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V.P Babak[1], Dr. Sci. (Tech.), Prof., Corresponding Member of National Academy of Science of Ukraine,
V.V. Shchepetov[1], Dr. Sci. (Tech.), Prof.,
S.D. Nedaiborshch[2]

1 – Institute for Technical Thermal Physics under National Academy of Science of Ukraine, Kyiv, Ukraine, e-mail: vdoe@ukr.net; vvs2020@ukr.net
2 – State Enterprise "PLANT 410", Kyiv, Ukraine, e-mail: nanoavia@ukr.net

WEAR RESISTANCE OF NANOCOMPOSITE COATINGS WITH DRY LUBRICANT UNDER VACUUM

В.П. Бабак[1], д-р техн. наук, проф., член-кор. НАН України,
В.В. Щепетов[1], д-р техн. наук, проф.,
С.Д. Недайборщ[2]

1 – Інститут технічної теплофізики НАН України, м. Київ, Україна, e-mail: vdoe@ukr.net; vvs2020@ukr.net
2 – Державне підприємство „ЗАВОД 410 ЦА", м. Київ, Україна, e-mail: nanoavia@ukr.net

ЗНОСОСТІЙКІСТЬ У ВАКУУМІ НАНОКОМПОЗИЦІЙНИХ ПОКРИТТІВ З ТВЕРДИМ МАСТИЛОМ

Purpose. To research tribotechnical characterization of the developed *Cr-Si-B* detonation nanocomposite coatings containing dry lubricant additives involving the dispersed molybdenum disulfide as an extra anti-friction component under vacuum conditions.

Procedure. To accomplish D-Gun spraying, the nanocomposite powders obtained by mechanochemical synthesis by means of an IES-1-0.5 laboratory attritor [2] were used. The particles of dry lubricant (fractions from 3 to 10 mμm) were mixed with the starting metallic nanopowders using the aqueous method. The thickness of the sprayed detonation layer upon treatment made up 0.20–0.25 mm, roughness was R_a= 0.63-0.32, strength of cohesion with a base was σ_{coh} = 87.5 MPa. The examination of the surface strength of the coatings when in friction, seizure susceptibility and a triboactivation degree have been evaluated in terms of wear intensity in the vacuum with rarefaction of $1.33 \cdot 10^{-5}$ Pa. The tribotechnical characteristics of the composite coatings studied have been analyzed and compared with the values of VK15 coating wear resistance and the surface layers produced from a thermodiffusion alloying with boron, vanadium and chromium.

The up-to-date physical techniques including X-ray spectral microanalysis and scanning electron microscopy have been applied to investigate rubbing surfaces.

Findings. By mechanochemical synthesis of starting materials, the nanocomposite powders composed of nanocomposite homogeneous mixture have been obtained. Controlling the operation procedure of producing nanocomposites, the authors succeeded in providing the desired chemistry. Moreover, the intended coating nanostructure with high resistance to wear under friction loading in vacuum has been obtained while spraying.

Originality. High resistance to wear of the developed nanocomposite coatings containing a dry lubricant additive involving the dispersed molybdenum disulfide as an extra anti-friction component has been practically established and theoretically substantiated. The effect of a coating structure and surface film composition on their operational characteristics has been found.

Practical value. The evidence obtained expands the store of achievements in contemporary tribotechnical material science and is of certain value in producing competitive products characterized by high service reliability.

Keywords: *detonation coating, wear resistance, surface layer, structural adaptability, molybdenum disulfide*

Introduction. The quality standards and reliability of machinery are largely due to surface strength and wear resistance of the usable materials. The surface strength of the material subjected to friction remains to be one of the major challenges in the domain of science and technology for it implies studying the issues, both with theoretical and applied methods, which require solution in a day-to-day engineering practice. In spite of certain achievements the solution of the problem still lags behind the present requirements. Thus, the problems relating to wear resistance and surface strength under the extreme operating conditions still remain to be of paramount importance. These conditions involve not only the limit loads and travel velocities but the ambient effects, vacuum, in particular, where a conventional lubricant is used restrictedly.

The relevant scientific publications do not abound in reasonable evidence on the effect of separate structural constituents in composite powder materials on the detonation coating strength properties. Moreover, the data concerning the impact of the molybdenum disulphide on the detonation coating wear resistance under vacuum is virtually unavailable. So far the principal method to develop coatings has been considered the empirical approach relying on a "composition-properties" relationship search.

In aircraft the bearings, gear and friction transmissions, sliding guide members, end supports, reciprocating travel twains, articulated joints, control surfaces system components are parts whose sliding joints being operated under friction loads undergo wear leading to failures because of adhesion and seizure. Servicing and maintaining them in operating availability are among the primary engineering challenges for aircraft maintenance systems [1]. Furthermore, antifriction wear resistant coatings are widely adopted to ensure reliable operation of friction assemblies in equipment used by minerals industry and operating under specific conditions [2].

Material and Research Technique. The materials to be sprayed were prepared following the procedure set forth in the paper [3]. The particles of dry lubricant (fractions from 3 to 10 mμm) were mixed with the starting metallic powders using the aqueous method, the mixture subsequently being dried to remove the moisture completely. D-gun spraying of the coatings was performed using the technology and equipment designed in IPMS NASU.

The thickness of the sprayed detonation layer upon treatment made up 0.20–0.25 mm, its roughness was R_a= 0.63-0.32, strength of cohesion with a base made σ_{coh}= 87.5 MPa. Testing under vacuum was conducted using an apparatus intended for the laboratory experimental evaluation of tribotechnical materials [4]. Examination of the surface strength for the coatings when in friction, seizure susceptibility and a triboactivation degree have been evaluated in terms of wear intensity in the vacuum (with rarefaction of $1.33\cdot10^{-5}$ Pa). The tribotechnical characteristics of the composite coatings studied have been analyzed and compared with the values of the VK15 coating wear resistance and the surface layers produced from a thermodiffusion alloying by boron, vanadium and chromium.

While contrasting the findings obtained upon testing at a standard atmospheric pressure [5] with those of the coating wear resistance under vacuum, it should be noted that with increasing air rarefaction and diminishing passivating capability of the medium there appear variations in quality with regard to the general friction trends, leading to sizeable quantity variations in the tribotechnical processes running in the contact area.

These nanocomposite coatings containing micro and nanophases revealed a structure inherited from mechanochemical synthesis products. Applying microindentation, the mechanical properties of the coatings produced were measured and the evidence on the strength of the rated mechanical characteristics attested that the structural state caused by the products of mechanochemical synthesis could be labelled as micronanocomposites.

To study the quality of the surface layers with activation processes running therein when loaded by friction, affecting the intensity of mechanochemical reactions, the overall procedure for physical analysis was applied. It included the following: metallography (optical microscope “Neofot-32” with an attachment), durometeric analysis (durometer Leco M-400 with a load of 0.249 and 0.496H), scanning electron microscopy (scanning electron microscope JSM-840), X-ray structural phase analysis (diffractometer DRON-UM1 with monochromatic radiation CuK_α).

Findings. The studies on the regularity of tribotechnical processes in oxygen-free medium are challenging, allowing the theoretical prerequisites to be created to attend practical application problems implying the investigation and creation of the wear resistance materials for coatings and their most efficient combination of friction couples operating in the vacuum.

In Fig. 1 the test data is plotted with wear intensities values and friction coefficients against those of sliding velocity with a 2.5 MPa load enabling the processes of friction of physical-chemical mechanics to be at most approximated to the actual operating environment.

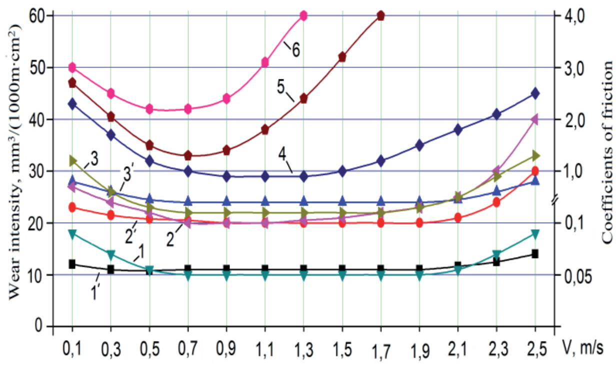


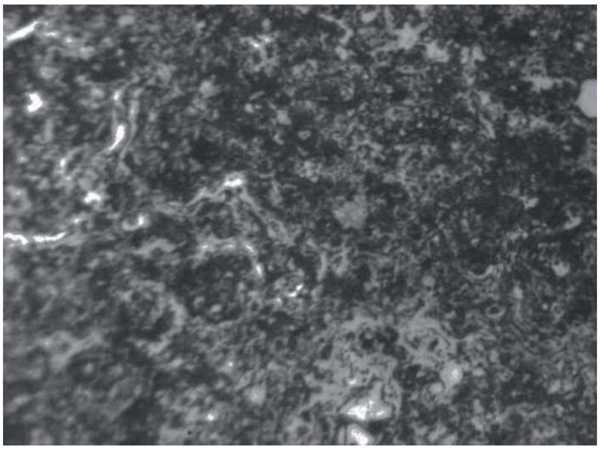
Fig. 1. Wear intensity (1,2,3) and coefficients of friction (1’,2’,3’) versus sliding velocity (P =2.5 MPa): 1,1’ – Cr-Si-B-MoS$_2$ coating; 2,2’ – VK-15 hard alloy coating; 3,3’ – vanadium-plated samples; 4 – chromium-plated samples; 5 – Cr-Si-B coating; 6 – boron-plated samples

The high wear resistance, under the given friction conditions, of the *Cr-Si-B-MoS$_2$* coatings (Fig. 1, curve 1) occurs due to structural adaptability which being a general occurrence, is implemented, in the first place, at the expense of a structure-free molybdenum disulphide that provides the formation of a protective film in course of friction (Fig.2.).

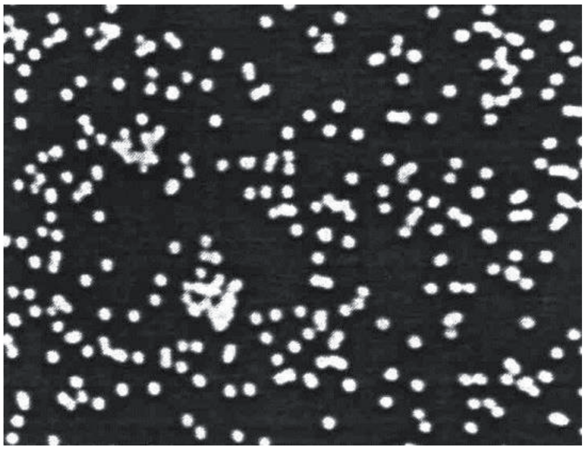
The metallographic data and examination of rubbing surfaces support the presence of a passivating hardphase lubricating film of the molybdenum disulphide, impeding the adhesive interaction of juvenile surfaces, some fracture nuclei becoming localized in the thin near-surface layers and annihilate when in grain boundary sliding thus eliminating damageability of any kind.

In the second place, a coating susceptibility to passivation is provided, under the given friction conditions, by the diffusion and hard phase tribochemical reactions of the components involving formation of superdispersed nanophases.

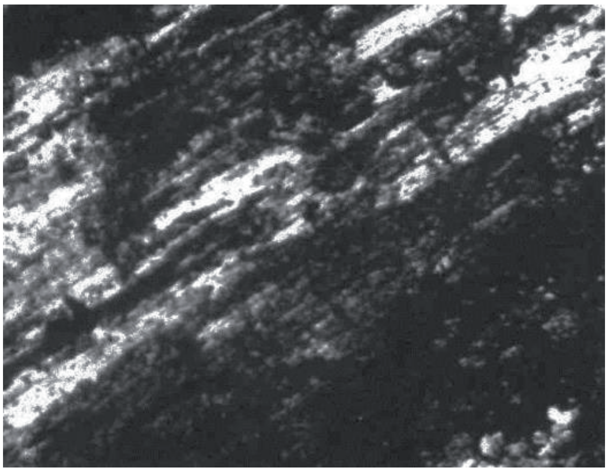
For the purpose of studying the surface layer with processes of activation running therein under friction, the electron diffraction analysis was applied. Fig. 3 presents the electron diffraction pattern of a rubbing surface of nanocomposite coatings with a change in fine structure and shows that the dispersion occurs with refinement of crystals in the suprasurface layer which is proved by a maximum of intensities available on the diffuse halos. From the diffraction theory it is known that diffusion halos are formed when the object under study has a superdispersed structure, the present textural maximums evidencing elements directionality of the superdispersed structure composed of friction-oriented crystals of an almost perfect structure and of about a few interatomic spacing sizes.



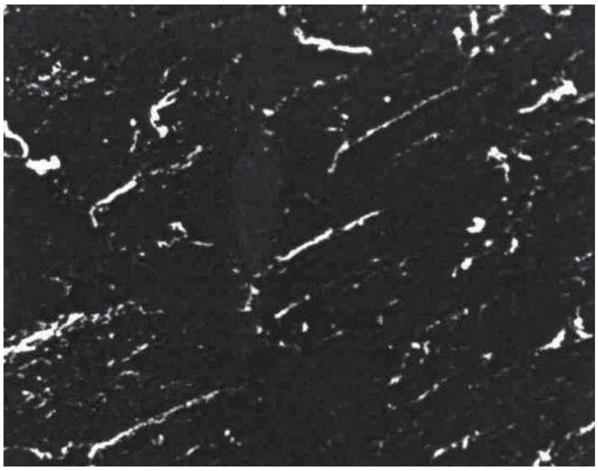
a



b



c



d

Fig. 2. Rubbing surface of Cr-Si-B-MoS_2 coating: a – the initial position; b – micro X-ray spectral distribution of MoS_2, x650; c – friction testing at V = 0.3 m/s, x320; d – friction testing at V =2.3 m/s, x320

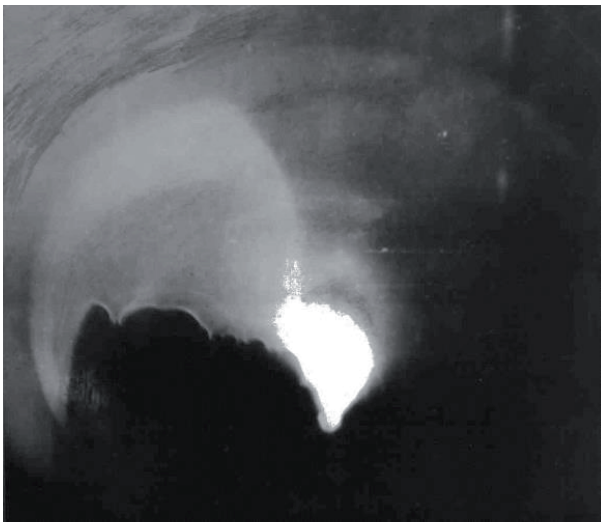


Fig. 3. Electron diffraction pattern of Cr-Si-B-MoS_2 coating rubbing surface tested at V =1.5 m/s

The above composition model does not only fit the experimental data when tested under friction, but is in agreement with the current notions about the character of a superdispersed crystalline solids state as well [6].

In studying the character and regularity of formation of a near-surface layer conducive to wear resistance, the layer has been found to be a MoS_2-based composite fine-dispersed quasistratified structure reinforced by Cr_5Si, $CrSi$, Cr_3Si, and $CrSi_2$ intermetallides; moreover, the molybdenum chalcogenide forms *CrS* sulphides through a tribochemical interaction with a deformed surface layer thus creating favourable conditions for substantial enhancement of wear resistance, and as established, increase of loading capacity.

The changed structure of the hardphase surface films determines the friction factor value as being 0.05–0.07 over the entire range of testing (Fig. 1, curve 1). Under the given conditions, as the authors believe, its value is not so much the function of a normal load as the function of tribophysical processes resulting from the additive load combination, sliding velocity, temperature, and a generalized vector of the friction profile (materials, environment, conditions, etc.). In this manner, a dry lubricant surface film or an active suprasurface layer does possess anti-wear properties in addition to anti-friction effect thus providing a high resistance of the *Cr-*

Si-B-MoS$_2$ coatings to wear under vacuum under the given friction conditions.

With the *Cr-Si-B* coatings where the molybdenum disulphide is absent (Fig. 1, curve 5), the behaviour of wear intensity and the dependence of the coefficient of friction on velocity vary appreciably.

For the purpose of examining the surface layer in which the processes of activation are running, the electron diffraction analysis with an ERM type apparatus (picture-taking for reflexes at U = 35 kV) was applied. The electron diffraction pattern (Fig. 4) with a change recorded in the thin structure shows that dispersion involving refinement of crystalline grains occurs in the surface layer. The thin-filmed object examined represents the superdispersed aligned structure of a thin surface layer which is 100–500 nm.

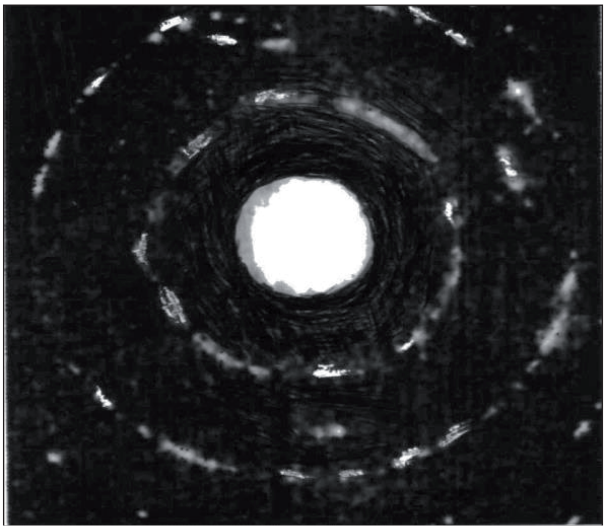


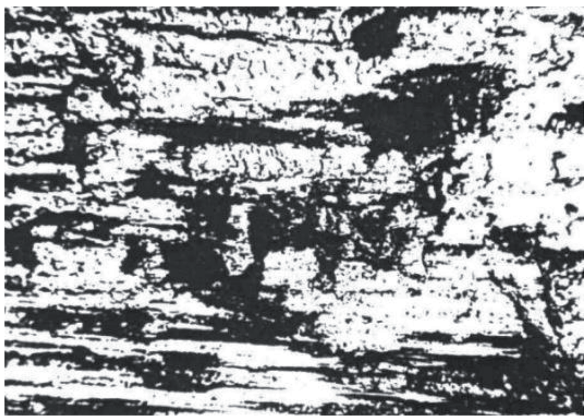
Fig. 4. Electron diffraction pattern of a Cr-Si-B coating frictional surface

It is to be noted that the *Cr-Si-B* coatings at sliding velocities under 0.9 m/s display minimal friction parameters. Wear resistance is provided here by the creation of a thin-filmed object dividing juvenile surfaces, which is the product of oxygen-free structures based on the metallic phases of the chemical elements incorporated into the coating and whose organization nature with an oxygen shortage involves phase transformations, in the authors' opinion. This occurs when the oxygen-free surface structures similar in mechanism of formation and properties to those of martensite phases are formed as a result of mechanical-thermal alloying and frictional hardening. Regarding the martensite mechanism and mechanical properties, the surface structures formed therewith under extreme temperature-time and loading conditions are different from those of the hardening martensite produced by a traditional heat treatment. So the martensite hardness upon heat treatment is ~7.5–9.5 GPa while the relevant values for the martensite structures on the frictional surfaces amount ~10.5–13.5 GPa.

With the testing velocities being over 1.0 m/s, the thermodynamic balance of a frictional system is broken and the properties of a hardphase surface film undergo irreversible changes due to destruction and disintegration of the surface martensite, which leads both to the loss of the protective thin-filmed object functions and to the loss of a screening ability. Under the given friction conditions, the growing seizure process appears as being the primary wearing mode for the MoS_2-free coatings. Fig. 5 shows the kinetics of the destruction of the *Cr-Si-B* coating surface layers as a function of test velocities.

a

b



c

Fig. 5. The rubbing surface of the Cr-Si-B coating tested at: a – 0.4 m/s; b – 0.6 m/s; c – 1.0 m/s (x320)

The coatings sprayed by the VK15 hard alloy powder show a high resistance to wear (Fig.1, curve 2). The VK15 coatings are known to be of a classic anti-friction material structure. The enhanced wear resistance of the hard-alloy coatings is due to either the nature of the components involved therein or to the structure. However, at the sliding velocities over 1.0 m/s the temperature, being a basic and drastic working parameter, starts exerting its influence.

Among the samples subject to diffusion alloying, the vanadium-plated surfaces prove to have minimal wear (Fig. 1, curve 3), which is due to formation of a working layer saturated with vanadium carbides characterized by high mechanical properties, by hardness and infusibility, particularly, [7], along with VC there being formed V_2C carbides having close-packed hexagonal crystalline lattice; furthermore, in the surface layer there occur compressive stresses also conducing to enhanced strength.

The wear behaviour of the steel samples hardened by thermodiffusion chromium-plating (Fig. 1, curve 4) is analogous to the general wear history of vanadium-plated steels. The raised wear values of the chromized samples are due to seizure tendency resulted from a rather low surface strength with friction in the vacuum [8].

The difficulties in obtaining and accumulating the methodically sound and statistically reliable tribotechnical research data are the major challenge to the development and implementation of coatings, being today a specific part of a common problem concerning the reliability growth and increased service life in aircraft building.

The needs of practical applications have their primary effect on the progress of the scientific application aspects. Being developed for application needs, the *Cr-Si-B-*MoS_2 detonation coatings studied displayed high tribotechnical characteristics over the entire range of tests to model the operation of a friction unit under rarefied air conditions. Here, as an agent to regulate wear and to provide a high anti-friction ability of the coatings in the vacuum, the dry lubricant is incorporated therein affecting the adaptation level through the structure, when in friction, due to the modified surface layers capable of blocking the destruction and shielding the inadmissible seizure processes.

In conclusion, it is worth noting that the development of the tribotechnical materials for coatings making use of the domestic mineral resources and their testing to define their optimal technoeconomic application conditions is an essential component of engineering and social advancements for both the science and the whole society.

Conclusions.

1. The appropriateness of techniques and algorithms to apply in the exploratory development under in-vacuum conditions of the *Cr-Si-B*-based heterogeneous coatings additionally incorporating the structurally free molybdenum disulfide (as an anti-friction component) used as a modified additive agent, has been established.

2. High resistance to wear for *Cr-Si-B-*MoS_2 coatings owing to the passivating hardphase lubricant film of the molybdenum disulfide that blocks the interaction of juvenile surfaces has been found. Here, some fracture nuclei, which are localized in near-surface layers are observed to annihilate when in grain-boundary gliding, thus blocking damageability of any kind over the given testing range.

3. While studying the character and regularities responsible for the coating tendency to passivation it has been observed that the realization of the latter is also due to the hardphase tribochemical and diffusion processes in the formation of MoS2-based quasilayered surface structures and fine-dispersed intermetallides from the components incorporated into the coating.

4. The protective thin-filmed surface structure has been found as assisting in the reduction of the adhesion constituent of frictional force, and its plastic deformation is by no means associated with appreciable losses of energy, rather it minimizes those. The character of dependency and values of a friction coefficient are at that in complete accord with a wear regularity being determined by the properties of the surface structures, while its stability is indicative of a high coating efficiency.

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Мета. Дослідження в умовах вакууму розроблених детонаційних покриттів системи *Cr-Si-B*, що додатково

містять в якості антифрикційного компонента добавки твердого мастила у вигляді диспергованого дисульфіду молібдену.

Методика. Для детонаційно-газового напилення використовували композиційні порошки, отримані методом механохімічного синтезу за допомогою лабораторного аттритора типу „ІЕЗ-1-10,5". Частинки твердого мастила, що відповідають фракціям 3–10 мкм, змішували мокрим способом з вихідними металевими нанопорошками. Товщина напиленого детонаційного шару після обробки складала 0,20–0,25 мм, шорсткість Ra = 0,63–0,32, міцність зчеплення з основою $\sigma_{шч}$ = 87,5 МПа. Дослідження поверхневої міцності покриттів при терті, їх схильність до схоплювання та ступінь трибоактивації оцінювалися за інтенсивністю зносу у вакуумі за розрідження $1{,}33 \cdot 10^{-5}$ Па. Характеристики тертя й зношування досліджуваних композиційних покриттів аналізувалися та порівнювалися з отриманими значеннями зносостійкості покриттів типу ВК15 і поверхневих шарів, отриманих у результаті термодифузійного легування бором, ванадієм і хромом.

При дослідженні поверхонь тертя використовували сучасні фізичні методи, включаючи рентгеноспектральний мікроаналіз і растрову електронну мікроскопію.

Результати. Отримані методом механохімічного синтезу композиційні порошки, що складаються з гомогенної суміші вихідних компонентів. Керуючи технологічним процесом отримання, вдалося забезпечити не тільки бажаний хімічний склад, але й отримати при напиленні задану структуру, оптимізуючу комплекс властивостей покриттів, що володіють високим опором зносу при навантаженні тертям у вакуумі.

Наукова новизна. Практично встановлено та теоретично обгрунтовано високий опір зносу розроблених нанокомпозиційних покриттів, що містять в якості антифрикційного компонента диспергований дисульфід молібдену. Виявлено вплив структури покриттів і складу поверхневих плівок на їх експлуатаційні характеристики.

Практична значимість. Отримані результати розширюють арсенал досягнень сучасного триботехнічного матеріалознавства та сприяють створенню конкурентоздатних виробів з високим рівнем експлуатаційної надійності.

Ключові слова: *детонаційні покриття, зносостійкість, поверхневий шар, структурна пристосованість, дисульфід молібдену*

Цель. Исследование в условиях вакуума разработанных детонационных покрытий системы *Cr-Si-B*, которые дополнительно содержат в качестве антифрикционного компонента добавки твердой смазки в виде диспергированного дисульфида молибдена.

Методика. Для детонационно-газового напыления использовали нанокомпозиционные порошки, полученные методом механохимического синтеза с помощью лабораторного аттритора типа „ИЭС-1-10,5". Частицы твердой смазки, соответствующие фракциям 3–10 мкм, смешивали мокрым способом с исходными металлическими нанопорошками. Толщина напыленного детонационного слоя после обработки составляла 0,20–0,25 мм, шероховатость R_a = 0,63–0,32, прочность сцепления с основой $\sigma_{сц}$ = 87,5 МПа. Исследование поверхностной прочности покрытий при трении, их склонность к схватыванию и степень трибоактивации оценивались по интенсивности износа в вакууме при разрежении $1{,}33 \cdot 10^{-5}$ Па. Характеристики трения и изнашивания исследуемых композиционных покрытий анализировались и сравнивались с полученными значениями износостойкости покрытий типа ВК15 и поверхностных слоев, полученных в результате термодиффузионного легирования бором, ванадием и хромом.

При исследовании поверхностей трения использовали современные физические методы, включая рентгеноспектральный микроанализ и растровую электронную микроскопию.

Результаты. Получены методом механохимического синтеза нанокомпозиционные порошки, состоящие из гомогенной смеси исходных компонентов. Управляя технологическим процессом получения, удалось обеспечить не только желаемый химический состав, но и получить при напылении заданную структуру, оптимизирующую комплекс свойств покрытий, обладающих высоким сопротивлением износу при нагружении трением в вакууме.

Научная новизна. Практически установлено и теоретически обосновано высокое сопротивление износу разработанных нанокомпозиционных покрытий, содержащих в качестве антифрикционного компонента диспергированный дисульфид молибдена. Выявлено влияние структуры покрытий и состава поверхностных пленок на их эксплуатационные характеристики.

Практическая значимость. Полученные результаты расширяют арсенал достижений современного триботехнического материаловедения и способствуют созданию конкурентоспособных изделий с высоким уровнем эксплуатационной надежности.

Ключевые слова: *детонационное покрытие, износостойкость, поверхностный слой, структурная приспосабливаемость, дисульфид молибдена*

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