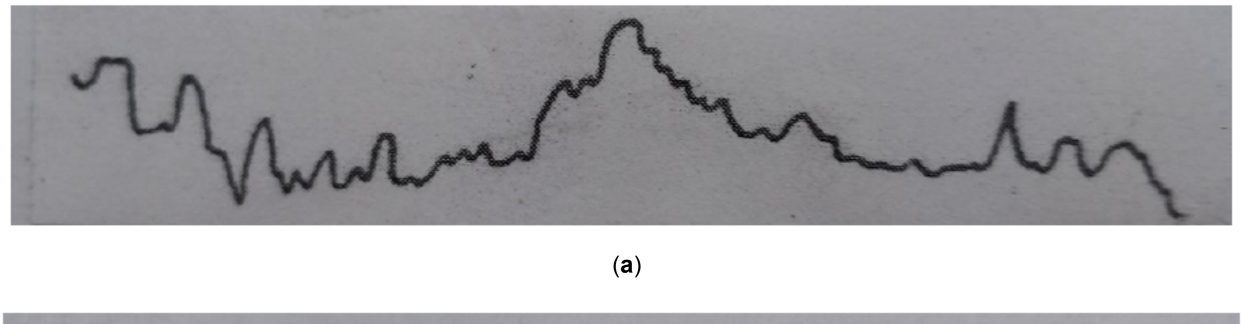
The topography of the working surface of silicate-based coatings in combination with physical and mechanical characteristics determines their operational properties, including wear resistance. Studies have shown that during the running-in process, the original technological relief is removed, the chemical composition, structure of the surface layer and its geometry are radically changed, which affects wear resistance. At the same time, a new surface quality is formed, which contributes to the formation of balanced roughness, which causes minimal and stable wear.

Thus, the initial technological roughness is converted into optimal operational roughness, which causes favorable wear. At the same time, the sprayed layer is characterized by a heterogeneous dispersed structure with a quasi-ordered lamellar appearance and fits tightly to the base, copying the relief, while the accumulation of films, slag inclusions and other contaminants, as well as defects in the form of micropores and microcracks, are not detected. Profiling of the contact zone (Figure **2**) indicates the absence of damage to the surface layers and leveling of the working surface, which mainly occurs due to the removal of protrusions, and contributes to the formation of continuous oxide high-temperature structures, which is also consistent with electron micrographs of friction surfaces.

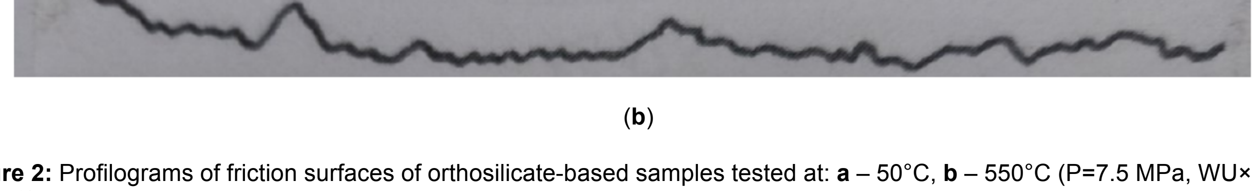
When determining the structure, we relied on the results of micro X-ray structural analysis (MRSA) performed on the Camebax SX installation, which allowed us to classify the structure of the studied coatings as a multicomponent fine-grained aggregate, the basis of which consists of homogeneous hexagonal magnesium orthosilicate and an almost uniformly defined significant amount of finely dispersed inclusions of carbides, especially silicon carbide (SiC) and a fine aggregate of high-temperature strengthening compounds, which are silicides Cr_2Si_3, $CrSi_2$, Zr_3Si_2, TiSi, TiSi2 and aluminides $TiAl_3$, TiAl, $ZrAl_3$, $CrAl_4$, as well as significant colonies of metal carbides that are part of the coating. In addition, significant intermetallic formations in the form of spherical nanoparticles of the $ZrCr_2$, ZrV_2, NiTi, NiAl types were identified, which stabilize the structure, and non-oxide fragments of ternary compounds in the form of MgSiC, Cr_2SiC, Ti_3SiC_2, TiZrC, ZrSiC, which are characterized by significant hardness and strength under high-temperature friction conditions. Qualitative determination of phases through the micro hardness of individual areas was also applied. Thus, micro areas with a micro hardness of 5.1-6.7 GPa are probably titanium carbosilicides, and zones with a micro hardness of almost 12.0 GPa are titanium carbides, values of 8.0 GPa most likely correspond to titanium silicides, while 9.3-10.2 GPa is a micro hardness that is close to the values of magnesium oxides. Thus, the structural-phase formations of coatings based on magnesium orthosilicate consist of chemical compounds, solid solutions and mechanical mixtures and are characterized by increased thermodynamic properties, namely hardness, strength and corrosion resistance, and provide considerable wear resistance and low friction coefficients under high-temperature friction conditions.

Thus, the specified structural components of orthosilicate-based coatings, due to quantitative formations, provide high-quality components of solid solutions, chemical compounds and mechanical mixtures, which have increased temperature stability, satisfactory hardness, strength and corrosion resistance at elevated temperatures.

The problem of coating quality is inextricably linked with the optimization of the technological process. To



(**a**)



(**b**)

Figure 2: Profilograms of friction surfaces of orthosilicate-based samples tested at: **a** – 50°C, **b** – 550°C (P=7.5 MPa, WU×1000, GU×40).

obtain improved coatings, technological parameters were investigated, primarily the particle size distribution, loading depth, barrel filling degree, working gas ratio and spraying distance [11]. In addition, by controlling the technological process of increasing the efficiency of the studied coatings, not only the required chemical composition was implemented, but also the predicted structure was obtained, which is determined by a set 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 characteristics in the samples of one batch that were sprayed was stably about 5-10%.

The study of the physical mechanisms of the formation and evolution of structural-phase states of secondary structures under conditions of mechanochemical activation at high-temperature friction is one of the important tasks of controlling the antifriction properties of coatings based on magnesium orthosilicate when regulating their tribotechnical properties. For comprehensive and reliable information in the study of thin surface layers in which the processes of structural-thermal activation occur, the X-ray photoelectron spectroscopy (XPS) method was additionally applied, with the help of which the microstructure was analyzed and the nature of the phases, their crystal structure and the parameters of the elementary cells, which are necessary for identifying the composition within the regions of their homogeneity, were determined. The obtained results allowed us to generalize that the initiation of physicochemical transformations due to elastic-plastic deformation is primarily manifested in the process of inversion of interaction with air oxygen and, as a result, the reformation of secondary films by additional formation of oxide compounds within the structural components of the orthosilicate composition, which, according to its stoichiometric composition, as a result of solid-phase tribochemical and diffusion processes, forms a powerful complex of stable thermodynamic compounds of the second type in the form of Al_2O, SiO_2, ZrO_2, TiO_2, Cr_2O_3, MgO, which additionally synthesize both solid solutions of the type $2Cr_2O_3$-SiO_2, MgO-Al_2O_3, and complex oxides in the form of aluminosilicates Al_2SiO_5, Al_2SiO_4, $AlSi_3O_8$, which constitute compounds with high thermal stability, as well as spinel phases with significant thermal stability, such as Mg_2TiO_4, $MgAl_2O_4$, $MgTi_2O_5$, $MgZrO_3$, $MgCr_2O_4$, in addition, the presence of binary compounds of the type TiO-ZrO_2, MgO-TiO_2, MgO-ZrO_2 has been identified, while the possibility of the presence of ternary compounds, such as Mg-ZrO_2-TiO_2, MgO-Al_2O_3-TiO_2, is not excluded. It is worth noting that at elevated temperatures, protective oxide structures that form a film on friction surfaces, in which shear deformation is localized during friction, determining the quality of friction, are in dynamic equilibrium and have the property of self-lubricating. However, due to statistical regularities, the processes of regulation of secondary self-lubricating structures on different parts of the working surface as a result of contact discreteness do not coincide in stages. The authors believe that the process of their formation does not occur simultaneously on the entire contact surface, but only on local fragments of the actual area, while their additive distribution is a stable structural-temporal state.

For a deeper understanding, the surface structure in which the activation processes occur was investigated using transmission electron microscopy. Figure **3** shows a typical topography of the surface of an orthosilicate-based coating and an electron diffraction pattern obtained from a section with an area of about 0.5 μm2, which consists of a large number of reflections, indicating a polycrystalline state and representing an oriented mixture of highly dispersed phases. The surface structure of this coating is an oriented composition of highly dispersed crystalline phases. The decrease in grain size is accompanied by an increase in their strength and hardness. In this case, the micro hardness of the surface layer is 19.0–21.0 GPa (with an initial one of about 16.0 GPa). Thus, low and stable values of both friction coefficients and wear rates of coatings at elevated temperatures are ensured by the formation of a coherent dynamically stable conglomerate of heat-resistant oxide structures, which are characterized by a small shear resistance. It should be noted that the structure itself can change within certain limits, but the general order, *i.e*. the dynamics of their formation and destruction, is constant. At the same time, it provides screening of adhesive-molecular interaction during friction and under conditions of local

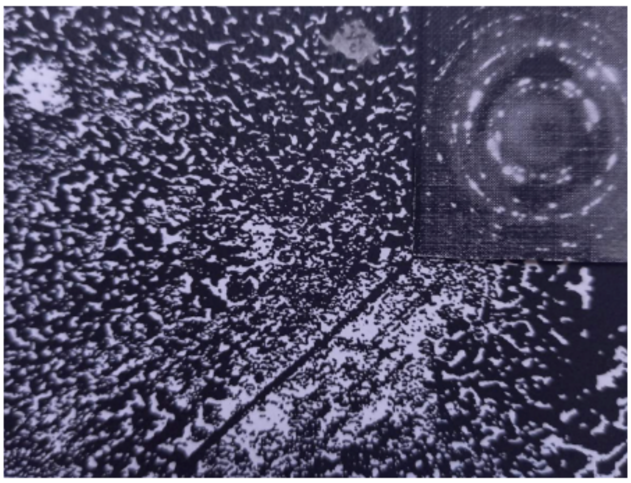


Figure 3: Friction surface and electron diffraction pattern orthosilicate-based coating (750°C, V=1.5 m/s, P=7.5 MPa.)

contact pressures and temperatures forms dense heterogeneous heat-resistant and fairly plastic surface films without cracks and chips, which by their properties have high adhesive activity to the surface and are a barrier to oxygen diffusion and contribute not only to reducing the oxidation rate and increasing heat resistance, but also play the role of solid lubricants.

Thus, the means of regulating wear and ensuring self-lubrication of magnesium silicate-based coatings under conditions of high-temperature friction is the action of heat-resistant surface oxide structures, which, during cooperative self-organization, provide an additive complex of properties of surface structures that have the ability to self-lubricate and prevent direct contact of surfaces, while effectively reducing the friction force, wear intensity, and preventing unacceptable destruction processes.

From the point of view of structural-thermodynamic mapping, the systemic ordering of surface oxide films under high-temperature conditions can be physically realized only through a structure that adapts through evolution and which can be considered during friction as adequate elementary physicochemical processes and mechanisms of self-ordering that cause self-lubrication under high-temperature friction conditions.

Figure **1** (curves 2, 2^1) also presents the results of tests of coatings of the type WK15, sprayed with tungsten carbide powder, which were used as reference coatings in the study of the patterns of friction and wear of coatings with orthosilicate. Coatings of the type WK-15, as a classic wear-resistant material, are widely implemented to protect against wear a significant range of parts of different design and purpose. As it was established, at sliding speeds of more than 1.7 m/s, the tendency to increase their wear is determined by the temperature factor, which ultimately turns out to be decisive in the development of destructive processes.

For coatings based on nichrome, alloyed with aluminum and boron, (Figure **1**, curves 3 and 3^1) is characterized by a slow increase in wear intensity with increasing temperature factor. The study of the phase composition revealed the presence in the composition of both a solid solution based on nickel, and, mainly, dispersed compounds of nickel aluminides (NiAl, Ni_3Al), chromium borides (Cr_2B, Cr_5B_3). The passive capabilities of secondary structures with increasing test temperature are suppressed by the development of plastic deformation, as a result, the dynamic equilibrium shifts towards increasing activation energy, and the type of wear changes qualitatively. The specifications of metallographic analysis of their friction surfaces at speeds of 1.8 m/s are random local tearing, scratches, and characteristic of the initial development of setting processes.

Thus, the detonation coatings based on magnesium orthosilicate, developed by the authors, are characterized by high antifriction properties and significantly exceed the control coatings in terms of operational capabilities, in addition, they are characterized by significant adhesion strength and the ability to vary secondary structures due to the composition, which cause self-lubrication. The conducted studies indicate the feasibility of using self-lubricating antifriction coatings to increase the operational reliability and durability of parts operating under high-temperature friction conditions. It can already be noted that their practical implementation will ensure reliability, increase the resource and, in case of operational damage to parts, reduce repair costs during their restoration. In technical systems, there are nodes that are subject to wear during the friction process and, as a rule, cause operational malfunctions over time. Such units include, for example, crankshafts, seats, disk and oval surfaces of products, housing parts, moving pairs, hinges of guide surfaces, cams, sliding supports, pairs with reciprocating movement, guide slides, lever parts, high-speed and heavily loaded joints, in which the use of traditional lubricants is undesirable. From our considerations, coatings developed on the basis of heat-resistant magnesium oxides can be considered as an alternative to other promising materials for operation in high-temperature units of modern technology, including aerospace.

It should be noted that the created composite powder based on magnesium orthosilicate for the formation of self-lubricating antifriction coatings operated under high-temperature friction conditions can be used by any technological methods using powder materials.

CONCLUSIONS

1. Magnesium orthosilicate-based coatings developed and tested under high temperature conditions are characterized by stable and low friction coefficients and wear rates. In high-temperature testing mode at a load of 7.5 MPa and a sliding speed of 1.5 m/s, they have friction parameters significantly lower than those of control coatings by 3.5-8.0 times.

2. Based on mechanochemical technology, composite powder mixtures based on magnesium orthosilicate were obtained, consisting of a nanocomposite conglomerate of micron-level base particles and nanoalloyed phases, and 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 spraying of orthosilicate compositions has been worked out, which reproduces not only the planned chemical composition, but also provides a predicted structure, which modernizes the friction surface and ensures guaranteed quality of coatings. At the same time, it is emphasized that during spraying, the variation of strength and plastic properties in samples of one batch is stable and is 5-10%.

4. The structural and phase composition of coatings based on magnesium orthosilicate has been established as a multicomponent fine-grained aggregate of hexagonal orthosilicate with an almost uniform distribution of finely dispersed high-temperature inclusions of carbides (TiC, ZrC, SiC), silicides (TiSi, $CrSi_2$, Zr_3Si_2), aluminides (TiAl, $ZrAl_3$,$CrAl_4$), in addition, intermetallic formations (NiAl, NiTi, $ZrCr_2$) have been identified, and ternary compounds in the form of MgSiC, TiZrC, ZrSiC have also been discovered, which are generally characterized by increased thermodynamic properties, high hardness and strength, and corrosion resistance.

5. It is noted that the tendency of coatings to passivation is due to diffusion and tribochemical processes, which cause the formation of a quasi-spherical oxide protective film, in which shear deformation is localized during friction. At the same time, it provides shielding of adhesive-molecular interaction, has high adhesive activity to the surface and under conditions of high-temperature friction increases heat resistance and performs the role of solid lubricants, while reducing the friction force, wear intensity and preventing unacceptable destruction processes.

6. The developed self-lubricating composite coatings based on magnesium oxide compounds extend the achievements of modern tribotechnical materials science. The studied self-lubricating compositions based on magnesium orthosilicate can be used both for strengthening and for high-quality restoration of worn parts by any technological methods using powder materials.

CONFLICTS OF INTEREST

The author declared no conflicts of interest.

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