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A STUDY OF AN EFFECT OF THE PARAMETERS OF NIOBIUM-BASED ION CLEANING OF A SURFACE ON ITS STRUCTURE AND PROPERTIES

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Проведено дослідження впливу потенціалу, поданого на підкладку, і зміни відстані «підкладка – катод» на процеси осадження, розпилення, а також механічні характеристики. Встановлено, що присутність аргону у процесі іонного бомбардування призводить до збільшення швидкості розпилення, а наявність активного газу азоту призводить до зменшення швидкості осадження. Це пов'язано з формуванням нітридів на поверхні

Ключові слова: вакуумно-дугове випаровування, потенціал зсуву, мікротвердість, імплантація, перемішування, розпилення, підкладка

Проведено исследование влияния потенциала, поданного на подложку, и изменения расстояния «подложка – катод» на процессы осаждения, распыления, а также механические характеристики. Установлено, что присутствие аргона в процессе ионной бомбардировки приводит к увеличению скорости распыления, а присутствие активного газа азота приводит к уменьшению скорости осаждения. Это связано с формированием нитридов на поверхности

Ключевые слова: вакуумно-дуговое испарение, потенциал смещения, микротвердость, имплантация, перемешивание, распыление, подложка

1. Introduction

Nowadays, a vacuum arc method is widely used for applying wear-resistant coatings based on nitrides of refractory metals, in particular titanium [1], zirconium [2], chromium [3, 4], molybdenum [5, 6], as well as multi-element alloys with them [7, 8]. These coatings have a high heat of forming the implementation phases and, consequently, a strong force of the covalent bonding. However, there is virtually no information on the materials of coatings with a strong metallic bond, such as niobium.

Quite often in practice, when large size products are sputtered for coating in a vacuum chamber, there happen gassing from the sides and a possible opening of pores in the metal, which results in a pressure spike in the chamber. These gases are mostly nitrogen and oxygen, which react with ionized niobium to form compounds; consequently, instead of cleaning and activating the workpiece surface, there occurs sedimentation of the coating. Such a coating does not have any good diffusing connection with the hardened piece, so the subsequent deposition of the protective coating will only lead to delamination. Therefore, it is very important to know the parameters of sputtering on the surface of products under different conditions of using reactive gases. This information allows suggesting a method with improved conditions of applying such coatings.

Thus, the relevance of the study lies in the scientific novelty of developing a technology of ionic sputtering in the plasma with heavy ions of Nb. This technology can be practically used in the preparation of steel surfaces with low roughness and high mechanical properties.

2. Literature review and problem statement

The vacuum arc coating technology has been successfully used to increase the resistance of machine parts and tools by increasing anti-corrosion, anti-friction and strength properties [9, 10]. To achieve high mechanical properties of a protective coating prior to applying such a coating to a product, it is necessary to create a diffusion layer to improve adhesion of the coating to the substrate [11].

It is known that bombardment with ions of a vaporizable material at a negative displacement potential (U_b) of about –1000 V and a subsequent application of a wear-resistant coating provide mutual penetration of the metal atoms of the coating and the substrate. This produces the desired diffusion layer with high adhesion bonding [12].

To create a diffusion layer, it is necessary to produce ion bombardment (purification) in high vacuum (about 0.001 Pa) to ensure a sputtering of the surface layers that contain various oxides and other contaminants which may impede the diffusion of the atoms of the vaporizable material into the substrate [13, 14]. There simultaneously happens an intensive heating of the surface layers, since the kinetic energy of the bombarding ions is mostly converted into heat [15]. These layers have abnormally low thermal conductivity, so their temperature can be several times higher than the temperature of the substrate itself [16], which in turn intensifies the diffusion processes [17, 18]. However, in case of the presence of gases in the vacuum chamber, the gasses (nitrogen, oxygen, etc.) can create a compound with the vaporizable metal, and these compounds can be deposited on the surface of the substrate, limiting the diffusion processes [19]. The actual processing conditions involve large loads of products in a vacuum chamber. Besides, almost always there is an intention to reduce the time of the production processes. Therefore, the process of cleaning the surface of a product in practice begins at higher pressures in the chamber, which often leads to delamination of the coatings [20].

3. The purpose and objectives of the study

The aim of the study is to determine the effect of the value of U_b (substrate potential) and the pressures of various gases in a vacuum chamber on the substrate sputtering processes under bombardment with ions of niobium. It is an important goal of research, both for the scientific bases of plasma physics and for industrial use.

The goal is achieved by doing the following tasks:

– to choose the most efficient modes of cleaning the samples' surfaces prior to coating them by means of bombarding with niobium ions;

– to determine the effect of the presence of argon and reactive gases (nitrogen) in the process of ion bombardment on the sputtering rate.

4. The procedure for preparing and studying the samples

The experiments were performed on samples obtained by the vacuum-arc method in the modernized vacuum chamber Bulat-6 (Ukraine) [21]. The cathode material was niobium Nb1. The coatings were applied to the surface of the samples such as 18×18×3 mm of stainless steel 12X18H9T that had been prepared by the standard methods of grinding and polishing. After polishing and washing the samples in an ultrasonic bath with an alkaline solution and wiping with calico soaked in Nefras C2 80/120, they were weighed on the analytical scales VLR-200. These scales were also used to weigh the samples after the experiments.

The distance from the evaporator (niobium) to the substrate was 300 mm or 485 mm. The arc current in the evaporators was 130 A, and the chamber pressure was varied from 0.002 Pa to 0.66 Pa by admitting argon, nitrogen or their mixtures in various proportions. In the experiments, the substrate was supplied with U_b in a range of –50...–1300 V. The bombardment time in each experiment was 10 minutes. The temperature of the substrate, as measured by the thermocouple chromel-alumel, was 150....550 °C. The surface morphology was investigated on the metallographic microscope XDS-3.

Microhardness was measured on the microhardness tester PMT-3, with a load of 10 g and 50 g, taking the average by the results of ten measurements.

5. The influence of the modes of bombardment with Nb ions on the processes of sputtering and depositing

Fig. 1 shows the results of changes in the volume weights in the cases of the coating deposition and the substrate sputtering after the niobium ion bombardment. When the values were positive, the calculation was based on the weight of niobium, and when the values were negative, the calculation was based on the weight of the stainless steel. It should be noted that at a U_b of –900 and –1300 V, the substrate temperature increased to 550 °C and 600 °C, respectively.

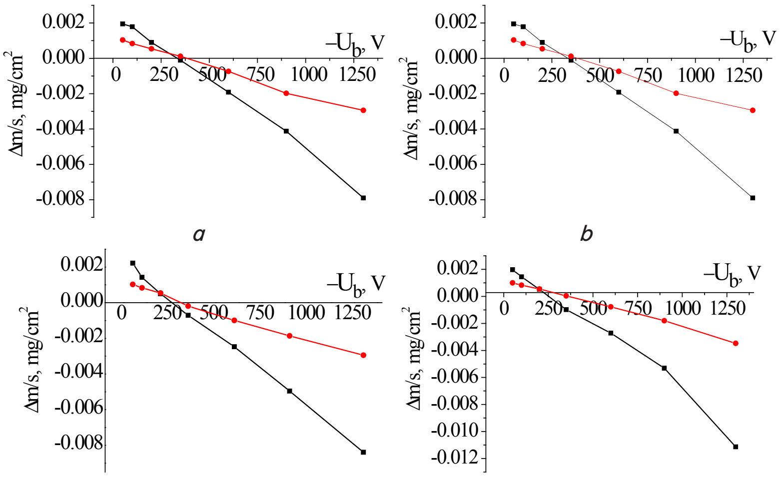


Fig. 1. Graphs of changes in the specific weight depending on the U_b when being bombarded with ions of niobium at various pressures of argon and distances to the samples: ■ – H=300 mm, ● – H=485 mm; *a* – P=0.002 Pa, *b* – P_{Ar}=0.04 Pa, *c* – P_{Ar}=0.09 Pa, and *d* – P_{Ar}=0.66 Pa

Of particular interest is the effect of impurity gases on the amount of sputtering the material. Fig. 1 shows the effect of the inert argon gas pressure on the rate of sputtering on the surface of the samples.

As can be seen from Fig. 1, *a*, when in a high vacuum the U_b is from –50 V to –350 V, the niobium coating is deposed, and its thickness decreases as the U_b increases as the result of sputtering. When U_b=–350 V, there is an equilibrium between the processes of sputtering and depositing, but with a further increase of the U_b, there prevail the sputtering processes. A significant effect on the rate of sputtering across the surface is produced by the distance from the samples to the cathode: when the distance decreases, the rate of sputtering increases. When argon pressure in the vacuum chamber increases, it significantly increases the sputtering rate on the samples within the range of all pressure values. And the equilibrium point "sputtering-depositing" (Fig. 1, *c, d*) is shifted to U_b=–250 V at a distance of 300 mm.

The increase in the sputtering rate at the increasing argon pressure in the chamber is associated with a significant increase in the concentration of niobium ions due to the intensive interaction of the plasma with the gas, which increases the intensity of niobium sputtering and diffusion into the substrate material.

For a fuller understanding of the nature of sputtering the substrate material, Fig. 2 shows a graph of the dependence of the sputtering magnitude on the U_b on the substrate under various pressures of argon in the chamber.

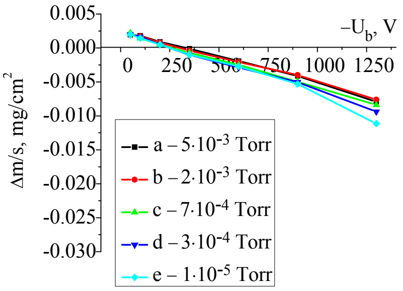


Fig. 2. A graph of changes in the specific weight depending on the U_b when being bombarded with ions of niobium at a distance of 300 mm from the cathode under the following argon pressures P_{Ar}: *a* – 0.66 Pa, *b* – 0.267 Pa, *c* – 0.09 Pa, *d* – 0.04 Pa and *e* – 0.002 Pa

It is noticeable that the critical value of the U_b for the transition from the sputtering process to the depositing process is U_b=–350 V. When the P_N value increases, there appears a tendency to a decline in the critical value of the U_b.

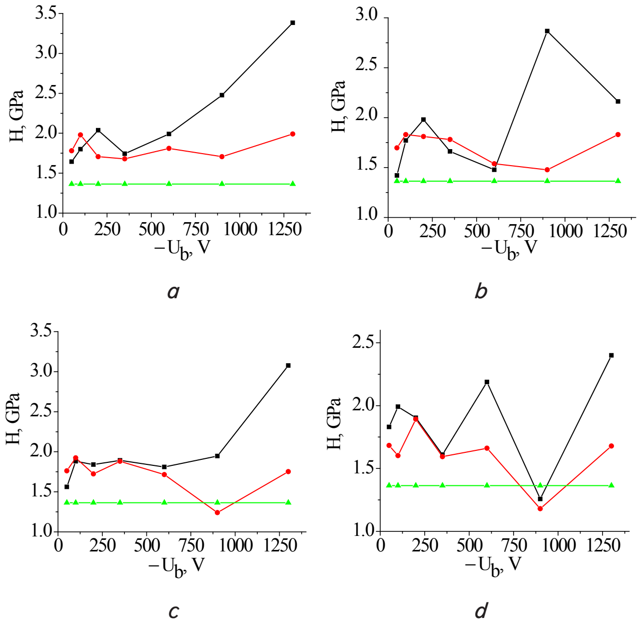
6. The influence of a potential displacement under the plasma processing on the mechanical properties and surface preparation of steel 12X18H9T

The use of the argon medium for bombarding steel with niobium ions increases the microhardness (Fig. 3).

It is necessary to take into account that bombardment with metal ions leads not only to sputtering on a sample surface but also to deposition followed by diffusion. Such sputtering and depositing on the surface of a sample increase the microhardness of the sample surface due to the formation of a solid solution (Fig. 3).

From the graphs of the microhardness dependence (Fig. 3) on the U_b, there appears to be an increase in the microhardness at all pressures of argon. The highest degree of microhardness arises at the maximum intensity of the surface sputtering when U_b=–1,300 V. This is due to the diffusion of niobium in the substrate and the creation of a saturated layer.

For a sample at a distance of 485 mm, the microhardness increases from the baseline to 1.8...2.0 GPa. However, it should be taken into account that the thickness of the coating is relatively small, and when the microhardness is measured at a load of 50 grams, it becomes pressed through. The most significant increase in the microhardness occurs in the process of sputtering on the surface of a sample at a high value of U_b=–1,300 V at a distance of 300 mm (Fig. 3), which is associated with the diffusion of niobium deep into steel.



a *b*

c *d*

Fig. 3. Graphs of changes in the substrate microhardness depending on the U_b after the bombardment with niobium ions at various pressures of argon located at various distances from the cathode to the samples: ■ – H=300 mm, ● – H=485 mm, and ▲ – the original; *a* – P=0.002 Pa, *b* – P=0.04 Pa, *c* – P=0.09 Pa and *d* – P=0.66 Pa

However, in the presence of nitrogen in the vacuum chamber, an increased pressure produces a displacement so that the equilibrium between sputtering and depositing is shifted towards a higher U_b (from a value of about –400 V at a P_N=0.02 Pa to –500 V at a P_N=0.08 Pa) (Fig. 4).

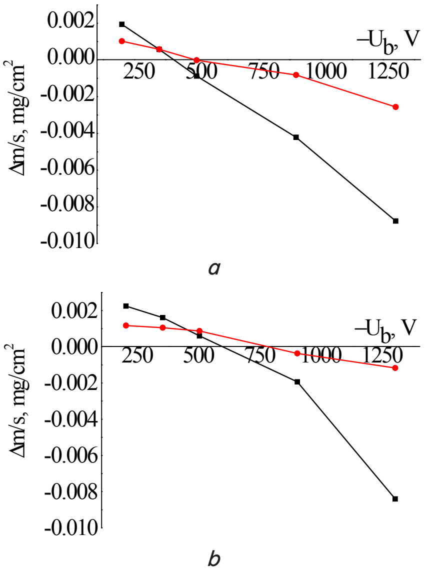


Fig. 4. Graphs of changes in the specific weight depending on the U_b when being bombarded with ions of niobium at various distances to the samples: ■ – H=300 mm and ● – H=485 mm; *a* – P_N=0.02 Pa and *b* – P_N=0.08 Pa

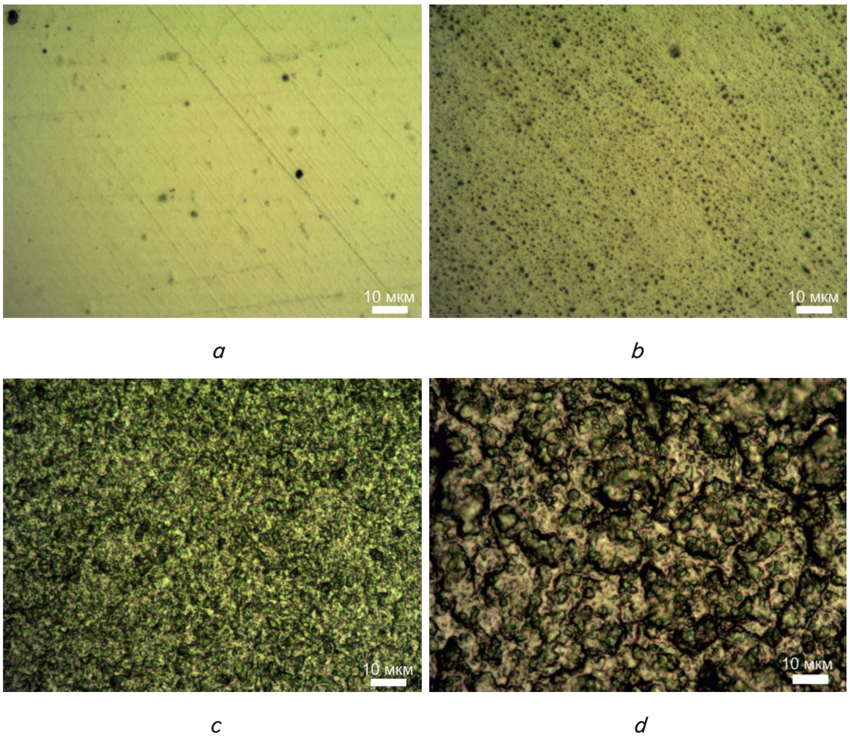
It can be noticed that the balance point between the sputtering and sputtering shifts (respectively, to –400 V and –500 V), depending on the distance of 300 mm and 485 mm (Fig. 4, *a*). A subsequent increase in the U_b also cleans the surface.

By increasing the nitrogen pressure in the vacuum chamber to P=0.08 Pa (Fig. 4, *b*), there is even a greater shift of the equilibrium point between the sputtering and sputtering. Thus, for the sample at a distance of 300 mm, the equilibrium point is –600 V, and the sample at a distance of 485 mm has an equilibrium point even at the level of –800 V.

The increased microhardness of the samples after adding nitrogen to the chamber is connected with the formation of niobium nitride on the substrate of the solid coating (Fig. 5).

The nitride phase creation leads to an increased microhardness of up to 2.2 GPa at small U_b=–200...–350 V, which is associated with the NbN coating deposition.

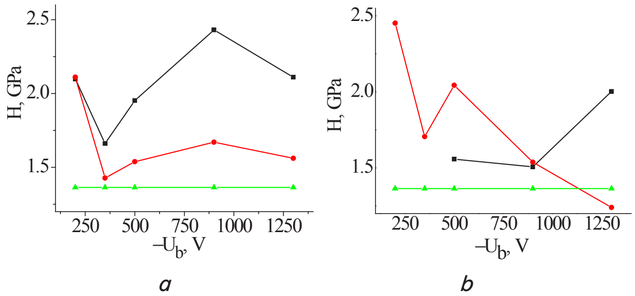
Fig. 6 shows photographs of the samples' surfaces where it is obvious that an increase in the U_b increases the sputtering intensity. At a small U_b, there is a deposition of the niobium-based coating (Fig. 6, *a*).



a *b*

c *d*

Fig. 6. Photos of the substrate surfaces after the bombardment with niobium ions at an argon pressure of 0.66 Pa under the following U_b: *a* – –200 V; *b* – –250 V, *c* – –900 V; *d* – –1,300 V



a *b*

Fig. 5. Graphs of changes in the substrate microhardness depending on the U_b after the bombardment with niobium ions at various distances to the samples: ■ – H=300 mm, ● – H=485 mm and ▲ – the original; *a* – P_N=0.02 Pa and *b* – P_N=0.08 Pa

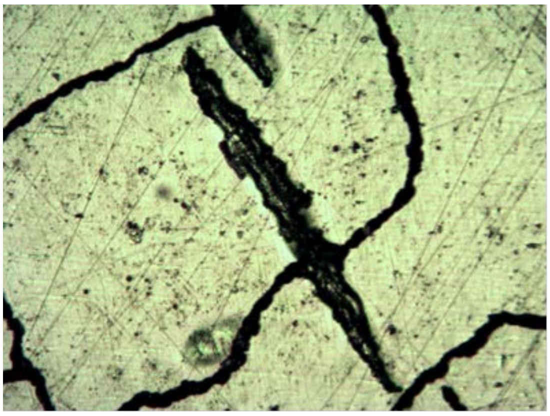


Fig. 7. A photo of the surface substrate after the bombardment with niobium ions with a thin coating layer of NbN that was created at a nitrogen pressure of 0.08 Pa and under U_b=–200 V

By increasing the U_b to –250 V and –350 V (depending on the distance from the sample to the cathode: 300 mm and 485 mm, respectively), there occurs its sputtering on the surface, as shown in Fig. 6, *b*.

At a further increase of the U_b in the substrate up to – 900 V, there is a significant change in its surface topography (Fig. 6, *c*).

The most efficient surface preparation takes place for the samples that have been treated at U_b=–1,300 V (Fig. 6, *d*).

Fig. 7 shows a coating that was created at a nitrogen pressure of 0.08 Pa and under U_b=–200 V.

The coating that was received at the lowest pressure is brittle, which is manifested by its spontaneous cracking.

7. Discussion of the results on the identified regularities as well as the physical and technological reasons of their existence

The study has determined that the cleaning of the surface with niobium ions takes place in a high vacuum at 0.002 Pa under U_b=–450...–700 V or more, but the most high-quality surface cleaning with niobium ions is carried out at a high value of U_b=–1300 V. The presence of argon in the ion bombardment increases the sputtering rate in a direct proportion to its pressure, and the presence of reactive gases (nitrogen) decreases the sputtering rate and increases the U_b. This is due to the fact that the presence of nitrogen in the chamber results in two competing processes: on the one hand, the supply of nitrogen (as well as argon) results in an increase of niobium ion concentration in the plasma volume and intensifies the ion bombardment of the surface. On the other hand, there appear niobium nitrides on the substrate surface, for sputtering which it is required to have a high energy of ions. As a result, there is a predominant influence of the mechanism of forming the nitrides, and the U_b, corresponding to the equilibrium process of "sputtering-depositing" is shifted towards higher values. A significant increase in the substrate surface hardness after cleaning with the Nb ion bombardment apparently happens due to a large diffusion saturation of the surface with Nb ions.

The findings are of interest because the cleaning technology of surface preparation is the key to ensuring adhesive strength of any vacuum plasma coatings. Undoubtedly, this study is far from complete; it requires additional research. It is planned to undertake further microscopic and structural-phase tests to obtain a complete and unambiguous picture of the process of ion cleaning.

8. Conclusions

1. It has been determined that the cleaning process produces a diffusion saturation of steel with niobium, which leads to an increase in its hardness and resistance to crack formation. In this article, an optimal cleaning mode is suggested at the following parameters: the distance from the cathode to the substrate should be 300 mm, with $U_b=-1300$ V and $P_{Ar}=0.002$ Pa.

2. It has been found that the presence of argon in the ion bombardment process increases the sputtering rate at an increased pressure, and the presence of reactive gases (nitrogen) leads to a decrease in the sputtering rate due to the formation of niobium nitride on the surface.

References

1. Sobol', O. Physical characteristics, structure and stress state of vacuum-arc TiN coating, deposition on the substrate when applying high-voltage pulse during the deposition [Text] / O. Sobol', A. Andreev, S. Grigoriev, V. Gorban', S. Volosova, S. Aleshin, V. Stolbovoy // Problems of Atomic Science and Technology. – 2011. – Issue 4. – P. 174–177.
2. Beresnev, V. Thermal stability of the phase composition, structure, and stressed state of ion-plasma condensates in the Zr-Ti-Si-N system [Text] / V. M. Beresnev, O. V. Sobol', A. D. Pogrebnjak, P. V. Turbin, S. V. Litovchenko // Technical Physics. – 2010. – Vol. 55, Issue 6. – P. 871–873. doi: 10.1134/s1063784210060216
3. Ulrich, S. Correlation between constitution, properties and machining performance of TiN/ZrN multilayers [Text] / S. Ulrich, C. Ziebert, M. Stuber, E. Nold, H. Holleck, M. Goken et. al. // Surface and Coatings Technology. – 2004. – Vol. 188-189. – P. 331–337. doi: 10.1016/j.surfcoat.2004.08.056
4. Xu, X. Effect of modulation structure on the growth behavior and mechanical properties of TiN/ZrN multilayers [Text] / X. M. Xu, J. Wang, J. An, Y. Zhao, Q. Y. Zhang // Surface and Coatings Technology. – 2007. – Vol. 201, Issue 9-11. – P. 5582–5586. doi: 10.1016/j.surfcoat.2006.07.132
5. Koshy, R. A. Synthesis and characterization of CrN/Mo2N multulayers and phases of Molybdenum nitride [Text] / R. A. Koshy, M. E. Graham, L. D. Marks // Surface and Coatings Technology. – 2007. – Vol. 202, Issue 4-7. – P. 1123–1128. doi: 10.1016/j.surfcoat.2007.07.090
6. Kazmanli, M. K. Effect of nitrogen pressure, bias voltage and substrate temperature on the phase structure of Mo-N coatings produced by cathodic arc PVD [Text] / M. K. Kazmanli, M. Urgen, A. F. Cakir // Surface and Coatings Technology. – 2003. – Vol. 167, Issue 1. – P. 77–82. doi: 10.1016/s0257-8972(02)00866-6
7. Pogrebnyak, A. Features of the structural state and mechanical properties of ZrN and Zr(Ti)-Si-N coatings obtained by ion-plasma deposition technique [Text] / A. D. Pogrebnyak, O. V. Sobol', V. M. Beresnev, P. V. Turbin, S. N. Dub, G. V. Kirik, A. E. Dmitrenko // Technical Physics Letters. – 2009. – Vol. 35, Issue 10. – P. 925–928. doi: 10.1134/s1063785009100150
8. Azarenkov, N. Vakuumno-plazmennye pokrytija na osnove mnogojelementnyh nitridov [Text] / N. Azarenkov, O. Sobol', V. Beresnev, A. Pogrebnjak, D. Kolesnikov, P. Turbin, I. Torjanik // Metallofizika i novejshie tehnologii. – 2013. – Vol. 35, Issue 8. – P. 1061–1084.
9. Pogrebnjak, A. D. The effect of the deposition parameters of nitrides of high-entropy alloys (TiZrHfVNb)N on their structure, composition, mechanical and tribological properties [Text] / A. D. Pogrebnjak, I. V. Yakushchenko, G. Abadias, P. Chartier, O. V. Bondar, V. M. Beresnev et. al. // Journal of Superhard Materials. – 2013. – Vol. 35, Issue 6. – P. 356–368. doi: 10.3103/s106345761306004x
10. Holmberg, K. Friction and wear of coated surfaces – scales, modelling and simulation of tribomechanisms [Text] / K. Holmberg, H. Ronkainen, A. Laukkanen, K. Wallin // Surface and Coatings Technology. – 2007. – Vol. 202, Issue 4-7. – P. 1034–1049. doi: 10.1016/j.surfcoat.2007.07.105
11. Sobol', O. V. Structural Engineering Vacuum-plasma Coatings Interstitial Phases [Text] / O. V. Sobol' // Journal of Nano- and Electronic Physics. – 2016. – Vol. 8, Issue 2. – P. 02024-1–02024-7. doi: 10.21272/jnep.8(2).02024
12. Azarenkov, N. Inzhenerija vakuumno-plazmennyh pokrytij [Text] / N. Azarenkov, O. Sobol', A. Pogrebnjak, V. Beresnev. – Kharkiv: HNU imeni V. N. Karazina, 2011. – 344 p.
13. Aksenov, I. Vakuumnaja duga v jerozionnyh istochnikah plazmy [Text] / I. Aksenov. – Kharkiv: NNC HFTI, 2005. – 212 p.

14. Pogrebnjak, A. D. The effect of nanolayer thickness on the structure and properties of multilayer TiN/MoN coatings [Text] / A. D. Pogrebnjak, V. M. Beresnev, O. V. Bondar, G. Abadias, P. Chartier, B. A. Postol'nyi et. al. // Technical Physics Letters. – 2014. – Vol. 40, Issue 3. – P. 215–218. doi: 10.1134/s1063785014030092
15. Sobol', O. V. Effect of high-voltage pulses on the structure and properties of titanium nitride vacuum-arc coatings [Text] / O. V. Sobol', A. A. Andreev, S. N. Grigoriev, V. F. Gorban', M. A. Volosova, S. V. Aleshin, V. A. Stolbovoi // Metal Science and Heat Treatment. – 2012. – Vol. 54, Issue 3-4. – P. 195–203. doi: 10.1007/s11041-012-9481-8
16. Sobol', O. V. Nanostructural ordering in W-Ti-B condensates [Text] / O. V. Sobol' // Physics of the Solid State. – 2007. – Vol. 49, Issue 6. – P. 1161–1167. doi: 10.1134/s1063783407060236
17. Sobol', O. V. The influence of nonstoichiometry on elastic characteristics of metastable β-WC1–x phase in ion plasma condensates [Text] / O. V. Sobol' // Technical Physics Letters. – 2016. – Vol. 42, Issue 9. – P. 909–911. doi: 10.1134/s1063785016090108
18. Sobol, O. V. Peculiarities of structure state and mechanical characteristics in ion-plasma condensates of quasibinary system borides W_2B_5-TiB_2 [Text] / O. V. Sobol, O. N. Grigoryev, Y. A. Kunitsky, S. N. Dub, A. A. Podtelezhnikov, A. N. Stetsenko // Science of Sintering. – 2006. – Vol. 38, Issue 1. – P. 63–72. doi: 10.2298/sos0601063s
19. Aksenov, I. Tehnika osazhdenija vakuumno-dugovyh pokrytij [Text] / I. Aksenov, D. Aksenov, V. Belous. – Kharkiv: NNC HFTI, 2014. – 280 p.
20. Belous, V. Cavitation and abrasion resistance of Ti-Al-Y-N coatings prepared by the PIII&D technique from filtered vacuum-arc plasma [Text] / V. Belous, V. Vasyliev, A. Luchaninov, V. Marinin, E. Reshetnyak, V. Strel'nitskij et. al. // Surface and Coatings Technology. – 2013. – Vol. 223. – P. 68–74. doi: 10.1016/j.surfcoat.2013.02.031
21. Andreev, A. A. Vacuum-arc coating [Text] / A. A. Andreev, L. P. Sablev, S. N. Grigorev. – Kharkiv: NNC KIPT, 2010. – 317 p.