MULTYLAYER VACUUM-ARC COATINS Ti-Mo-N PRODUCTION AND STUDY

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Composite materials are a good example of systems in which functional properties can be significantly increased compared to the original components. As such composite material in this paper we consider a multilayer system of alternating layers of TiN and Mo_2N. Single-layer TiN and Mo_2N components are characterized by the following structure and properties. The hardness of Mo-N coatings is 32…55 GPa, X-ray analysis of the coatings showed that the molybdenum nitride composition Mo_2N contains two structural modifications of the high-temperature γ-Mo_2N phase with a cubic lattice and low-temperature phase β-Mo_2N with a tetragonal lattice. TiN coatings, deposited using pulsed implantation during the deposition, also show the hardness $\geq$ 40 GPa, and provide resistance increase of tools and equipment up to 10 times.
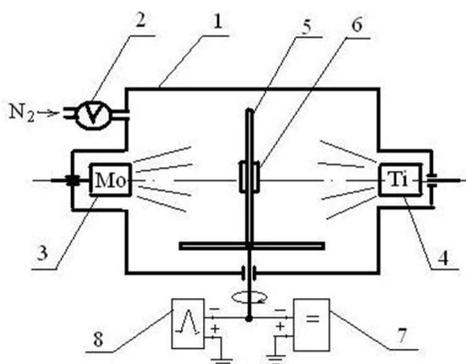

Fig. 1 - scheme of the plant for multilayer coatings deposition.1 – vacuum chamber; 2 – automatic maintenance of the nitrogen pressure; 3 – molybdenum evaporator; 4 – titanium evaporator; 5 – substrate holder; 6 – substrate; 7 – constant voltage source; 8 – pulsed voltage generator.

Multilayer coatings Ti-Mo-N, obtained by simultaneous evaporation of titanium and molybdenum cathodes with continuous rotation of the substrate, in the case of deposition on a cutting tool show resistance increase in 2 ... 4 times more than the TiN coatings, especially in-cut tough materials. Therefore the study of multilayer coatings is of scientific and practical interest. Two-phase multilayer nanostructured coatings TiN-MoN were deposited in the modernized vacuum-arc plant

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"Bulat-6". *Fig. 1* shows the scheme of plant for multi-layer coatings deposition which provides a clear boundary between the layers of TiN and MoN.

The deposition was carried out under the following technological conditions. After the deposition of the first layer in a time of 10 or 20 s. both evaporators were turned off, substrate holder was turned at 180° and then both evaporators were turned on at the same time. The arc current during deposition was 85...90 A for titanium and 140 A for molybdenum, the nitrogen pressure in the chamber was 0.665 Pa, the distance from the evaporator to the substrate was - 250 mm, the substrate temperature was in the range of 250...350° C. Pulsed negative potential with duration of 10 ms, repetition rate of 7 kHz and amplitude of 2 kV and constant negative potential of 5…400 V was applied on the substrate during the deposition process.

Annealing of the samples was carried out in a vacuum oven at the residual gas pressure of 0.0013 Pa and the temperature of 800 C° for two hours after reaching this temperature. Photomicrographs of coatings were studied by scanning electron microscope (SEM) JEOL JSM-840. Automatic microindentation was performed with "Micron-Gamma" indenter with a Berkovich pyramid load within 50 g. The X-ray diffraction studies of the samples were carried out on DRON-3 diffractometer in Cu-Kα radiation at the discrete shooting mode of the scattering registration with a scanning pitch changing in the interval $\Delta(2\vartheta)=0.01...0.05^{0}$.

The average thickness of the coatings defined by electron microscopic images of coating fractures was 6-8 micron (*Table 1*).

Mass ratio of Ti and Mo atoms in coating is 49…44 mass% of Ti and 51…56 mass% of Mo. This corresponds to an atomic ratio of Ti / Mo for samples with small and medium-thick layers of 2-10 nm Ti/Mo $\approx$ 60/40, and for more layer deposition time 20 s (layer thickness $\approx$ 20 nm), this ratio shifts to Ti/Mo $\approx$ 70/30.

Table 1 – deposition parameters, mechanical characteristics, thickness, composition and structure of coatings. P_N = 0,665 Pa, U=2000 V, f=7 kHz.

Sample	U, V	Time, s	H, GPa		E, GPa		Relation TiN/Mo$_2$N, vol.%	Texture	Coating thickness, micron
			basic	anneal	basic	anneal			
1	-230	2	47	38	470	370	90/10	(111)	6,7
2	-230	10	26	24	370	355	60/40	(111)	7,2
3	-230	20	39	31	440	380	80/20	(111)	7
4	-40	2	31	24	380	370	TiN – 100	(200)	8
5	-40	10	42	30	430	430	60/40	(200)	6,7
6	-40	20	40	37	480	480	80/20	(200)	8,6

It can be noted that composition changes were not observed after annealing in vacuum (two hours, 800^0 C).

For TiN layer thickness of about 2 nm and substrate potential -40 V due to alleged epitaxial growth of layers X-ray phase analysis shows the contents of only one phase with a cubic fcc lattice (NaCl structural type) which is typical at low temperature for TiN. Alternation of Ti and Mo metal evaporators during sputtering in a nitrogen environment should lead to layer-by-layer generation of TiN and MoN with thickness ratio close to atomic ratio of metal atoms, which according to elemental analysis corresponds to the ratio of Ti/Mo equals to 60/40. In this case the lack of interface indicates the epitaxial growth of thin layers which lattice spacing is determined by the stronger bonds in titanium nitride layer. Mo_2N lattice spacing is 0.419 nm, i.e. less than TiN which helps of compression stress relaxation in TiN layers during epitaxial growth and is accompanied by period decrease in unstressed section to 0.4248 nm (sample 4).

When the substrate potential is -230 V the X-ray phase analysis shows the formation of two-phase material with the same type of TiN crystal lattice (fcc type NaCl) and high-temperature γ-Mo_2N phases with phase correlation TiN/Mo_2N equals to 90/10. In this case the reason for the appearance of two-phase state is an intense ion bombardment which contributes to grains refinement and beginning of interface formation. At the same time formation of Mo_2N as a separate layers with a cubic lattice and hence formation of the interface leads to stress increase in TiN phase and period increase in unstressed section (sample 1).

Increase of substrate potential leads to change of deposited coating texture from axis [100] to [111] which is accompanied by hardness increase.

For the second series of samples with a layer thickness of 10 nm table 1 (samples 2 and 5) it is significant that formation of two-phase structure with an average grade of TiN and γ-Mo_2N cubic phases as 60 vol.%-40 vol.% begins during the deposition which is close to the data results of X-ray fluorescence elemental analysis of atomic % components of metal atoms.

The occurrence of significant interface specific volume due to the high content of the second γ-Mo_2N-phase is accompanied by development of high compression stress in titanium nitride and achievement of sufficiently high hardness of 42...44 GPa at a relatively high elastic modulus 430...450 GPa. An exception is the sample obtained at substrate potential -230 V which hardness is relatively low. The most likely reason for the relatively low hardness appears to be a lack of nitrogen atoms in the coating compared with the stoichiometric composition as judged by reduction of titanium nitride lattice spacing which is 0.42378 nm (table value for stoichiometric composition is 0,42417 nm).

We should also mention that this series is characterized by more uniform surface morphology of the coating, but at substrate potential -230V cell is larger than at -40 V (*Fig.2*). At the same time fractures have enough correct

shape that is typical for destruction of material under the action of compression stress.

Samples with the most thick alternating layers of TiN and Mo$_2$N up to 20 nm also have two-phase structure (*Fig. 3*), but the volume content of molybdenum nitride phase prior to annealing (20%, Table. 1, Fig. 1a) is slightly lower in comparison with the data expected based on the results of X-ray fluorescence elemental analysis (30%). At the same time after annealing the volume content of phases accurately corresponds to data expected for the elemental analysis 70% TiN - 30% Mo$_2$N.

This fact can be explained by the appearance of diffused interface in coatings with a layer thickness up to 20 nm, which increases contribution to the diffraction effect of the phase with high volume content, in this case the phase of titanium nitride.
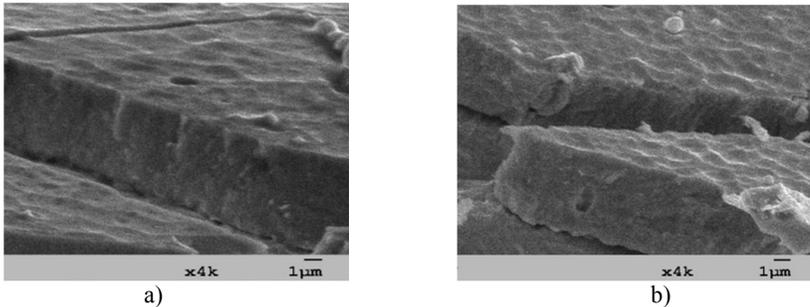

a)   b)

Fig. 2 – Photomicrographs of fractures of multilayer TiN-Mo$_2$N coating deposited on copper substrate, substrate potentials are -230 V (sample 2) a) and -40 V (sample 5) b).
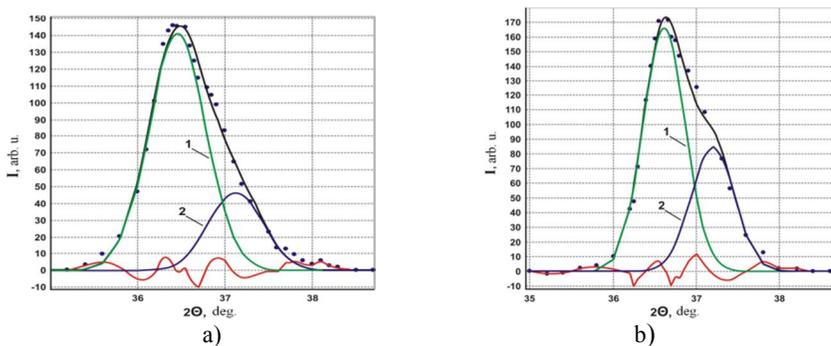

a)   b)

Fig. 3 – Separation of diffraction spectrum for component peaks of two phases (111) TiN and (111) γ-Mo$_2$N (sample 3) prior to annealing (a) and after annealing (b). 1 – separated peak (111) TiN; 2 – separated peak (111) γ-Mo$_2$N.

Because of diffused interface correspondence of the phase composition to elemental appears after annealing, when bound contribution is substantially reduced as a result of border area material transition from the amorphous to the crystalline state.

It should also be noted that this series of samples is characterized by lower hardness dependence on the magnitude of U. If you change U from -40 to -230 V total hardness varies from 40 to 39 GPa, and thus, in both cases, samples can be considered as superhard.

So:

There is a possibility of epitaxial growth of cubic isostructural modifications of titanium nitride and molybdenum nitride without formation of two-phase state in the case of small layer thickness up to $\approx$ 2 nm.

Layer thickness increase of multilayer system from 2 nm to 20 nm leads to increase of mechanical properties thermal stability of these coatings, which results in smaller decrease in hardness of coatings subjected to a high temperature annealing.

At greater layers thickness up to 10...20 nm two-phase material in which the second phase is an isostructural to titanium nitride high temperature molybdenum nitride γ-Mo_2N with a cubic lattice is formed. This leads to the fact that at the maximum layer thickness up to 20 nm during annealing at 800º C hardness decrease does not exceed 25% remains coating in a superhard state.