JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. 8 No 1, 01043(4pp) (2016)
ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том 8 № 1, 01043(4cc) (2016)

Influence on the Mechanical Characteristics of the Layer Thickness in MoN/CrN Multilayer Coatings Deposited Under a Negative Bias Potential

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(Received 16 February 2016; published online 15 March 2016)

A complex study of the influence of layer thickness of MoN/CrN multilayer composition on the phase and structure state and mechanical properties of the coatings during applying a constant negative U_b has been held using structure engineering method. It was found that mixing in the interboundary areas of the layers at high $U_b = -150$ V leads to a sharp decrease of mechanical properties at layer thickness of $h \leq 40$ nm. The highest hardness of 39.8 GPa and abrasive strength for $L_{C5} = 145$ N was reached at $h \approx 12$ nm at applying a small $U_b = -20$ V.

Keywords: MoN/CrN multilayer coating, Layer thickness, Bias potential, Structure, Crystallite nanosize, Mixing, Hardness, Abrasive strength.

DOI: 10.21272/jnep.8(1).01043 PACS numbers: 61.46. – w, 62.20.Op. 62-65. – g

1. INTRODUCTION

Vacuum-arc wear resistant coatings based on nitrides of IV-VI groups of the Mendeleev periodic system of elements are widely used to improve the operating characteristics of tools and machine parts produced of highly alloyed steels and other materials [1, 2].

These coatings possess high hardness and good adhesion to the substrate [1-3]. However, such high characteristics are achieved in these coatings during their transition to the nanostructured state, which, as known [4-9], is unstable to temperature and other external impacts. It is possible to increase stability of these states by fabricating multilayer composite materials [10-13], in which alternation of layers from different components serves as a good diffusion barrier and provides increased stability of the properties under external influences. At that, the superhard state in multilayer nanocomposites presupposes the suppression of the growth processes of embryonic cracks, generation and propagation of dislocations providing the plastic strain relief with decreasing nanocrystallite sizes to 10 nm, and absence of the anomalous Hall-Petch dependence typical for the nanostructured materials [5].

MoN/CrN [14-18] has recently been considered as one of the most promising multilayer systems, where the utilized combination of nitrides allows to achieve high hardness and wear resistance combined with good resistance to oxidation and other impacts in the aggressive environment.

The aim of this work was to study the influence of such a parameter as the layer thickness on the phase composition, structure, and mechanical properties (hardness) of the coatings deposited at different negative bias potential applied to the substrate (U_b) that provides the difference in the energies of deposited particles.

2. METHODS OF PRODUCTION AND STUDY OF THE SAMPLES

The coatings were obtained by vacuum-arc method on the modernized setup "Bulat-6" [1, 10]. The working (nitrogen) atmosphere pressure during the deposition was equal to $P_N = 3 \times 10^{-3}$ torr, deposition rate in this case was about 3 nm/s. The deposition was performed from two sources (Mo and Cr) for the specified exposure time or at constant rotation of the samples fixed on the substrates with the speed of 8 rpm. The total thickness of the coatings was approximately equal to 10 μm for the deposition time of about 1 hour. A constant negative bias potential of the value of $U_b = -20$ V and -150 V was applied to the substrates during the deposition.

The structural-phase analysis was carried out using X-ray diffractometry method with Cu-K$_\alpha$-radiation. Separation of the profiles into components was performed by the program package "New Profile". The elemental composition was investigated by the energy-dispersive method on the scanning electron microscope FEI Nova NanoSEM 450. Hardness was measured by the microindentation method with the Vickers diamond pyramid acted as an indenter under the loads of 50 and 100 g. The study was conducted on the device DM-8 intended for microhardness tests. Determination of adhesion and corrosion stability, resistance to scratching, and clarification of the mechanism of coating destruction was carried out by a scratch-tester Revetest (CSM Instruments). Scratches were done with a continuously increasing load on the coating surface by a diamond spherical indenter of the "Rockwell C" type with the curvature radius of 200 μm. The signal strength of acoustic emission (AE), friction coefficient, and indenter penetration depth were recorded simultaneously as well as the normal load. To obtain reliable results, three scratches were scored on

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the surface of each coated sample. The tests were implemented under the following conditions: the load on the indenter increased from 0.9 дto 70 N, indenter velocity was equal to 1 mm/min, scratch length – 10 mm, rate of load application – 6.91 N/min, signal frequency – 60 Hz, signal strength of AE – 9 dB. As a result of the tests, the minimum (critical) loads were determined: L_{C1} corresponds to the beginning of indenter penetration into the coating, L_{C2} – to the appearance of crack aggregates, and L_{C5} – to the coating cleavage or its plastic abrasion to the substrate.

3. RESULTS AND DISCUSSION

As shown by the energy-dispersive analysis, the elemental composition of metal components for all series obtained at both low $U_b = -20$ V and high $U_b = -150$ V is close to the equiatomic one (Mo/Cr atomic ratio varies from 0.90 to 0.93) that in relation to the layer thickness, defined by each component (Mo and Cr), indicates that the resulting layers are almost equal in thickness. The content of nitrogen atoms determined integrally for the composite multilayer coating was changed from 31.14 to 30.80 wt. % relative to the metal components with increasing U_b from – 20 to – 150 V.

In this case, the X-ray diffraction spectra show that the value of U_b significantly influences the formed structural state. It is seen from the comparison of Fig. 1a and Fig. 1b that at low $U_b = -20$ V for the same type of the crystal lattices of phases formed in the layers (crystal lattices of the B1 structural type (fcc-NaCl) that is typical for CrN and γ-Mo_2N) one observes a preferential orientation of the crystallite growth with the [311] axis perpendicular to the growth plane that is manifested in a relative intensity strengthening of the corresponding reflex. At that, such texture type is more pronounced in CrN layers.

We should note that the analysis of the elemental composition of single-layer coatings showed that content of the nitrogen component in both Cr-N and Mo-N layers is lower than the stoichiometric composition. At that, the relative content of nitrogen in the Mo-N system for the pressure of $P_N = 3 \cdot 10^{-3}$ torr despite the formation of the γ-Mo_2N phase is slightly higher than in the Cr-N system making Mo – 64.83 wt. %, N – 35.17 wt. % and Cr – 67.87 wt. %, N – 32.13 wt. %, respectively. Although the γ-Mo_2N phase formed in this case in the Mo-N layer is described as for the stoichiometric ratio Me/N = 2/1, but in practice it has a larger homogeneity range [17] up to the filling of all octahedral interstices in the lattice by nitrogen atoms, i.e. for the mononitride stoichiometry. Moreover, isostructural (cubic lattice of the NaCl structural type) CrN phase has a larger homogeneity range. The reason for stabilization of the isostructural phases in Cr-N and Mo-N layers is the stability of this lattice type to radiation effects and a large homogeneity range that makes structural states with this lattice type the most often formed in vacuum-arc coatings of the transition metal/nitrogen systems [1, 5, 6].

At larger $U_b = -150$ V, another texture type [111] is formed, whose degree of perfection increases with the growth of the layer thickness. At that, it is seen from Fig. 1 that in contrast to a small bias potential, when explicit separation of the reflexes from the corresponding phases of two layers occurs at large diffraction angles, this separation at $U_b = -150$ V is not observed that indicates the formation of a solid solution. In this case, as the scanning electron microscopic images show, the interlayer boundaries are not revealed.

At the substructural level, crystallite sizes are close to the layer thickness, and microstrain of crystallites is slightly higher in the coatings obtained at low U_b that, apparently, is defined by lower mobility of atoms deposited in this case. The latter leads to the decrease in the probability of diffusion healing of growth defects.

The investigation results of hardness of such coatings showed (Fig. 2) that increase in hardness of a multilayer composite is observed with decreasing layer thickness at low bias potential applied to the substrate $U_b = -20$ V.

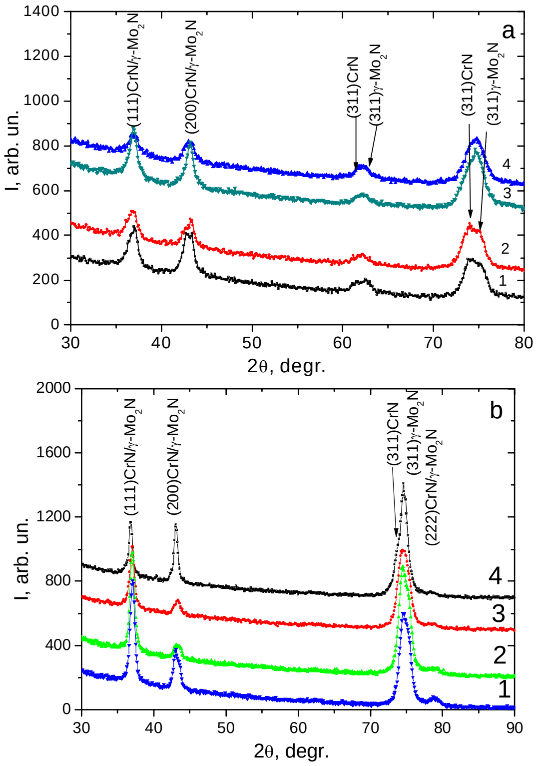

Fig. 1 – Diffraction spectral regions of the coatings obtained at $U_b = -20$ V (a) and – 150 V (b) for different layer thickness *h*: 1 – 300 nm, 2 – 70 nm, 3 – 20 nm, 4 – 12 nm

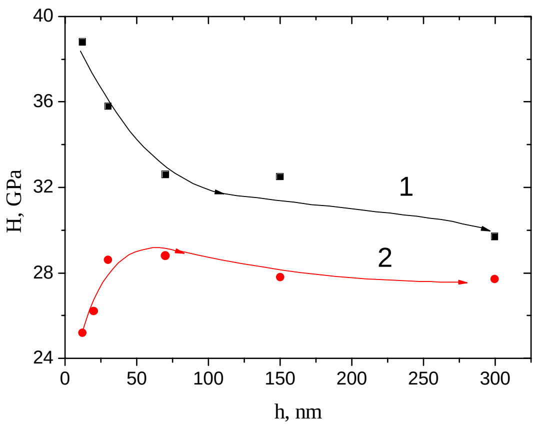

Fig. 2 – Dependence of microhardness *H* depending on the layer thickness *h* during the formation when applying a negative bias potential of the value of – 20 V (1) and – 150 V (2) to the substrate

This can be associated with the typical effects of decreasing grain size (the Hall-Petch equation) [5].

At larger $U_b = -150$ V, such a tendency is maintained up to the layer thicknesses of about 40 nm, below which a decrease in hardness is observed.

In comparison with the structural data, it is possible to assume that the reason for this decrease is the loss in this case of barrier properties by the interphase boundary due to the formation of mixing of high-energy particles on the boundary of a solid solution (Mo, Cr)N.

The samples with the greatest hardness obtained in conditions of low radiation exposure ($U_b = -20$ V) also exhibit high adhesion properties.

Thus, according to the scratch-test data, the critical damage load is equal to 145 N.

The destruction itself is fairly homogeneous that is manifested in the absence of pronounced cleavages on all stages of wear defined by the critical points L_C (Fig. 3).

The friction coefficient in this case is approximately equal to 0.15 and it is almost constant at the first three regions (up to L_{C3}) of wear.

4. CONCLUSIONS

Thus, when using a negative bias potential applied to the substrate during deposition, the layer thickness of a multilayer composite coating has a critical value determined by mixing in the interboundary area. In MoN/CrN system, for $U_b = -150$ V and layer thickness less than 40 nm, mixing with the formation of a solid solution leads to a sharp decrease in hardness of a multilayer composition. To achieve the highest mechanical properties for the layer thickness of $h \approx 12$ nm, the applied (to improve adhesion) negative bias potential should not be larger than it was achieved by applying $U_b = -20$ V.

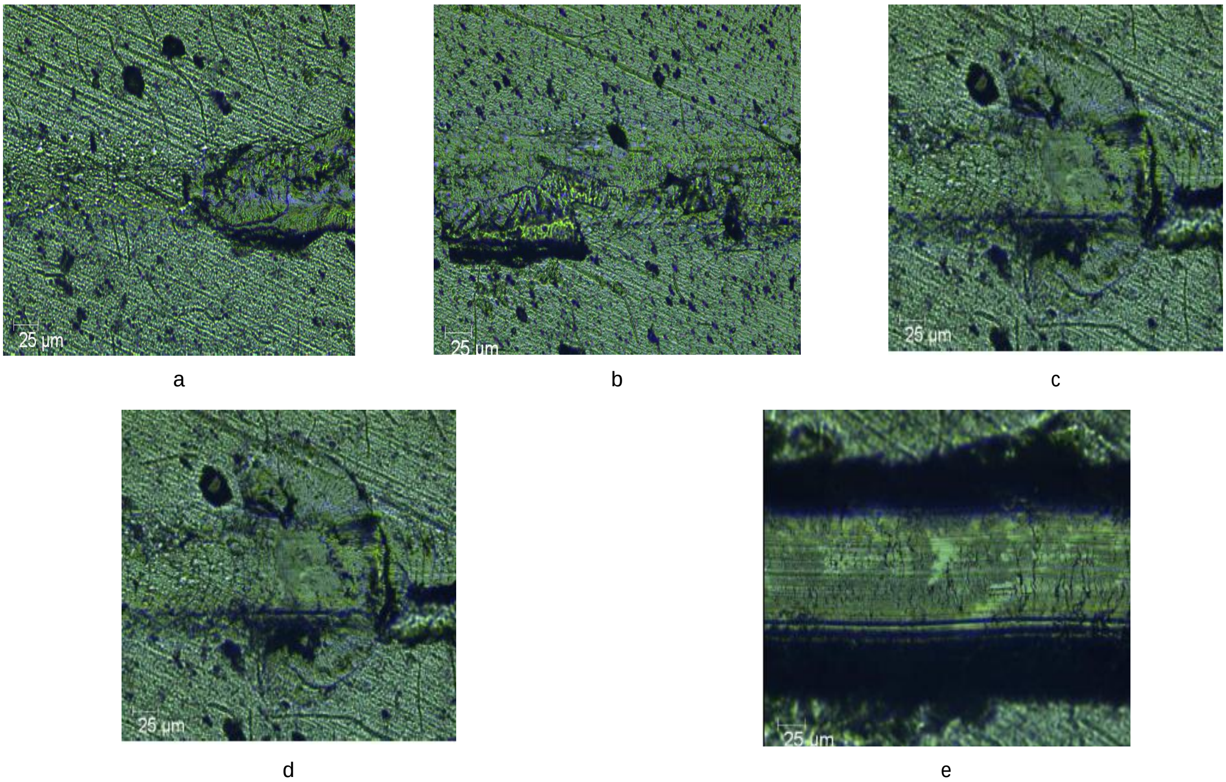

Fig. 3 – Wear paths for the corresponding stages L_{C1} (a), L_{C2} (b), L_{C3} (c), L_{C4} (d), and L_{C5} (e) in scratch tests of the coating obtained at $U_b = -20$ V and $h \approx 12$ nm

REFERENCES

1. A.A. Andreyev, L.P. Sablev, S.N. Grigor'yev, *Vakuumno-dugovyye pokrytiya* (Kharkov: NNTs KhFTI: 2010).
2. *Nanostrukturnyye pokrytiya. Per. s angl.* (Pod red. A. Kavalyero, D.T.M. Khossona) (Moskva: Tekhnosfera: 2011).
3. R.L. Boxman, V.N. Zhitomirsky, I. Grinberg, L. Rapoport, S. Goldsmith, B.Z. Weiss, *Surf. Coat. Technol.* 125, 257 (2000).
4. P.H. Mayrhofer, C. Mitterer, L. Hultman, H. Clemens, *Progr. Mater. Sci.* 51, 1032 (2006).
5. N.A. Azarenkov, O.V. Sobol′, V.M. Beresnev, A.D. Pogrebnyak, S.V. Litovchenko, O.N. Ivanov, *Materialovedeniye neravnovesnogo sostoyaniya modifitsirovannoy poverkhnosti* (Sumy: Sumskoy gos. un-t: 2012).
6. O.V. Sobol′, *Phys. Solid State* 53 No 7, 1464 (2011).
7. P.H. Mayrhofer, C. Mitterer, J.G. Wen, J.E. Greene, I. Petrov, *Appl. Phys. Lett.* 86 No 2, 131909 (2005).
8. S. Veprek, M. Veprek-Heijman, P. Karvankova, J. Prochazka, *Thin Solid Films* 476, 1 (2005).
9. Ph.V. Kiryukhantsev-Korneev, D.V. Stansky, M.I. Petrznik, E.A. Levashov, B.N. Mavrin, *Surf. Coat. Tech.* 201, 6143 (2007).
10. M.K. Samani, X.Z. Ding, N. Khosravian, B. Amin-Ahmadi, Yang Yi, G. Chen, E.C. Neyts, A. Bogaerts, B.K. Tay, *Thin Solid Films* 578, 133 (2015).
11. Z.H. Xie, M. Hoffman, P. Munroe, R. Singh, A. Bendavid, P.J. Martin, *J. Mater. Res.* 22 No 8, 2312 (2007).
12. J.M. Lackeri, L. Malor, M. Kot, *Bull. Polish Academy Sci. Tech. Sci.* 59 No 3, 343 (2011).
13. M. Ertas, A.C. Onel, G. Ekinci, B. Toydemir, S. Durdu, M. Usta, L. Colakerol Arslan, *Int. J. Chem., Nuclear, Mater. Metallurgical Eng.* 9, No 1, 53 (2015).

14. K. Lukaszkowicz, L.A. Dobrzański, A. Zarychta, L. Cunha, *J. Achievement. Mater. Manufacturing Eng.* 15 No 1-2, 47 (2006).
15. A. Gilewicz, B. Warcholinski, *Tribol. Int.* 80, 34 (2014).
16. A.D. Pogrebnjak, V.M. Beresnev, A.A. Demianenko, V.S. Baidak, F.F. Komarov, M.V. Kaverin, N.A. Makhmudov, D.A. Kolesnikov, *Phys. Solid. State* 54 No 9, 1882 (2012).
17. A.G. Guglya, I.M. Neklyudov, *Uspekhi Fiz. Met.* 6, 197 (2005).
18. S.S. Grankin, V.M. Beresnev, O.V. Sobol, V.A. Stolbovoy, V.Yu. Novikov, S.V. Lytovchenko, U.S. Nyemchenko, A.A. Meylehov, M.G. Kovaleva, A.A. Postelnik, I.N. Toryanik, *J. Nano- Electron. Phys.* 7 No 4, 04050 (2015).