



Nanostructural glass composite coatings

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Abstract

The results of the study of glass-composite nanostructured self-lubricating coatings are presented. The developed glass composite is an antifriction material with an ultrafine structure. The structural components of these coatings significantly affect the graphitization process and provide an antifriction surface layer of α -graphite. The formation of this layer makes it possible to significantly minimize the contact parameters in the friction region.

The developed antifriction nanostructured glass-ceramic self-lubricating coatings containing magnesium carbide and structural components that promote surface graphitization do not contain expensive and scarce components, meet environmental safety requirements, and have high performance characteristics. A significant effect of aluminoborosilicate in the form of a glass phase on the tribological properties of coatings is noted. An increase in adhesive strength is achieved by forming a surface layer of glassy sodium silicate. Using X-ray phase analysis, it was found that the intercalating elements in the subsurface zone-graphite system at the initial stage of the process were Mg^{2+} , Al^{3+} , Cu^{2+} ions, which randomly penetrated into the interlayer space of the graphite matrix. 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 system of graphite. Their intercalation is accompanied by a sequence of repetitive stages, which are reversible with a change in tribological parameters and are characterized by a specific transformation of the structure and, above all, by an increase in the distance between layers due to the influence of various types of interlayer defects and the introduction of intercalants.

The presence of near-surface particles in the graphite layer does not affect the tribotechnical characteristics of the coatings. The developed glass-composite nanostructured self-lubricating coatings have high antifriction characteristics throughout the entire load-speed range.

Key words: nanostructured coatings, wear intensity, glass composite, glass phase, graphitization

Introduction

Preservation of operational characteristics limited by friction and wear, both of individual units and technical systems as a whole, can be ensured by modern surface engineering tools that implement the basic principle of minimum costs with maximum results. Structural engineering methods that use modification through the use of solid lubricants have taken a leading position in recent years in providing anti-friction contact interfaces. Coatings containing solid lubricants are among the innovative and most promising antifriction materials, the high quality of which is especially noticeable in conditions where traditional liquid lubricants are ineffective [1, 2]. They are used in various fields of technology from lubrication of precision aircraft mechanisms to preventing jamming of threaded joints [3,4].

The development of antifriction nanostructured glass-composite self-lubricating coatings meets the modern priorities of tribotechnical materials science aimed at increasing the wear resistance of friction-loaded movable interfaces and, on their basis, the development of scientific and applied solutions in the interests of improving the efficiency of using high-quality production technologies [5,6].



Objective

Ensuring high quality antifriction properties of nanostructured glass-composite self-lubricating coatings with increased adhesive strength due to the presence of aluminoborosilicate and structurally free magnesium carbide in the composition of the glass phase, as well as the selection of structural components that promote graphitization.

Materials and methods of research

As is known from the comparative characteristics of gas-thermal coatings, which are similar in their structural-phase composition, detonation-gas coatings have maximum operational properties [7]. On this basis, for the deposition of the coatings under study, the detonation method was used using nanostructured powders obtained by the mechanochemical method, the composition of SiC-Ni-Cu-Al-Si-C with a uniform distribution of the aluminoborosilicate glass phase ($\text{SiO}_2\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3$). According to the developed technology, structurally free magnesium nanocarbide (MgC_2) was added to the resulting nanoglass composition, after which it was mixed, ensuring its uniform distribution in the powder mixture ready for spraying. All powder materials used in the work are obtained from the mineral resource base of the country.

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

The study of contact interfaces, in which activation processes occur during friction, which determine the intensity of surface reactions and tribophysical phenomena, was carried out using modern methods of physical analysis, involving metallography (an optical microscope of the type Neofot-32 with an attachment), an X-ray electronic microanalyzer of the Camscan 4 DW type with a program for the distribution of chemical elements. The 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 monochromatic $\text{CuK}\alpha$ radiation.

Increasing the adhesive strength, as a criterion for the performance of glass composite coatings, was carried out by preliminary deposition on the working surface of a sublayer of glassy sodium silicate $\text{Na}_2\text{O}(\text{SiO}_2)_2$. The exclusion of unproductive losses and adherence to the measurement technology using the conical pin method determined the correctness of the obtained results of the adhesion strength, which amounted to 145-150 MPa [8].

Research results

The contact interaction of surfaces is a complex sequence of cooperative influence of both external factors and internal transformations, the qualitative agreement of which reflects the commonality of quantitative patterns and determines their ordered causal relationship. According to the results of interactions of coatings under friction loading, Fig. 1 shows experimental values representing the averaged functional dependences of the wear intensity and friction coefficients, which change with time and stabilize after running in, in the field of sliding velocities at a constant load of 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 rates and the corresponding friction coefficients correspond to nanostructured glass-composite coatings (curves 1 and 1'). The structure of nanoglass composites, which determines their properties, practically consists of a finely dispersed mixture representing both solid solutions and, mainly, intermetallic compounds with a significant presence of a glass phase. The invariance of the chemical composition and the constancy of the parameters of technological deposition determine the stability of the coating structure, the relative density of which was up to 99%. The cross section of the nanocomposite coating is shown in Fig.2. Metallographic analysis has established that the deposited layer has a quasi-ordered lamella-like appearance, which closely adheres to the base material, completely copying the surface topography, while accumulations of component oxides, as well as slag contamination, are practically absent, and defects in the form of pores and cracks are not detected.

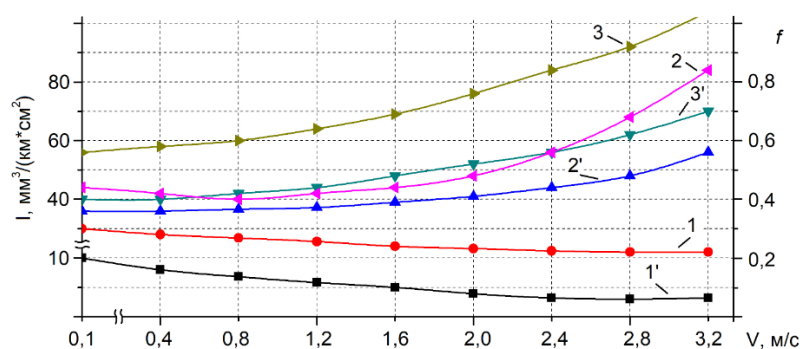


Fig.1. Dependence of wear intensity (1,2,3) and friction coefficient (1',2',3') on sliding speed of coatings SiC-Ni-Cu-Al-Si-C+glass phase+MgC2 (1,1'), WC-Co (2,2') and Ni-Cr-Al-B (3,3') on sliding speed ($P=10.0$ MPa).

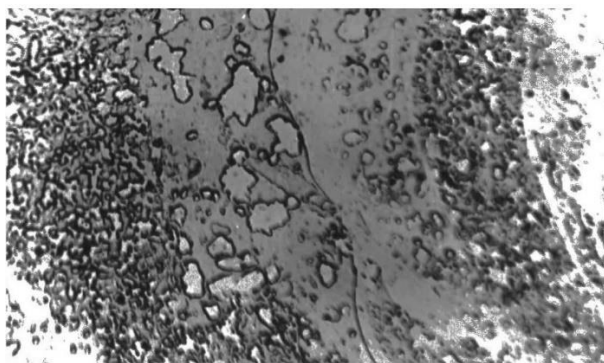


Fig.2. Coating structure (x5000)

The synthesis and study of solid solutions based on refractory compounds, in particular silicon carbide, are being carried out quite intensively, but the capabilities of the latter and its complex of tribological properties are far from the expected results. The developed glass composite is an antifriction material with an ultrafine structure. It is generally accepted that elastoplastic 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 a derivative of it. It can be said that the evolution of the structure during contact interactions has pronounced scale levels, and the processes occurring at different scale levels are interdependent. The layer-by-layer picture of plastic deformation obtained by the diffraction method reveals the main regularities of the formation of a scale structure and makes it possible to establish uniform transitions from a dispersed polycrystalline fragmented structure on the surface through intermediate textured layers to the original crystalline, inherent in deep material. As can be seen from Fig. 3, in the coating under study, as it approaches the friction surface and the contact pressure increases, and the intensity of deformation, the structure is gradually replaced by an ultrafine one. In this case, high contact compressive and shear stresses create conditions for the implementation of significant plastic deformations in the near-surface layer of the coating material, which cause the formation of ultrafine structures.

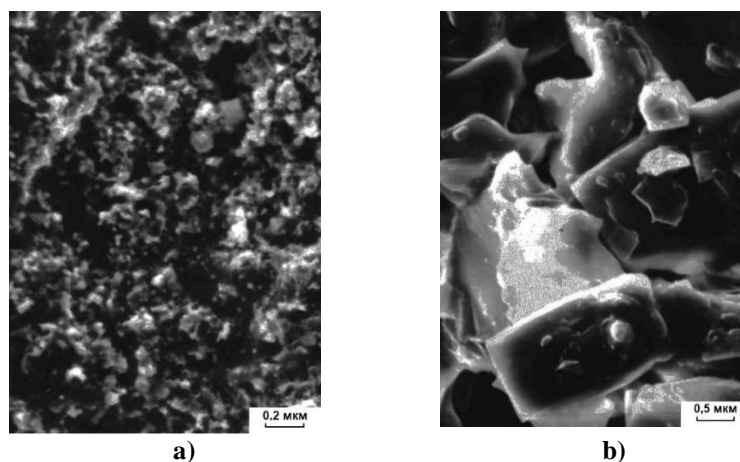


Fig.3. Changes in the structure of the nanoglass-composite coating with increasing distance from the friction surface in a layer ~ 6 μm thick: a) near-surface zone; b) undeformed structure.

This gives grounds to single out in a structure subjected to tribotechnical loads a near-surface zone, in which deformation processes that develop inhomogeneously in microvolumes form a specific layer at the near-surface level, in which structural-thermal activation causes a complex of physico-chemical interactions that determine the concomitant and leading type of wear. The surface zone is a structurally heterogeneous finely dispersed composition.

As evidenced by the results of X-ray microanalysis (MRSA) performed on the "Camebax SX", the basis 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 predominate, 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. However, the high thermomechanical properties of SiC carbide are discredited by significant brittleness. We noted that the substitutional solid solution that forms Al and SiC causes a slight distortion of the crystal lattice of the carbide, since the differences in the masses of Al atoms and Si are extremely small, as a result of which the microhardness does not change, while plasticity increases. A similar effect on the composition of SiC, forming substitutional solid solutions by replacing Si atoms, is exerted by Cu and Ni. The formation of phases in the coating, as tests have shown, is determined not only by the ratio of components, temperature, dispersion, but also depends on their defectiveness and external conditions. Undoubtedly, as an axiom, tribochemical interaction takes place when the molecules receive the necessary activation energy. Endothermic reactions generally do not proceed without activation. The interaction of SiC with Mg, which is formed during the thermal decomposition of structurally free magnesium carbide under running-in conditions and depends on the process temperature, is accompanied by the formation of magnesium silicide and acetylenide magnesium, the latter, under the influence of thermomechanical action, promotes 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, under thermodynamic action, the presence of a catalyst in the form of Al promotes the decomposition of magnesium carbide. The basis of physical phenomena that initiate the mechanism of decomposition of carbide graphite are structural transformations in the solid phase, caused by thermal effects. The factors that determine the qualitative level of thermomechanical carbide graphitization include both the degree of dispersion of structural components, specific pressure, operating temperature, and temperature in the contact zone, the presence of elements that initiate decomposition processes, as well as the influence of the environment (in vacuum, the probability of the amount of graphite increases), in addition, internal factors associated with the composition of the material, its structure, the presence of defects, etc. The contact zone constituting the near-surface layer (initial scale level) separating the coating material from the antifriction film consisting of polydisperse graphite particles is a deformed zone, which, according to the results of X-ray microanalysis performed on MAR-3 (probe diameter 1 μm), represents finely dispersed heterogeneous structural -phase compounds of the components that make up the coating. Among which, the presence of Ni, as a structural component, is due to its distinctive properties, so, on actual contact spots, when a temperature of about 450-500 °C is reached, depending on the dispersion and external influences in a local high-temperature field, Ni interacts with SiC, forming nickel silicides with a predominance of metal-enriched Ni_2Si . As a result, carbon is reduced, which is transformed in the form of a solid phase of elementary polydisperse graphite colonies combined into surface structures.

However, magnesium carbide remains the main component of the antifriction surface layer, consisting of a carbonaceous product - graphite. The value of the specific wear work characteristic of the initial running-in moment, as shown by calculations, is up to 10 kJ/mm^3 , which is both a necessary and sufficient condition for initiating the thermal decomposition of MgC_2 , which causes 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, a high-quality, thickened anti-friction layer was obtained, which determines the operational properties of coatings.

In 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, being a high-temperature phase, has a significant hardness, as shown by measurements, most likely about 3.8 GPa. The presence of an ordered solid solution based on nickel monoaluminide with a reduced Al content (~20–25 wt %) was also found, which leads to increased ductility. According to the results of elemental and X-ray phase analyzes, the presence of a solid solution of Ni in Cu was noted, but their compounds were not found. Solid solutions of Ni in Si and Si in Ni, as well as their intermetallic compounds Ni_2Si , Ni_3Si_2 , and NiSi_2 , have been revealed. In addition, the presence of small amounts of colonies of solid solutions of Si in Cu was established, and the formation of their chemical compounds such as copper silicates is also likely, since the microhardness increases significantly. However, it was difficult to identify them accurately.

Powders of aluminoborosilicate glasses, the dispersion of which was 25–30 μm , in the process of mechanochemical treatment and thermomechanical action, being products of inorganic synthesis, caused, along with the preservation of the original components, the formation of new stable compounds, as was found, from solid solutions of Al_2O_3 and SiO_2 obtained rhombic syngony, close to the structure of sillimanite, most likely it is the lowest mullite obtained by reaction as a result of the interaction of the oxidation products of the original components. From the point of view of glass-ceramic technologies, the greatest interest, in our opinion, is the

presence of components that form refractory metal oxides, primarily Al and Si oxides. The presence of B_2O_3 was also established, which, as a result of partial oxidation, formed a solid solution of $Al_2O_3 - B_2O_3$.

From the point of view of condensed matter physics, the addition of a glassy component affects the quality of the coating material through the structural state and, as practice shows, interest in these technical products is steadily increasing. When studying glass composites, their optimal composition was established experimentally, in which the rational use of glass structures contributes to an increase in heat resistance and chemical resistance, in addition, the manifestation of high cohesive strength, an increase in the density of nanocomponents, crack resistance with significant corrosion resistance and ensures high adhesion (more than 127 MPa) with materials 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 antifriction layer consisting of polydisperse graphite particles is the thinnest film several micrometers thick. Studies have shown that the pressure in it is uneven, and the areas of tensile and compressive stresses, which are inevitable under the conditions of deformation of heterogeneous phases, are close in structure to a conglomerate of finely dispersed (quasi-amorphous) structures, having dimensions in the range of 5-15 nm, and representing 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 physicochemical properties, including reactivity, and affect the intensity of chemical reactions in the solid phase.

At the same time, the thermal conductivity of a finely dispersed conglomerate having an increased porosity and forming a near-surface zone is lower than that of a solid material, therefore, the heating temperature of the 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 introduction of kinetically active components of the dispersed zone through the weakening of the bond between the polyarene planes into the interlayer space of graphite and thus the formation of intercalated graphite.

Using X-ray phase analysis, it was established that the intercalating elements in the subsurface zone-graphite system at the initial stage of the process were Mg^{2+} , Al^{3+} , Cu^{2+} ions, which randomly intruded into the interlayer space of the graphite matrix. 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 system of graphite. Their intercalation is accompanied by a sequence of repetitive stages, which are reversible with a change in tribological parameters and are characterized by a specific transformation of the structure and, above all, by an increase in the distance between layers due to the influence of various types of interlayer defects and the introduction of intercalants. Note that today there is no general intercalation model that explains the electrochemical mechanism of the synthesis of layered systems. From the energy point of view, the intercalation process, which represents reversible topo-taxial chemical reactions, can be considered as an adequate way of self-organization of surface layers in the process of structural adaptability of the friction system.

We have found that quantitative changes during the intercalation of the graphite layer, which causes a high level of antifriction, does not affect the expected degree on the qualitative values of tribological parameters during testing for related characteristics associated with the electromagnetic properties of intercalated graphite, judging by the analysis of literature data, it has a significant effect.

The developed antifriction nanostructured glass-ceramic self-lubricating coatings containing magnesium carbide and structural components that promote surface graphitization do not contain expensive and scarce components, meet environmental safety requirements, and have high performance characteristics. The most effective use of nanostructured glass-ceramic self-lubricating coatings is to improve the operational reliability of friction units during their hardening and restoration of moving parts of control mechanisms, sliding bearings, lever parts, high-speed and thermally loaded interfaces, in which the use of traditional lubricants is not desirable.

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

It should be noted that the developed nanostructured glass-composite powder can be used for strengthening and restoring worn parts by any technological methods used in powder materials.

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

Conclusions

1. By means of theoretical prerequisites and experimental studies, the optimal structural-phase composition of nanostructured glass-composite coatings of the SiC-Ni-Cu-Al-Si-C system containing a glass phase of the $SiO_2-Al_2O_3-B_2O_3$ type and structurally free magnesium carbide was realized. To improve the adhesion strength, a sublayer of glassy sodium silicate was applied to the substrate. The role of the glass phase in the formation of glass composites is disclosed, which contributes to an increase in the cohesive component,

continuity and strength of the nanostructure, and an increase in the anticorrosion properties and chemical resistance of coatings.

2. It is noted that the assessment of the quality of the coatings under study is inextricably linked with the problem of the reproducibility of their technological process. By controlling the deposition of nanostructured glass-composite powders, it turned out to be possible to provide not only the desired chemical composition, but also to obtain a given nanostructure as a result, optimizing a set of properties that contribute to the stable manifestation of minimization of tribotechnical characteristics.

3. The physical mechanism and the main factors that determine the level of thermomechanical graphitization are considered, the nature and chemical interactions of the structural components of the friction system are noted, in ensuring high anti-friction properties of glass-composite coatings.

4. The synthesis of layered graphite compounds as a result of topo-taxial reactions has been studied. The nature of intercalants in a graphite matrix is established and it is noted that reversible topo-taxial chemical reactions in the solid phase represent one of the mechanisms of self-organization of the surface layers of a friction system under conditions of structural adaptability.

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

6. Structural engineering, driven by the analysis and innovative provision of the functional properties of the developed materials, opens up promising opportunities associated with the modernization of friction surfaces.

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Харченко С.Д., Харченко О.В. Склокомпозиційні наноструктурні покриття

Наведено результати дослідження склокомпозиційних самозмащувальних наноструктурних покриттів. Розроблений склокомпозит є антифрикційним матеріалом з ультрадрібнодисперсною структурою. Структурні складові даних покриттів суттєво впливають на процес графітизації та забезпечують одержання антифрикційного поверхневого шару α -графіту. Формування даного шару дозволяє істотно мінімізувати контактні параметри у зоні тертя.

Розроблені антифрикційні самозмащувальні наноструктурні склокерамічні покриття, містять карбід магнію та структурні складові, що сприяють поверхневій графітизації, не мають у складі дорогих і дефіцитних компонентів, відповідають вимогам екологічної безпеки, мають високі робочі характеристики. Відзначено значний вплив алюмоборосилікату у вигляді склофази на триботехнічні властивості покриттів. Підвищення адгезійної міцності досягається шляхом утворення поверхневого шару зі склоподібного силікату натрію. Методом рентенофазового аналізу встановлено, що інтеркалюючими елементами в системі підповерхнева зона-графіт, на початковому етапі процесу з'явилися іони Mg^{2+} , Al^{3+} , Cu^{2+} , що хаотично впроваджувалися в міжшаровий простір графітової матриці. При швидкостях ковзання більше 3,0 м/с виявлено у шаруватій системі графіту інтрекаляти бінарних молекулярних сполук цих елементів з киснем. Їх інтрекаляція супроводжується послідовністю повторюваних стадій, які при зміні триботехнічних параметрів є оборотними і характеризуються специфічним перетворенням структури і, насамперед, збільшенням відстані між шарами за рахунок впливу різних типів міжшарових дефектів та впровадження інтрекалантів.

Наявність у графітовому шарі частинок поверхневого шару не впливає на триботехнічні характеристики покриттів. Розроблені склокомпозиційні самозмащувальні наноструктурні покриття, мають на всьому навантажувально-швидкісному діапазоні високі антифрикційні характеристики.

Ключові слова: наноструктурні покриття, інтенсивність зношування, склокомпозит, склофаза, графітизація