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MECHANICAL PROPERTIES OF MULTILAYERED COATINGS MoN/CrN OBTAINED BY MEANS OF VACUUM-ARC DEPOSITION METHOD

S.S. Grankin¹, V.M. Beresnev¹, O.V. Sobol², U.S. Nyemchenko¹,
V.A. Stolbovoy³, P.V. Turbin^{1,4}, A.A. Meylehov², M.Ju. Arsenko⁵

¹ Karazin Kharkiv National University
Svobody Sq. 4, Kharkiv, 61022 Ukraine

² National Technical University "Kharkiv Polytechnic Institute"
Frunze St., 21, Kharkiv, 61002 Ukraine

³ National Science Center "Kharkiv Institute of Physics and Technology"
Academicheskaya St., 1, Kharkiv, 61108, Ukraine

⁴ Scientific Center of Physical Technologies of MES and NAS
Svobody Sq. 6, Kharkiv, 61022 Ukraine

⁵ Belgorod National Research University
Koroleva St., 2a, Belgorod, 308015 Russia

e-mail: beresnev-scpt@yandex.ru

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Transition metal nitrides of Mo and Cr are characterized by a relatively low heat of formation. The possibilities of elemental and structural engineering of vacuum-arc coatings based on Mo and Cr under the influence of the bias potential U_s and the reaction gas pressure P_N have been studied. 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, vacuum-arc, multilayered coatings, nanocomposite coatings

МЕХАНИЧЕСКИЕ СВОЙСТВА МНОГОКОМПОНЕНТНЫХ ПОКРЫТИЙ MoN/CrN, ПОЛУЧЕННЫХ МЕТОДОМ ВАКУУМНО-ДУГОВОГО ОСАЖДЕНИЯ

С.С. Гранкин¹, В.М. Береснев¹, О.В. Соболев², У.С. Немченко¹,
В.А. Столбовой³, П.В. Турбин^{1,4}, А.А. Мейлехов², М.Ю. Арсенко⁵

¹ Харьковский национальный университет имени В.Н. Каразина
пл. Свободы 4, Харьков, Украина, 61022

² Национальный технический университет "Харьковский политехнический институт"
ул. Фрунзе 21, Харьков, Украина, 61002

³ Национальный научный центр "Харьковский физико-технический институт"
ул. Академическая 1, Харьков, Украина, 61108

⁴ Научный центр физических технологий МОН и НАН Украины
пл. Свободы 6, Харьков, Украина, 61022

⁵ Белгородский национальный исследовательский университет
ул. Королева 2а, Белгород, Россия, 308015

Нитриды переходных металлов Мо и Сг характеризуются сравнительно низкой теплотой образования. Были изучены возможности элементной и структурной инженерии вакуумно-дуговых покрытий на основе Мо и Сг под влиянием потенциала смещения U_s и давления реакционного газа P_N . Было обнаружено, что при сравнительно небольшой толщине слоев нанометрового порядка, который обеспечивает сверхтвердое состояние покрытий, подача U_s величиной, превышающей критическое значение, приводит к падению твердости, что можно объяснить перемешиванием слоев межфазной границы.

КЛЮЧЕВЫЕ СЛОВА: вакуумно-дуговые покрытия, многослойные покрытия, нанокompозитные покрытия

МЕХАНИЧНІ ВЛАСТИВОСТІ БАГАТОЕЛЕМЕНТНИХ ПОКРИТТІВ MoN/CrN, ОТРИМАНИХ МЕТОДОМ ВАКУУМНО-ДУГОВОГО ОСАДЖЕННЯ

С.С. Гранкін¹, В.М. Береснев¹, О.В. Соболев², У.С. Немченко¹,
В.А. Столбовой³, П.В. Турбін^{1,4}, А.А. Мейлехов², М.Ю. Арсенко⁵

¹ Харківський національний університет імені В.Н. Каразіна
м. Свободи 4, Харків, Україна, 61022

² Національний технічний університет "Харківський політехнічний інститут"
вул. Фрунзе 21, Харків, Україна, 61002

³ Національний науковий центр "Харківський фізико-технічний інститут"
вул. Академічна 1, Харків, Україна, 61108

⁴ Науковий центр фізичних технологій МОН та НАН України
м. Свободи 6, Харків, Україна, 61022

⁵ Белгородський національний дослідницький університет
вул. Корольова 2а, Белгород, Росія, 308015

Нітриди перехідних металів Мо та Сг характеризуються порівняно низькою теплою утворення. Було вивчено можливості елементної та структурної інженерії вакуумно-дугових покриттів на основі Мо та Сг під впливом потенціалу зсуву U_s та тиску реакційного газу P_N . Було виявлено, що при порівняно невеликій товщині шарів нанометрового порядку, який забезпечує надтвердий стан покриттів, подача U_s величиною, що перевищує критичне значення, призводить до падіння твердості, що можна пояснити перемішуванням шарів міжфазної границі.

КЛЮЧОВІ СЛОВА: вакуумно-дугові покриття, багатшарові покриття, нанокмпозитні покриття

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].

Thus, the aim of this work was to obtain the coatings MoN/CrNc with nanometer sizes of the layers by means of vacuum-arc deposition and study of their physical and mechanical characteristics.

EXPERIMENTAL PART

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 $P_N = (7 \dots 30) \times 10^{-4}$ 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-K α . 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.

RESULTS AND DISCUSSION

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].

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 .

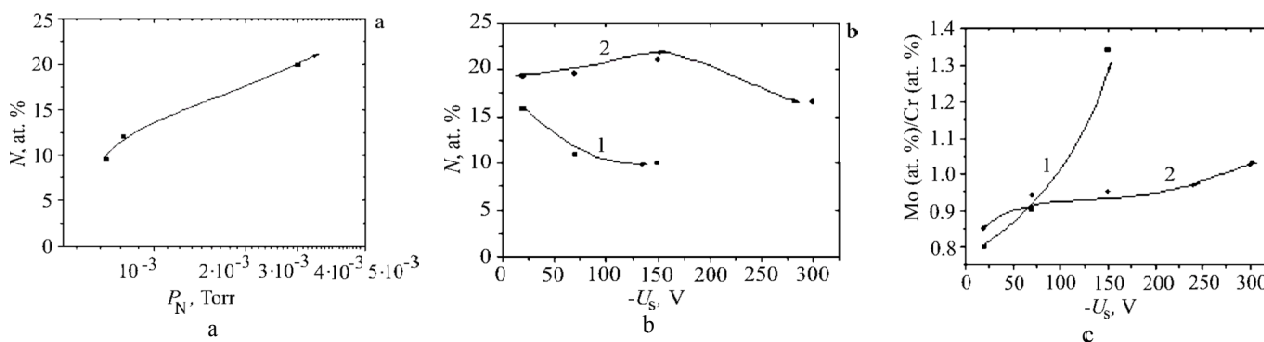


Fig. 1. The changing the content of nitrogen in the coating depends on:

a – pressures during the deposition (P_N) at a constant $U_s = -70$ V; b – from U_s at a constant $P_N = 7 \cdot 10^{-4}$ Torr (curve 1) and $P_N = 3 \cdot 10^{-3}$ Torr (curve 2); c – dependence of the correlation of the atoms Mo/Cr from U_s at $P_N = 7 \cdot 10^{-4}$ Torr (curve 1) and $P_N = 3 \cdot 10^{-3}$ Torr (curve 2).

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 -Cr₂N (hexagonal lattice, JCPDS 35-0803) и γ -Mo₂N (cubic fcc, JCPDS 25-1366) takes place, with the compliance of interplane distances of the planes (111) β -Cr₂N/(200) γ -Mo₂N and (110) β -Cr₂N/(111) γ -Mo₂N. 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 -Cr₂N/(200) γ -Mo₂N 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 -Cr₂ 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 nitrogen 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.

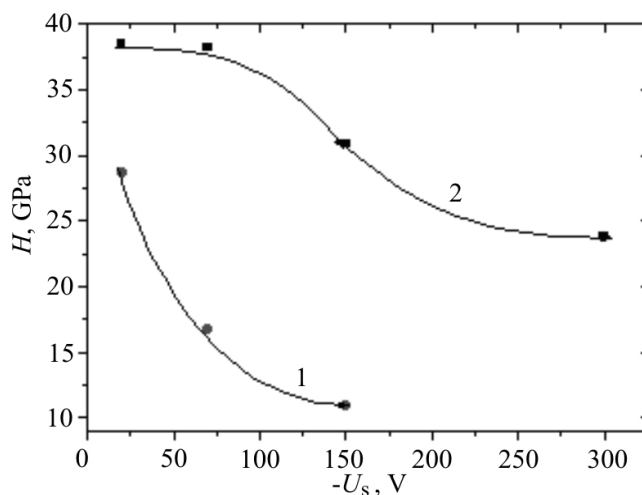


Fig. 2. The dependence of hardness of the coatings of the applied negative bias potential during the deposition: 1 - $P_N = 7 \times 10^{-4}$ Torr, 2 - $P_N = 3 \times 10^{-3}$ Torr

CONCLUSIONS

1. With the decrease of working pressure of nitrogen atmosphere from 3×10^{-3} Torr to 7×10^{-4} Torr, the depletion of the coating MoN/CrN by the nitrogen compound takes place. On a phase and structural level this leads to transition from two alike cubic structures γ -Mo₂N with a wide homogeneity area in the layers of MoN and Cr₂N in the layers of CrN, to formation of lower phase by nitrogen β -Cr₂N with hexagonal crystal lattice.

2. The hardness of the coatings corresponds to high hardness state reaching 38 GPa which lowers with the decrease of pressure during the deposition and applying of negative bias potential, which stimulates selective secondary spraying and depletion by light nitrogen atoms.

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REFERENCES

1. Xie Z.H., Hoffman M., Munroe P., Singh R., Bendavid A., Martin P.J. Microstructural response of TiN monolithic and multilayer coatings during microscratch testing // Journal of Materials Research. - 2007. - Vol. 22. - No. 08. - P. 2312–2318.
2. Sobol' O.V., Andreev A.A., Grigoriev S.N., Gorban' V.F., Volosova M.A., Aleshin S.V., Stolbovoi V.A. Effect of high-voltage pulses on the structure and properties of titanium nitride vacuum-arc coatings // Metal Science and Heat Treatment. - 2012. - Vol. 54. - No. 3-4. - P. 195–203.
3. Lackner J.M., Major L., Kot M. Microscale interpretation of tribological phenomena in Ti/TiN soft-hard multilayer coatings on soft austenite steel substrates // Bulletin of the polish academy of sciences technical sciences. - 2011. - Vol. 59. - No. 3. - P. 343–355.
4. Gilewicz A., Warcholinski B. Tribological properties of CrCN/CrN multilayer coatings // Tribology International. - 2014. - Vol.80. - P. 34–40.

5. Ertas M., Onel A.C., Ekinci G., Toydemir B., Durdu S., Usta M., Colakerol L. Investigation of VN/TiN Multilayer Coatings on AZ910 Mg Alloys // *International Journal of Chemical, Nuclear, Materials and Metallurgical Engineering*. - 2015. - Vol. 9. - No.1. - P. 53–57.
6. Sobol' O.V., Andreev A.A., Stolbovoi V.A., Fil'chikov V.E. Structural-phase and stressed state of vacuum-arc-deposited nanostructural Mo-N coatings controlled by substrate bias during deposition // *Technical Physics Letters*. - 2012. - Vol. 38. - No. 2. - P. 168–171.
7. Guglya A.G., Neklyudov I.M. Coatings on the Basis of Chromium Nitride. Experience of Design and Investigation // *Progress in Physics of Metals*. - 2005. - Vol. 6. - P. 197–232.
8. Pogrebnyak A.D., Shpak A.P., Azarenkov N.A., Beresnev V.M. Structures and properties of hard and superhard nanocomposite coatings // *Advances in Physical Sciences*. - 2009. - Vol. 179. - No. 1. - P. 35–64.
9. Beresnev V.M., Sobol' O.V., Pogrebnyak A.D., Turbin P.V., Litovchenko S.V. Thermal stability of the phase composition, structure, and stressed state of ion-plasma condensates in the Zr-Ti-Si-N system // *Technical Physics*. - 2010. - Vol. 55. - No. 6. - P. 871–873.
10. Andreev A.A., Sablev L.P., Grigoryev S.N. Vacuum-arc coatings. - Kharkiv: NSC KIPT, 2010. - 318 p.
11. Klepikov V.F., Lonin Yu.F., Lytvynenko V.V., Pashenko A.V., Ponomarev A.G., Uvarov V.V., Uvarov V.T., Sheremet V.I. The formation of strengthening coats by microsecond duration high-current relativistic electron beam // *Problems of Atomic Science and Technology. Ser. Nucl. Phys. Inv.* - 2008. - No. 5(50). - P. 91–95.
12. Batracov A.B., Bazaleev M.I., Donets S.E., Klepikov V.F., Lytvynenko V.V., Lonin Yu.F., Ponomarev A.G., Uvarov V.V., Uvarov V.T. The particularities of the high current relativistic electron beams influence on construction materials targets // *Problems of atomic Science and Technology. Ser. Nucl. Phys. Inv.* - 2013. - No. 6(88). - P. 225–229.