Structure Engineering in Vacuum-Arc-Deposited Coatings of the MoN−CrN System

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Abstract—The possibilities of structure engineering in multilayer coatings of the MoN−CrN system with relatively low heats of formation of component transition metal nitrides are demonstrated by varying pressure P_N of reactive gas (nitrogen) and negative bias voltage $−U_s$ applied to a metal substrate. It is established that, by changing P_N from 7×10^{-4} to 3×10^{-3} Torr, it is possible to obtain coatings in two significantly different structural-phase states. A multilayer nonisostructural composite with hexagonal crystalline lattice in CrN layers and cubic type lattice in MoN layers is formed at low pressure, whereas an isostructural state with cubic lattice in both nitride layers is formed at high pressure. The existence of two types of structural states allows multilayer coatings with controlled hardness to be obtained, which reaches 38 GPa in the isostructural state.

Using the deposition of multilayer systems, it is possible not only to model the structural state of each separate layer, but also to select the necessary thickness, material, and number of layers per period so as to create artificial structures possessing unique functional properties [1−5].

In single-layer coatings based on MoN and CrN, the structure and properties can be varied within broad limits depending on the voltage applied to a substrate and the pressure of nitrogen-containing atmosphere during deposition [6, 7]. For this reason, one can expect high sensitivity for these parameters for the structural states and properties of coatings obtained using MoN and CrN as component layers in a multilayer system. The most significant effects can be expected in systems with component layer thicknesses in a nanometer range, which is related to the fact that the highest mechanical properties of nitrides are observed on this scale [8, 9].

The present work was devoted to studying the influence of negative bias voltage $−U_s$ (which determines the energies of deposited particles) and the pressure of nitrogen-containing atmosphere in the reactor chamber (determining the content of nitrogen in the deposit) on the structural-phase state of deposited layers (structure engineering) and their mechanical properties (in particular, hardness).

The samples of multilayer coatings of the MoN−CrN system were obtained by vacuum-arc-deposition in a modified setup of the Bulat-6 type [10]. The pressure of working (nitrogen-containing) atmosphere during deposition was varied within $P_N = (7−30) \times 10^{-4}$ Torr and the deposition rate was about 3 nm/s. The component metals (Mo and Cr) were supplied from two sources (evaporators) to substrates continuously rotating at 8 rpm, which allowed component layers with thicknesses about 10 nm and coatings with a total number of component layers of up to 960 (480 bilayers) and total thickness of about 9 μm to be obtained. During deposition, a constant negative voltage of $−U_s = 20, 70, 150,$ or 300 V was applied to the substrates.

The structural-phase state of samples was studied by X-ray diffraction (XRD) using CuK_α radiation. Deconvolution of XRD profiles into components was performed using a NewProfile program package. The elemental composition of coatings was determined by energy-dispersive X-ray (EDX) spectroscopy on a scanning electron microscope (FEI Nova NanoSEM 450). The coating thicknesses were measured on the
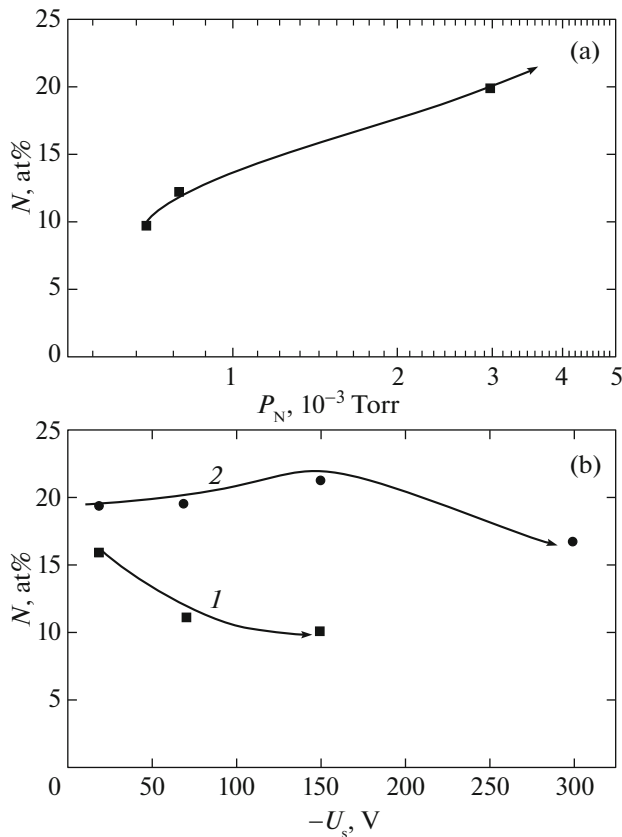
Fig. 1. Plots of the nitrogen content in coatings (a) vs. pressure P_N during deposition at constant $U_s = -70$ V and (b) vs. U_s at constant $P_N = 7 \times 10^{-4}$ Torr (curve *1*) and 3×10^{-3} Torr (curve *2*).

same instrument using cross sections of coating–substrate samples. The hardness was measured by the micro-Vickers method using a DM 8 hardness meter at an indenter load of 0.2 N.

Figure 1 shows the results of analysis of the elemental composition of coatings as dependent on nitrogen pressure P_N during deposition and on bias voltage $-U_s$. As can be seen, the content of nitrogen (light interstitial impurity) is most significantly influenced by P_N (Fig. 1a), while the dependence on $-U_s$ is much less pronounced (Fig. 1b) as manifested by a relative decrease in the atomic concentration of nitrogen (caused by selective secondary sputtering from the growth surface) at large $-U_s$ values. It should be noted that increased binding of deposited metal to atmospheric nitrogen at high P_N leads to stabilization of the coating composition at significantly greater values of $-U_s$ (see Fig. 1b, curve *2*). An increase in the absolute value of bias voltage $-U_s$ leads to a significant increase in the homogeneity of coatings (decrease in the droplet spray fraction). Another way to decreasing the droplet fraction is provided by using pulsed evaporation beams [11, 12].

Data on the relative content of metal components (Mo and Cr) in the coating depending on the bias voltage are given in Table 1, from which it follows that the Mo/Cr atomic ratio strongly depends on $-U_s$ at lower nitrogen pressure. This behavior is explained as being a result of a higher average energy of Mo and Cr ions bombarding the growing layer, which is related to smaller collisional losses of ion energies at lower nitrogen pressure P_N.

To study the influence of the technological parameters ($-U_s$, P_N) determining the energy of deposited particles and their composition, respectively, we have prepared two series of samples. The first series was deposited at $P_N = 7 \times 10^{-4}$ Torr and various bias voltages $-U_s = 20$, 70 and 150 V; the second series was prepared at the same bias voltages and a higher nitrogen pressure of $P_N = 3 \times 10^{-3}$ Torr. Figures 2a and 2b show fragments of the XRD patterns observed for these series of coatings. As can be seen, a lower pressure of nitrogen ($P_N = 7 \times 10^{-4}$ Torr) leads to the formation of lower nitrides β-Cr_2N (hexagonal lattice, JCPDS 35-07803) and γ-Mo_2N (FCC lattice, JCPDS 25-1366) with coinciding interplanar spacing for $(110)\beta$-$Cr_2N/(111)\gamma$-Mo_2N planes and non-coinciding distances between $(002)\beta$-Cr_2N and $(200)\gamma$-Mo_2N. An increase in the absolute value of bias voltage $-U_s$ in this system is accompanied by preferential growth of $(002)\beta$-Cr_2N and $(200)\gamma$-Mo_2N (Fig. 2a, curves *3*), which leads to increasing interlayer mismatch.

The deposition at higher nitrogen pressure $P_N = 3 \times 10^{-3}$ Torr leads to the formation of chromium mononitride CrN and γ-Mo_2N with cubic NaCl type lattices in both layers (Fig. 2b). In this case, an increase in the absolute value of bias voltage $-U_s$ is accompanied by a transition from a semicrystalline nontextured state at $-U_s = 20$ V to predominant orientation of grains during deposition with [100] axial texture at bias voltages $-U_s$ above 70 V (Fig. 2b, curves *3* and *4*). Note that the appearance of this type of texture is apparently related to a relative decrease in the content of nitrogen in the coating with increasing absolute value of $-U_s$. The presence of structures with coinciding interplanar distances may be indicative of a mutually related growth of these structures.

The obtained spectrum of structural states in multilayer coatings determined significant variations in

Table 1. Dependence of Mo/Cr atomic ratio on the applied bias voltage $-U_s$ and nitrogen pressure P_N

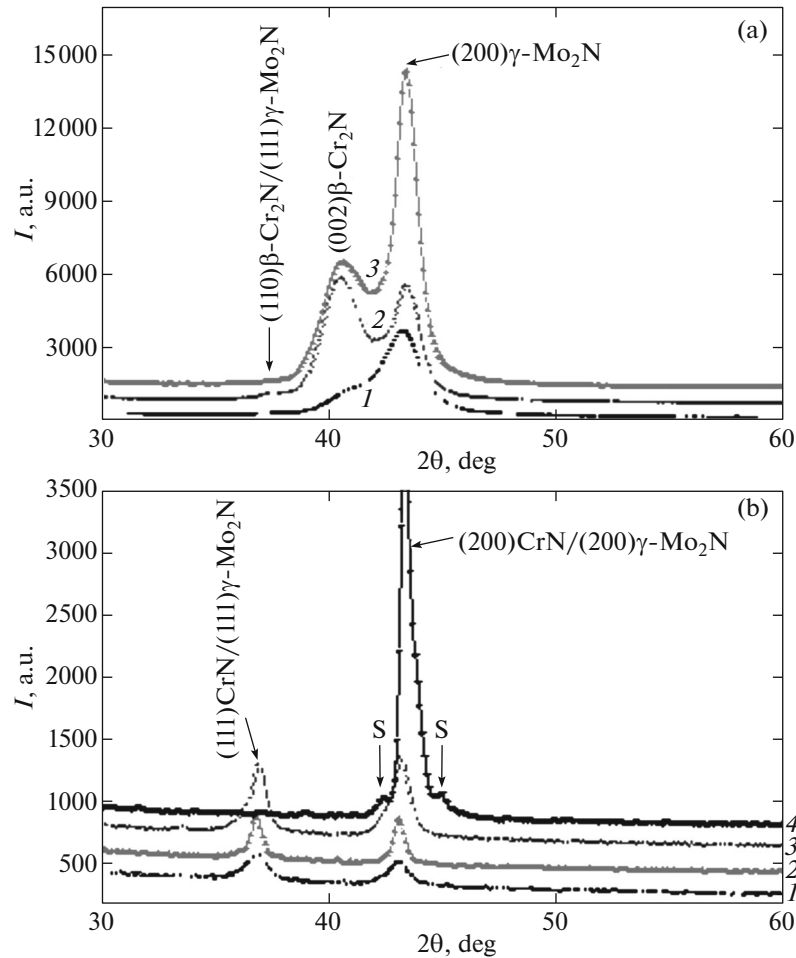| Nitrogen pressure P_N, Torr	Bias voltage $-U_s$, V						
	25	50	100	150	200	250	300
7×10^{-4}	0.80	0.85	0.99	1.35	—	—	—
3×10^{-3}	0.86	0.90	0.92	0.93	0.95	0.97	1.05

Fig. 2. Fragments of the XRD patterns of coatings deposited at various conditions: (a) $P_N = 7 \times 10^{-4}$ Torr and $-U_s = 20$ V (*1*), 70 V (*2*) and 150 V (*3*); (b) $P_N = 3 \times 10^{-3}$ Torr and $-U_s = 20$ V (*1*), 70 V (*2*), 150 V (*3*), and 300 V (*4*) (arrows S indicate super-structural reflections).

their mechanical characteristics. As can be seen from the data presented in Table 2, the maximum value of hardness was achieved under conditions of small bias voltage U_s and high nitrogen pressure P_N, which ensure the isostructural state of component layers and maximum content of nitrogen in the coating. A decrease in the hardness of coatings formed at lower pressure may be related to the appearance of vacancies in the nitrogen sublattice because of its significantly lower content in comparison to the stoichiometric nitride composition. A comparison of data in Tables 1 and 2 shows that, as the Mo/Cr ratio increases from 0.80 to 1.35, the coating hardness significantly decreases. The drop in hardness is most pronounced at the lower nitrogen pressure γ-Mo$_2$N, which can be explained by comparing the phase compositions of coatings using the XRD data presented in Fig. 2. Indeed, at both $P_N = 7 \times 10^{-4}$ and 3×10^{-3} Torr, a γ-Mo$_2$N phase with a large region of composition homogeneity is formed in the Mo−N layers. In contrast, layers of the Cr−N subsystem exhibit the formation of phases of two types depending

on the pressure: β-Cr$_2$N with hexagonal lattice is formed at $N = 7 \times 10^{-4}$ Torr and CrN phase with cubic lattice and relatively small region of homogeneity is formed at $P_N = 3 \times 10^{-3}$ Torr. According to the obtained results, a higher hardness is achieved when this cubic CrN phase is present in the Cr−N layers. The maximum value (38 GPa) was observed for Mo/Cr atomic ratios below 0.9 (cf. data in Tables 1 and 2). In addition, a decrease in the hardness of coatings deposited at increasing U_s is probably also caused by growing intensity of mixing in the boundary layer with the formation of a solid solution of reduced hardness, which is in agreement with data presented in [13].

Thus, the results of our work demonstrate the possibilities of structure engineering in a multilayer system based on transition metals with relatively low heats of nitride formation with transition from a non-isostructural to an isostructural interlayer state at relative small change in nitrogen pressure P_N. A bias volt-

Table 2. Dependence of the hardness (H, GPa) of coatings on bias voltage $-U_s$ and nitrogen pressure P_N during deposition

Nitrogen pressure P_N, Torr	Bias voltage $-U_s$, V			
	20	70	150	300
7×10^{-4}	28	18	12	—
3×10^{-3}	38	38	32	27

age that is usually applied for improving connectivity of layers during deposition, positively influences properties of the multilayer system with nanometer-thick layers only at low $-U_s$ values (bellow 70 V) for which the region of mixing in the interlayer space during deposition does not play a determining role. The obtaining of coatings possessing high mechanical properties in this case is favored by the mutual cohesion of layers in the isostructural state.

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