

Effect of Preparation Conditions in the Pressure Range of Atmospheric Nitrogen ($2 \dots 50$) 10^{-4} Torr on the Structural and Phase State of the Vacuum-Arc Coatings of Mo-N

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This work deals with the impact of the reactive atmosphere (N_2) pressure and bias potential values on the phase-structural state of the coatings being formed. It has been found that at a low bias potential $U_b = (0 \dots -40)$ V, and with pressure increase from $2 \cdot 10^{-4}$ up to $5 \cdot 10^{-3}$ Torr, phase formation takes place in the following sequence: supersaturated solid solution of nitrogen in the bcc lattice of Mo ($Mo_{(N)}$) $\rightarrow \gamma$ - Mo_2N $\rightarrow \gamma$ -MoN phases with the NaCl-type lattice and with different degrees of octahedral interstitial site occupation with nitrogen. At $U_b = (-40 \dots -100)$ V, the sequence of phase-structural states is as follows: Mo ($Mo_{(N)}$) $\rightarrow \gamma$ - Mo_2N $\rightarrow \varepsilon$ -MoN (hexagonal lattice) $\rightarrow \delta$ -MoN. At highest U_b (with a strong radiation factor effect) values ranging between -150 V and -200 V and with pressure increase, the composition changes to Mo ($Mo_{(N)}$) $\rightarrow \gamma$ - Mo_2N $\rightarrow \beta$ - Mo_2N $\rightarrow \varepsilon$ -MoN $\rightarrow \delta$ -MoN.

Keywords: Vacuum-Arc coatings, Nanostructured, Mo-N system, Bias potential, X-ray diffraction.

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1. INTRODUCTION

Nanocrystalline vacuum-arc nitride coatings possess the totality of unique structural states and properties (high hardness, wear resistance, oxidation stability, etc.) [1]. The coatings of the Mo-N system show a high hardness and low solubility of nonferromagnetic materials, thereby attracting great interest in their industrial use [2]. Unfortunately, at present there is an apparent lack of information on the regularities of phase-structural state formation in the Mo-N system.

Mo-N coatings can be deposited by various techniques such as ion beam deposition stimulated, dc and r.f. magnetron sputtering, arc PVD-technique and ion implantation of nitrogen into the film-coated pure molybdenum. Among these techniques arc PVD is one of the most versatile processes due to the high degree of ionization and good adhesion properties of the coatings.

Formation phases in Mo-N coatings is strongly dependent on process parameters. Currently there is a lack of information in the literature concerning the systematic investigation of relations between the parameters and deposition properties of the coatings Mo-N. For this system, characterized by two stable compounds: δ -MoN and Mo_2N . Recently, the compound exists in two versions: the low-temperature – (β) and high (γ). The transformation $\gamma \Rightarrow \beta$ is a martensitic. Phase δ -MoN has a hexagonal lattice with parameters $a = 0.572$ nm and $c = 0.560$ nm (Fig. 1a). The homogeneity region Mo_2N is (27.5 ... 30.1) at.% N. Phase Mo_2N has an fcc lattice with a structural type of NaCl ($a = 0.4137$ nm at 27.5 atm.% N, Fig. 1b). β - Mo_2N – an ordered tetragonal modification γ - Mo_2N

pseudo cell face centered tetragonal ($a = 0.4200$ nm, $c = 0.4005$ nm, Fig. 1c) [3].

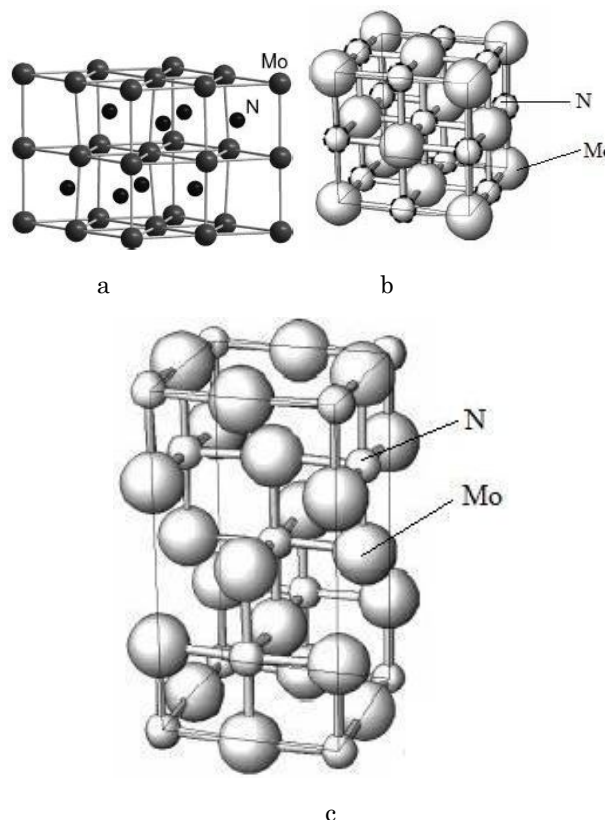


Fig. 1 – Crystal structure of δ -MoN (a), γ - Mo_2N (b) and β - Mo_2N (c)

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Also in the case of vacuum-plasma condensates in analogy to that described in [4] for coatings in the system Mo-N to form a nanostructured state can expect the appearance of the crystallite space group P6/mmm, which for the nitrides was recorded in the system TaN. MoN phase with a hexagonal lattice of the space group P6/mmm, denoted by analogy with the phase of ϵ -TaN [5], as ϵ -MoN phase with a hexagonal crystal structure shown in Fig. 2.

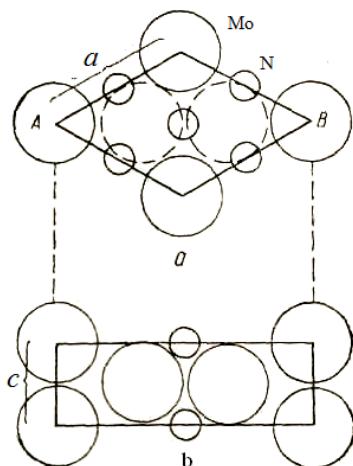


Fig. 2 – The crystal structure of TaN: a – the unit cell; b – its vertical section on AB [5]

An attempt to systematize the structural and phase state was first made in [6] for the system Mo-N at relatively high pressure reactive atmosphere (more than $2 \cdot 10^{-3}$ Torr). However, studies have shown the mechanical properties of the vacuum-arc coating system Mo-N [7] to the highest mechanical properties of the system can be expected at lower pressures. Moreover, this pressure provides a technological process, as proceeds at a net formation conditions. In this context, this paper attempts to summarize accumulated in this area by the authors of data for relatively low pressure range form ($2 \cdot 10^{-4}$ – $5 \cdot 10^{-3}$) Torr.

It should be noted that the identification phase state compared with X-ray diffraction data given in [6] shows the possibility of using all of the phase states, and at a lower pressure, but increased intensity because of the use of the process nitride formation additional magnetic block [8], increases ionization, and by improving the process of forming by supplying high-voltage pulse to the substrate bias potential. If we consider the sub-bands in the pressure range studied ($2 \cdot 10^{-4}$ – $5 \cdot 10^{-3}$) Torr, in accordance with the characteristic of phase-structural state can be distinguished interval $P_N = (2 \dots 6) \cdot 10^{-4}$ Torr. This interval is characterized by the formation of single-phase structural state of Mo phase with a bcc lattice. Constant flow of negative bias potential leads to the appearance of the texture of growth (110) (Fig. 3a).

In the case of low value of the bias potential (-40 V) at a pressure of $8 \cdot 10^{-4}$ Torr instead supersaturated on nitrogen atoms of molybdenum is formed γ -Mo₂N (structural type NaCl) with a relatively low

lattice period and texture (311), see Fig. 3b.

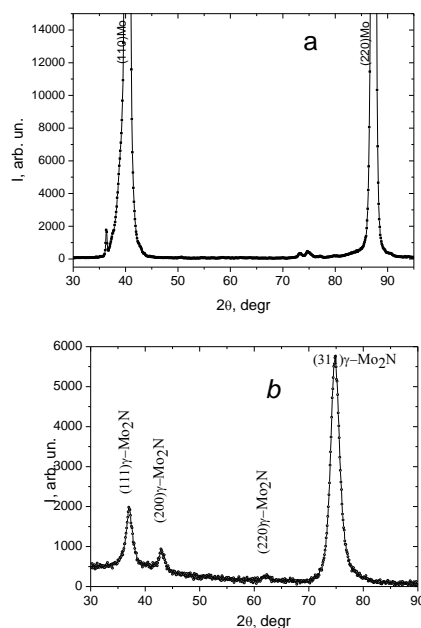


Fig. 3 – X-ray diffraction spectrum from the coating produced by $P_N = 8 \cdot 10^{-4}$ Torr and $U_b = -200$ V (a) and spectrum from the Mo-N coatings obtained at $U_b = -40$ V and a nitrogen pressure of about $7 \cdot 10^{-4}$ Torr at length storage at 10 seconds (radiation Cu-K α , identification of the phase γ -Mo₂N) (b)

Feeding of a higher amount of negative bias potential results in a phase with a low nitrogen content, even at relatively high pressure $P_N = 2 \cdot 10^{-3}$ Torr. In the two-phase coating stabilized condition in which, in addition to the solid solution of nitrogen in the bcc molybdenum nitride formed γ -Mo + N with very poor texture (311).

The lattice periods of nitrides are close to the value of 0.416 nm. Apparently, this value corresponds to the period of the stoichiometric composition of the phase Mo₂N with NaCl-type lattice in which nitrogen occupies half of the possible places to fill the octahedral interstices. As the pressure decreases the value of a work environment macrodeformation from -1.92% at a pressure of $8 \cdot 10^{-4}$ Torr (-40 V) up 0.53% at $P_N = 2 \cdot 10^{-3}$ Torr. Such a reduction in the stress-strain state with increasing pressure may be due to a significant loss of energy film-forming particles at high pressure. In the latter case, a phase according Mo « $\sin^2 \psi$ »-method developed tensile strain value 0.28% (corresponding to step macrostresses tension value 0.67 GPa).

For coatings produced at a relatively high pressure nitrogen $P_N = 0.2$ Pa, and a relatively small $U_b = -40$ V and -70 V at diffraction spectra also revealed the texture (311) (see Fig. 5), and the values were large periods and amounted to 0.4184 nm and 0.4189 nm, respectively. The value of macrodeformation was -0.97% for $U_b = -40$ V and -2.05% for $U_b = -70$ V.

In this connection identified in the characteristic values of two frames (close to 0.416 nm and 0.419 nm, respectively, Fig. 4) can be classified into two types of ordering in the lattice structural type NaCl. In the first case corresponds to the ordering of the stoichiometry of γ -Mo₂N, while the second - MoN with fcc metal sublattice.

At higher pressure $P_N = (2 \dots 6) \cdot 10^{-3}$ Torr and $U_b = (-150 \dots -200)$ V occurs in the formation of ϵ -MoN phase

with a hexagonal crystal structure (Fig. 5).

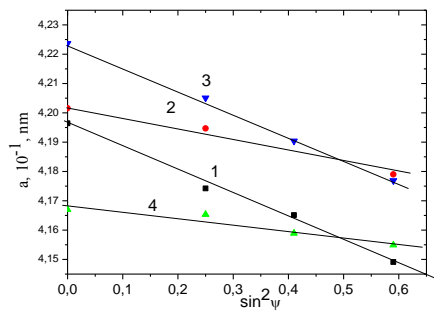


Fig. 4 – « $a\text{-sin}^2\psi$ »-graphs for determining the macrodeformation in coatings Mo-N system, obtained at no bias potential supply (when "floating" potential) and a pressure $P_N = 7 \cdot 10^{-4}$ Torr (1), when the $P_N = 1,3 \cdot 10^{-3}$ Torr and $U_b = -40$ V(2), $U_b = -70$ V (3) and $U_b = -200$ V (4)

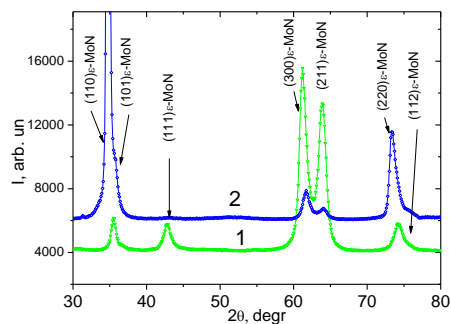


Fig. 5 – X-ray diffraction spectra from the coating Mo-N system, obtained by pressure at $P_N = 3 \cdot 10^{-3}$ Torr, $U_b = -200$ V and and high-voltage pulse with an amplitude of stimulation: 1 – 1.2 kV, 2 – 2 kV

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Thus, a generalized phase diagram coordinates P_N – U_b for range pressures $P_N = (7 \dots 50) \cdot 10^{-4}$ Torr and $U_b = (0 \dots 200)$ V has the form shown in Fig. 6.

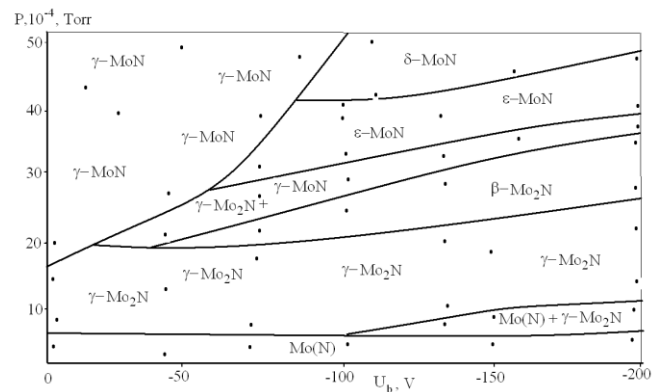


Fig. 6 – The phase diagram for vacuum plasma coating Mo-N system in the coordinates P_N – U_b

It is seen that the vacuum plasma nanostructured coating of the Mo-N system with an increase in bias potential observed with the formation of phases disadvantage nitrogen atoms and a non-cubic crystal lattice type.