INFLUENCE OF HIGH-VOLTAGE CONSTANT POTENTIAL BIAS ON STRUCTURE AND PROPERTIES OF MoN/CrN MULTILAYER COMPOSITE WITH DIFFERENT LAYER-THICKNESS

S.S. Grankin[1], V.M. Beresnev[1], O.V. Sobol'[2], S.V. Lytovchenko[1], V.A. Stolbovoy,
D.A. Kolesnikov[4], A.A. Meylekhov[2], A.A. Postelnyk[2], I.N. Toryanik[1]
[1]V.N. Karazin Kharkiv National University, Kharkov, Ukraine,
E-mail: beresnev@ yandex.ru;
[2]National Technical University "KhPI", Kharkov, Ukraine;
[3]National Scientific Center "Kharkov Institute of Physics and Technology",
Kharkov, Ukraine;
[4]Belgorod state national research university, Belgorod, Russia

Influence of high-voltage constant potential bias, pressure of nitrogen atmosphere, and thickness of layers on the phase and elemental composition, structure and mechanical properties of the composite multilayer coatings CrN/MoN, which were prepared by the nitrogen vacuum-arc evaporation in atmosphere, was studied. It was determined that when the layer thickness is reduced from 200 to 15 nm at almost invariable phase the structural hardness decreases from 34 to 13 GPa what may be accounted for increase of the specific contribution of nonequilibrium at boundaries. When the layers thickness is smaller, e.g. of about 5 nm, the hardness increases, and adhesion strength reaches 187.17 H of the coating destruction critical point. Some possible mechanisms of the fixed increase of the coating mechanical properties are considered.

At present some new materials for cutting tools are actively developed and applied in industry. Besides production of new kinds of hard alloys and fast-cutting steel grades much attention is paid to protection of the tool coating surface against its wear and preservation of its geometry at the harder processing rates. One of the major trends in this sphere is development of wear proof coatings and their deposition on cutting tools [1, 2]. The fact that the coatings are capable to increase the tool efficiency and to improve the property of the processed surface is considered to be proved.

As long as coating forming is one of the most effective ways to provide the necessary functional properties to a surface (superficial engineering) [3−6] more attention is paid to studying the relation between the conditions for deposition and the coating structure. Use of the high-efficiency vacuum-arc deposition method allows to prepare coatings which can work under high temperature and pressure, in corrosive medium and under intensive wear [7−10]. One of the most promising materials providing good wear and corrosion resistance of edge tools working at high speed of cutting is chromium nitride [11−14]. Unlike titanium nitride TiN which is more widely used now in the industry, CrN shows high temperature stability and has lower friction factor.

However single-layer coating made of chromium-nitride has not sufficient hardness and is substantially subject to abrasive wear. One of the most promising ways to increase performance characteristics of nitrides by transferring them into nanostructure state is creation of multilayer structures with nano-dimensioned thickness of layers [15−17]. At that, by alternation of two or more layers of materials with various physical-mechanical properties it is possible to change substantially properties of a system, including pressure concentration and cracks extension, thus increasing the

material fracture toughness. MoN compound whose high mechanical properties [18] amplify sufficiently CrN properties may be promising as the other layer in such a system.

The purpose of this work was to develop a method of structural engineering as applied to CrN/MoN composite with different thickness of its layers that are deposited at pressure variation of the working hydrogen atmosphere and of the value of negative potential bias applied to the substrate in the course of deposition.

SPECIMENS AND TECHNIQUES OF THEIR STUDY

Specimens have been prepared by vacuum-arc method using "Bulat 6" modernized device [19]. Pressure of the working atmosphere (nitrogen) at the coating deposition made $P_N = (7…30) \cdot 10^{-4}$ Torr, the rate of deposition being 3 nm/s. Deposition was carried out from two sources (Mo and Cr) at continuous rotation of the fixed specimens at the rate of 8 turns a minute. At 60-minute deposition the total number of the coating layers was 960 (or 480 bi-layered periods) with total thickness of about 9 μm. In the course of deposition the substrates were subjected to the constant negative potential $U_s = 20, 40, 150, 300$ V.

The phase structural analysis was carried out by X-ray diffraction method with Cu-k_α radiation. Profile fragmentation was carried out using software package "NewProfile".

The hardness was measured by Microindentation method with Vickers diamond pyramid used as an indenter at loads of 25, 50 and 100 g. The analysis was carried out using the device 402MVD of Instron Wolpert Wilson Instruments Company.

Determination of adhesive and cohesive strength, scratch resistance, as well as finding-out the mechanism

of the coating destruction was performed by using the scratch tester Revetest (CSM Instruments).

Cracks were made on the coating surface with a diamond spherical indenter having curvature radius of 200 μm at linearly increasing loading. Signal intensity of acoustic emission (AE), friction factor, the indenter penetration depth and the value of normal loading on it were registered simultaneously with the loading. To obtain statistically reliable results three scratches were made on the surface of each sample. In the process of tests the load on the indenter increased from 0.9 to 70 N at the rate of 6.91 N/min, the speed of the indenter displacement was 1 mm/min, the scratch length was 10 mm, the frequency of the acoustic emission discrete signal was 60 Hz, the acoustic emission signal power was 9 dB. The surface morphology, the fractogramme and friction tracks were studied using FEI Nova NanoSEM 450 scanning electron microscope. The coatings elemental composition was analyzed by the spectra of characteristic x-radiation obtained with the energy dispersive x-ray spectrometer of PEGASUS (EDAX) system built into the microscope.

RESULTS AND THEIR CONSIDERATION

The analysis data of the coating elemental composition related to the nitrogen pressure P_N and the negative potential U_s are presented in Fig. 1. The nitrogen content (light element to be implanted) when deposited depends to a large extent on P_N value (see Fig. 1,a). Influence of U_s is less essential (Fig. 1b), which becomes evident from relative reduction of atomic nitrogen concentration at high U_s (see Fig. 1,b, curve 1).
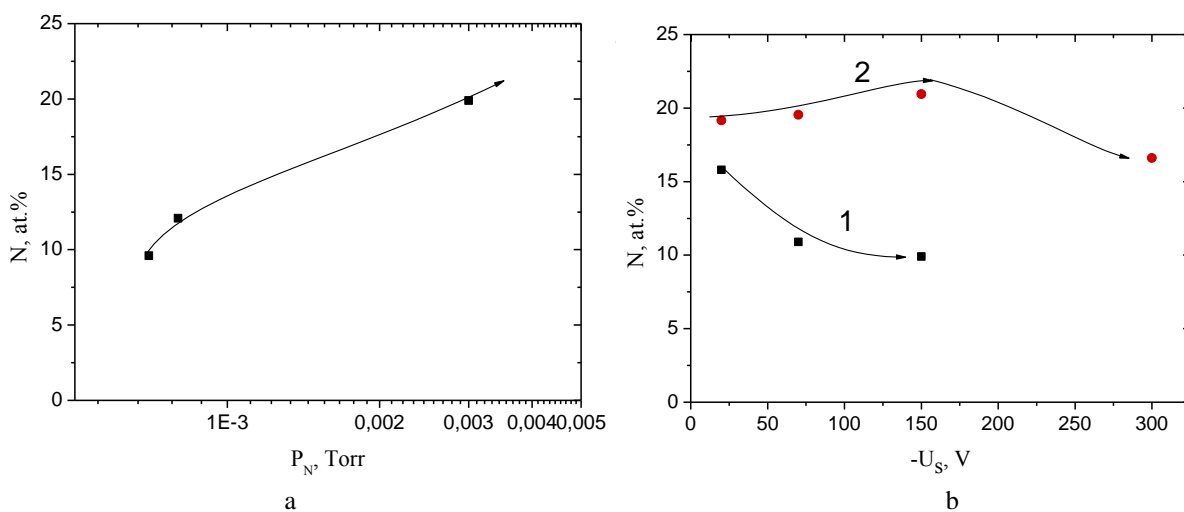

Fig. 1. Change of the nitrogen content in the coating related to: a – pressure at deposition (P_N) at constant $U_s = -70$ V, b – potential bias at constant $P_N = 7 \cdot 10^{-4}$ Torr (1) and $P_N = 3 \cdot 10^{-3}$ Torr (2)

Selective secondary dispersion from the growth surface may be the reason for such decrease. Note, that strengthening of bond of the deposited metal and the atmospheric nitrogen at high pressure PN results in stabilization of the coating composition to much higher value of U_s (see Fig. 1,b, curve 2), in this case growth of U_s is accompanied by increase of the coating uniformity due to decrease of the drop component in the coating (Fig. 2).

The ratio of metals Mo and Cr (Fig. 3,a) in a coating depends on U_s (see Fig. 3,b), and at low pressure of nitrogen this dependence is stronger (see Fig. 3,b, curve 1) than at the high pressure (see Fig. 3b, curve 2). The reason of the observed effect is the higher average energy of Mo- and Cr-ions bombarding the growing coating and smaller energy loss of ions at low P_N.

The results show that the most sensitive, and, hence, the most variable, are the coatings deposited at the highest $U_s = -300$ V. The coatings prepared under such conditions are studied in more detail.

X-ray examination of coatings (Fig. 4) have shown that in coatings with thickness of about 7 nm prepared under continuous rotation of samples the nitrogen phases are lowest. For Mo-N layer the γ-Mo_2N phase has a cubic lattice (structural type – NaCl , JCPDS 25-1366), and for Cr-N system layers the β-Cr_2N phase has a hexagonal lattice (JCPDS 35-0803). γ-Mo_2N phase has a larger homogeneity area, and the cubic lattice is more stable when strongly nonequilibrium vacuum-arc methods of preparation are used [18], and therefore this phase remains basic in the Mo-N system interlayers with increase of the layers thickness. With thickness increase an isomorphic phase is formed in Cr-N interlayers relative to γ-Mo_2N phase of CrN with a cubic lattice (structural type NaCl, JCPDS 11-0065). Note, that with the increase of the layers thickness specific contribution of interfacial interaction decreases, and on the diffraction spectra one can see only isostructural peaks (200) CrN/(200)γ-Mo_2N (Fig. 4, spectra 4−6).
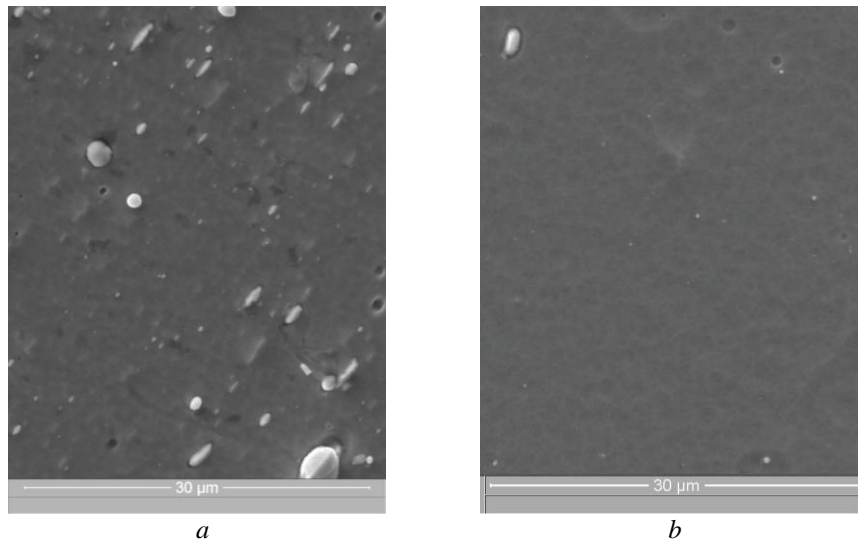
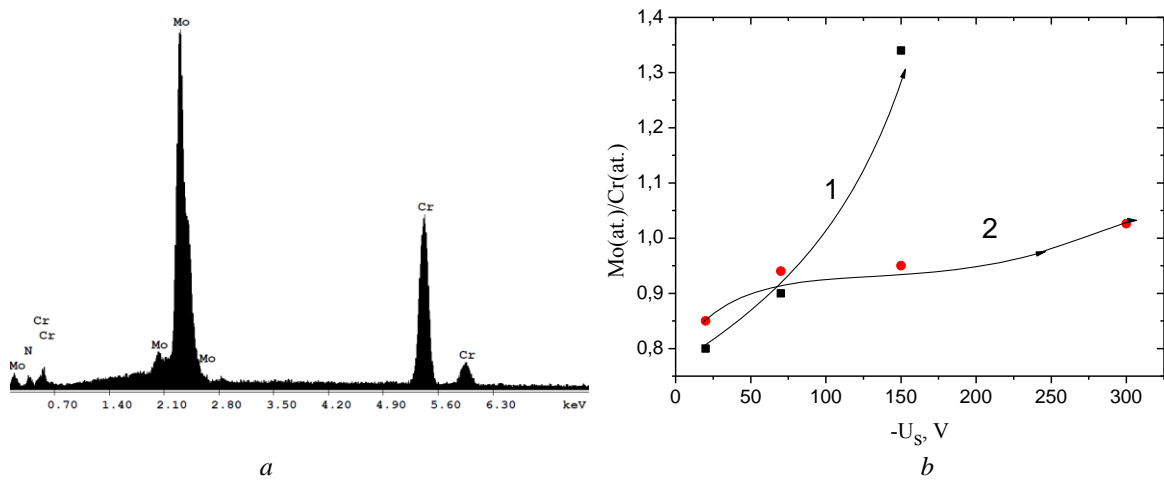*Fig. 2. Morphology of the coating surface at $U_s = -20$ V (a), for $U_s = -150$ V (b)*

Fig. 3. Metals in the coating (a), and dependence of their ratio on U_s
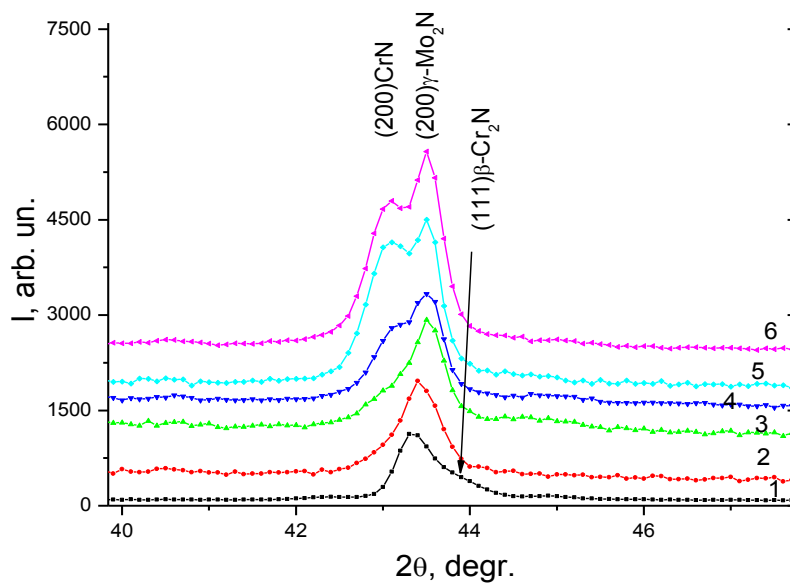*at $P_N = 7\cdot10^{-4}$ Torr (1) and $P_N = 3\cdot10^{-3}$ Torr (2) (b)*

Fig. 4. Segments of the coatings spectra formed at: $P_N = 3\cdot10^{-3}$ Torr and $U_s = -300$ V at layers thickness: of about
7 nm, a continuous mode (1), of about 12 nm (2), of 25 nm (3), of 50 nm (4), of 100 nm (5), of 200 nm (6)

Studies of such coatings mechanical properties (by the most express and universal characteristic – hardness) show that for the thickness of 10 nm or more some hardening is observed with increase of the layers thickness, when the contribution of interfacial interaction is minimized (Fig. 5,a).

Rather high hardness of the layers with smallest thickness (in the coatings prepared under continuous rotation) may be caused by the dimensional effect or formation of incoherent interphase boundary (with different type of crystal lattices) in the layers.

Formation of the lowest phases in the both systems at smaller pressure (when the nitrogen content in a coating is not more than 17 at.%) results in strong decrease in hardness (see Fig. 5,b) which is accounted for the presence of a great number of vacancies in nitrogenous sub-lattice at strongly nonequilibrium state of the coating.
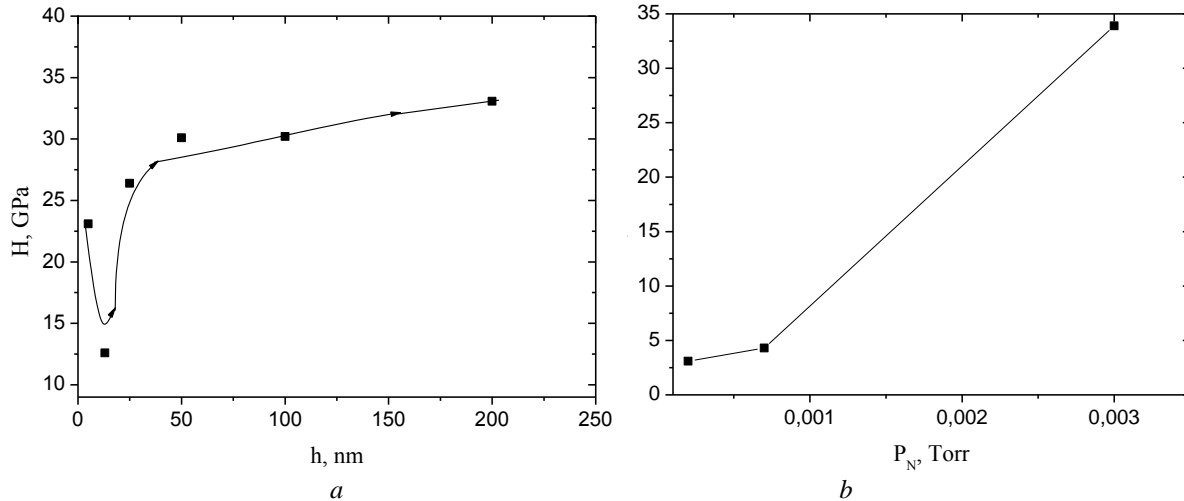

Fig. 5. The coating hardness dependence on the layers thickness (a) and pressure (b); deposition at $U_s = - 300$ V

Tests of adhesive strength of coatings with the thinnest layers, in which the greatest dimensional effect of hardness increase was expected, have shown (Fig. 6) rather uniform change of characteristics at loading growth on the indenter. The coating wears out without formation of avalanche cleavages, what confirms, in particular, the character of the acoustic emission curve. The friction factor changes from 0.18 to 0.36 in the process of the coating wear.
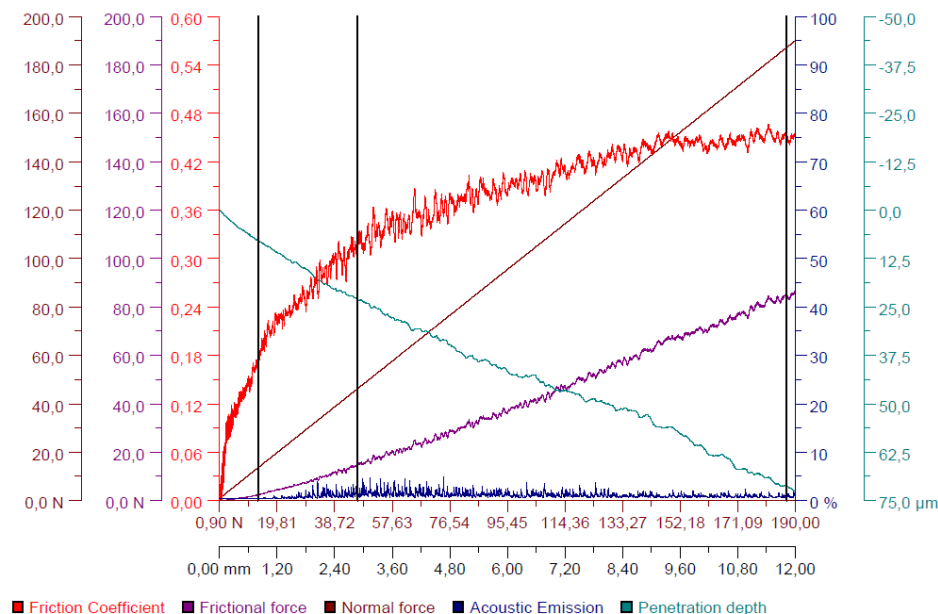

Fig. 6. Results of sclerometry of coatings with thickness of about 5 nm

Flexible and uniform wear pattern of the coating allows to obtain high values of its cohesive and adhesive destruction (Lc_1 = 13.56 H, Lc_2 = 46.3 H, Lc_3 = 187.17). Uniformity of wear is well illustrated by the image of wear tracks (Fig. 7); such coating property may be accounted for plastification and strength increase at transition to the nano-level of structural components.
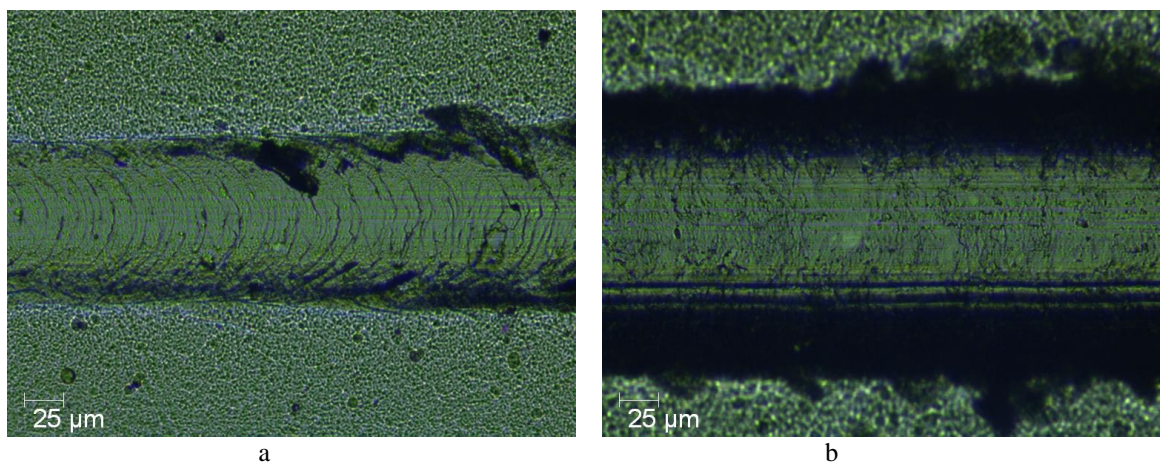
Fig. 7. Wear tracks in the area of loads at critical points Lc_1 (a) and Lc_2 (b)
for MoN/CrN coating with the thickness of about 5 nm, obtained in the course of continuous rotation,
when $P_N = 3 \cdot 10^{-3}$ Torr and $U_s = -300$ V

CONCLUSION

In the course of deposition of nitrides with relatively low formation heat (system Mo-N and Cr-N) the high negative constant potential bias (-150 and-300 V) results in formation of the lowest nitrogen phases in nanometer thin layers.

Pressure of the working atmosphere at deposition essentially influences on the phase-structural state of coatings. Pressure decrease results in lack of nitrogen in a coating as compared to its stoichiometric composition what is accompanied by instability of the coating phase-structural state and abrupt decrease of its hardness.

Increase of the layers thickness to 100 nm or more results in increase of the coating hardness and adhesion strength, which is caused by decrease of specific contribution of the unstable boundaries.

Acceptable hardness level of thin (less than 10 nm) coatings may be determined by nano-dimensional effects providing high adhesive strength and uniform coatings wear.

REFERENCES

1. *Nanostructured Coatings* / Edited by: Cavaleiro, Albano; De Hosson, Jeff Th. M. Springer – Verlag, 2006, 648 p.

2. P.H. Mayrhofer, C. Mitterer, L. Hultman, H. Clemens. Microstructural design of hard coatings // *Progress in Materials Science*. 2016, v. 51, p. 1032-1114.

3. O.V. Sobol'. Control of the Structure and Stress State of Thin Films and Coatings in the Process of their Preparation by Ion-Plasma Methods // *Physics of the Solid State*. 2011, v. 53, N 7, p. 1464-1473.

4. O V.Sobol', O.N. Grigorjev, Yu.A. Kunitsky, S.N. Dub, A.A. Podtelezhnikov, A.N. Stetsenko. Peculiarities of Structure State and Mechanical Characteristics in Ion-Plasma Condensates of Quasibinary System Borides W_2B_5-TiB_2 // *Science of Sintering*. 2006, v. 38, p. 63-72.

5. R.A. Andrievsky. Vlijanie obluchenija na svojstva nanomaterialov // *Fizika Metallov i Metallovedenie*. 2010, v. 110, p. 243-254 (in Russian).

6. R.A. Andrievski. Behavior of radiation defects in nanomaterials // *Review on Advanced Materials Science*. 2011, v. 29, p. 54-67.

7. F. Lomello, F. Sanchette, F. Schuster, M. Tabarant, A. Billard. Influence of bias voltage on properties of AlCrN coatings prepared by cathodic ars deposition // *Surf. AND Coat. Tech*. 2013, v. 224, p. 77-81.

8. Z.H. Xie, M. Hoffman, P. Munroe, R. Singh, A. Bendavid, P.J. Martin. Microstructural response of TiN monolithic and multilayer coatings during microscratch testing // *Journal of Materials Research*. 2007, v. 22, N 8, p. 2312-2318.

9. K. Lukaszkowicz, L.A. Dobrzański, A. Zarychta, L. Cunha. Mechanical properties of multilayer coatings deposited by PVD techniques onto the brass substrate // *J. of Achievements in Materials and Manufacturing Engineering*. 2006, v. 15, N 1-2, p. 47-52.

10. R. Krause-Rehberg, A.D. Pogrebnyak, V.N. Borisyuk, M.V. Kaverin, A.G. Ponomarev, M.A. Bilokur, K. Oyoshi, Y. Takeda, V.M. Beresnev, O.V. Sobol. Analysis of local regions near interfaces in nanostructured multicomponent (Ti-Zr-Hf-V-Nb) N coatings produced by the cathodic-arc-vapour-deposition from an arc of an evaporating cathode // *Physics of Metals and Metallography*. v. 114, N 8, p. 672-680.

11. Juergen M. Lackner, Wolfgang Waldhauser, Lukasz Majo, Marcin Kot. Tribology and Micromechanics of Chromium Nitride Based Multilayer Coatings on Soft and Hard Substrates // *Coatings*. 2014, N 4, p.121-138.

12. A.G. Guglya, I.M. Nekhlyudov. Pokrytiya na baze nitrida khroma // *Uspekhi Fiziki Metallov*. 2005, N 6, p. 197-232 (in Russian).

13. A. Gilewicz, B. Warcholinski. Tribological properties of CrCN/CrN multilayer coatings // *Tribology International*. 2014, v. 80, p. 34-40.

14. M. Ertas, A.C. Onel, G. Ekinci, B. Toydemir, S. Durdu, M. Usta, L. Colakerol Arslan. Investigation of VN/TiN Multilayer Coatings on AZ91D Mg Alloys // *International Journal of Chemical, Nuclear, Materials*

and Metallurgical Engineering. 2015, v. 9, N 1, p. 53-57.

15. H.C. Barshilia, K.S. Rajam. Deposition of TiN/CrN hard superlattices by reactive d.c. magnetron sputtering // *Bull. Mater. SCI*. 2013, v. 26, N 2, p. 233-237.

16. M.S. Konchady, S. Yarmolenko, D.M. Pai, J. Sankar. Nanoindentation, Nanoscratch and Wear Studies on Nanoscale Multilayer TiN/CrN Coatings // *ASME 2009 International Mechanical Engineering Congress and Exposition 2009*, v. 14: *Processing and Engineering Applications of Novel Materials*, p. 55-59.

17. O.V. Sobol', A.A. Andreev, V.A. Stolbovoi, V.E. Fil'chikov. Structural-phase and stressed state of vacuum-arc-deposited nanostructural Mo-N coatings controlled by substrate bias during deposition // *Technical Physics Letters*. 2012, v. 38, N 2, p. 168-171.

18. O.V. Sobol', A.A. Andreev, S.N. Grigoriev, V.F. Gorban', M.A. Volosova, S.V. Aleshin, V.A. Stolbovoy. Physical characteristics, structure and stress state of vacuum-arc tin coating, deposition on the substrate when applying high-voltage pulse during the deposition // *Problems of Atomic Science and Technology*. 2011, N 4 (74), p. 174-177.

ВЛИЯНИЕ ВЫСОКОВОЛЬТНОГО ПОСТОЯННОГО ПОТЕНЦИАЛА СМЕЩЕНИЯ НА СТРУКТУРУ И СВОЙСТВА МНОГОСЛОЙНОГО КОМПОЗИЦИОННОГО МАТЕРИАЛА MoN/CrN С РАЗНОЙ ТОЛЩИНОЙ СЛОЕВ

С.С. Гранкин, В.М. Береснев, О.В. Соболь, С.В. Литовченко, В.А. Столбовой,
Д.А. Колесников, А.А. Мейлехов, А.А. Постельник, И.Н. Торяник

Исследованы влияния высоковольтного постоянного потенциала смещения, давления азотной атмосферы и толщины слоев на фазовый и элементный составы, структуру и механические свойства композиционных многослойных покрытий CrN/MoN, полученных вакуумно-дуговым испарением в атмосфере азота. Установлено, что при уменьшении толщины слоев от 200 до 15 нм при практически неизменном фазовом составе твердость снижается с 34 до 13 ГПа, что можно связать с повышением удельного вклада неравновесных границ. При меньшей толщине слоев, около 5 нм, происходит увеличение твердости, а адгезионная прочность достигает высокого значения (187,17 Н) критической точки разрушения покрытия. Обсуждены возможные механизмы зафиксированного повышения механических свойств покрытия.

ВПЛИВ ВИСОКОВОЛЬТНОГО ПОСТІЙНОГО ПОТЕНЦІАЛУ ЗМІЩЕННЯ НА СТРУКТУРУ І ВЛАСТИВОСТІ БАГАТОШАРОВОГО КОМПОЗИЦІЙНОГО МАТЕРІАЛУ MoN/CrN З РІЗНОЮ ТОВЩИНОЮ ШАРІВ

С.С. Гранкін, В.М. Береснєв, О.В. Соболь, С.В. Литовченко, В.А. Столбовий, Д.О. Колесніков,
А.О. Мейлехов, Г.О. Постельник, І.Н. Торяник

Досліджено вплив високовольтного постійного потенціалу зміщення, тиску азотної атмосфери і товщини шарів на фазовий і елементний склад, структуру і механічні властивості композиційних багатошарових покриттів CrN/MoN, отриманих вакуумно-дуговим випаром в атмосфері азоту. Встановлено, що при зменшенні товщини шарів від 200 до 15 нм при практично незмінному фазовому складі твердість знижується з 34 до 13 ГПа, що можна зв'язати з підвищенням питомого внеску нерівноважних меж. При меншій товщині шарів, близько 5 нм, відбувається збільшення твердості, а адгезійна міцність досягає високого значення 187,17 Н критичної точки руйнування покриття. Обговорено можливі механізми зафіксованого підвищення механічних властивостей покриття.