

# Antifriction Nanostructural Glass-Composite Self-Lubricating Coatings

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Received February 7, 2022; revised June 20, 2022; accepted June 21, 2022

**Abstract**—The results of a study of the friction and wear characteristics of the developed nanostructured glass-composite self-lubricating detonation coatings with the composition SiC–Ni–Cu–Al–Si–C additionally containing a SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub> aluminoborosilicate glass phase and structurally free MgC<sub>2</sub>, which forms α-graphite during thermal decomposition are presented. It is indicated that their synergistic effect promotes the creation of an antifriction surface layer that minimizes contact parameters. An increase in the adhesion strength of the coatings is achieved by preliminarily applying a sublayer of glass-like sodium silicate Na<sub>2</sub>O(SiO<sub>2</sub>)<sub>2</sub> onto the working surface. It is noted that the intercalation of the graphite layer by the particles of the subsurface zone does not affect the tribotechnical characteristics of the coatings. The developed coatings show high performance properties; here, the way of wear stabilization is the presence of a thin-film antifriction layer based on α-graphite, which shields unacceptable processes of molecular adhesion interaction.

**Keywords:** friction, wear, wear intensity, glass composite, nanostructure, contact parameters, graphite, self-lubricating, glass phase

**DOI:** 10.3103/S1068366622030023

## INTRODUCTION

The retention of performance characteristics limited by friction and wear of both separate units and technical systems as a whole can be provided by modern means of surface engineering, which implement the fundamental principle of minimum expenses with maximum results. The methods of structural engineering utilizing modification due to the application of solid lubricants have occupied a leading position in providing antifrictionality of contact interfaces over recent years. Coatings containing solid lubricants are one of the most innovative and promising antifriction materials, the high quality of which is especially noticeable under the conditions, where traditional liquid lubricants are not very effective [1, 2]. They are used in various technical fields from lubrication of precision aviation mechanisms to prevention of jamming of threaded connections [3, 4].

The development of antifriction nanostructural glass-composite self-lubricating coatings meets the current priorities of tribotechnical materials science aimed at increasing the resistance to wear of friction-loaded mobile interfaces and development of scientific and applied solutions for the benefit of improving the efficiency of application of high-quality production technologies [5, 6].

**Objective**—To provide a high quality of the antifrictionality of nanostructural glass-composite self-lubri-

cating coatings with an increased adhesion strength due to the presence of a glass phase of the type of aluminoborosilicate and structurally free magnesium carbide in the composition as well as selection of structural components promoting graphitization.

## METHODS AND MATERIALS

As is known from the comparative characteristics of gas-thermal coatings similar in their structural and phase composition, gas-detonation coatings possess the maximum performance properties [7]. Based on this, a detonation method with the use of nanostructural powders, obtained by the mechanochemical method with the composition SiC–Ni–Cu–Al–Si–C with the uniform distribution of the aluminoborosilicate glass phase (SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub>), was used for the spraying of the coatings under study. According to the developed technology, structurally free magnesium nanocarbide (MgC<sub>2</sub>) was added to the obtained nano-glass composition, after which it was stirred, providing its uniform distribution in the powder mixture ready for spraying. All the powder materials used in the study were procured from the available mineral resources of the country.

The antifriction properties of the coatings were assessed upon the friction of ring samples according to the end-type scheme in the mode of continuous slid-

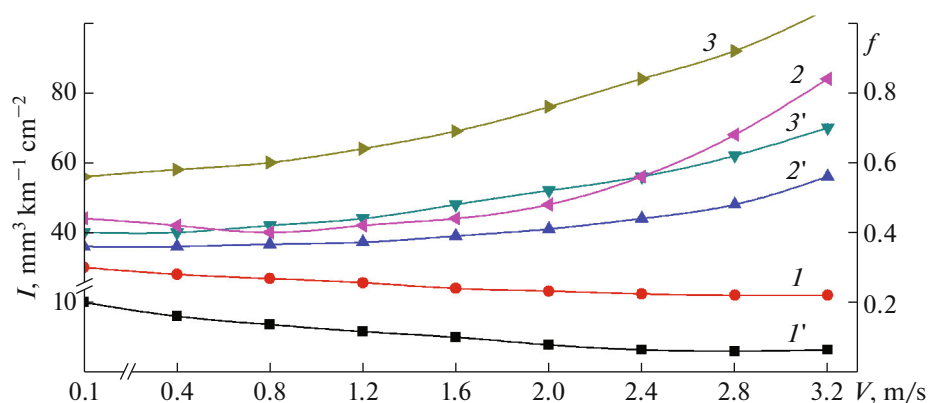


Fig. 1. Dependence of the ( $I$ ,  $2$ ,  $3$ ) wear intensity and ( $I'$ ,  $2'$ ,  $3'$ ) friction coefficient of the ( $I$ ,  $I'$ ) SiC–Ni–Cu–Al–Si–C + glass phase + MgC<sub>2</sub>, ( $2$ ,  $2'$ ) WC–Co, and ( $3$ ,  $3'$ ) Ni–Cr–Al–B coatings on the sliding speed ( $P = 10.0$  MPa).

ing at a load of 10.0 MPa. The effect of the environment, speed, and load implemented upon testing was chosen taking into account the maximum approximation of the processes of physicochemical friction mechanics to the real-life conditions of contact interaction; in addition, the program of the study of the nanostructural glass-composite coatings anticipated a comparative analysis of their antifriction characteristics with similar values obtained upon the testing of tungsten-containing coatings of the VK15 type and coatings sprayed with a doped nichrome powder.

The study of the contact interfaces, in which the processes of activation upon friction proceed which determine the intensity of surface reactions and tribo-physical phenomena, were executed by modern methods of physical analysis anticipating metallography (a Neophot-32 optical microscope with an accessory; a Camscan 4DW electron probe X-ray microanalyzer with the program of distribution of chemical elements). The phase composition of the surface layers was determined on a DRON-3 general-purpose X-ray diffractometer with a monochromatized CuK<sub>α</sub> radiation.

The increase in the adhesion strength as a criterion of the working capacity of glass-composite coatings was executed by the preliminarily application of a sub-layer of glass-like sodium silicate Na<sub>2</sub>O(SiO<sub>2</sub>)<sub>2</sub> onto the working surface. The exclusion of unproductive losses and observance of the measurement technology by the taper pin method [8] determined the correctness of the results for adhesion strength, which were 145–150 MPa.

## RESULTS AND DISCUSSION

Contact interaction of surfaces is a complex sequence of the cooperative action of both external factors and internal transformations proper coordination of which reflects the commonness of the quantitative regularities and determines their ordered causal relationship. Based on the results of the interactions of

the coatings under friction loading Fig. 1 presents the experimental values that are averaged functional dependences of the wear intensity and friction coefficients, which change in time and stabilize after running-in in the field of sliding speeds at a constant load of 10.0 MPa. As is seen from the graph, the minimum values of wear intensities and corresponding to them friction coefficients correspond to nanostructural glass-composite coatings (curves  $I$ ,  $I'$ ) throughout the entire testing range at a monotonically increasing sliding speed. The structure of the nanoglass compositions that determines their properties actually consists of a finely dispersed mixture presenting both solid solutions and, mainly, intermetallic compounds with a significant presence of a glass phase. The invariability of the chemical composition and constancy of the parameters of technological spraying determine the stability of the structure of the coatings the relative density of which was up to 99%. The cross section of the nanocomposite coating is presented in Fig. 2. It has been found by metallographic analysis that the layer being sprayed has a quasi-ordered lamellar appearance, which stands against the base material, fully copying the relief of the surface; here, there were almost no accumulations of the oxides of the components as well as slag impurities, and no defects in the form of pores and cracks were detected.

The synthesis and study of the solid solutions based on high-melting compound, in particular, silicon carbide, are being quite intensively carried out; however, the capabilities of the latter and its set of tribotechnical properties are far from the expected results.

The developed glass composite is an antifriction material with an ultrafine structure. It is generally considered that elastoplastic deformation is the key factor determining the development of the process of external friction and, moreover, in our opinion, the formation of a gradient structure is a derivative of it. It can be said that the evolution of the structure upon contact interactions has pronounced scale levels, and

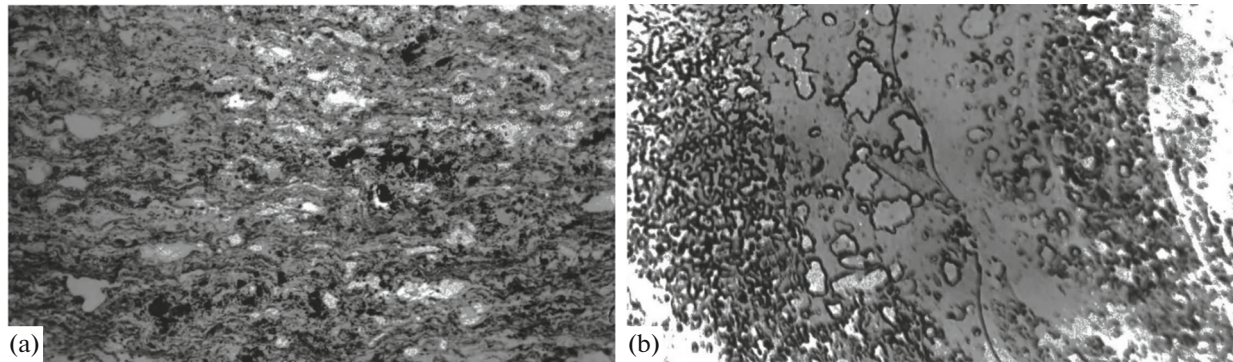


Fig. 2. Structure of the coating: (a)  $\times 120$  and (b)  $\times 5000$ .

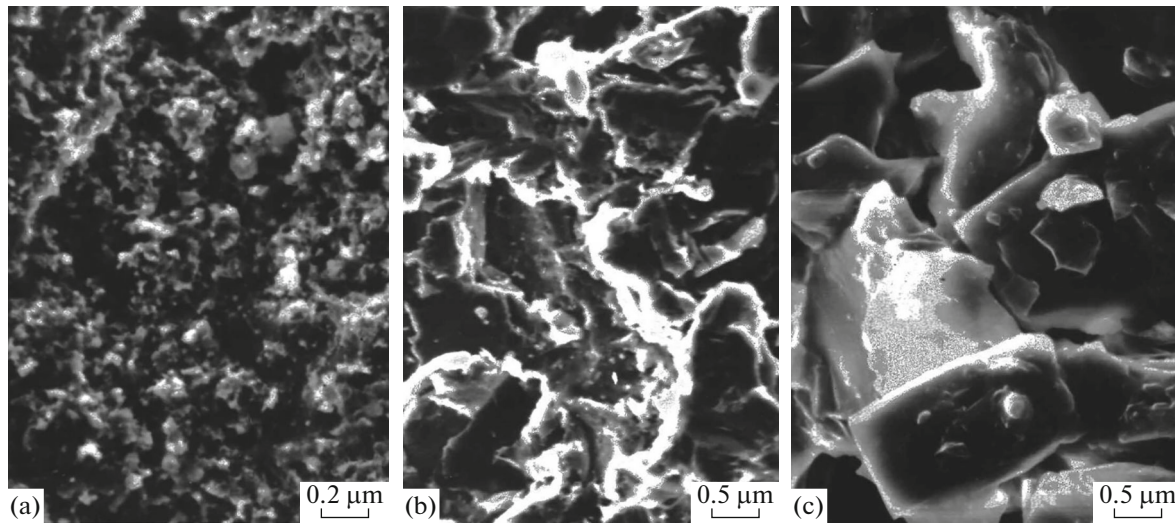


Fig. 3. Change in the structure of the nanoglass-composite coating with increasing distance from the friction surface in a layer with a thickness of  $\sim 6 \mu\text{m}$ : the (a) near-surface zone, (b) intermediate layer, and (c) undeformed structure.

the processes occurring at different scale levels are interdependent. The layer-by-layer pattern of plastic deformation obtained by diffraction uncovers the key regularities of formation of the scale structure and makes it possible to determine uniform transitions from a dispersed polycrystalline fragmented structure on the surface via intermediate textured layers to the initial crystal structure intrinsic to the subsurface material. As is seen from Fig. 3, in the coating under study, as the friction surface is approached and contact pressure and intensity of deformation increase, the structure is gradually replaced by an ultrafine structure. Here, the high contact compression and shear stresses generate conditions for the implementation of significant plastic deformations in the near-surface layer of the material of the coating, which determine the formation of ultrafine structures.

This gives us the ground to distinguish a near-surface zone in the structure subjected to tribotechnical loads, in which the deformation processes inhomoge-

neously developing in the microvolumes form a specific layer at the near-surface level, in which structural thermal activation is responsible for the set of physico-chemical interactions determining the accompanying and leading types of wear. The near-surface zone is a structurally nonuniform finely dispersed composition.

As is evidenced by the results of electron probe X-ray microanalysis (EPMA) executed on a Camebax SX unit, the main component of the nanoglass composition is nonstoichiometric silicon carbide, along the grain boundaries of which silicate compounds are located, among which inclusions corresponding to the composition of silica predominate; also, distributed along the boundaries oxides  $\text{Al}_2\text{O}_3$  and intermetallic inclusions in the form of spherical nanograins act as the dispersion-strengthened components in the carbide structure. However, the high thermomechanical properties of carbide SiC are compromised by significant fragility. We have noted that the solid substitutional solution formed by Al and SiC induces insignif-



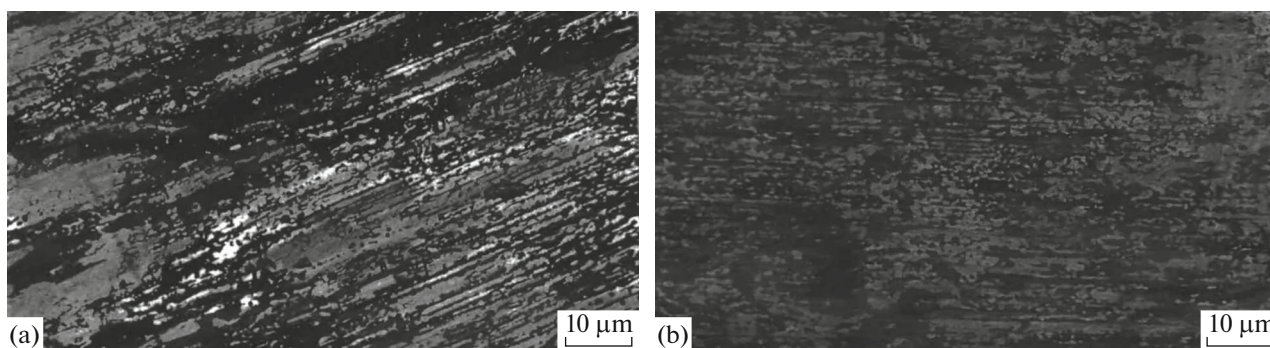


Fig. 4. Topography of the friction surface upon the formation of a graphite film:  $V =$  (a) 0.8 and (b) 1.5 m/s.

ificant distortion of the crystal lattice of carbide because the differences in the weights of Al and Si atoms are extremely small, as a result of which microhardness remains unchanged, and plasticity increases. Cu and Ni have a similar effect on the composition of SiC, forming solid substitutional solution by means of replacement of Si atoms. As it was shown by testing, the formation of phases in the coating is determined not only by the ratio of the components, temperature, and dispersity but also depends on their defectiveness and external conditions. Undoubtedly, as an axiom, a tribochemical interaction takes place when the molecules receive the required activation energy. Endothermic reactions do not at all proceed without activation. The interaction of SiC with Mg that is formed upon the thermal decomposition of structurally free magnesium carbide under the conditions of running-in and depends on the process temperature is accompanied by the formation of magnesium silicide and magnesium acetylenide, the latter promotes the formation of graphite via intermediate dimagnesium tricarbonide under the action of a thermomechanical action ( $2\text{SiC} + 5\text{Mg} \rightarrow 2\text{Mg}_2\text{Si} + \text{MgC}_2$ ,  $\text{MgC}_2 \rightarrow \text{Mg}_2\text{C}_3 \rightarrow \text{Mg} + \text{C}$ ). It should be noted that the presence of a catalyst in the form of Al in the structure promotes the decomposition of magnesium carbide upon a thermodynamic action. The basis of the physical phenomena initiating the mechanism of decomposition of carbide graphite is structural transformations in the solid phase determined by the thermal actions. The factors determining the qualitative level of thermomechanical carbide graphitization include both the degree of dispersity of the structural components, specific pressure, and operating temperature and the temperature in the contact zone, presence of elements initiating the decomposition processes as well as the effect of the environment (the probability of the amount of graphite increases in vacuum) and, in addition, internal factors associated with the composition of the material, its structure, presence of defects, etc.

Figure 4 presents the topographies of the friction surface obtained at sliding speeds of 0.8 and 0.15 m/s. As is seen, the antifriction layer of graphite almost

screens the working surface, providing an increase in the actual contact area and promoting a decrease in the specific load as a result of an increase in the bearing length due to the filling and levelling of the micro-roughnesses and fixation of graphite microparticles in the microvalleys. The contact zone constituting the near-surface layer (the initial scale level) that separates the material of the coating from the antifriction film consisting of polydispersed graphite particles is a deformed zone that represents, according to the results of electron probe X-ray microanalysis executed on MAP-3 (the probe diameter of  $1\ \mu\text{m}$ ), finely dispersed heterogeneous structural and phase compounds of the components present in the composition of the coating. Among them, the presence of Ni as a structural component is determined by its distinguishing properties, thus, Ni interacts with SiC on the actual contact patches upon reaching about  $450\text{--}500^\circ\text{C}$  depending on the dispersity and external actions under the conditions of a local high-temperature field to form nickel silicides with the predominance of metal-enriched  $\text{Ni}_2\text{Si}$ . As a result, reduction of carbon takes place, which is transformed in the form of a solid phase of elementary polydispersed colonies of graphite united into surface structures.

However, magnesium carbide remains to be the main component of the antifriction surface layer consisting of a carbon product, graphite. As it has been shown by calculations, the value of the specific wear work characteristic for the initial moment of running-in is up to  $10\ \text{kJ}/\text{mm}^3$ , which is both a necessary and sufficiency condition of initiation of thermal decomposition of  $\text{MgC}_2$ , which determines the formation of carbon in the form of a solid phase.

Using the natural ability of chemical elements to graphitization via the formation of carbide graphite, a high-quality, thickened antifriction layer determining the performance properties of the coatings was obtained.

The presence of intermetallic compounds based on Al and Ni of the type of  $\text{NiAl}$  and  $\text{Ni}_2\text{Al}_3$  has been noted upon the structural and phase study of the glass-

composite coatings; here, monoaluminide, being a high-temperature phase, possesses significant hardness, as it was shown by the measurements, most likely about 3.8 GPa. Also, the presence of an ordered solid solution based on nickel monoaluminide with a decreased concentration of Al (~20–25 wt %) has been found, which determines increased plasticity. The presence of a solid solution of Ni in Cu has been noted based on the results of elemental and X-ray diffraction analyses; however, their compounds have not been detected. Solid solutions of Ni in Si and Si in Ni as well as their intermetallics Ni<sub>2</sub>Si, Ni<sub>3</sub>Si<sub>2</sub>, and NiSi<sub>2</sub> have been found. In addition, the presence of small amounts of the colonies of solid solutions of Si in Cu has been found, the formation of their chemical compounds of the type of copper silicates is also probable because microhardness substantially increases. However, it was significantly challenging to accurately identify them.

During the process of mechanochemical processing and thermomechanical action, the powders of aluminoborosilicate glass with the dispersity of 25–30 μm, being the products of inorganic synthesis, have also provided the formation of new stable compounds in addition to the retention of the initial components; as it was established, a rhombic system similar to the structure of sillimanite has been obtained from the solid solutions of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, most likely, this is the simplest mullite obtained by way of reaction as a result of interaction of the oxidation products of the initial components. In our opinion, from the perspective of glass–ceramic technologies, the presence of components forming high-melting metal oxides and, first of all, Al and Si oxides, is of the greatest interest. The presence of B<sub>2</sub>O<sub>3</sub> has also been determined, which constituted an Al<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub> solid solution as a result of partial oxidation.

From the perspective of condensed matter physics, the addition of a glass-like component affects the quality of the material of the coatings through the structural state and, as is shown by practice, the interest in these technical products steadily increases. Upon studying glass compositions, their optimum composition has been experimentally found, in which the rational use of glass structures promotes an increase in the high-temperature strength and chemical resistances and, in addition, appearance of high cohesion strength and increase in the density of the nanocomponents and crack resistance with significant corrosion resistance, and provides obtaining high adhesion (above 127 MPa) with materials of different chemical natures; in addition, the formation of a silicate barrier layer prevents interdiffusion of the structure-forming particles of the coating and the substrate.

The surface zone immediately adjacent to the friction surface and separating the material of the coating from the antifriction layer consisting of polydispersed graphite particles is a super-thin film with a thickness

of several micrometers. Studies have shown that the pressure in it is nonuniform, and the regions of tension and compression 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 with sizes in a range of 5–15 nm and are mechanical mixtures, oxygen-free, and oxide compounds of the structure-forming components. The effect 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.

Here, the thermal conductivity of the finely dispersed conglomerate that has an increased porosity and forms the near-surface zone is lower when compared to a solid material, because of which the heat-up temperature of the finely dispersed fragments of the zone is higher than the temperature of the regions of the surface.

The temperature factor stimulates physicochemical processes, in particular, reaction diffusion of the structure-forming particles at the atomic and molecular level, which promotes the intercalation of the kinetically active components of the dispersed zone through the weakening of the bond between the polyaniline planes into the interlayer space of graphite and, thus, formation of intercalated graphite.

It has been found by X-ray diffraction analysis that, at the initial stage of the process, the intercalating elements in the near-surface zone–graphite system are Mg<sup>2+</sup>, Al<sup>3+</sup>, and Cu<sup>2+</sup> ions that are chaotically intercalated into the interlayer space of the graphite matrix. Intercalants of binary molecular compounds of these elements with oxygen have been detected in the layered system of graphite at sliding speeds above 3.0 m/s. Their intercalation is accompanied by a sequence of repeating stages that are reversible upon changing the tribotechnical parameters 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 effect of various types of interlayer defects and intercalation of intercalants. Note that, to date, there is no general intercalation model explaining the electrochemical mechanism of the synthesis of layered systems. From the energy perspective, the intercalation process that is reversible topotaxial chemical reactions can be considered as an adequate method for the self-organization of the surface layers in the process of structural adaptability of a friction system.

It has been found that the quantitative changes upon the intercalation of the graphite layer determining a high level of antifrictionality do not affect the qualitative values of the tribotechnical parameters in the process of testing to the expected extent, but judging by the analysis of the published data, substantially affect the accompanying characteristics associated

with the electromagnetic properties of intercalated graphite.

The developed antifriction nanostructural glass–ceramic self-lubricating coatings containing magnesium carbide and structural components promoting surface graphitization do not have expensive and sought-after components in their composition, meet environmental safety requirements, and have high performance characteristics. It is most effective to apply nanostructural glass–ceramic self-lubricating coatings for increasing the performance reliability of friction units upon their strengthening and recovery of the mobile parts of control mechanisms, sliding bearings, lever parts, and high-speed and thermally loaded interfaces in which the application of traditional lubricants is undesirable.

### CONCLUSIONS

(1) The optimum structural and phase composition of nanostructural glass–composite coatings of the SiC–Ni–Cu–Al–Si–C system containing a glass phase of the SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub> type and structurally free magnesium carbide has been implemented by means of theoretical prerequisites and experimental studies. To improve the adhesion strength, a sublayer of glass-like sodium silicate was applied onto a substrate. The role of the glass phase upon the formation of glass compositions has been revealed, which promotes an increase in the cohesion component, continuity, and strength of the nanostructure and an increase in the anticorrosion and chemical resistance of the coatings.

(2) It has been noted that the assessment of the quality of the coatings under study is inseparably associated with the problem of reproducibility of their technology process. Governing the spraying of nanostructural glass–composite powders, it has turned out to be possible to provide not only the required chemical composition but also to obtain as a result the pre-defined nanostructure optimizing the set of properties promoting robust manifestation of the minimization of the tribotechnical parameters under study.

(3) The physical mechanism and key factors determining the level of thermomechanical graphitization have been considered and the nature and chemical interactions of the structural components of the friction system in the provision of high antifrictionality of glass–composite coatings have been noted.

(4) The synthesis of layered graphite compounds as a result of topotaxial reactions has been studied. The nature of the intercalants in the graphite matrix has been determined, and it has been noted that reversible topotaxial 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 adaptability.

(5) The fundamental ideas about the formation and structure of the antifriction surface structures based on polydispersed carbide graphite have been supplemented, which has made it possible to expand the range of achievements of modern tribological engineering.

(6) Structural engineering determined by the analysis and innovation provision of the functional properties of the materials under development opens up promising possibilities associated with the modernization of friction surfaces.

### CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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Translated by E. Boltukhina