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NANOCOMPOSITE COATINGS FOR WEAR PROTECTION AT HIGH TEMPERATURES

Abstract. *The investigation results of friction and wear of the developed detonation composite coatings $FeAl_2$-Ti-Si-B under high-temperature friction conditions are presented. The choice of $FeAl_2$-Ti-Si-B composition and its optimal content for spraying wear-resistant coatings loaded with friction under high-temperature conditions are justified. It is noted that the alloying elements at definite concentrations and technological parameters of spraying have a positive influence on the structure, properties, and quality assurance of multicomponent coatings. It is shown that the introduction of silicon and boron contributes the formation of hard-alloy high-temperature compounds with increased wear resistance. The maximum microhardness corresponds to the Cr-Si coatings with ~ 28 % titan content. In addition, the mechanical properties of the obtained material are improved by additional alloying of ~ 22 % silicon and bor. In turn, the coatings plating at a working gas flow rate in a ratio for acetylene ~ (20/25) l/min and oxygen ~ (22/27) l/min provides the chemical composition and spraying process parameters permanence as well as constant properties of coatings. The obtained results show that for the coatings of $FeAl_2$-Ti-Si-B system at loading 5.0 MPa, sliding speed 1.5 m/s, and temperature up to 650 °C the stable performance of structural adaptability, which ensures the friction and wear parameters minimization, is demonstrated. The metallographic analysis and strip chart recording of specimens indicate that the friction surfaces are characterized by the absence of visible defects; the separate cold-welded regions are located in thin-film surface layers. The composition, structure, and tribological durability of coatings produced from the elements of the country's resource base were studied; their high adhesion, physical and mechanical characteristics and wear resistance under high-temperature conditions were defined. The thin-film surface structure patterns and properties were investigated with the help of modern physical and chemical methods of analysis. It was determined that the combination of mechanical, physical, and chemical properties of the investigated coatings provides vide opportunities for their usage as effective materials under high-temperature wear conditions. According to the test results, the application of the investigated composite coatings for friction unit efficiency improvement provides their operational reliability in accordance with requirements and opportunities that appear with the development of a new competitive material for wear-resistant coatings obtained with the help of the detonation method.*
Keywords: detonation coating: wear resistance, surface layer, structural adaptability, temperature.

1. Introduction

Friction and wear processes are among the most important scientific-technical domains where the challenges to be faced in day-to-day life are investigated by using theoretical and applied approaches. Typical to the majority of mating and moving machinery parts operating under friction is to perform their working and production functions at elevated temperatures.

Temperature as one of the operational factors, being an important friction characteristic, as well as the thermal processes resulting therewith, affect directly the shaping of the physicochemical and mechanical properties of surface layers.

Nonetheless, despite being vitally important, the theoretical and practical studies dealing with the high temperature wear of detonation coatings are fairly limited in number in scientific publications while some individual papers and published works available do not help make up for this gap. Thereby the investigations aimed at discovering the effects of thermal factors on a detonation coating wear behavior remain a matter of topical interest nowadays.

The aim of this work was to summarize the theoretical and practical findings on the tribological stability of resistant to temperature $FeAl_2$-Ti-Si-B type coatings developed to protect the machine elements operating in a high temperature friction environment.

The economic attractiveness was an important factor to consider at the point of choosing and substantiating the composition and coating structure. The coatings of interest do not contain scarce and costly components.

2. Experimental Procedure

The research was based on the general technical requirements consistent with the procedure for testing material wear resistance at high temperatures [1]. To approximate as much as possible the physicochemical mechanics of friction and wear to real operating conditions, the appropriate changes have been made therewith. The tests have been carried out with a sliding velocity of 1.5 m/s and, a load of 5.0 MPa, using a M-22PV unit, the equipment designed at Frantsevich Institute for Problems in Materials Sciences under the National Academy of Sciences of Ukraine (IPMS NASU) [2].

The friction temperature of specimens has been measured using the chrome-compel thermocouples fabricated from a categorized wire.

Inherent to the current status of triboengineering material science is a large-scale application of physical research techniques. The physicochemical properties, micro-phase analysis of the surface layers state responsible for activation trends, intensification of mechano-chemical oxidation, and frictional seizure have been studied by electron diffraction technique. The investigations have been carried out using an electron diffraction camera EMP-100 (reflection shooting at 100 kV) and X-ray microspectral analysis made with a microanalyzer "Kameka". In determining true concentrations, some corrections for the main effects have been introduced using suitable software [3].

The data on qualitative and quantitative compositions, element chemical state, presence of defects, and functional groups in the near-surface layers have been obtained by the Auger-electron spectroscopy method with a "Jamp-10S" plant under the "JEOL" procedure. Auger spectra have been registered at $5\text{-}10^{-8}$ A, 10 кV accelerating voltage, $2\text{-}10^{-7}$ Pa vacuum, with a 30 μm diameter probe. Metallographic research has been done with the help of a MIM-8M microscope.

Obtaining microsections manufactured by the technique outlined in the work [4] was an important step in the qualitative study of the coating structure.

3. Results and Discussion

Most of the tasks involved with friction and wear, despite the exceptional role the protection coatings play in engineering, are still being solved by way of experiments. Also, the choice of a rational composition such as the $FeAl_2$-Ti-Si-B coatings, was involved with a component effect estimation which was made on the structural basis [5].

The relationship between titanium and silicon content and microhardness (Hμ) and wear intensity (Iw) in the coatings is plotted in Figures 1 and 2.

As seen in the plot, the detonation $FeAl_2$-Ti-Si-B coatings with a titanium content of ~ 28 % have total microhardness. With a titanium content taken as uniform in the system, we determine an optimal content of silicon.

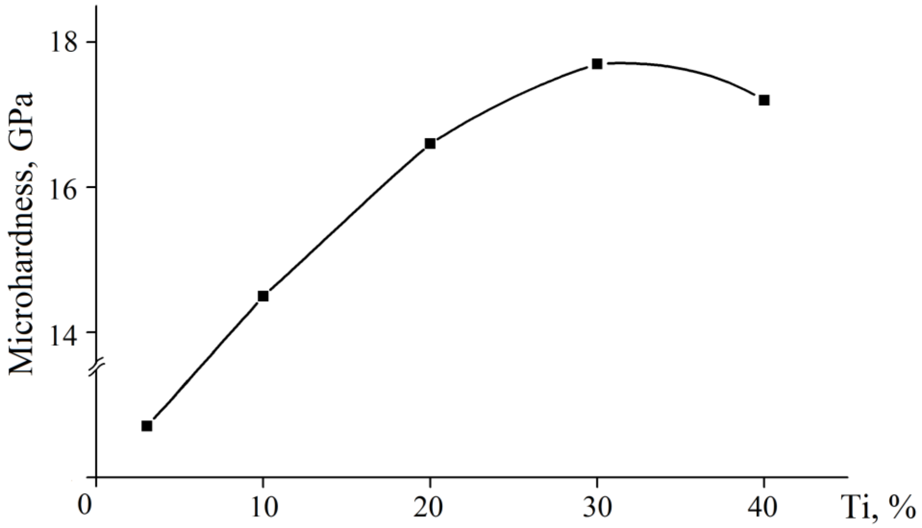


Fig. 1. Dependence of microhardness on Ti content

The choice of iron powder as a starting material, being rather inexpensive, not critical, and standard [6], has been also governed by its capability of being repeatedly alloyed, especially, by elements with limited solubility [7–9]. The thermodiffusion impregnation with aluminum and bor is beneficial to a solid solution hardening and formation of iron aluminides and borides refractory phases, exhibiting a trend for grain refinement and improving durability therewith. The incorporation of titanium and silicon, which form part of an iron solid solution and harden it, is conducive to the formation of intricately alloyed high-temperature structures causing a dispersed hardening, thus increasing wear resistance due to the formation of a considerable body of strengthening phases with high thermodynamic stability. As found in the tests, the alloying elements exert a positive effect on the structure and coating properties only with definite concentrations whose best values have been specified by the experiment.

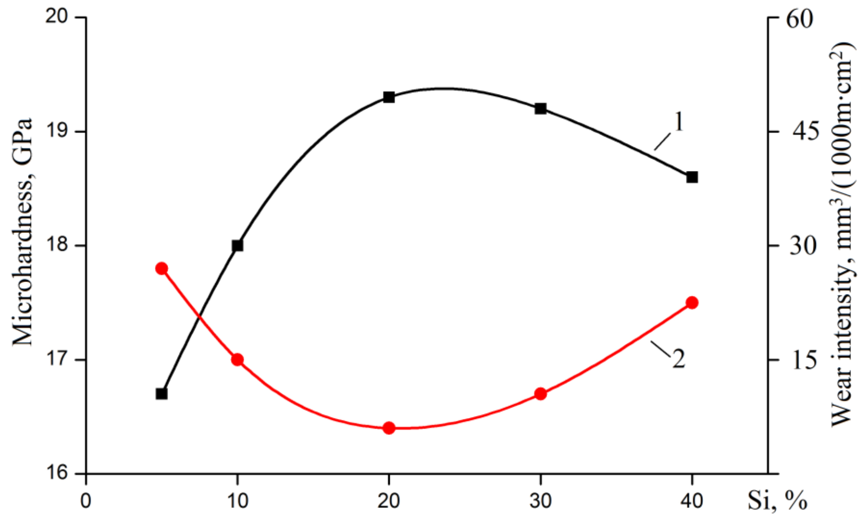


Fig. 2. Dependence of microhardness (1) and wear intensity (2) on Si content

The spraying process parameters play a great role in providing high-quality multicomponent coatings. A set of tests has been performed to define the effect of a working gas ratio and the extent of barrel filling with the gaseous mixture on the operating characteristics of the coatings.

Figure 3 shows the relationship between wear intensity and barrel filling with acetylene-oxygen mixture (in a ratio of 1 to 1.1). Spraying, involving a working gas flow with a ratio of 22/27 – 24/29 for acetylene-oxygen, provides a maximum wear resistance which correlates explicitly with a coating bond strength as illustrated in Fig. 3.

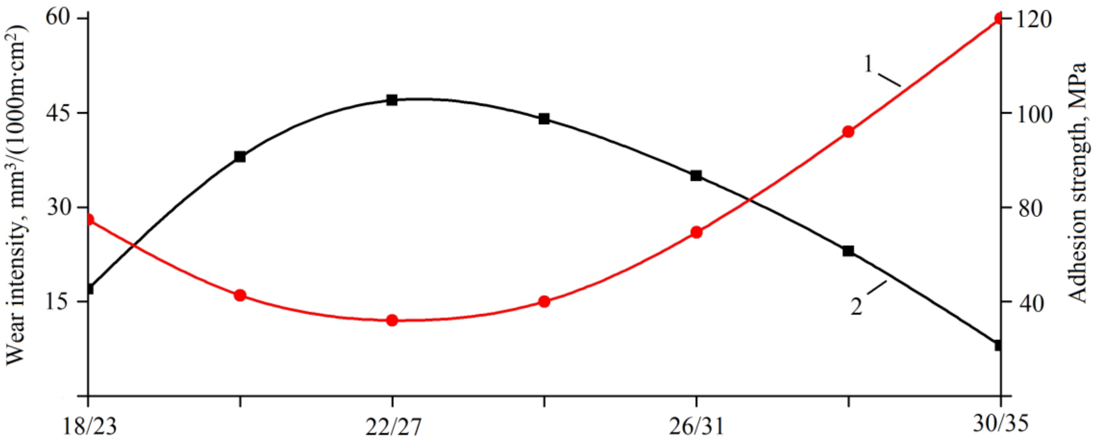


Fig. 3. Dependence of coating wear intensity, and adhesion strength on gas flow rate in spraying

The invariance of chemical composition and spraying process variables dictates the fixed properties of the coatings whose relative density comes to ~ 95 %.

The findings obtained upon optimizing the $FeAl_2$-Ti-Si-B coatings, by a X-ray microspectral analysis, allow the structure to be categorized as a fine conglomerate of inclusions (more than 65 % of volume) like aluminides of iron (Fe_3Al, $FeAl_2$, Fe_3Al_5, $FeAl_3$), titanium (Ti_3Al, $TiAl_2$, $TiAl_3$), and silicides (Fe_3Si, Fe_2Si, Fe_5Si_3; TiSi, $TiSi_2$), except for binomial intermetallic inclusions. Imposition of associated concentration maximums points to a possible existence of the complex refractory phases like (Fe, Ti)Al, (Fe, Si)AI, solid solutions Ti_5Si_3-Fe_5Si_3. The Intermetallic compounds have been found to be responsible for the formation of solid solutions by dissolving initial components. The changes in the physical-mechanical properties of the coatings as a result of alloying are presented in Table 1.

Table 1. Physical-mechanical properties of the coatings

Coating content	Thickness, mm	$\sigma_в$, GPa	$\sigma_{изг}$, MPa	$\sigma_{сц}$, MPa	Hμ, MPa
$FeAl_2$	0.15–0.25	0.45–0.50	380–430	45–51	11 000
$FeAl_2$-Ti	0.15–0.25	0.53–0.66	550–600	62–79	17 000
$FeAl_2$-Ti-Si	0.17–0.27	0.65–0.82	630–790	71–92	18400
$FeAl_2$-Ti-Si-B	0.20–0.30	0.80–0.97	670–840	89–110	19 500

A surface layer being friction-loaded is known to pass, in consequence of plastic deformation, into a thermodynamically unbalanced activated state from which by diffusion and chemical interaction with the environment it tends to transit to the passive state, resulting in the formation of the secondary thin-filmed structures [10–12].

The test data indicating the functional dependence of wear intensity on the temperature near the friction surfaces of the coatings under study are presented in Fig. 4. In elevating temperature as high as 600 °C, the wear process of coatings $FeAl_2$-Ti-Si (curve 1) remains practically stable with normal mechanochemical wear. According to the test findings the composition of the surface films, shielding the adhesive interactions in the area of a friction contact, represents along with a main phase the solid supersaturated solutions based on Fe, Si in α-Al, oxides Fe_2O_3–Al_2O_3, Al_2O_3-TiO_2, as well as a conglomerate of complex oxide compounds of Fe_2TiO_5, $Fe_2(TiO_3)_3$, $FeAl_3O_4$, β- tillite Al_2TiO_5, mullite Al_2SiO_5 type, and silicate of fayalite type $FeSiO_4$, which, as a result of sintering, are responsible for the formation of thin-filmed heterogeneous surface structures, with a microhardness being 28÷35GPa versus the primary one of up to 19GPa. Thus, with temperatures increased, the thermomechanical processes and essential structural-phase changes proceed intensively on account of shearing and compressive stresses in the surface structures and a near-surface layer.

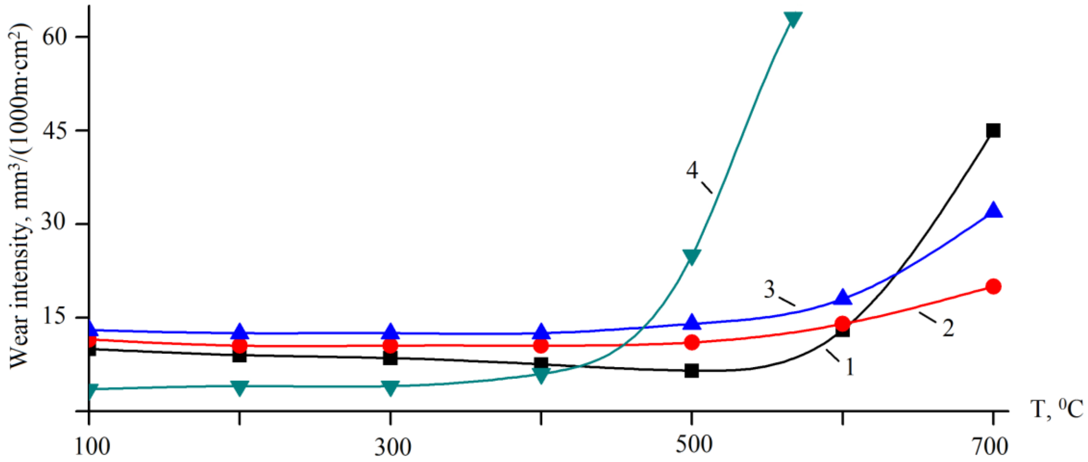
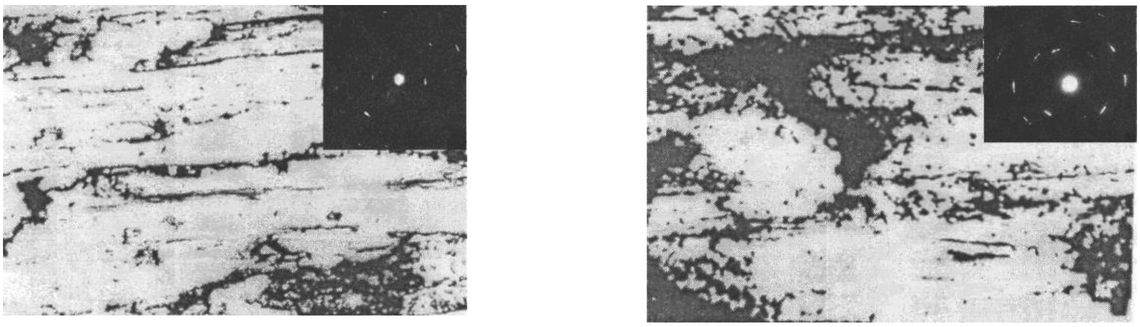


Fig. 4. Dependence of wear intensity on temperature:
1 – $FeAl_2$-Ti-Si-B; 2 – Ni-Cr-Al-B; 3 – Al_2O_3-Cr_2O_3; 4 – WC-Co (V=1,5m/s; P=5,0 MPa)

In Fig. 5. are given microstructures and electronograms displaying the kinetics of decomposition in the structures on the rubbing surfaces of $FeAl_2$-Ti-Si-B coatings.

The rise in temperature activates the processes of coagulation and recrystallization developing on various scaled levels, which is evidenced by progressive disappearing of rings and appearing of point reflections on electronograms.



a) b)

Fig. 5. Microstructures and electron diffraction patterns of rubbing
surface of $FeAl_2$-Ti-Si-B coatings tested at temperatures: a) 400 °C (x320); b) 550 °C (x320)

In terms of energy the given secondary structure transformation may be regarded as an adequate elementary mechanism of a surface layers adaptation in the process of a structural adaptability of friction system. So, on the one hand, due to the statistical law, the formation and fragmentation phases of secondary structures do not coincide on the different sections of contact surfaces, but their additive distribution represents a stable structure-time state. On the other hand the formation of a surface layer structure is not determinative but follows the principals underlying the minimal dissipative processes [8, 9]. As temperature is raised (Fig. 4), the totality of surface effects is intensified, which in our opinion is due to a crystal lattice distortion by plastic deformation on account of fluctuating stresses occurring with friction; in addition, the occurrence of point and multidimensional defects activates tribochemical reactions.

However, a temperature growth of up to ~ 650 °C, which is critical for the coating under test (curve 1, Fig. 4), gives rise to destruction processes and leads to inadmissible damaging effects (Fig. 6).

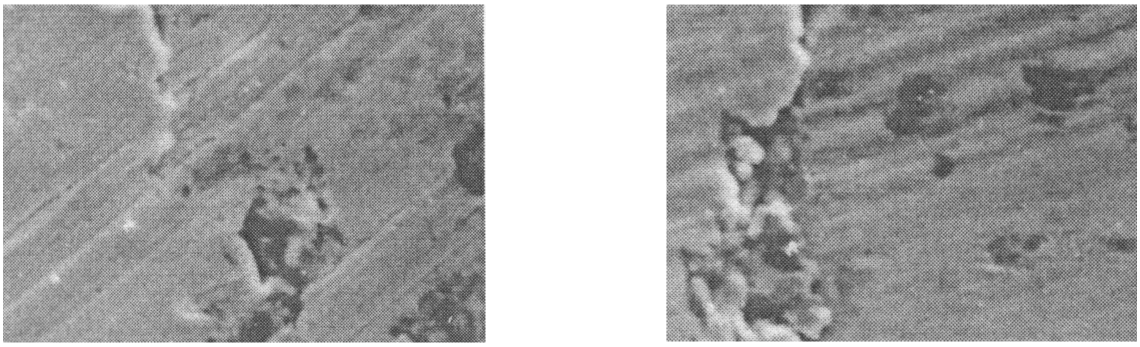


Fig. 6. Rubbing surfaces of the $FeAl_2$-Ti-Si-B coating illustrating destruction kinetics upon testing at 650°C (x3000)

The critical temperature limit for the Al_2O_3-Cr_2O_3 (curve 3, Fig.4) coatings under the given rubbing conditions is ~ 680 °C, a range of normal friction for the coatings of Ni-Cr-Al-B type (curve 2, Fig. 4.) is limited to ~ 600 °C, while WC-based coatings (curve 4, Fig. 4) remain efficient up to 530 °C.

A thin-filmed oxide phases conglomerate, obstructing the adhesive-molecular interaction of the surfaces in contact, is a complex object whose integral properties in turn are a function of characteristic traits and individual properties of simple oxides as substantive self-contained constituents whose properties can be examined in terms of peculiarity of their structures.

The microhardness of wustite FeO, forming on the rubbing surfaces of $FeAl_2$-Ti-Si coatings, decreases steadily with temperature lowering while a microhardness jump is observed in the vicinity of 520 °C, which results from a solid-phase transformation of FeO into more stable oxide Fe_2O_3. As this takes place, the microhardness values of these oxides, by lowering temperature, do not agree with the results drawn while heating, which, in our opinion, is accounted for by different values of a structural-thermal activation and hence by a contact plastoelastic deformation affecting the anomalous diffusion activity of both oxygen and other elements, iron included.

The microhardness of hematite Fe_2O_3, in raising the temperature, goes down with a microhardness jump occurring as a consequence of a polymorphic $\beta \rightarrow \alpha$ transformation. In cooling hematite with a retention at the moment of measuring the microhardness, the latter has been observed to decrease spasmodically down to values concurrent with those of the microhardness in magnetite Fe_3O_4 more spongy and less dense than γ-Fe_2O_3. The grit is a dark brown powder. The X-ray phase analysis data corroborate the transformation of hematite into magnetite which proves to be more stable than iron oxide under the given conditions.

The microhardness of titanium monoxide, which does not undergo polymorphic transformation, decreases steadily with rise in temperature. It should be also noted that simple oxides are prone to forming solid solutions in which the dissolution of alloying elements normally leads to increasing the microhardness.

The titanium dioxide TiO_2 undergoes polymorphic transformation at 500 °C, the increase of microhardness at the moment of transformation indicating the transition of a less densely packed brookite cristaline lattice (rhomb-shaped) into a more densely packed rutile tetragonal lattice. With dissolution of iron in the titanium dioxide, its microhardness remains nearly unchanged.

In incorporating silicon as an alloying addition into a detonation coating composition, there is formed a dioxide on the rubbing surface, undergoing, in the temperature range under test, two polymorphous changes, the first at 500 °C and the second at 700 °C. In the first occurrence, a low-temperature β-quartz has been found by an X-ray phase analysis to transform into a high temperature α-quartz.

The microhardness of the oxide films of three-valence metals, in this case, Fe_2O_3 and Al_2O_3, formed on the rubbing surfaces, goes down as temperature is increased, however, an Al_2O_3 microhardness curve in close proximity to 550÷600 °C has a knee which points to a polymorphous transformation.

As a result of studying the microhardness of the oxide structures being raised under high temperature wear on the rubbing surfaces of detonation coatings, certain distinctive characteristics should be mentioned, that is the structures involved, because of their chemical composition, can be found in different states. With higher temperatures the oxide structures transit to a more stable condition, which causes the change of their physical properties. The relationship between microhardness of surface structures and temperature is normally monotone, if those are not polymorphous, and spasmodic in case the polymorphous changes or transformations of metastable states into more stable and steady occur with heating or cooling. The curve bends of the microhardnesses are mostly smooth since the particles of interstitial implantations and impurities, which markedly affect the microhardness and hence the oxide properties both of simple and complex compounds, are dissolved and present in the oxide structures.

4. Conclusions

With all the spectrum of structural forms and functional characteristics of machinery, wear resistance is a general parameter that determinates their reliability and longevity, and yet the creation of the multifunctional coating to protect them against wear involves the same problem as that of the production of a wear resistant monolithic material which could cover all the requirements relevant to mechanical engineering.

Thus, creating new materials is of common interest in this field. In developing the materials, techno-economic restrictions imposed by a production process, including expenditure of scarce and expensive components, have been taken into account.

The composition, structure, frictional resistance of $FeAl_2$-Ti-Si-B coatings (using nationally available resources to produce them), have been studied, the increased level of their adhesive ability, of physical-mechanical characteristics, and of wear resistance under elevated temperatures, which may be comparable to heat resistance of heavily alloyed materials, have been proved. The structure and properties of thin-filmed secondary structures have been tested by using the up-to-date physicochemical techniques.

As proved by the test findings, the introduction of the composition coatings under study for the purpose of improving the wear resistance of tribological units enhances their functional reliability according to the requirements thereto and opportunities to be offered by developing a new competitive material for wear resistant coatings fabricated via detonation spraying technique.

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НАНОКОМПОЗИЦІЙНІ ПОКРИТТЯ ДЛЯ ЗАХИСТУ ВІД ЗНОШУВАННЯ В УМОВАХ ВИСОКИХ ТЕМПЕРАТУР

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Анотація. *Наведено результати дослідження тертя та зношування детонаційних композитних покриттів $FeAl_2$-Ti-Si-B в умовах високотемпературного тертя. Обґрунтовано вибір композиції $FeAl_2$-Ti-Si-B та її оптимальний склад для напилення зносостійких покриттів, навантажених тертям в умовах високих температур. Відзначено, що легуючі елементи при певних концентраціях і технологічних параметрах напилення позитивно впливають на структуру, властивості та забезпечення якості багатокомпонентних покриттів. Показано, що введення кремнію та бору сприяє утворенню твердосплавних жаростійких з'єднань з підвищеними показниками зносостійкості. Максимальна мікротвердість відповідає покриттям Cr-Si з вмістом титану ~ 28 %. Крім того, механічні властивості отриманого матеріалу покращуються шляхом додаткового легування ~ 22 % кремнію та бору. У свою чергу, нанесення покриттів при витраті робочого газу в співвідношенні ацетилену ~ (20/25) л/хв та кисню ~ (22/27) л/хв забезпечує постійність хімічного складу та параметрів процесу напилення, а також стабільні властивості покриттів. Отримані результати показують, що для покриттів системи $FeAl_2$-Ti-Si-B при навантаженні 5,0 МПа, швидкості ковзання 1,5 м/с і температурі до 650 °С стабільні показники структурної адаптивності, що забезпечує мінімізацію параметрів тертя та зношування. Металографічний аналіз та електронограми зразків свідчать про те, що поверхні тертя характеризуються відсутністю видимих дефектів, окремі ділянки острівків зварювання розташовані в тонкоплівкових поверхневих шарах. Досліджено склад, структуру та трибологічну довговічність покриттів, отриманих з елементів сировинної бази країни, визначено їх високу адгезію, фізико-механічні характеристики та зносостійкість в умовах високих температур. За допомогою сучасних фізико-хімічних методів аналізу досліджено структуру та властивості тонкоплівкової поверхні. Встановлено, що сукупність механічних, фізичних і хімічних властивостей досліджуваних покриттів дає можливість використовувати їх як ефективні матеріали в умовах високотемпературного зношування. За результатами випробувань встановлено, що застосування досліджуваних композиційних покриттів для підвищення ефективності вузлів тертя забезпечує їх експлуатаційну надійність відповідно до вимог і можливостей, що з'являються з розробкою нового конкурентоспроможного матеріалу, отриманого детонаційним методом.*

Ключові слова: детонаційне покриття, зносостійкість, поверхневий шар, структурна пристосовуваність, температура.

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