# ADHESION AND PHYSICO-MECHANICAL CHARACTERISTICS OF COATINGS OF CHROMIUM CARBONITRIDE, GENERATED ON STEEL SUBSTRATES

# АДГЕЗИОННЫЕ И ФИЗИКО-МЕХАНИЧЕСКИЕ ХАРАКТЕРИСТИКИ ПОКРЫТИЙ КАРБОНИТРИДА ХРОМА, СФОРМИРОВАННЫХ НА СТАЛЬНЫХ СУБСТРАТАХ

Phd Chekan N.M.[1], Ass.prof, dr.Eng. Auchynnikau Y.V.[2], Phd Akula I.P.[1], Ass.prof. Phd Eisymont Y.I.[2], Pinchuk T.I.[3]
Physicotechnical Institute, National Academy of Sciences of the Republic of Belarus[1], Yanka Kupala State University of Grodno,Grodno, Belarus[2], Institute of Powder Metallurgy of the National Academy of Sciences of the Republic of Belarus[3]
e-mail: pec@bas-net.by,ovchin_1967@mail.ru

***Abstract.*** *In the present work, the adhesion and physico-mechanical characteristics of heat-resistant vacuum coatings formed on steel substrates are investigated. An increase in the values of adhesion and physico-mechanical parameters of coatings formed from multicomponent compounds is established. The tribotechnical characteristics of coatings based on chromium carbonitride have been studied.*
*KEYWORDS: adhesion, coating, morphology, friction, microhardness*

## 1. Introduction

Chrome coatings are widely used to create antifriction anti-adhesion layers for various functional purposes. Wide distribution found coatings on the basis of electrolytic chromium in the manufacture of various types of products of automotive and automotive tractors. In works [1-3] it was shown that the use of composite coatings based on chromium modified with ultradisperse clusters of synthetic carbon (UDD) is an effective direction of increasing the life of friction units of automobile shock absorbers. Such coatings have a higher hardness (by 23-40%), wear resistance (1.6-2.2 times) compared with base chromium and can be applied in one cycle without additional grinding and polishing of the parts. This allows to significantly reduce the thickness of the working layer (up to 5-10 microns) while maintaining the main performance characteristics. At the same time, when applying composite chromium coatings of small thickness, the role of microdefects caused by the presence of aggregates of the solid phase modifier (UDD) in the electrolyte solution increases substantially. Therefore, the corrosion resistance of modified UDD coatings decreases significantly with decreasing thickness, which significantly reduces the efficiency of their use in engineering. Coating with a thickness of more than 5-10 microns from the modified chromium is economically expedient, so it allows to significantly increase the wear resistance of the modified products, even despite the rather high cost of UDD (1, -1, 5 US dollars per carat of the modifier). In [4-5], it was proposed to apply the Foleoks fluorine-containing oligomers F-1, F-8 and F-14 to the working surface when creating electrolytic coatings, which provides not only a significant increase in the wear resistance of the interface, but also a corrosive durability of coatings. After 150 hours of soaking in salt fog at 600 °C, the test samples have no visible traces of corrosion damage, while the samples with a base coating after 48 hours of testing have a significant number of local corrosion sites. At the same time, the microhardness of the coating and its hydrophobicity increase substantially. The use of composite coatings will not only significantly increase the service life of shock absorbers, but also significantly reduce their energy intensity [4-6].

A promising area in the field of creating chrome coatings and compositions based on it is the use of vacuum technologies. One of the promising types of these coatings is chromium nitride (CrN), which is a new alternative in the field of protective high-temperature layers. Coatings of CrN, CrCN have good thermal stability, low deposition temperature, high wear resistance and corrosion resistance. The disadvantage is the lack of precise information for the formation of these coatings, which affects the porosity of the coating and, as a consequence, reduces the corrosion resistance and tribological properties. Further development of studies on the characteristics of vacuum coatings was the creation of two-layer systems Cr-CrN, Cr-CrCN. These coatings are characterized by increased wear resistance, low coefficient of friction and high microhardness in comparison with CrN coatings. Usually this system is obtained by magnetron sputtering. This method gives advantages in deposition rate and low content of impurities. In addition, this method allows the creation of thin films with different variations in the crystallographic structure and morphology of the structure [7]. Multilayer coatings of Cr-CrN, CrCN are formed by changing the deposition parameters of the coating, which makes it possible to obtain composite that are gradient in structure, that is, a layer close to the substrate exhibits increased crystallinity and the upper layers are amorphous [8-9]. One of the main parameters determining the physical and mechanical characteristics of surface layers, coatings, and films are surface energy. By surface energy is meant an excess of energy in the surface layer at the interface of two phases in comparison with energy in the volume of two phases [10].

According to established ideas, the surface layers of solids, whose size does not exceed the action of the radius of molecular forces, have a structure different from the structure of the bulk phase of the condensed body. In the structure of a solid body, boundary, transition layers are distinguished, which can have a significant effect on the values of the surface energy determined experimentally. One of the methods for determining the surface energy of solid substrates is to measure the contact angles of the polar and non-polar liquids wetting [11]. Based on the values of the contact angle, it is possible to calculate the value of the surface energy. In the scientific literature there are works showing the relationship between the value of surface energy and physical characteristics, so in [12] it is proposed to consider surface energy as an additional tool for providing in space the constancy of positioning, i.e. stationary state of the two contacting parts. This arrangement is recommended to receive with the help of such a phenomenon as setting effect. To create a certain energy state of the contacting parts, in which connections (bridging bridges) arise, it is proposed to use the technological process. Thus, the process of formation of the energy state of the surface layer of two (and more) parts with predetermined physico-mechanical properties is controlled [12].

The purpose of this work was to study the adhesion and physico-mechanical characteristics of chromium carbonitride coatings formed on steel substrates

**2. Research methodology.**

Adhesion characteristics were studied by the scratch analysis method. Standard equipment used for indenting uses a module for measuring scoring, research of wear and profilometry. A feedback system is used to control the applied load, the force acting on the sample, which does not depend on the topography of the surface. The pre-scan procedure allows you to measure the actual penetration depth for a scratch test to characterize the elastic recovery using the post-scan procedure [13]. Scratch testers are equipped with an easy-to-use software package that allows the user to perform a scratch test in a wide variety of test modes, including simple scratching, an extended scratch test (with pre-scanning and post scan), simple scratch mapping, scratch mapping with different modes, defined by the user.

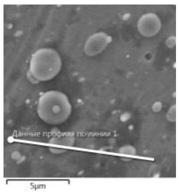
Morphological features of coatings formed on the basis of refractory metals after determining the adhesion characteristics were studied by scanning electron microscopy.

Scanning electron microscope is a device with great possibilities, which allow to characterize heterogeneous materials and surfaces at such a high level. In the scanning electron microscope (SEM), the surface under investigation is irradiated by a thin-focused electron beam, which can either rest or unfold in a raster over the surface of the sample. As a result of the interaction, secondary electrons, reflected electrons, characteristic X-ray radiation, Auger electrons and photons of different energies arise. They are produced in certain volumes (generation areas within the sample) and are used to measure many of its characteristics (composition, surface topography, crystallographic orientation, etc.).

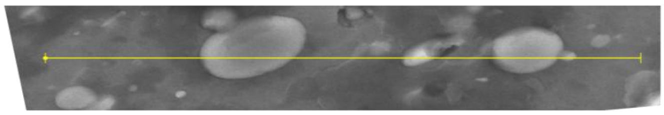
The scanning electron microscope is one of the most versatile instruments for studying and analyzing the microstructural characteristics of solids. The main reason for the wide use of SEM is the high resolution in the study of massive objects, reaching today 10-15 nm (100-150 Å). One of the important features of SEM is that it allows you to observe the topography of a solid with a resolution and depth of field that is significantly higher than the corresponding parameters of light microscopes. Information in the study of the surface is transferred by reflected secondary electrons and other simulating signals. The thickness of the sample is not particularly important, as is the case in transmission electron microscopy, where information is transferred by transmitted electrons that penetrate the sample by no more than 0.1 μm. Dielectric materials are particularly difficult to investigate in SEM. When an electron probe hits a dielectric, its absorbed electrons accumulate on its surface because of the absence of a charge flowing to the ground. The accumulation of electrons leads to the appearance of charged regions on the surface of the sample, which during subsequent scanning can irregularly deflect the primary beam, leading to serious distortions. In addition, the presence of a surface charge greatly changes the secondary electron emission. From the charging effect, you can get rid of the conductive coating on the surface of the sample. The criterion for choosing the material for deposition is usually the production of the maximum number of secondary electrons. Based on the consideration of the physical aspects of secondary electron emission, it was concluded that a 15-nm gold coating should give optimal secondary electron emission. In the "Sputter coater" installation, the conductive layer is created by cathode sputtering of gold. The prepared samples are placed in a scanning electron microscope and imaged at different magnifications. Acceleration voltage is one of the main parameters of shooting in EMS. Samples were sampled at an accelerating voltage of 20 kV. The morphology of the samples was studied using a high-resolution scanning electron microscope "Mira" from Tescan (Czech Republic). The microscope is equipped with secondary electron (SE) detectors and back-reflected electrons (BSE), which allow for the study of samples in two modes. When shooting samples in the secondary electron (SE) mode, the contrast in the image is created by reflecting the electron beam from the sample surface. In the case of an inverse-reflected electron (BSE) detector, the contrast in the picture is created by the atomic number of the sample elements. The type of detector used, the magnification and other shooting parameters are indicated in the information line at the bottom of each frame. The elemental composition was investigated using an INCA 350 microspectral analyzer from Oxford Instruments (UK). Defined elements from B to U. The minimum detection limit of an element is 0.5%. The error of the method is 5-15 relative percent.

**3. Research results.**

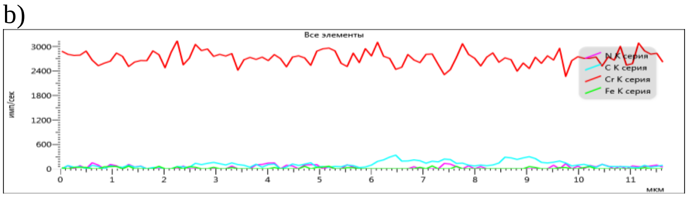
According to the data presented in Fig. 1a, chromium carbonitride coatings formed by plasma-chemical methods are composite coatings. There is a matrix in which globular formations with increased nitrogen concentration and a reduced carbon concentration are included with respect to the content of these chemical elements in the coating matrix.



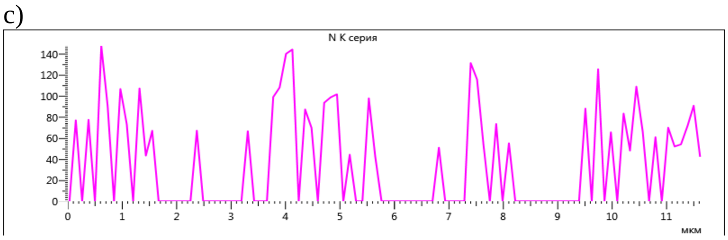
a)



b)

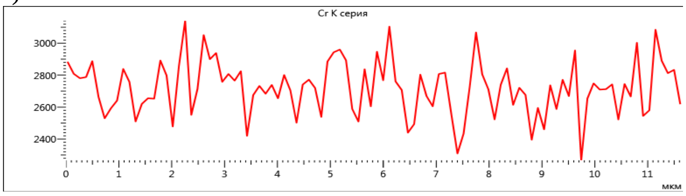



c)

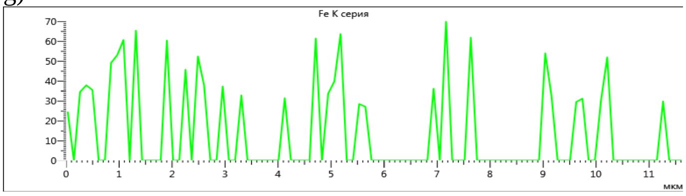



d)


f)




g)

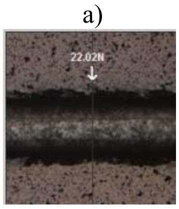



h)

***Figure 1*** *Dependence of the distribution of chemical elements in the coatings of chromium carbonitride: a-coating of chromium carbonitride; b-surface area of the coating for which the content of the chemical elements was measured, c-the total distribution of the chemical elements in the CrCN coating, d - the nitrogen distribution in the CrCN coating, f - the carbon distribution in the CrCN coating, g - the chromium distribution in the CrCN coating, h -iron in the coating of CrCN.*

The presence of iron in CrCN coatings is due to the fact that the thickness of the coating is on the order of 2-5 µm and does not completely shield the steel substrate. The structure and chemical composition of the coating have a significant effect on the adhesion and physico-mechanical characteristics of the coatings.

a)




b)

***Figure 2*** *- Type of scratch on the CrCN coating obtained by the scratch analysis method. a - a shape of a scratch, b - a fragment of a scratch where there is a full peeling of a covering from a substrate*

Coatings of CrCN begin to peel off at values that are in the region of 12 - 13 N. The complete peeling of the coating from the substrate is observed at values of ~ 23 N. These values are 1.8-2 times higher than the adhesion characteristics of vacuum chrome coatings. According to the data of [14-15], the effect of the load on the coefficient of friction depends on the type of contact interaction - elastic or plastic. In the general case, the function f (N) is nonmonotonic and is determined by a quadratic function (Figure 2). It is believed that the position of the minimum of this curve depends on the ratio of the molecular and mechanical components. In the case where the ratio of the coefficient of friction responsible for the molecular component to the friction coefficient responsible for the mechanical component is greater than unity, the minimum of the curve f (N) is shifted to the region of smaller values of N. In the region of small loads, the plastic contact [14-15] f is determined mainly by the molecular component of friction.

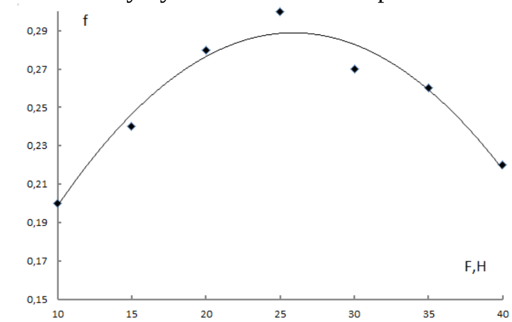



***Figure 3*** *- Dependence of the friction coefficient of the pair "CrCN-ShKh 15" from the load*

The decrease in the coefficient of friction with increasing N is due to the fact that N increases faster than the increase in the area of the actual contact caused by this increase, and, as a consequence of the frictional force. That is, an increase in the load by n times entails an increase in the number of frictional bonds and their dimensions, and, consequently, an increase in the total shear resistance by a smaller number of times. After reaching the f minimum a plastic contact is realized in the main. The position of the minimum of the curve depends on the ratio of the molecular and mechanical components. In the course of tribological tests of diamond-like coatings, the reverse effect is observed. At low loads, the friction coefficient of the CrCN coating over steel increases. Then, under loads in the region of 25-30 N, an extremum point is observed. Further increase in the values of the normal load is accompanied by a significant decrease in the coefficient of friction. Thus, the behavior of the tribotechnical characteristics of chrome coatings differ from the classical views when the normal load changes.

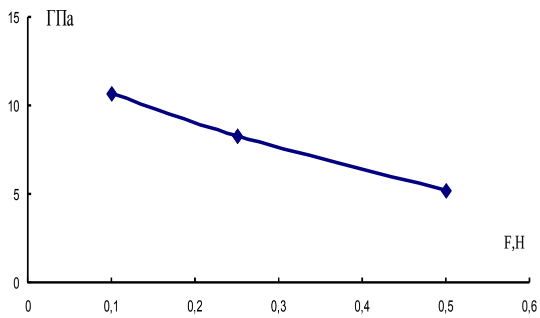



***Figure 4*** *- Dependence of the change in the microhardness of the CrCN coating formed on 40X steel from the applied load on the pyramid*

This dependence of the friction coefficient on the load for these coatings is explained by the fact that in the structure of CrCN there is a carbon with a high concentration in comparison with the base chrome coating. The increase in load promotes the diffusion of carbon into the friction zone and the formation of a separation film with low shear stress values, which is expressed by a decrease in the friction coefficient with increasing load. Determination of the microhardness of CrCN coatings by the Vickers method leads monotonic decrease in values with increasing load on the indenter. The microhardness parameters of the coatings are reduced three times with the load increasing from 0.1 to 0.5 N. Thus, at loads of 0.25-0.5 N, the coating is impressed into the material of the steel substrate. However, carrying out measurements with these loads makes it possible to establish a modifying effect of high-hard coatings, since the microhardness of the steel substrate is no more than 2-3 GPa.

**4. Conclusion.**

Based on the obtained data, it is established that the microhardness values of steel substrates are in the range from 2,400 to 3,000 MPa and do not depend on the load on the diamond pyramid. The microhardness values of chromium carbonitride coatings decrease monotonically with increasing load on the diamond pyramid. This effect is due to the indentation of the coating in the structure of the steel substrate material. The adhesion characteristics of CrCN coatings are 1.8-2 times higher than the adhesive characteristics of vacuum chrome ones. The tribological characteristics of CrCN coatings are investigated. It is shown that diffusion of carbon into the friction zone and formation of a separation film with low shear stresses is possible, which is expressed by a decrease in the friction coefficient with increasing load.

**Bibliography:**

1. Novye materialy i tekhnologii, primeniaemye pri proizvodstve kardannykh peredach [Tekst]/ V. I. Kravchenko, V. A. Struk, G. A. Kostiukovich, E. V. Ovchinnikov // Vestnik Belorussko-Rossiiskogo universiteta. – 2006. – № 4 (13). – S. 91-99.

2. Kompozitsionnye pokrytiia na osnove elektroliticheskogo khroma, modifitsirovannogo ul'tradispersnym uglerodom / S.D. Leshchik, A.I. Mamonchik, V.A. Struk, E.V. Ovchinnikov // Problemy i puti realizatsii nauchno-tekhnicheskogo potentsiala voenno-promyshlennogo kompleksa: Tezisy dokladov mezhdunarodnoi konferentsii, Kiev, 15-17 marta 2000 g. Kiev, 2000. – S. 98 - 99.3 .

3. Funktsional'nye nanokompozitsionnye materialy dlia konstruktsii kardan-nykh peredach [Tekst] / V. I. Kravchenko, G. A. Kostiukovich, V. A. Struk, E. V. Ovchinnikov // Trans and motoauto'04: Proceedings of International conference, Plovdiv, 14 – 17 oct. 2004. / Scientific-technical union of mechanical engineering of Bulgaria; editor: D. Damianov. – Sofia, 2004. – Vol. 2. – rr. 66-67.

4. Metallopolimernye pokrytiia na osnove modifitsirovannogo khroma i ftorsoderzhashchikh oligomerov / A.I. Mamonchik, E.V. Ovchinnikov, S.D. Leshchik, A.F. Sen'ko // Materialy. Tekhnologii. Instrumenty. - 1998. – T.3, №2. – S.101

5. Tribotekhnicheskie kharakteristiki kompozitsionnykh mnogosloinykh pokrytii [Tekst] / E. V. Ovchinnikov, S. D. Leshchik, V. A. Struk, O. V. Kholodilov, D. I. Fedorov // Trenie i iznos. – 2000. – T. 21, № 2. – C. 147-155.

6. Ovchinnikov, E. V. Tonkie plenki ftorsoderzhashchikh oligomerov: osnovy sinteza, svoistva i primenenie [Tekst] / E. V. Ovchinnikov, V. A. Struk, V. A. Gubanov. – Grodno: GGAU, 2007. – 326 s.

7. Kelly PJ, Arnell RD (2000)Magnetron sputtering: a review of recent developments and applications. Vacuum 56:159–172

8. Majzoobi GH, Hojjati R, NematianM, Zalnejad E, Ahmadkhani AR, Hanifepoor E (2010) A new device for fretting fatigue testing. Trans Indian Inst Metals 63(2–3):493–497

9. Chunyan Y, Linhai T, Yinghui W, Shebin W, Tianbao L, Bingshe X (2009) The effect of substrate bias voltages on impact resistance of CrAlN coatings deposited by modified ion beam enhanced magnetron sputtering. Appl Surf Sci 255:4033–4038

10. .Khimicheskii entsiklopedicheskii slovar'. - Pod red. Knuniants I.L. - M.: Sovetstkaia entsiklopediia, 1983. – s.793.

11. Akhmatov A.S. Molekuliarnaia fizika granichnogo treniia. – M.: «Fizmatgiz», 1963, 472 s.

12. Musokhranov M. V., Antoniuk F. I. , Kalmykov V. V. Poverkhnostnaia energiia i protsess skhvatyvaniia kontaktiruiushchikh poverkhnostei Nauka i Obrazovanie. MGTU im. N.E. Baumana. Elektron. zhurn. 2014. № 11. S. 45–51.

13. 1. CSM INSTRUMENTS. Tekhnicheskoe opisanie. Mikro Skretch Tester (MST 2) [Elektronnyi resurs] / OOO «Nienshants-Saintifik». – Rezhim dostupa: http://lab-nnz.ru/wp-content/uploads/02-MST2_Technical-Features_2011-RUS.pdf. – Data dostupa: 29.11.2016.

14. Tribotekhnicheskii mekhanizm deistviia epilamov pri trenii. 2. Tribotekhnicheskie kharakteristiki epilamirovannykh materialov / I.I. Garbar [i dr.] // Trenie i iznos. − 1990. − T. 11. − №6. − S. 987-996.

15. Poplevich, V.I. Zashchitnaia effektivnost' ftorirovannykh karbonovykh kislot / V.I. Poplevich // Khimiia i tekhnologiia topliv i masel. - 1990.- №8. – S. 22-23.