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FORMATION OF ANTIFRICTION SURFACE STRUCTURES UNDER FRICTION

The results of the formation of anti-friction surface structures of the developed glass-composite self-lubricating nanocoatings, the structural components of which have a qualitative effect on the graphitization process and ensure the production of a surface layer of α -graphite that minimizes contact parameters, are presented. The positive role of the glass phase in the form of aluminoborosilicate, which affects the tribotechnical properties of coatings, has been established. It is noted that the increase in adhesive strength is achieved due to the formation of a surface layer of vitreous sodium silicate during sputtering. It was established that the intercalation of the graphite layer with particles of the subsurface zone does not significantly affect the tribotechnical characteristics. The developed nanostructured glass composite coatings showed high anti-friction characteristics in the entire load-speed range of tests.

Key words: friction, wear, intensity of wear, glass composite, nanostructure.

Preservation of operational characteristics, limited to friction and wear, of both individual units and technical systems as a whole, is ensured by modern means of surface engineering, which implement the basic principle of minimum costs for maximum results. Structural engineering methods using modification through the use of solid lubricants have made significant progress in ensuring antifriction of contact joints in recent years. Coatings containing solid lubricants are one of the innovative and most promising antifriction materials, the high quality of which is especially noticeable in conditions where traditional liquid lubricants are not very effective [1,2]. They are used in various fields of technology, from the lubrication of precision aviation mechanisms to the prevention of jamming of threaded joints [3,4].

The development of anti-friction nanostructured glass-composite self-lubricating coatings corresponds to the modern priorities of tribotechnical materials science, aimed at increasing the wear resistance of moving joints, and the development of scientific and applied solutions in the interest of improving the efficiency of the use of high-quality production technologies [5,6].

The purpose of the work is related to the study of nanostructured glass-composite self-lubricating coatings that have increased antifriction due to the presence of a glass phase of aluminoborosilicate and structurally free magnesium carbide and the use of structural components that promote graphitization.

Research materials and methods. As is known from the comparative characteristics of gas-thermal coatings, similar in structural and phase composition, the maximum operational properties have detonation-gas [7]. Based on this, the technology of detonation-gas spraying of nanostructured powders of the composition SiC-Ni-Cu-Al-Si-C with a uniform distribution of aluminoborosilicate glass phase ($\text{SiO}_2\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3$) was used for sputtering the investigated coatings. Structurally free magnesium nanocarbide (MgC_2) was added to the nanoglass composition obtained by the

mechanical method, after which it was mixed, ensuring its uniform distribution in the obtained powder mixture, ready for sputtering. All components of the powder materials used in the work are taken from the mineral and raw material base of Ukraine.

The anti-friction properties of the coatings were evaluated when the ring samples were rubbed according to the end scheme under conditions of distributed contact in continuous sliding mode under a load of 10.0 MPa. The influence of the environment, speed, and load implemented during the tests were chosen taking into account the maximum approximation of the processes of physico-chemical mechanics of friction to the real conditions of contact interaction, in addition, the research program of nanostructured glass composite coatings provided for a comparative analysis of their antifriction characteristics with similar values obtained during tests coatings of the VK15 type and coatings sprayed with alloyed nichrome powder.

The study of contact joints, in which friction activation processes occur, which determine the intensity of surface reactions and tribophysical phenomena, was carried out using modern methods of physical analysis, which includes metallography (optical microscope type Neofot-32 with an attachment), X-ray electronic microanalyzer type "Camscan 4DW» with a program for the distribution of chemical elements. Determination of the phase composition of the surface layers was carried out on a general-purpose X-ray diffractometer of the DRON-3 type with monochromatized $\text{CuK}\alpha$ radiation.

Increasing the adhesive strength, as a criterion for the performance of glass composite coatings, was carried out by previously applying a sublayer of vitreous sodium silicate $\text{Na}_2\text{O}(\text{SiO}_2)_2$ to the working surface. The exception of unproductive losses and compliance with the measurement technology [8] determined the correctness of the obtained results of the adhesion strength, which amounted to 145-150 MPa.

Research results. The contact interaction of surfaces is a complex sequence of cooperative influence of both external factors and internal transformations, the qualitative coordination of which reflects the commonality of quantitative regularities and determines their orderly causal relationship. According to the results of the interaction of the coatings under friction loading, Fig. 1 shows the experimental values representing the averaged functional dependences of wear intensity and friction coefficients, which change over time and stabilize after running-in, in the field of sliding speeds under a constant load equal to 10.0 MPa. As can be seen from the graph, in the entire range of tests with a monotonically increasing sliding speed, the minimum values of wear intensities and the corresponding friction coefficients correspond to nanostructured glass composite coatings (curves 1 and 1'). The structure of nanoglass compositions, which determines their properties, consists practically of a finely dispersed mixture representing solid solutions and, mainly, intermetallic compounds and the presence of a glass phase. The invariance of the chemical composition and the constancy of the properties of technological spraying determine the stability of the coating structure, the relative density of which reaches 99%. The cross-section of the nanoglass composite coating is shown in Fig. 2. Metallographic analysis established that the sprayed layer has a quasi-ordered lamella-like appearance and tightly adheres to the base material, completely copying the surface relief, while the accumulation of component oxides, as well as slag contamination, are practically absent, and defects in the form of pores and cracks are not detected.

The synthesis and research of solid solutions based on refractory compounds, in particular silicon carbide, are being conducted quite intensively, but the capabilities of the latter and its set of tribotechnical properties are far from the expected results.

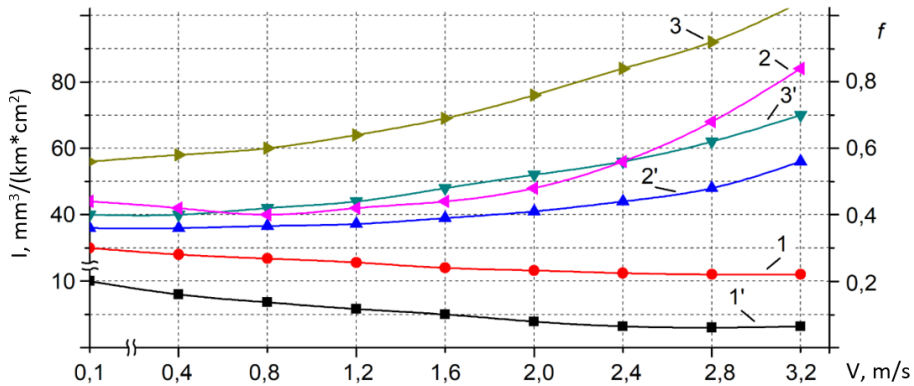


Fig. 1. Dependence of wear intensity (1, 2, 3) and friction coefficient (1', 2', 3') on sliding speed of coatings SiC-Ni-Cu-Al-Si-C+glass phase+MgC₂ (1, 1'), WC-Co (2, 2') and Ni-Cr-Al-B (3, 3') ($P = 10.0$ MPa)

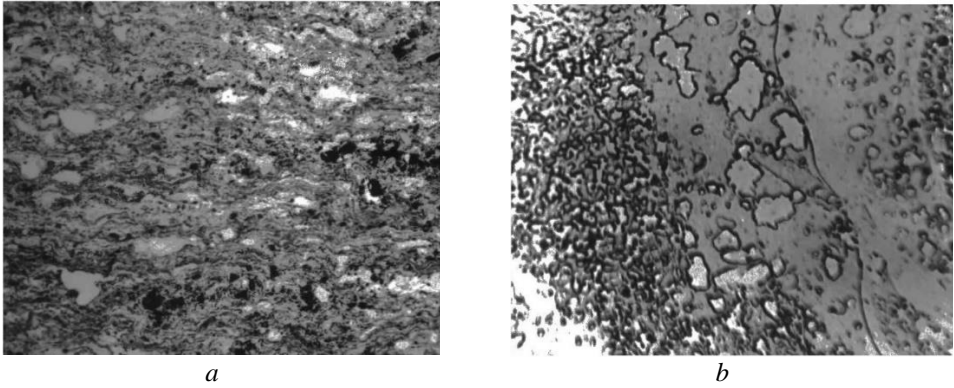


Fig. 2. Coating structure: *a* – $\times 120$; *b* – $\times 5000$

The developed glass composite is an anti-friction material with an ultrafine structure. It is generally accepted that elastic-plastic deformation is the main factor determining the development of the process of external friction, and in addition, in our opinion, the formation of a gradient structure is derived from it. It can be said that the evolution of the structure during contact interactions has pronounced scale levels, and the processes taking place at different scale levels are mutually dependent. The layer-by-layer picture of plastic deformation, obtained by the diffraction method, reveals the main regularities of the formation of a large-scale structure and allows establishing uniform transitions from a dispersed polycrystalline fragmented structure on the surface through intermediate textured layers to the original crystalline material inherent in the depth. Thus, the structure of the investigated coating gradually changes to ultradispersed as it approaches the friction surface and increases in contact pressure and intensity of deformation. At the same time, high contact compressive and shear stresses create conditions for realizing significant plastic deformations in the surface layer of the coating material, which lead to the formation of ultradispersed structures.

This gives reason to distinguish a near-surface zone in a structure subjected to tribotechnical loads, in which deformation processes that develop inhomogeneously in microvolumes form a specific layer at the near-surface level, in which structural-thermal activation conditions a complex of physico-chemical interactions that determines

concomitant and dominant type of wear. The near-surface zone has a structurally inhomogeneous finely dispersed composition.

As evidenced by the results of X-ray microspectral analysis (XMR) performed on the "CamebaxSX" installation, the basis of the component of the nanoglass composition is silicon carbide of non-stoichiometric composition, along the grain boundaries of which silicate compounds are located, among which inclusions corresponding to the composition of silicon dioxide prevail, also in the carbide structure the role of dispersion-strengthened components is performed by Al_2O_3 oxides distributed along the boundaries and intermetallic inclusions in the form of spherical nanograins. But the high thermomechanical properties of SiC carbide are discredited by significant brittleness. We noted that the solid replacement solution that forms Al and SiC causes a slight distortion of the carbide crystal lattice, since the differences in the masses of Al and Si atoms are extremely small, as a result of which the microhardness does not change, while the plasticity increases. Cu and Ni have a similar effect on the composition of SiC, which form substitutional solid solutions by replacing Si atoms. The formation of phases in the coating, as the tests showed, is determined not only by the ratio of components, temperature, dispersion, but also depends on their defects and external conditions. There is no doubt that tribochemical interaction occurs when molecules receive the necessary activation energy. Endothermic reactions do not proceed at all without activation. The interaction of SiC with Mg, which is formed during the thermal decomposition of structurally free magnesium carbide under working conditions and depends on the temperature of the process, is accompanied by the formation of magnesium silicide and acetylenedimagnesium, the latter under the influence of thermomechanical interactions contributes to the formation of graphite through the intermediate dimagnesium tricarbonide ($2\text{SiC} + 5\text{Mg} \rightarrow 2\text{Mg}_2\text{Si} + \text{MgC}_2$, $\text{MgC}_2 \rightarrow \text{Mg}_2\text{C}_3 \rightarrow \text{Mg} + \text{C}$). It should be noted that during thermodynamic action, the presence of a catalyst in the form of Al in the structure contributes to the decomposition of magnesium carbide. The basis of the physical phenomena that initiate the mechanism of carbide graphite decomposition are structural transformations in the solid phase caused by thermal effects. In our opinion, the factors that determine the quality level of thermomechanical carbide graphitization include the degree of dispersion of structural components, specific pressure, operating temperature, and the temperature in the contact zone, the presence of elements that initiate decay processes, as well as the influence of the environment (in vacuum, the probability of the amount of graphite increases), in addition, internal factors related to the composition of the material, its structure, the presence of defects, etc. Figure 3 shows topographies of friction surfaces obtained at sliding speeds of 0.8 m/s and 0.15 m/s. As can be seen, the anti-friction layer of graphite covers almost the entire working surface with all its capacity, providing an increase in the actual contact area, contributing to a decrease in the specific load due to an increase in the support length due to the filling and leveling of micro-unevennesses and fixing of graphite micro-particles in micro-indentations. The contact zone, which is the near-surface layer (initial scale level), which separates the coating material from the antifriction film consisting of polydispersed graphite particles, represents a deformed zone, which, according to the results of micro-X-ray spectral analysis performed on MAR-3 (probe diameter 1 μm), represents finely dispersed heterogeneous structural-phase compounds of components. Among which the presence of Ni, as a structural component, is due to its specific properties, namely, on the spots of actual contact when the temperature reaches 450-500 °C depending on the dispersion and external influences

in the conditions of a local high-temperature field, Ni interacts with SiC, forming nickel-enriched silicides metal (Ni_2Si). As a result, there is a recovery of carbon, which is transformed into a solid phase of elementary polydisperse graphite colonies united into surface structures.

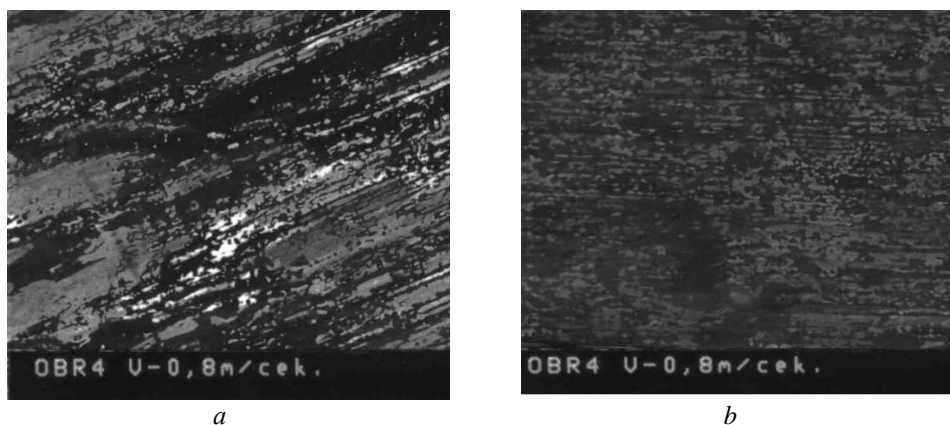


Fig. 4. Topography of the friction surface during the formation of a graphite film:
a – $V = 0.8$ m/s; *b* – $V = 1.5$ m/s.

But the dominant component of the formation of the anti-friction surface layer, consisting of a carbon product - graphite, remains magnesium carbide. The value of the specific work of wear, characteristic of the initial moment of running-in, as shown by the calculations, is up to 10 kJ/mm^3 , which is both a necessary and a sufficient condition for initiating the thermal decomposition of MgC_2 , which leads to the formation of carbon in the form of a solid phase.

Using the natural ability of chemical elements to graphitize through the formation of carbide graphite, we obtained a high-quality, anti-friction layer that determines the operational properties of the coatings.

During the structural-phase study of glass composite coatings, the presence of intermetallic compounds based on Al and Ni such as NiAl and Ni_2Al_3 was noted, while monoaluminide, which is a high-temperature phase, has significant hardness, as shown by measurements, most likely close to 3.8 GPa. The presence of an ordered solid solution based on nickel monoaluminide with an Al content of $\sim 20\text{-}25$ wt. %, which causes increased plasticity. According to the results of elemental and X-ray phase analysis, the presence of a solid solution of Ni in Cu was noted, but their compounds were not detected. Solid solutions of Ni in Si and Si in Ni, as well as their intermetallics Ni_2Si , Ni_3Si_2 , NiSi_2 , were established. In addition, the presence of small amounts of colonies of solid solutions of Si in Cu was proven, probably also the formation of their chemical compounds of the type of copper silicates, since the structural microhardness increases significantly, but identifying them presented significant difficulties.

Powders of aluminoborosilicate glass, the dispersion of which was $25\text{-}30 \mu\text{m}$, in the process of mechanochemical treatment and thermomechanical influence, as products of inorganic synthesis, caused, as was determined, along with the preservation of the initial components, the formation of new stable compounds from solid solutions of Al_2O_3 and SiO_2 with rhombic syngonia, which is close to the structure of sillimanite, it is most likely a lower mullite obtained by reaction as a result of the interaction of oxidation products of the initial components. From the point of view of glass-ceramic technologies, the most interesting, in our opinion, is the presence of components that

form refractory metal oxides and primarily Al and Si oxides. The presence of B_2O_3 , which as a result of partial oxidation became part of the Al_2O_3 - B_2O_3 solid solution, was also established.

From the standpoint of the physics of the condensed state, the addition of a vitreous component affects the quality of the coating material through the structural state, and, as practice shows, interest in these technical products is steadily growing. When studying glass compositions using an experimental method, their optimal composition was established, in which the rational use of glass structures contributes to increasing heat resistance and chemical resistance, in addition, the manifestation of high cohesive strength, increasing the density of nanocomponents, crack resistance and, with significant corrosion resistance, provides high adhesion (more than 127 MPa) with materials of different chemical nature, in addition, the formation of a silicate barrier layer prevents the mutual diffusion of structure-forming particles of the coating and substrate.

The surface zone directly adjacent to the friction surface and separating the coating material from the anti-friction layer consisting of polydisperse graphite particles is the thinnest film with a thickness of several micrometers. Studies have shown that the pressure in it is uneven, and the regions of tensile and compressive stresses, which are inevitable under the conditions of deformation of heterogeneous phases, are similar in structure to a conglomerate of finely dispersed (quasi-amorphous) structures, which have dimensions in the range of 5-15 nm, and are mechanical mixtures, oxygen-free and oxide compounds of structure-forming components. The influence of plastic deformation is associated not only with the dispersion of the surface zone, but also with the accumulation of defects that change its physical and chemical properties, including reactivity, and affect the intensity of chemical reactions in the solid phase.

At the same time, the thermal conductivity of finely dispersed conglomerate has increased porosity and forms a near-surface zone lower than that of solid material, therefore the heating temperature of finely dispersed fragments of the zone is higher than the temperature of the surface areas.

The temperature factor stimulates physicochemical processes, in particular, the reactive diffusion of structure-forming particles at the atomic-molecular level, which contributes to the penetration of kinetically active components of the dispersed zone due to the weakening of the bond between polyarene planes into the interlayer space of graphite and, thus, the formation of intercalated graphite.

Using the X-ray phase analysis method, it was established that Mg^{2+} , Al^{3+} , Cu^{2+} ions, which randomly penetrate into the interlayer space of the graphite matrix, appeared as intercalating elements in the subsurface zone-graphite system at the initial stage of the process. At sliding speeds of more than 3.0 m/s, intercalates of binary molecular compounds of these elements with oxygen were found in the layered graphite system. Their intercalation is accompanied by a sequence of repeated stages, which are reversible when the tribotechnical parameters are changed and are characterized by a specific transformation of the structure and, first of all, an increase in the distance between the layers due to the influence of various types of interlayer defects and the penetration of intercalants. Note that today there is no general intercalation model that explains the electrochemical mechanism of synthesis of layered systems. From the energy point of view, the process of intercalation, representing reverse topotaxial chemical reactions, can be considered as an adequate mechanism of self-organization of surface layers in the process of structural adaptability of the friction system.

We found that the level of quantitative changes during the intercalation of the graphite layer, which causes a high level of antifriction, does not affect the qualitative values of tribotechnical parameters in the test process to the expected extent.

The developed anti-friction nanostructured glass-ceramic self-lubricating coatings, which contain magnesium carbide and structural components that contribute to surface graphitization, do not contain expensive and scarce components, meet the requirements of environmental safety, and provide high performance properties. The use of nanostructured glass-ceramic self-lubricating coatings is most effective for increasing the operational reliability of friction nodes when strengthening and restoring moving parts of control mechanisms, sliding supports, lever parts, high-speed and thermally loaded couplings, in which the use of traditional lubricants is not desirable.

The development of nanostructured glass-ceramic anti-friction self-lubricating coatings, the substantiation of their structural components, the results of applied tests and the ability to work in production conditions allow to significantly expand the arsenal of achievements of modern tribotechnical materials science.

It should be noted that the developed nanostructured glass composite powder can be used to strengthen and restore worn parts by any technological methods using powder materials.

The presented work continues the cycle of research on the creation of promising nanomaterials designed to reduce friction coefficients and increase the wear resistance of tribotechnical compounds of machine and equipment parts.

Conclusions

1. Through theoretical and experimental research, the optimal structural and phase composition of nanostructured glass composite coatings of the SiC-Ni-Cu-Al-Si-C system, containing a glass phase of the SiO₂-Al₂O₃-B₂O₃ type and structurally free magnesium carbide, was realized. To improve the adhesive strength, a sublayer of vitreous sodium silicate was applied to the substrate. The role of the glass phase in the formation of glass compositions, which contributes to the increase of the cohesive component, the integrity and strength of the nanostructure, and the increase in the chemical resistance of coatings, is revealed.

2. It is noted that the assessment of the quality of the investigated coatings is related to the problem of the reproducibility of the technological process. Controlling the sputtering of nanostructured glass composite powders, it turned out to be possible to provide not only the required chemical composition, but also to obtain a given nanostructure that optimizes a complex of properties that contribute to the stable manifestation of the minimization of tribotechnical parameters in the conditions of structural adaptability.

3. The physical mechanism and main factors determining the level of thermomechanical graphitization were considered, the nature and chemical interactions of the structural components of the friction system in ensuring high antifriction of glass composite coatings were noted.

4. The synthesis of layered compounds of graphite as a result of topoaxial reactions was investigated. The nature of the intercalants in the graphite matrix was established and it was noted that reversible topoaxial chemical reactions in the solid phase are one of the mechanisms of self-organization of the surface layers of the friction system under the conditions of structural adjustment.

5. The fundamental ideas about the formation and structure of anti-friction surface structures based on polydisperse carbide graphite were supplemented, which made it possible to expand the arsenal of achievements of modern tribotechnics.

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ФОРМУВАННЯ АНТИФРИКЦІЙНИХ ПОВЕРХНЕВИХ СТРУКТУР ПРИ ТЕРТІ

Наведено результати формування антифрикційних поверхневих структур розроблених склокомпозиційних самозмашувальних нанопокриттів, структурні складові яких мають якісний вплив на процес графітизації та забезпечують отримання поверхневого шару α -графіту, що мінімізує контактні параметри. Встановлено позитивну роль склофази у вигляді алюмоборосилікату, що впливає на триботехнічні властивості покриттів. Відзначено, що підвищення адгезійної міцності досягається за рахунок формування при напилюванні поверхневого шару зі склоподібного силікату натрію. Констатовано, що інтеркаляція графітового шару частинками підповерхневої зони суттєво не впливає на триботехнічні характеристики. Розроблені наноструктурні склокомпозиційні покриття показали високі антифрикційні характеристики у всьому навантажувально-швидкісному діапазоні випробувань.

Ключові слова: тертя, знос, інтенсивність зношування, склокомпозит, наноструктура.

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