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Effect of High-Entropy Components of Nitride Layers on Nitrogen Content and Hardness of (TiN-Cu)/(AlNbTiMoVCr)N Vacuum-Arc Multilayer Coatings

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An integrated research of links in the "content-structure-properties" chain in structural engineering of (TiN-Cu)/(AlNbTiMoVCr)N multilayer coatings was carried out with application of elemental and X-ray diffraction analysis as well as microhardness testing. It has been found that formation of the second layer based on a high-entropy alloy even with a relatively small content of components (below 1 wt. %) leads to formation of a solid solution FCC lattice phase. Compared to TiN-Cu single-layer coatings, the multilayer coating based on a (TiN-Cu)/(AlNbTiMoVCr)N system has an increased nitrogen content and an enhanced hardness of up to 24.5 GPa.

Keywords: (TiN-Cu)/(AlNbTiMoVCr)N multilayer coating, Nitrogen content, Structure, Process gas pressure, Hardness.

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1. INTRODUCTION

The actuality of constructing new hard coatings based on the use of multi-element systems is caused by constantly emerging new problems of modern materials science, since it is already clear that the characteristics of known hard coatings (are currently most widely used in the Ti industry) cannot provide modern requirements for their effective functioning.

The additional introduction of transition metals and, thus, the production of multi-element and/or multilayer materials, which are used in this context, is due to the need to increase such functional properties as oxidation resistance, heat resistance, viscosity increase to material destruction, etc. (see, for example, [1-8]).

A new, very promising direction in the coating materials engineering developed in recent years is associated with the use of multi-element (high-entropy) nitride coatings, as well as the compositions on their basis [9].

The aim of this work was to create a multi-element multilayer coating from the base Ti-Cu cathode by its evaporation in nitrogen atmosphere until the formation of a composite TiN-Cu structure in combination with nitride layers of high-entropy AlNbTiMoVCr system and to determine the influence of its composition on the structural-phase state and mechanical properties.

2. SAMPLES AND METHODS OF STUDY

The samples were obtained by vacuum-arc method on the modernized installation "Bulat-6". The pressure of the working (nitrogen) atmosphere during deposition was equal to $P_N = (1.2…4.5) \times 10^{-3}$ torr. The deposition was carried out from two sources (Ti-12 wt. % of Cu) and (AlNbTiMoVCr) with continuous rotation of the samples attached to the substrates at a speed of 8 rpm that allowed to obtain a layer about 8 nm thick with the total number of layers of 960 (or 480 bilayer periods). The total deposition time of the coating was equal to 1 hour. A constant negative potential of a value of $-U_s = -100$ and -200 V was applied to the substrates during the deposition. The modes of obtaining coatings and their hardness are presented in Table 1 (I_a is the arc current of the first and the second cathodes, respectively, above and below; U_{cp} is the constant negative potential applied to the substrate during deposition; P_N is the nitrogen atmosphere pressure; H is the hardness).

Table 1 – Cathode materials, deposition parameters of the coatings and their microhardness

Sample No	Cathode materials	I_a, A	U_{cp}, V	P_N, torr	H, GPa
853	Ti-12 % Cu	80	200	$4.5 \cdot 10^{-3}$	22.1
854	(Ti-12 % Cu) + (AlNbTiMoVCr)	80 110	200	$4 \cdot 10^{-3}$	23.2
855	(Ti-12 % Cu) + (AlNbTiMoVCr)	80 140	100	$4 \cdot 10^{-3}$	24.5
856	(Ti-12 % Cu) + (AlNbTiMoVCr)	80 140	200	$1.2 \cdot 10^{-3}$	23.3
857	(Ti-12 % Cu) + (AlNbTiMoVCr)	80 140	100	$1.2 \cdot 10^{-3}$	19.9

The structural-phase analysis was performed by X-ray diffractometry in Cu-k_{α}-radiation on the installation DRON-4. The separation of profiles into components was implemented by the software package "NewProfile".

The hardness was measured by a microindentation method with a Vickers diamond pyramid as an indenter at loads of 50 g. The investigation was conducted on a microhardness tester using a DM-8 hardness meter by the micro-Vickers method.

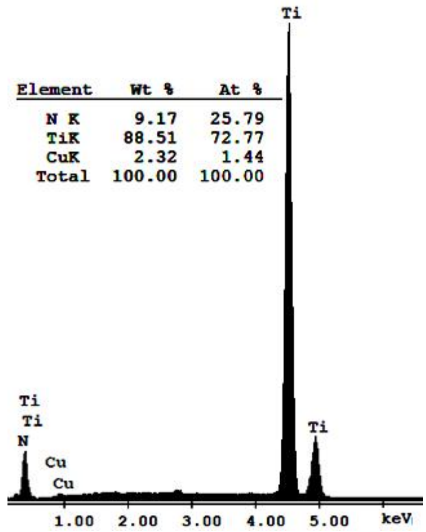
Analysis of the elemental composition was performed based on the energy-dispersive spectra obtained on a scanning electron microscope FEI Nova NanoSEM 450.

3. RESULTS AND DISCUSSION

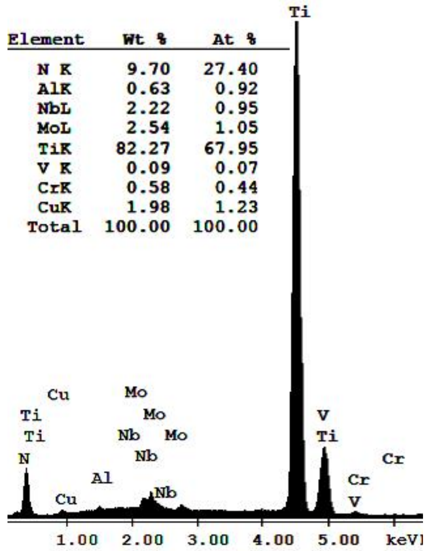
Since the aim of the work was to clarify the regularities in a classical materials science sequence: composition – structure – properties, then the first stage in the study was the determination of the elemental composition of the coatings obtained under different technological conditions. In Fig. 1 we illustrate the energy-dispersive spectra and the results of their processing for examining the elemental composition. It is seen that for a single-layer coating obtained by evaporation of Ti + 12 wt. % of Cu cathode at a pressure of $P_N = 4.5 \times 10^{-3}$ torr (see Fig. 1a), the nitrogen content is equal to 25.8 wt. %. When producing a multilayer (TiN-Cu)/(AlNbTiMoVCr)N coating, the nitrogen content in the coating increases to 27.4 wt. % and, here, practically is not changed in the range of the applied negative bias potential of – 100 … – 200 V (Fig. 1b). A slightly higher nitrogen concentration revealed in the coating, which is obtained at a potential of – 200 V, can be caused by a high content there of strong nitride-forming elements Mo and Al (Fig. 1b). With decreasing pressure to $P_N = 1.2 \cdot 10^{-3}$ torr, the nitrogen content in the coating expectedly decreases that is mostly manifested in the coating obtained by applying a potential of – 100 V (Fig. 1c, d). The latter is also due to the above noted tendency to increase the content of strong nitride-forming elements Mo and Al that promotes the nitrogen retention during deposition under the condition of applying a larger negative bias potential.

The study of the structural state using the X-ray diffraction method showed that during evaporation of the Ti + Cu cathode in a nitrogen atmosphere, the system of peaks of the TiN phase (with the texture axis [111]), as well as α-Ti and Cu (Fig. 2, spectrum from the sample 853), is the main system of diffraction peaks in the obtained coatings. The introduction of a high-entropy alloy (AlNbTiMoVCr)N layer results in the appearance of a system of reflexes from the fcc-crystal lattice with a period of 0.4452 nm and increase in the degree of texturing of the TiN component with the texture axis [111].

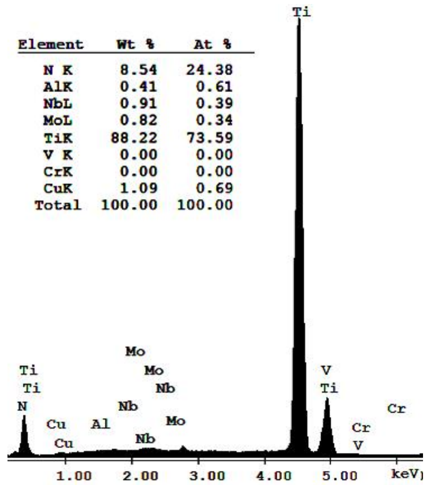
In deposition, when a lower (in magnitude) potential $-U_s = -100$ V is applied (spectrum 855 in Fig. 2), this leads to a decrease in the degree of preferred orientation [111] and appearance of preferred orientation with the axis [100] perpendicular to the growth plane. When the nitrogen atmosphere pressure decreases in deposition to $P = 1.2 \times 10^{-3}$ torr, one observes a preferential growth of crystallites with the axis [100], to which the relative increase in the intensity of the reflex (200) corresponds (see Fig. 2, spectra 856 and 857).



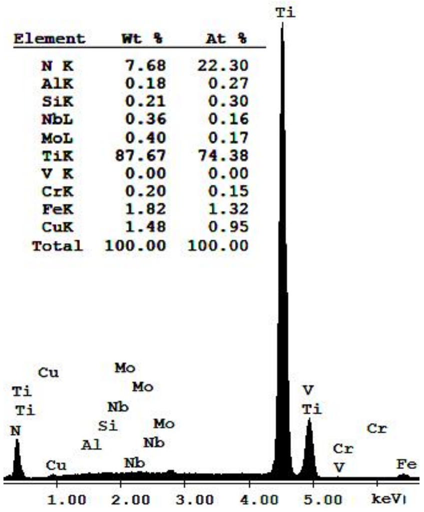
a



b



c



d

Fig. 1 – Energy-dispersive spectra and determined from them elemental composition of the coatings of the multilayer system (TiN-Cu)/(AlNbTiMoVCr)N, whose production modes are given in Table 1: a – 853, b – 854, c – 856, d – 857

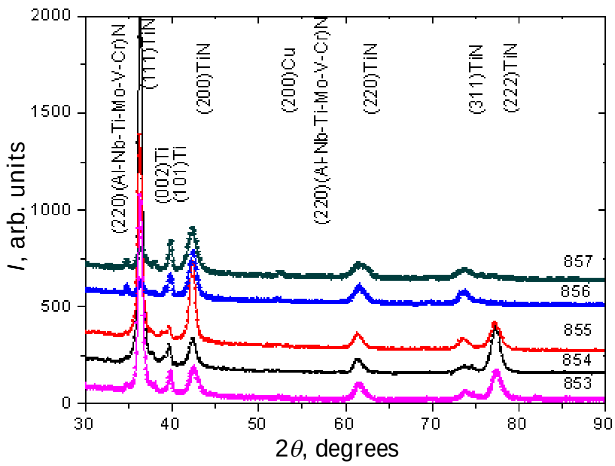


Fig. 2 – Regions of the diffraction spectra with identification of diffraction peaks for the coatings of (TiN-Cu)/(AlNbTiMoVCr)N system (the numbers of the curves correspond to the numbers of the samples in Table 1)

Formation of a texture with the axis [100] is defined by the surface energy minimum and observed in the case of a relatively low deformation of the crystal lattice due to "atomic peening", i.e. the effect [10] during implantation of film-forming particles in deposition of the coatingi [11, 12].

In the work, the hardness determined by the micro-indentation method was used as a universal characteristic of the mechanical properties of the coatings. As seen from the results given in Table 1, deposition of a high-entropy alloy nitride layer leads to an increase in hardness (compare samples 853 and 854 in Table 1). At the time, an increase in hardness is caused by an increase in the content of strong nitride-forming element Ti in the coating (sample 855), when the hardness reaches the maximum value of 24.5 GPa (in Fig. 3 we present the coating surface after indentation).

A reduction in the nitrogen content in the coatings obtained at a lower working pressure of $P = 1.2 \times 10^{-3}$ torr leads to a decrease in hardness to 19.9 GPa (see sample 857 in Table 1).

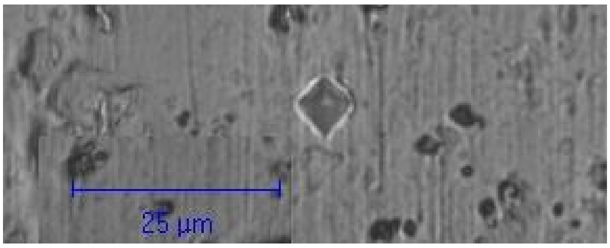


Fig. 3 – View of the coatings surface after indentation with a puncture mark of a diamond pyramid when measuring hardness

4. CONCLUSIONS

1. It is established that the use of one evaporating (Ti-12 wt. % Cu) cathode leads to the formation in the coatings deposited in a nitrogen atmosphere of the three-phase state based on the TiN phase with the preferred orientation axis of the crystallites growth [111].

2. The introduction of the second high-entropy alloy layer even with low relative content of the constituent elements (to 1 wt. %) is accompanied by the formation of the solid solution fcc-lattice phase.

3. A multilayer coating obtained as a result of evaporation of (Ti-Cu) and (AlNbTiMoVCr) cathodes with continuous rotation differs from the single-cathode (Ti-Cu) evaporation by an increased content of nitrogen component in the coating and an enhanced hardness.

REFERENCES

1. *Nanostructured coatings* (Ed. by A. Cavaleiro, J.T.M. De Hosson) (New York: Springer: 2006).
2. W.D. Munz, *J. Vac. Sci. Technol. A* 4, 2717 (1986).
3. O. Knotek, R. Elsing, M. Atzor, H.G. Prengel, *Wear* 133, 189 (1989).
4. O.V. Sobol′, A.A. Andreev, V.A. Stolbovoi, V.E. Fil′chikov, *Tech. Phys. Lett.* 38 No 2, 168 (2012).
5. G. Hakansson, J.E. Sundgren, D. Mcintyre, J.E. Greene, W.D. Munz, *Thin Solid Films* 153, 55 (1987).
6. O. Knotek, M. Atzor, H.G. Prengel, *Surf. Coat. Technol.* 36, 265 (1988).
7. R.A. Andrievskiy, *Russ. Chem. Rev.* 66 No 1, 53 (1997).
8. A.D. Pogrebnjak, A.A. Bagdasaryan, I.V. Yakushchenko, V.M. Beresnev, *Russ. Chem. Rev.* 83 No 11, 1027 (2014).
9. V.M. Beresnev, O.V. Sobol′, I.N. Toryanik, A.A. Meylekhov, U.S. Nyemchenko, P.V. Turbin, I.V. Yakushchenko, M.O. Lisovenko, *J. Nano-Electron. Phys.* 6 No 1, 01030 (2014).
10. O.V. Sobol′, *Phys. Metals Metallography* 91 No 1, 60 (2001).
11. U.S. Nyemchenko, V.Ju. Novikov O.V. Sobol′, S.S. Grankin, E.M. Tulibiyev, A. Radko, *J. Nano-Electron. Phys.* 7 No 1, 01041 (2015).
12. U.S. Nyemchenko, V.Yu. Novikov, S.S. Grankin, V.V. Ganenko, M.Yu. Arseenko, O.V. Sobol′, O.P. Tkach, *J. Nano-Electron. Phys.* 7, No 2, 02040 (2015).