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Tribotechnical properties of coatings based on magnesium compounds

V.V. Shchepetov[1] 0000-0003-1644-6042, **N.M. Fialko[1]** 0000-0003-0116-7673, **S.S. Bys[2*]** 0000-0002-7518-3310

[1]*Institute of Technical Thermophysics of the National Academy of Sciences of Ukraine*
[2]*Khmelnytskyi National University, Ukraine*
**E- mail : serhiibys@gmail.com*

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Abstract

The article summarizes the results of studies of tribotechnical properties of detonation coatings based on magnesium orthosilicate under conditions of constant load in the sliding velocity field. The structural and phase composition of the coatings was studied using modern physical analysis methods. The developed and studied coatings based on magnesium orthosilicate have high and stable antifriction properties in the entire load-velocity range of tests. It is emphasized that the result of antifriction under friction conditions is the additive effect of both the carbide graphite film and dispersed surface oxide structures, the synthesis of which provides modification of the surface of the structure, which is capable of self-lubrication and at the same time limits the development of unacceptable destruction processes.

Key words: detonation coating, wear intensity, structural and phase composition, graphitization.

Introduction

Magnesium compounds, due to their exceptional properties, are widely used in innovative technologies. Without them, the functioning of technical structures from alloys and chemical current sources to fireproofing and military equipment systems is impossible [1-2]. Their use in tribotechnical materials science is associated with modern achievements in tribology. Thus, as structural components of coatings, they are used to protect machines and mechanisms from the manifestation of destructive wear processes during friction [3-4]. Widely used methods of reducing friction forces and combating wear are the use of a lubricating medium in the friction contact zone. In modern tribotechnical systems, contact interaction in the absence of lubricants is practically not carried out. The effective functioning of friction units of machines and mechanisms is ensured mainly by the use of various lubricants, which significantly reduce friction parameters, and the use of which is determined in each specific case by their lubricating properties. Thus, polymer lubricants are an effective material from room temperature to 300ºC; laminar solid lubricants extend the range to 450ºC; graphite, being a layered solid material, is an exception, since it provides lubricating ability at temperatures exceeding 450ºC. Stable fluorides and metal oxides are used at temperatures from 500ºC to 1000ºC [5-6]. Despite the positive results in achieving the quality of antifriction materials through the use of solid lubricants, the applied problems of friction and wear of machines remain the most complex technical areas of knowledge that have to be solved during the operation of modern technology. A significant need arising from current production tasks and the internal logic of scientific development requires new solutions in the study of the general material science imperative, which determines the relationship between the chemical composition and structure formation with the technology of formation and functional properties of materials. At the same time, the use of coatings containing solid lubricants is becoming increasingly necessary to ensure the long-term operation of moving joints [7]. Summing up, it can be noted that the development of powder compositions for high-quality antifriction coatings is a priority area of modern tribotechnical materials science and a relevant task related to the extension of the operational life of machine parts in industrial production conditions.

The purpose of the work is the determination, within the framework of the phenomenological approach, of the patterns of friction and wear of composite coatings based on magnesium compounds with structurally free magnesium carbide, the study of the structural and phase composition and its influence on the formation and self-organization of surface structures that have self-lubricating ability.

Materials and research methods.

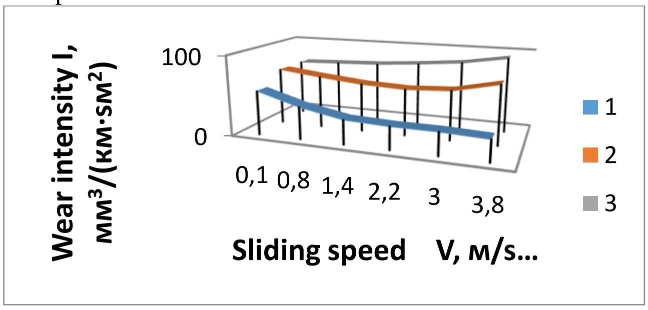
Deserved attention in the field of tribotechnical materials is attracted by compounds of complex oxides and, first of all, compounds with magnesium oxide due to their high thermo mechanical properties. As a basis for self-lubricating coatings, studied in the work, magnesium orthosilicate (forsterite) with the chemical formula $2MgO \cdot SiO_2$ was purposefully used, which exists in only one modification, that is, as a material, it does not have polymorphic transformations. Doped impurities from chromium, zirconium, nickel, titanium, aluminum, silicon and carbon powders were added to magnesium orthosilicate, as a basis. The initial composition of crystalline powders of complex chemical composition for subsequent spraying was obtained by the method of mechanochemical synthesis (MCS). The use of which made it possible to obtain a nanocomposite conglomerate of micron-sized base particles and nanosized doped phases. To the powder conglomerate obtained in this way, a magnesium compound was added in the appropriate proportion, namely structurally free carbide (MgC_2), and the resulting mechanical mixture was mixed until the structural components were completely and uniformly distributed. Magnesium orthosilicate-based coatings were formed by the detonation-gas method on samples of high-strength steel type 30HGSNA. Steel 65G (HRC 62-65) was used as a counter body. The physical and mechanical properties and patterns of friction and wear of orthosilicate-based coatings were studied using the end-face scheme in the continuous sliding mode at a constant load of 14.5 MPa. At the same time, the research program provides for a comparative analysis of the friction parameters of the developed coatings with the values of coatings based on tungsten carbide type WK15 and coatings of alloyed nichrome. The adhesion strength was determined by the pin method, which for coatings based on magnesium orthosilicate was over 93 MPa with a porosity of about 0.5%, along with this, after preliminary finishing grinding, their initial roughness was Ra 0.32-0.63.

Both the wear intensity and friction coefficient, as well as the condition of the working surfaces, were used as criteria for the performance of magnesium silicate-based coatings. When studying the patterns of friction and wear, when explaining the technology-structure and structure-properties relationships, a complex of modern physicochemical methods of structural-phase analysis was used, which are capable of determining the consideration of surface layers at the macro- and microscopic levels. In this case, the complex research methodology included metallography (optical microscope "Neophot-32" with a prefix); durometric analysis (hardness tester M-40 from LECO); scanning electron microscopy (scanning electron microscope JSM-840); X-ray structural phase analyzer (diffractometer DRON-UM1).

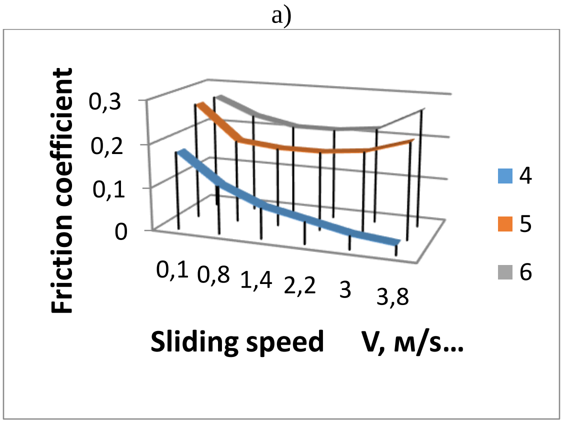
Research results and their discussion.

The main factors on which the patterns that determine the course of friction and wear processes depend are external influences. They determine the degree and gradients of elastic-plastic deformation, temperature, activation level, a number of accompanying phenomena, and ultimately determine the leading type of wear.

The test results of the studied coatings (fig. 1) are presented in the form of graphs of functional average values of wear intensities and friction coefficients obtained in a field of monotonically increasing sliding velocities at a constant load, which corresponds to 14.5 MPa.



a)



b)

Fig. 1. Dependences of wear intensities (a) and friction coefficients (b) on the sliding speed of coatings based on magnesium compounds (1, 4), WK15(2, 5) and alloyed nichrome (3, 6) at P=const=14.5 MPa.

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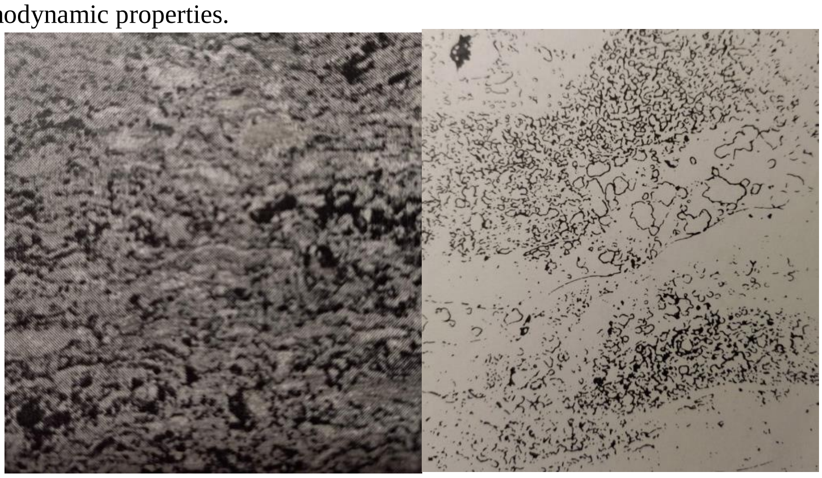
In the working range of the studies, the values of the controlled parameters for coatings based on magnesium orthosilicate compared to the control coatings are minimal and stable (curves 1 and 2, respectively), which determines normal mechanochemical wear.

The micro geometry of the working plane of silicate-based coatings in combination with the physical and mechanical properties of the surface sphere determines their operational state. The results of the studies showed that during the running-in process, the initial technological relief disappears, the chemical composition, structure of the surface layer and its geometry radically change. It is possible to determine that running-in is one of the manifestations of the self-organization process, in which the quasi-relaxation of the surface structure from the equilibrium state will pass to a stable state. At the same time, a new surface quality is formed, characterized by the formation of a balanced roughness, which is not only optimal for specific friction conditions, but also ensures stable wear in the entire test range. Thus, the initial technological roughness is transformed into an optimal operational roughness, which for silicate-based coatings corresponds to the value of Ra 2.5-1.5. At the same time, the sprayed layer is distinguished by a heterogeneous finely dispersed structure with a quasi-ordered lamellar appearance, which tightly adheres to the base and copies the surface relief, at the same time, no accumulation of films, slag inclusions and other contaminants, as well as defects in the form of micropores and micro cracks, was detected.

From the results of micro X-ray structural analysis (MRSA), it was established that the studied coatings have 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 conglomerate of strengthening compounds, which are silicides Cr_2Si_3, $CrSi_2$, Zr_3Si_2, TiSi, $TiSi_2$ and aluminides $TiAl_3$, TiAl, $ZrAl_3$, $CrAl_4$, as well as intermetallic formations such as $ZrCr_2$, ZrV_2, NiTi. In addition, the presence of high-temperature compounds of mullite Al_2SiO_4 was established, which, in our opinion, is formed with the appearance of cristobalite β-SiO_2 with a further increase in temperature, and particles of β-tialite were also found, which should have formed as a result of the interaction of solid solutions according to the reaction: $Al_2O_3 + TiO_2 = Al_2TiO_5$. Thus, a heterophase finely dispersed layered structure was established, which has increased physical, thermal and chemical properties both at normal and elevated temperatures. Also, the studied structure consists of small fragments of ternary compounds of transition metals in the form of Cr_2SiC, TiAlC, TiZrC, SiZrC, in addition, reflexes corresponding to magnesium aluminate ($MgAl_2O_4$) were found against the background of solid solutions, the crystals of which have a spinel structure and correspond to increased thermodynamic properties.



a b

Fig. 2. Cross-sectional microstructure of coatings sprayed with composite powder based on magnesium orthosilicate (a - ×120; b - ×5000).

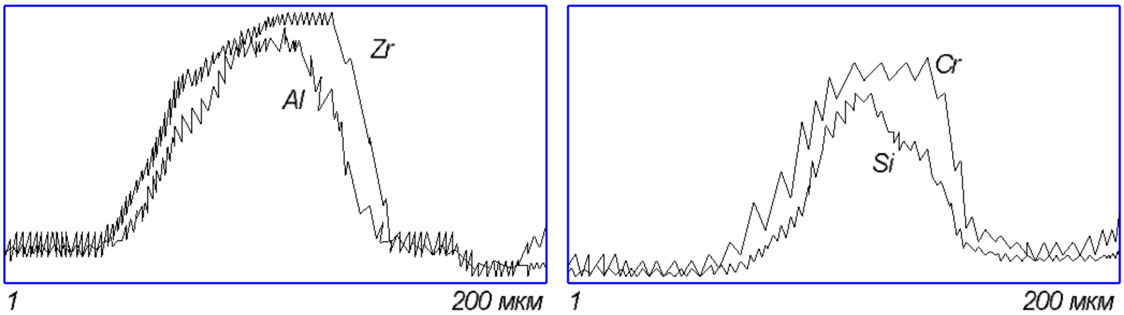
The specified structural components of coatings based on magnesium orthosilicate form solid solutions, chemical compounds and mechanical mixtures and have increased temperature resistance, significant hardness and strength, and corrosion resistance, which ensures their high wear resistance under friction conditions, especially at elevated temperatures.

The problem of coating quality is inextricably linked to the assessment of reproducibility and optimization of the spraying technological process. Changing technological modes leads to changes in the properties of coatings. Based on the cause-and-effect relationships between technological and operational factors, for the formation of high-quality coatings by optimizing the spraying mode, a comprehensive treatment of the main technological parameters was implemented, including the granulometric composition, loading depth, barrel filling degree, working gas ratio and spraying distance [8]. Thus, in the conditions of the technological process of forming the studied coatings, not only the required chemical composition was implemented, but also the predicted stable structure was obtained during spraying, which determines the set of properties that determine the stability of structural adaptability. At the same time, the possibilities of obtaining constant quality were achieved, namely, the variation of strength and plastic characteristics in samples of one batch that were sprayed was stably about 5-10%.

Studying the physical mechanisms of formation and evolution of structural-phase states of secondary structures under conditions of mechanochemical activation is one of the important tasks of controlling the surface strength of coatings based on magnesium orthosilicate while regulating their tribotechnical properties.

For comprehensive and reliable information in the study of thin surface layers in which structural-thermal activation processes occur, the secondary ion mass spectroscopy (SIMS) method was additionally applied, which analyzed the change in the microstructure and established 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.

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 surface oxide films by additional formations that form within the structure of the orthosilicate composition and, by stoichiometric composition, represent a complex in the form of oxides Al_2O, SiO_2, ZrO_2, TiO_2, Cr_2O_3, MgO, which, interacting, form both solid solutions of the Cr_2O_3-SiO_2, ZrO_2-Al_2O_3 type, as evidenced by the coincidence of concentration maxima (fig. 3), and spinel phases $NiCrO_4$, $MgAlO_4$, Zr_2SiO_4, Al_2SiO_5, Cr_2TiO_5, in addition, the presence of binary compounds of the TiO-ZrO_2, MgO-TiO_2, MgO-ZrO_2 type was identified, also not the probability of the presence of ternary compounds such as Mg-ZrO_2-TiO_2, MgO-Al_2O_3-TiO_2 is excluded. It should be noted that the secondary oxide structures that have been detected are characterized by significant strength, hardness, thermal stability and chemical inertness. In this case, the processes of formation and destruction of oxide structures are in dynamic equilibrium and automatically self-regulate, which determines the manifestation and stability of the phenomenon of structural adaptation [9]. However, due to statistical regularities, the processes of decomposition of ultra disperse secondary structures on different parts of the working surface as a result of contact discreteness do not coincide in stages. At the same time, there is an opportunity to assume that the process of their formation does not take place on the entire tribosurface, but only on separate uneven fragments of the actual working area, but their additive distribution is a stable structural-temporal state.



a b

Fig. 3. Distribution of elements in the oxide film on the surface area of the orthosilicate-based coating

In order to study the state of the oxide surface layer, in which the activation processes occur during friction, electron diffraction analysis was used, performed on the EPM-100 installation (reflection recording at U=5 kV). Fig. 4 shows an electron diffraction pattern from the surface of the coating based on magnesium orthosilicate, which records a change in the fine structure, which indicates the presence of intensity maxima on diffusion halos. The studied thin-film layer represents an ultra disperse oriented structure. In this case, the micro hardness of the surface layer is 21.0–23.0 GPa (with an initial one of about 16.0 GPa). Thus, low and stable values of both friction coefficients and wear rates of coatings are ensured by the formation of a coherent dynamically stable conglomerate of oxide structures that screen the adhesive-molecular interaction during friction and have a finely dispersed structure and, under local contact pressures and temperatures, form dense heterogeneous heat-resistant and sufficiently plastic surface structures without cracks and chips, which contribute not only to reducing the oxidation rate and increasing heat resistance, but also play the role of solid lubricants during friction.

Fig. 4. Electron pattern from the surface of the contact ball orthosilicate-based coating at V=1.5m/s and P=14.5 MPa.

When the sliding speed increases to 0.14 m/s, the specific work of wear reaches approximately 104 kJ/mm^3, which corresponds to the necessary and sufficient condition for the thermal decomposition of magnesium carbide and, as a result, fragments of structurally free α-graphite appear on the friction surface (fig. 5). The shape of the particles of the graphite structure is close to scaly, consisting of polydisperse crystallites oriented in the direction of friction. It should be noted that the strength of graphite as an antifriction material is its weak interaction between the layers. Thus, running-in, in a certain sense, can be considered as a specific type of heat treatment accompanied by graphitization.

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

Fig. 5. Surface topography during graphite film formation (v=0.17 m/s).

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

Self-lubrication of magnesium orthosilicate-based coatings depends on the formation of a graphite film, the dynamic equilibrium of which is maintained by the further formation of graphite. At test speeds of more than 0.21 m/s, the frictional self-lubricating surface film of graphite covers more than half of the friction area and, at the same time, is a layer of an ordered set of polydisperse graphite particles, the self-equilibrium of which is maintained by their active formation as a result of pyrolysis. At the same time, the higher the temperature, the greater the amount of carbon converted into a graphite-forming self-lubricating film, and the longer the contact areas interact, the more graphite is formed.

Thus, the means of regulating wear and ensuring self-lubrication of coatings based on magnesium orthosilicate are both the use of magnesium carbide, which, through its structure, affects the adaptation process during friction by modifying the surface layers with carbide graphite, and the joint use of stable surface oxide structures, which, with cooperative self-organization, provide an additive complex of heat-resistant surface structures that prevent direct contact of surfaces and effectively reduce the friction force, wear intensity, and prevent unacceptable destruction processes.

From the point of view of structural thermodynamics, the systemic ordering of self-adapting surface films due to changes in composition and structure can be considered as adequate elementary physicochemical processes and adaptation mechanisms in the process of structural adaptability [10].

Fig. 1 also presents the results of testing coatings of the type WK15 (curves 2, 4), sprayed with tungsten-cobalt powder. Coatings of this type, as a classic wear-resistant material, are widely used to protect against wear a significant range of different design and purpose of critical parts. As established, at sliding speeds of more than 1.9 m/s, the temperature factor has a tendency to reduce their speed against wear, which ultimately turns out to be decisive in the development of destructive processes during friction.

For coatings based on nichrome (fig. 1, curves 3, 6) doped with aluminum and boron, a monotonic increase in wear intensity with increasing speed is characteristic. The study of the phase composition showed the presence in the coating composition of both a solid solution based on nickel and dispersed compounds of nickel aluminides ($NiAl$, Ni_3Al), chromium borides (Cr_2B, Cr_5B_3), as well as the presence of complex borides of the type (Cr, Ni). The passive capabilities of secondary structures with increasing test speed are suppressed by the development of plastic deformation and, as a result, the dynamic equilibrium shifts towards increasing activation energy, and the type of wear changes qualitatively. According to metallographic analysis, their friction surfaces at speeds of 1.8 m/s have random local tearing, scratches, characteristic of the initial development of setting processes.

Thus, the detonation coatings based on magnesium compounds, 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 increased adhesion strength and the ability, through their composition, to influence structural properties that are capable of self-lubrication. The conducted studies indicate the feasibility of their use in order to increase antifriction due to self-lubrication in real operating conditions. However, it can already be noted that their use will ensure reliability, increase the resource and reduce repair costs when restoring worn parts. The most appropriate application of the studied coatings is to increase the reliability of operation of friction units, for example, for moving pairs of control mechanisms, hinges of guide surfaces, cams, sliding supports, pairs with reciprocating movement, bearings, sliding guides, lever parts of high-speed and heavily loaded units, in which the use of traditional lubricants is undesirable.

It should be noted that the developed composite powder material for forming self-lubricating coatings based on magnesium compounds can be implemented by any technological methods that use powder materials. The presented work continues the cycle of research on the development of promising coatings to minimize friction coefficients and wear rates through the use of materials containing magnesium compounds.

Conclusions.

1. The developed and investigated detonation coatings based on magnesium compounds, which are characterized by stable and minimal values of friction coefficients and wear intensities under test conditions at a sliding speed of up to 4.0 m/s and a load of 14.5 MPa, have friction parameters significantly lower than those for control coatings by almost 2.5-7.0 times.

2. The creation of a powder mixture based on magnesium orthosilicate was carried out by the method of mechano-chemical synthesis, which made it possible to obtain a nanocomposite conglomerate of micron-sized base particles and nanosized alloyed phases with the subsequent addition of structurally free magnesium carbide to the powder composition.

3. A comprehensive treatment of the main technological parameters was implemented and the optimal mode of detonation-gas spraying of composite powders based on orthosilicate was worked out, while not only the planned chemical composition was reproduced, but also the predicted structure was obtained, which modernizes the friction surface and minimizes tribotechnical properties. At the same time, it was emphasized that the variation of strength and plastic properties in samples of one batch is stable and is 5-10%.

4. The structural-phase composition of coatings with magnesium orthosilicate was studied by modern means of physicochemical analysis, while the main components of the composite particles are solid solutions based on binary oxides and inclusions of chemical compounds of simple and complex carbides and intermetallics, as well as mechanical mixtures of component compounds. The determined components of the composition have increased temperature stability, significant hardness and strength and chemical inertness. In addition, there is the presence of dense and rather plastic heterogeneous oxide surface structures, which cause not only a decrease in the oxidation rate and an increase in heat resistance, but also perform an active role of solid lubricants under friction conditions.

5. The physical mechanism and main factors determining the level of thermodynamic graphitization have been determined. The nature and regularities that determine the tendency of coatings to passivation have been studied. It is noted that its implementation is carried out both due to solid-phase tribochemical reactions, which cause the formation of quasi-spherical polydisperse surface films integrated on the basis of carbide α-graphite and finely dispersed oxide compounds.

6. The developed self-lubricating antifriction coatings based on magnesium orthosilicate expand the achievements of modern tribotechnical materials science. At the same time, the studied self-lubricating coatings can be used both for strengthening and for high-quality restoration of worn parts by any technological methods using powder materials.

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Щепетов В.В., Фіалко Н.М., Бись С.С. Триботехнічні властивості покриттів на основі сполук магнію

У статті узагальнено результати досліджень триботехнічних властивостей детонаційних покриттів на основі ортосилікату магнію в умовах постійного навантаження у полі швидкостей ковзання. Методами сучасного фізичного аналізу досліджено структурно-фазовий склад покриттів. Розроблені та досліджені покриття на основі ортосилікату магнію мають високі та стабільні антифрикційні властивості у всьому навантажувально-швидкісному діапазоні випробувань. Підкреслено, що результатом антифрикційності умовах тертя є адитивна дія як плівки карбідного графіту, так і дисперсних поверхневих оксидних структур, синтез яких забезпечує модифікацію поверхні структури, що спроможня до самозмащування та водночас обмеження розвитку неприпустимих процесів руйнування.

Ключові слова: детонаційне покриття, інтенсивність зношування, структурно-фазовий склад, графітизація.