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STRUCTURE AND PHASE COMPOSITION OF Mo-N COATINGS PRODUCED BY CATHODIC ARC PVD AT VARIOUS NITROGEN PRESSURE

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Mo-N coatings deposited at various nitrogen partial pressures ranging from $2\cdot10^{-3}$ to $1\cdot10^{-2}$ Torr have been investigated. The structure and chemical composition of the coatings were investigated by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Also, the structure of the coatings was analyzed by Raman spectroscopy. The microhardness of the coatings varied from 2000 to 2400 HV. Samples deposited at lower nitrogen pressures ($2\cdot10^{-3}$ to $7\cdot10^{-3}$ Torr) exhibit weaker Raman responses, suggesting a lower degree of nitridation and possibly reduced structural disorder. The Raman data indicate that elevated nitrogen pressure during deposition fosters the formation of highly disordered, potentially amorphous or nanocrystalline Mo-N phases.

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INTRODUCTION

Among transition metal nitrides such as Ti, Zr, W, or Cr nitrides, Mo nitrides have been much less studied although they exhibit hardness values ranging from 28 to 34 GPa, whereas those for Ti or Cr nitrides range between 18 and 24 GPa [1, 2]. Because of their strong covalent bonding, the calculated values of the bulk modulus of the stoichiometric MoN phase of hexagonal or cubic structure are comparable to those of c-BN and even diamond. Although the phase formation in Mo-N coatings is strongly dependent on the parameters of the coating process, presently there is a lack of information in the literature regarding the systematic investigation of the deposition parameters–property relations of the Mo-N coatings.

Beside the solid solution of nitrogen in molybdenum, the so-called α-phase, which contains 1.08 at.% nitrogen, three molybdenum nitride phases are stable in thermal equilibrium according to the binary phase diagram determined in [3]. The γ-$Mo_2N_{1\pm x}$ phase is stable at high temperature. Its structure is cubic of NaCl-B1-type and can be described as a face centered cubic array of Mo atoms with N atoms randomly occupying one half of the octahedral interstices of the host metal (Fm3m, space group). Tagliazucca et al. [4] have reported another structure for the γ-$Mo_2N_{1\pm x}$ phase, which consists of an ordered array of vacancies (Pm3m, space group) distinguished from the Fm3m space group by the presence of superstructure reflections. Molybdenum nitrides also crystallize in a structure similar to γ-Mo_2N with an excess of nitrogen in the lattice and with the formula Mo_3N_2 [5].

The β-$Mo_2N_{1\pm x}$ phase is stable at low temperature. Its structure is a face centered tetragonal structure of metal atoms with an ordered array of nitrogen atoms. This structure is often considered as a tetragonal modification of the cubic γ-$Mo_2N_{1\pm x}$ phase with the lattice constant c doubled (I41/amd, space group) [6]. Both phases exist over a wide range of stoichiometry, the transition between them depends on the stoichiometry and lies in the temperature range from 673 to 1123 K. Another tetragonal molybdenum nitride phase has been produced with the formula $Mo_{16}N_7$.

It should be noted, that Arc-PVD Mo_2N coatings exhibit a strong dependence on nitrogen pressure during deposition, influencing their structure, composition, and mechanical properties. Increasing nitrogen pressure generally leads to a higher nitrogen content in the coating, potentially favoring the formation of different nitride phases like Mo_2N and MoN, and impacting the hardness and wear resistance. At lower nitrogen pressures, the coating may primarily consist of a cubic molybdenum nitride phase (like γ-Mo_2N). The nitrogen content will be lower compared to coatings deposited at higher pressures [7]. As nitrogen pressure increases, the nitrogen content in the coating increases, potentially leading to the formation of a mixture of phases like β-Mo_2N, γ-Mo_2N, and δ-MoN.

In this research, the cathodic arc evaporation method (Arc-PVD) is used to deposit Mo-N coatings, with the ability to vary nitrogen pressure to control the coating's structure and properties.

1. EXPERIMENTAL SETUP

The "Bulat"-type experimental setup was used for coating deposition. AISI 430 steel samples, with dimensions 20×20×1.5 mm, were placed in the working volume of the Bulat-6 chamber (Fig. 1). Each sample was fixed onto an L-shaped holder, which was mounted vertically on a turntable, allowing its rotation around the vertical axis.

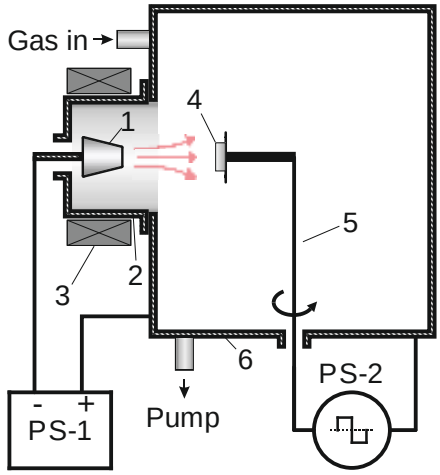

Fig. 1. Experimental Set-up:
1 – cathode; 2 – anode; 3 – coil; 4 – sample;
5 – sample holder; 6 – vacuum chamber;
PS-1 – arc discharge power supply;
PS-2 – pulsed power supply

To obtain the MoN coatings, a molybdenum cathode at a purity of 99.99% was used. The distance between the cathode and the samples was 30 cm. The chamber was evacuated to a pressure of $7.0 \cdot 10^{-5}$ Torr. A negative potential of 1200 V at a frequency of 45 kHz was applied to the sample. A vacuum-arc plasma source with a Mo cathode was used to clean the samples' surface by ion bombardment. The vacuum arc current was set to 120 A. After 50…60 s of cleaning, the amplitude of the negative potential was reduced to -50 V, and within 2 min, the Mo coating was deposited.

Next, nitrogen was introduced into the chamber, with the N_2 pressure set to various values: $2.0 \cdot 10^{-3}$; $4.5 \cdot 10^{-3}$; $7.0 \cdot 10^{-3}$, and $1.0 \cdot 10^{-2}$ Torr. The Mo-N coatings were deposited at these nitrogen gas pressures. The thickness and surface Vickers microhardness of the produced coatings are presented in Table.

Nitrogen pressure, Torr	$2.0 \cdot 10^{-3}$	$4.5 \cdot 10^{-3}$	$7.0 \cdot 10^{-3}$	$1.0 \cdot 10^{-2}$
Film thickness, μm	4	5	4	6.3
Microhardness, $H_v(0.05)$	2000	2400	2000	2400

Structure and chemical composition of the coatings were investigated by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) by using ZEISS EVO® MA10.

The structure of the coatings was additionally analysed by Raman spectroscopy using a Virsa fibre-optic-coupled Raman analyser (Renishaw, UK). The excitation source was an argon ion laser with a wavelength of 532 nm, and the spectral range analyzed extended from 120 to 3200 cm^{-1}.

2. RESULTS AND DISCUSSION

Fig. 2 depicts SEM surface morphology images from Mo-N coatings deposited at various nitrogen pressure. The surface is rather smooth with a low number of microparticles.

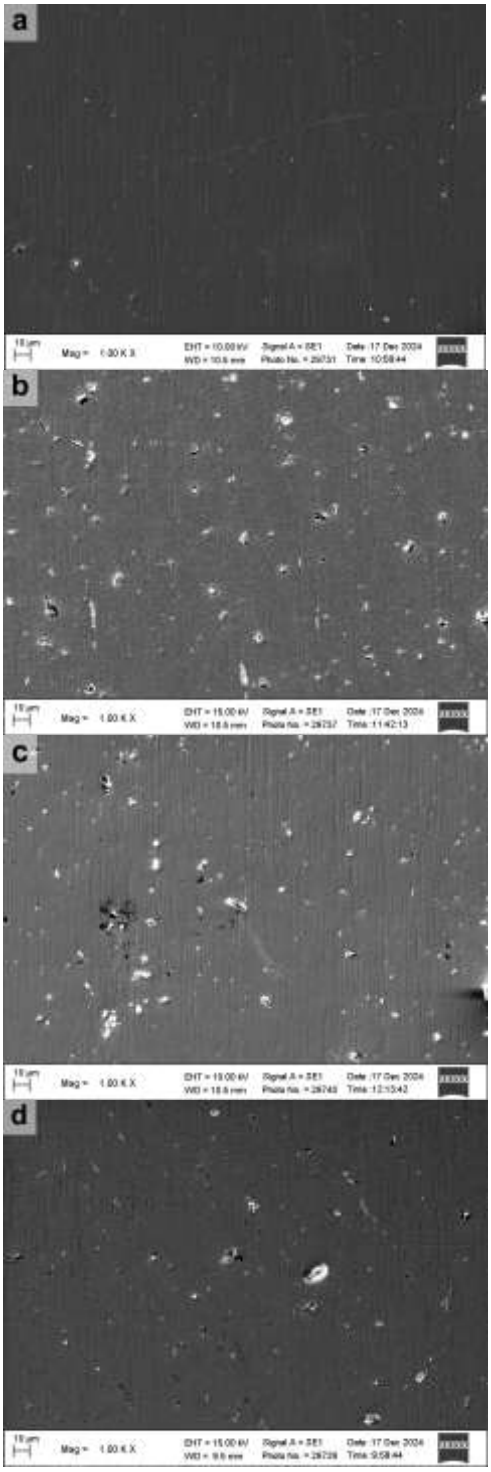

Fig. 2. SEM surface morphology of Mo-N coatings at various N_2 pressure: a – $2.0 \cdot 10^{-3}$ Torr; b – $4.5 \cdot 10^{-3}$ Torr; c – $7.0 \cdot 10^{-3}$ Torr; d – $1.0 \cdot 10^{-2}$ Torr

The number of microdroplets on the surface is the lowest at $2 \cdot 10^{-3}$ Torr as it is seen from the Fig. 2,a.

Fig. 3 depicts typical EDX spectra and Fig. 4 EDS mapping of selected chemical elements from the surface of one chosen coating.

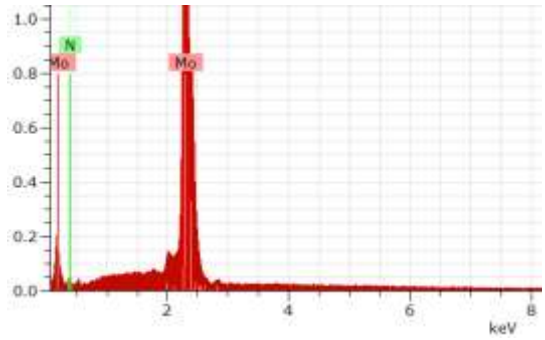

Fig. 3. Typical EDX spectra of the selected chemical elements

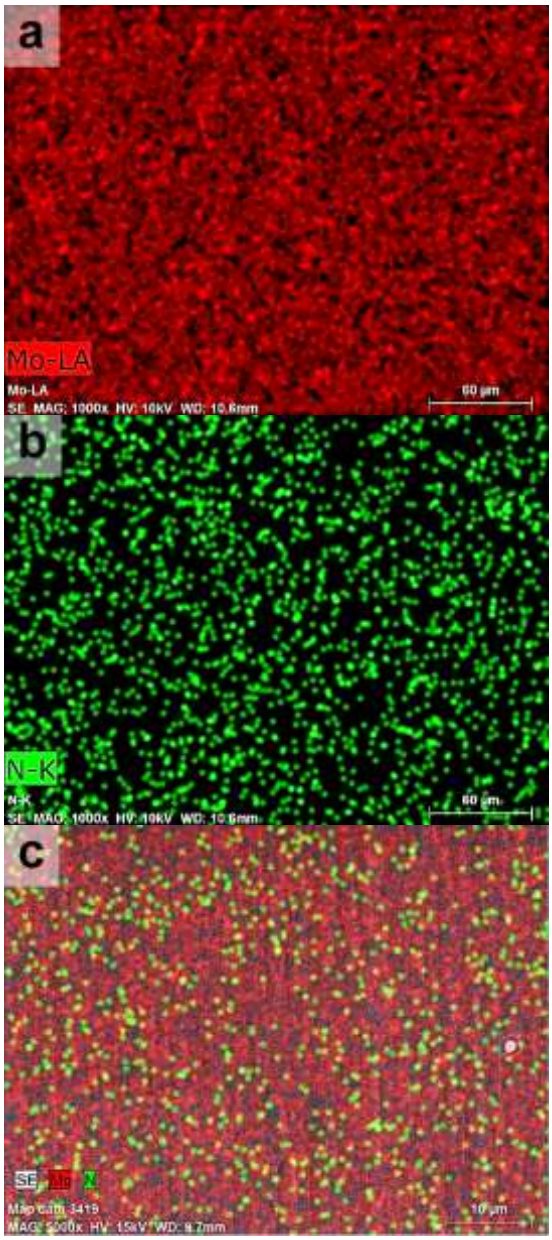

Fig. 4. EDS mapping of the selected chemical elements (a–c)

Fig. 5 shows the Raman spectra of Mo-N coatings deposited at various nitrogen partial pressures ranging from $2 \cdot 10^{-3}$ to $1 \cdot 10^{-2}$ Torr. All spectra exhibit relatively broad bands and lack of well-defined Raman-active peaks, which is consistent with the expected metallic or semi-metallic nature of γ-Mo_2N and/or disordered MoN_x (mainly – δ-MoN) phases. The absence of sharp vibrational modes further supports the assumption that the coatings are either amorphous or nanocrystalline [8, 9] with a high density of defects.

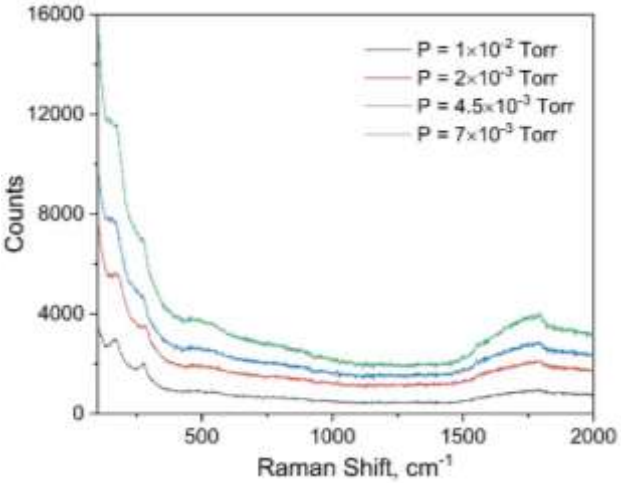

Fig. 5. Raman spectra of Mo_2N coatings

It is well established that for metallic and metal-based materials, Raman bands in the range 100…300 cm^{-1} typically correspond to vibrations of metallic atoms, whereas high-frequency modes above 400 cm^{-1} are predominantly associated with non-metallic atoms such as nitrogen or oxygen [10].

A notable tendency observed in this study is the significant variation in the overall spectral intensity as a function of nitrogen pressure during deposition. The sample prepared at the highest nitrogen pressure ($1 \cdot 10^{-2}$ Torr) exhibited the most intense and broadened background signal, particularly in the low-wavenumber region (100…400 cm^{-1}). The observed bands in the spectrum are likely to be associated with Mo-Mo vibrational modes. However, the pronounced broadening and increased intensity of the background may also be attributed to defect-induced scattering and enhanced electronic conductivity, both of which are characteristic of disordered transition metal nitrides [11].

In contrast, samples deposited at lower nitrogen pressures ($2 \cdot 10^{-3}$ to $7 \cdot 10^{-3}$ Torr) exhibit weaker Raman responses, suggesting a lower degree of nitridation and possibly reduced structural disorder. The relative suppression of low-wavenumber intensity in these samples may also reflect a lower density of Mo-N bonding environments or reduced carrier concentration, affecting the electronic Raman background.

Furthermore, a marginal increase in intensity was observed in the 1300…1800 cm^{-1} range, most notably in the spectrum of the sample deposited at $7 \cdot 10^{-3}$ Torr. This broad peak may be indicative of defect-induced scattering or weak contributions from oxygen-containing phases, although no distinct Mo-O vibrational modes are observed.

CONCLUSIONS

The Raman data indicates that elevated nitrogen pressure during deposition fosters the formation of highly disordered, potentially amorphous or nanocrystalline Mo_2N phases, characterised by an enhanced defect density and Raman background. Conversely, coatings formed at lower nitrogen pressures are likely to be less nitrogen-rich and more structurally ordered. The nitrogen pressure during ARC-PVD deposition of Mo_2N coatings is a crucial parameter that significantly impacts the coating's structure, composition, and mechanical properties.

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СТРУКТУРА ТА ФАЗОВИЙ СКЛАД Mo-N-ПОКРИТТІВ, ОТРИМАНИХ МЕТОДОМ ВАКУУМНО-ДУГОВОГО ОСАДЖЕННЯ ПРИ РІЗНОМУ ТИСКУ АЗОТУ

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Досліджені покриття Mo-N нанесені при різному парціальному тиску азоту в діапазоні $2\cdot10^{-3}…1\cdot10^{-2}$ Торр. Структура та хімічний склад покриттів досліджувались за допомогою скануючої електронної мікроскопії (СЕМ) та енергодисперсійної спектроскопії (ЕДС). Структуру покриттів також аналізували за допомогою раманівської спектроскопії. Мікротвердість покриттів змінювалася від 2000 до 2400 по Віккерсу. Зразки з покриттями, що нанесені при нижчому тиску азоту (від $2\cdot10^{-3}$ до $7\cdot10^{-3}$ Торр), демонструють слабші раманівські відгуки, що свідчить про нижчий ступінь азотування та, можливо, зменшення невпорядкованості структури. Дані раманівського розсіювання вказують на те, що підвищений тиск азоту під час осадження сприяє утворенню сильно невпорядкованих, потенційно аморфних або нанокристалічних фаз Mo-N.