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About Peculiarities of the Influence of the Negative Bias Potential Applied to the Substrate During the Deposition Process on the Structural State and Properties of the Multilayer system MoN-CrN

V.M. Beresnev[1,*], O.V. Sobol'[2], A.D. Pogrebnjak[3], U.S. Nyemchenko[1], S.S. Grankin[1],
V.A. Stolbovoy[4], P.V. Turbin[1,5], A.A. Meylehov[2], M.Ju. Arseenko[6]

[1] *V.N. Karazin Kharkiv National University, 4, Svobody Sq., 61022, Kharkiv, Ukraine*
[2] *National Technical University "Kharkiv polytechnic institute", 21, Frunze Str., Kharkiv 61002, Ukraine*
[3] *Sumy State University, 2, Rymsky Korsakov Str., 40007 Sumy, Ukraine*
[4] *National Science Center "Kharkiv Institute of Physics and Technology",*
1, Akademicheskaya St., Kharkiv 61108, Ukraine
[5] *Scientific Center of Physical Technologies of MES and NAS of Ukraine,*
Svobody sq., 6, 61022, Mail Box 4499, Kharkiv, Ukraine
[6] *National Research University "Belgorod State University", 85, Pobedy Str., Belgorod 308015, Russia*

Applying transition metal nitrides of Mo and Cr, which are characterized by a relatively low heat of formation, as the components of the multilayer coating, the possibilities of elemental and structural engineering of vacuum-arc coatings under the influence of the bias potential U_s and the reaction gas pressure P_N are revealed. It was found that at a relatively small thickness of the layers of nanometer range, which provides superhard state of the coatings, the supply of U_s with the value of above the critical leads to a drop in hardness, which can be explained by mixing of layers at the interphase boundary.

Keywords: Vacuum-arc coatings, Multilayer coating, Hard coatings, Vacuum-arc deposition.

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Using multilayer systems allows to carry out simulation during the deposition, not only for the structural state of each of the layers individually, but also by adjusting the thickness, the type of material and the number of layers in a period; creation of artificial structures with unique functional properties is also possible [1 - 5].

Structure and properties of the coatings based on MoN and CrN in monolayer state may vary in a wide range depending on the potential applied to the substrate and the pressure of nitrogen atmosphere during the deposition process [6, 7]. In connection to this, we can expect considerable sensitivity of structural states and properties of the coatings obtained by combining CrN and MoN as layers of the multilayer system. Thus, the greatest effects can be expected in the nanometer size of the layers, which is due to the high mechanical properties of nitrides in this size range [8, 9].

The samples of multilayer coating were obtained by means of vacuum-arc method by means of the modernized "Bulat-6" installation [10]. The pressure of working atmosphere (nitrogen) during the deposition was $P_N = (7...30) \times 10^{-4}$ Torr, the deposition speed was about 3 nm/s. The deposition was implemented from two sources (Mo and Cr) with continuous rotation with a speed of 8 rpm of fixed samples on the substrates, which allowed to obtain the layers with a thickness of about 10 nm, with a total amount of layers 960 (or 480 bilayer periods) and total thickness of the coating of about 9 μm during one hour deposition. In the process of deposition the constant negative potential with a value of $U_s = -20$ V, -70 V, -150 V and -300 V was applied to the substrates.

Phase and structural analysis was carried out by means of X-ray diffraction method in the emission of Cu-Kα. The separation of profiles into components was carried out by means of the software package "New Profile".

The elemental composition was investigated by energy dispersive method by means of scanning electron microscope FEI Nova NanoSEM 450. The hardness of the coatings was measured by means of durometer DM-8 by micro-Vickers method, at a load on indenter of 0.2 N.

Fig. 1 shows the data of elemental analysis depending on the pressure P_N and the applied negative bias potential U_s. It can be seen that the content of nitrogen as a light interstitial element in determining way depends on the magnitude of P_N during the deposition (Fig. 1a). The effect of U_s affects lesser (Fig. 1b) and appears in a relative decrease (due to selective secondary sputtering from the growth surface) of the atomic concentration of nitrogen at high U_s. It should be noted, that the strengthening of connections between the deposited metal and the atmospheric nitrogen at high pressure P_N leads to stabilization of the coating composition to a substantially larger in magnitude U_s (Figure 1b, dependence 2).

Increasing the bias potential U_s leads to a significant increase in uniformity (reduction of dropping component) of the coatings (microscopic image of the morphology on the left of fig. 1c for $U_s = -20$ V, and on the right for $U_s = -150$ V).

It should be also noted, that using of pulsed beams to vaporize the material deposited on the substrate allows to eliminates the presence of drop component [11, 12].
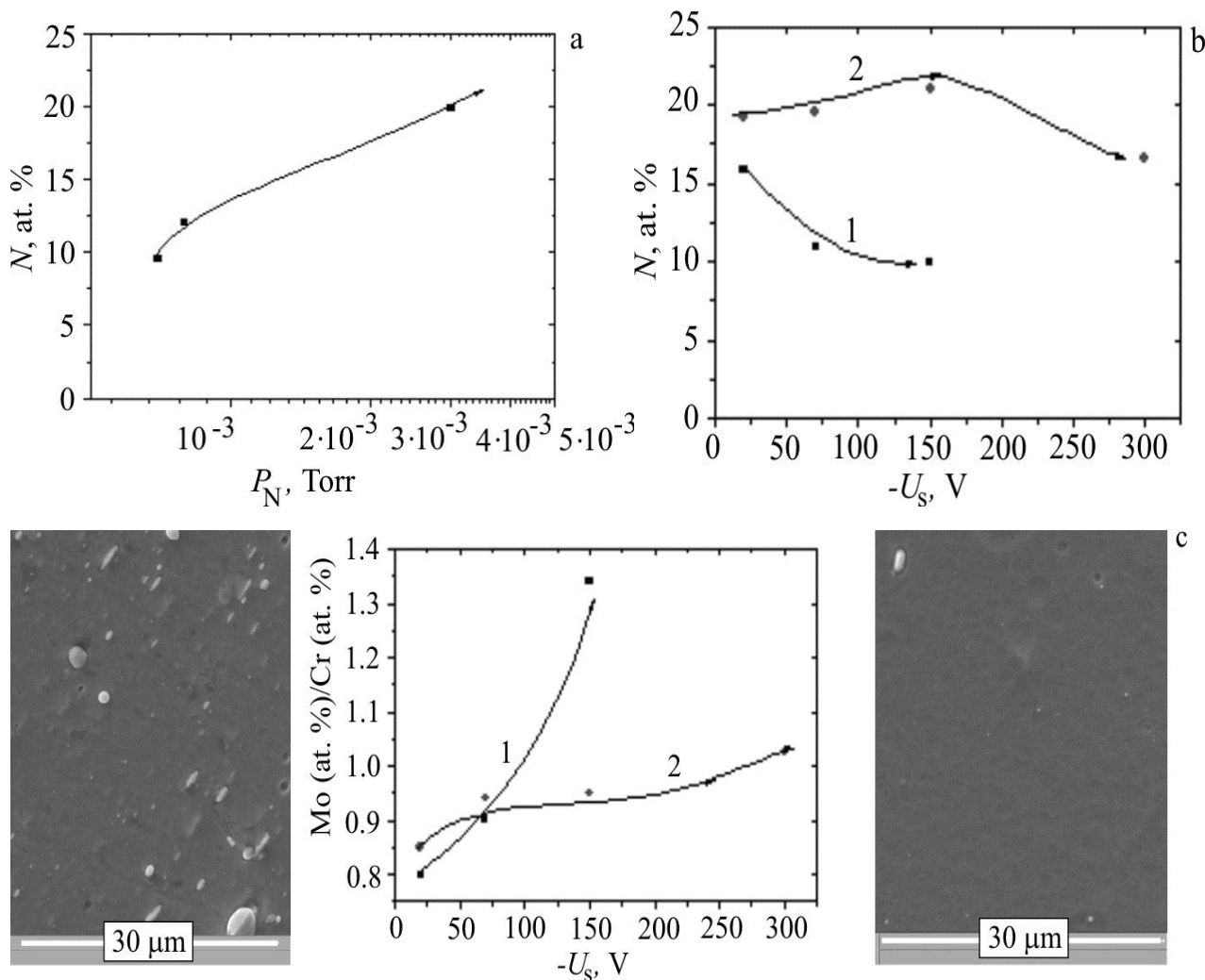
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* beresnev-scpt@yandex.ru

Fig. 1 – The changing the content of nitrogen in the coating depends on: a – pressures during the deposition (P_N) at a constant U_s = -70 V; b – from U_s at a constant $P_N = 7 \cdot$ x 10^{-4} Torr (curve 1) and $P_N = 3$ x 10^{-3} Torr (curve 2); c – dependence of the correlation of the atoms Mo/Cr from U_s at $P_N = 7 \times 10^{-4}$ Torr (curve 1) and $P_N = 3 \times 10^{-3}$ Torr (curve 2) (on the left and on the right side of the graph the images of morphology of the surface at U_s = -20 V and U_s = -150 V)

The change in the content of metal components of the coating (Mo and Cr) from the bias potential U_s are shown in Figure 1c, which implies a significant change of Mo/Cr ratio depending on the U_s at low pressure. The cause of the observed effect is a higher average energy of ions, bombarding the growing coating of the ions Mo and Cr, which is due to smaller losses of energy on collision at low P_N.

For structural studies of the influence of the main technological parameters during the deposition (values of the negative bias potential and pressure) two series of coatings were obtained: series 1, formed at $P_N = 7 \times 10^{-4}$ Torr and U_s = -20 V, -70 V, -150 V and series 2, formed at $P_N = 3 \times 10^{-3}$ Torr and U_s = -20 V, -70 V, -150 V and -300 V. At low pressure of $P_N = 7 \times 10^{-4}$ Torr the formation of lower nitrides β-Cr$_2$N (hexagonal lattice, JCPDS 35-0803) и γ-Mo$_2$N (cubic fcc, JCPDS 25-1366) takes place, with the compliance of interplane distances of the planes (111)β-Cr$_2$N/(200)γ-Mo$_2$N and (110)β-Cr$_2$N/(111)γ-Mo$_2$N. The presence of structures with the same interplanar spacings in the contacting layers may indicate the correlated growth of these two structures.

With the increase of bias potential U_s predominant growth of (111)β-Cr$_2$N/(200)γ-Mo$_2$N is observed.

At a pressure $P_N = 3 \times 10^{-3}$ Torr, occurs the formation of cubic (structural type NaCl) lattice in both layers. At the same time, with an increase of U_s, the transition from polycrystalline non-oriented state at U_s = -20 V to the preferred orientation of the growth of crystallites during the deposition with the axis of the axial texture [100] at the bias potential U_s, which is greater than the absolute value of -70 V. The appearance of this type of texture is apparently due to the relative decrease in the nitrogen content in the coating with the increase in the absolute value of U_s, which is expressed by the appearance in of chromium nitride phase β-Cr$_2$ in the layers at U_s = -300 V.

The obtained wide range of structural states of multilayer coatings defines the significant changes in its mechanical characteristics. Thus, from the dependence of hardness on the bias potential U_s shown in Fig.2 it is seen, that the highest hardness value is achieved at the lowest U_s and high pressure P_N, providing stoichiometric nitrogen composition.

The reduction of hardness at lower pressure can be associated with the formation of vacancies in the nitro-

gen sublattice due to its smaller content in the coating in comparison with the stoichiometric composition.

The reason of the decrease in hardness with increasing U_s is the intensification of the mixing process in the border area, which leads to the formation of a significant part of the solid solution with low hardness for relatively thin (about 10 nm) layers.

Fig. 2 – The dependence of hardness of the coatings of the applied negative bias potential during the deposition: 1 - $P_N = 7 \times 10^{-4}$ Torr, 2 - $P_N = 3 \times 10^{-3}$ Torr

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12. A.B. Batracov, M.I. Bazaleev, S.E. Donets, V.F. Klepikov, V.V. Lytvynenko, Yu.F. Lonin, A.G. Ponomarev, V.V. Uvarov, V.T. Uvarov, *Probl. Atomic Sci. Technol. Ser.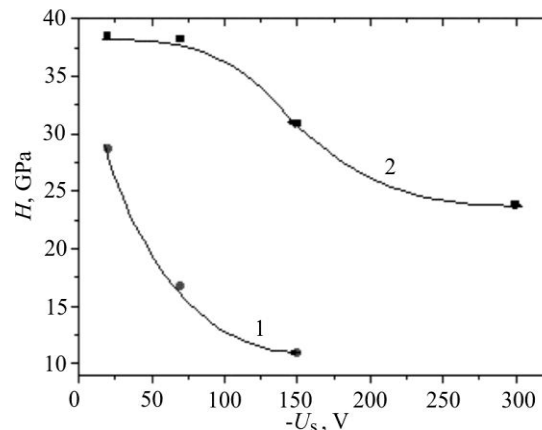 Nucl. Phys. Inv.* No6(88), 225 (2013).