Influence of nitrogen concentration on structure, composition and properties of nitride coatings deposited by vacuum arc plasma-assisted method

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Abstract. The coatings based on molybdenum nitride have been obtained by vacuum arc plasma-assisted method and have been investigated in a complex. For generation of gas-metal plasma two types of plazmagenerator were used: arc evaporator based on self-sustained arc discharge with cathode spot and a source of gas plasma on the basis of the non-self-sustained arc discharge with the combined hot and hollow cathode. The influence of the modes of plasma assistance on characteristics, composition and structure of MoN coatings was studied. It is revealed that the increase of arc current of a gas plasma source leads to increase in a share of nitrogen in gas-metal plasma, to increase the concentration of nitrogen in a coating, to increase in a share of molybdenum nitrides in coating and significant improvement of characteristics: to increase of hardness and wear resistance.

1. Introduction
Development and creation of surface functional layers and coatings with the required properties on a surface of the used products is an important problem not only from the view point of fundamental science, but also for many application-oriented directions, for example, for instrumental and mechanical engineering industry (wear-resistant coatings), medical applications (biocompatible coatings), etc. [1–2] MoN coating has the high mechanical characteristics and good adhesion to the tool and also chemical inertness in relation to non-ferrous metals, therefore it is an attractive to industrial applications, for example, for processing of non-ferrous metals. High hardness and low friction coefficient of molybdenum nitrides define their high tribological properties. Under normal friction conditions in thin (~0.1 nm) surface layers there are temperature above 1000°C on microroughnesses of the rubbing surfaces, at which molybdenum nitrides turn into the molybdenum, its microhardness becomes equal to 11-12 GPa. In case of friction the microroughnesses on a coating surface is smoothed, a molybdenum is oxidized by oxygen from air, the secondary structures are formed, its steady against abrasive and adhesive wear. The friction coefficient decreases also due to the lubricating effect of the molybdenum oxides which are formed due to oxygen from air atmosphere [1]. It is known from literature [3-8] that the best characteristics of MoN coatings have one phase coating formed by δ-MoN with a hexagonal lattice [9]. There are several ways for synthesis MoN coating with necessary phase composition.

First, it can be reached by increase of nitrogen pressure in the working chamber [3, 5-8]. Secondly, the authors of [4] tried to obtain the dominance of δ-MoN phase over Mo and γ-Mo2N in MoN coatings by increase in partial nitrogen pressure in a working gas mixture at the total pressure of 0.2 Pa. Thirdly,
change of phase composition can be achieved by means of additional ion bombardment including due to increase of energy of the ions bombarding a surface of the growing coating [3-5]. In [4] at using the IBAD method for MoN coating deposition with increase of ion energy from 300 to 1000 eV the dominance of δ-MoN phases over γ-Mo2N a phase is observed. Fourthly, the temperature of a substrate on which surface MoN coating is synthesized influences to its phase composition [3]. Here at lower temperatures of 300-380°C only the delta phase is observed, in the case of increase in temperature up to 410–510 °C – a gamma phase.

In this work, increase δ-MoN phase over Mo and γ-Mo2N in coating is reached by additional ionization of gas by means of a source of gas-discharge plasma based on non-self-sustained discharge with the combined hot and hollow cathode [9–10].

The purposes of the work are synthesis of single-layered nitride MoN coatings by vacuum arc plasma-assisted method with different concentration of nitrogen and investigation of influence of nitrogen concentration on its structure, composition and properties. To vary the nitrogen concentration of coating the share of nitrogen ions in gas-metal plasma will be varied by change of parameters of gas-discharge plasma at constant working gas pressure and arc current of arc evaporator.

2. Material and research techniques

The substrate material was a hard alloy WC-8%Co. MoN coatings were deposited by vacuum arc plasma-assisted method on “QUINTA” setup. The experiments on MoN coatings deposition were carried out using the “QUINTA” automated plasma-ion facility [11, 12]. “QUINTA” setup is equipped with five plasma sources: three arc evaporators based on arc self-sustained discharge with cathode spot, and two gas-plasma source based on arc non-self-sustained discharge with combined hot and hollow cathode [9, 10]. Two plasma sources (source of metal plasma and source of gas-discharge plasma) have been developed with extended dimensions (length is about 400 mm).

Figure 1. Dependence of density of ion current to the substrate on the discharge current for the sources of gas-discharge plasma (1) and arc evaporator (2). Gas – nitrogen; cathode material – molybdenum.

The used in the present work source of gas discharge plasma with combined hot and hollow cathode consists of a stainless-steel cylindrical cathode cavity with Ø 80 mm and h=240 mm. The filament cathode is made of tungsten wire (Ø 1.5 mm) and is fixed at the copper water-cooled current leads. The cathode assembly is placed into a longitudinal magnetic field of induction 2.5·10⁻² T created by a solenoid located outside the gas-plasma source. The principle of the PINK plasma source is based on the use of a non-self-sustained arc discharge with a combined hot and hollow cathodes. The used in the present work metal plasma source was a DI-100 arc evaporator based on a self-sustained arc discharge
with cathode spot [10]. The DI-100 arc evaporator provides the stable ignition and steady burning of the low-pressure arc with the current of 45-250 A at the burning voltage of 20-40 V. The cathode diameter is 100 mm. Cathode material is commercially pure molybdenum ($C_{Mo} \geq 99.96\%$).

Deposition parameters were the following: gas pressure $p_{N_2}=0.2$ Pa and negative bias voltage $U_b=150-250$ V, current of arc evaporator $I_d=80$ A. The deposition duration was chosen so that the coating thickness was $\approx 3$ $\mu$m. The discharge current density of the gas-discharge plasma source was varied parameters. Ion current density to the substrate vs the discharge current for the sources of gas plasma is presented in figure 1. The ratio of ion current densities of gas-discharge plasma source and arc evaporator ($j_p/j_d$) is varied from zero to 1.

After deposition we analyzed the surface morphology and elemental composition of formed MoN coatings by optical ($\mu$Vizo-MET-221 metallographic microviewer) and scanning electron microscopy (Philips SEM 515 microscope, EDAX ECON IV microanalyzer), its phase state by x-ray analysis (XRD 6000 diffractometer), microhardness (PMT-3 tester), and wear resistance (TRIBOtechnic device).

3. Results and discussion

In the figure 2a typical SEM image of MoN coating surface is presented. The coating is defect-free, dense, microdroplet-free. The x-ray analysis showed that the synthesized coatings are formed by MoN and Mo crystallites. At the increase of $j_p/j_d$ the concentration of nitrogen in a coating increases too. This fact is confirmed by results of the energy dispersive analysis. The maximum concentration of nitrogen in the chosen range of parameters is reached at $j_p/j_d=1$ and it is equal to 28.8 at. % (figure 2b, table 1). It can demonstrate to increase of a volume fraction of a molybdenum nitride phase in a coating in comparison with the case when the source of gas plasma isn't used to form MoN coating.

![Figure 2. SEM image of MoN coating surface (a); EDAX analysis results for MoN coating (b).](image)

**Table 1.** Properties of MoN coatings: $HV$ – Vicker’s hardness, $E$ – Young’s modulus, $\mu$ – friction coefficient; $V$ – wear factor, $C_{N_2}$ – nitrogen concentration, $CSR$ – the size of coherent scattering regions.

| $j_p/j_d$ | $C_{N_2}$ (a.u.) | $HV_{0.05}$ (GPa) | $E$ (GPa) | $\mu$ | $V$ ($\mu$m$^3$/N·m) | $CSR$ (nm) |
|----------|-----------------|-----------------|---------|------|-------------------|--------|
| 0        | 19.4            | 27.5            | 486.2   | 0.18 | 412.5             | 64     |
| 0.5      | 24.9            | 43.5            | 605.7   | 0.19 | 167.3             | 24     |
| 0.7      | 28.4            | 43.8            | 562.1   | 0.18 | 150.8             | 22     |
| 1        | 28.8            | 44.7            | 579.2   | 0.16 | 120.6             | 21     |
At increase of $j_p/j_d$ the increase of MoN coating hardness up to 44.7 GPa and the increase of wear resistance (it is inversely proportional to wear factor) are observed (table 1). MoN coating obtained in the mode with plasma assistance ($j_p/j_d=1$) has hardness in 1.6 times higher and wear resistance in 3.4 times higher in the comparison with the case when plasma assistance isn’t used. The friction coefficient slightly decreases to 0.16 at increasing $j_p/j_d$. It should be noted that size of coherent scattering regions (CSR) at increase of $j_p/j_d$ decreases to 21 nm. It testifies about reduction of the crystallites size in MoN coating at constant of elastic deformation value ($\Delta d/d$).

4. Conclusion
The results of researches of influence of the plasma assistance modes on the structure, composition and properties of coatings based on molybdenum nitride have shown followings:

1) The increase of the relation of densities of ion currents of a source of gas plasma and the arc evaporator leads to increase of nitrogen concentration in MoN coating. It in turn leads to increase in a volume fraction of molybdenum nitride phase.

2) The increase of $j_p/j_d$ leads to significant increase of hardness of molybdenum nitride coating (by 1.6 times) and to increase in its wear resistance (by 3.4 times).

3) Plasma assistance also leads to size reduction of the crystallites formed MoN coatings.

Thus, the method of increase in gas ions offered in the present work in gas-metal plasma with a constant pressure of nitrogen and constant current of the arc evaporator is quick-response and simple in application. It is possible to use that for formation of MoN coatings with high share of a molybdenum nitride phase. The coatings have superhardness and high wear resistance. Besides such effect can be used for obtaining single-layered, gradient or multilayered coatings not only based on molybdenum and its nitrides, but also based on other metals and their nitrides (Ti and TiN, Al and AlN, Zr and ZrN, and etc.).

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