



The properties of molybdenum nitride coatings obtained by cathodic arc evaporation

A. Gilewicz^{*}, B. Warcholinski, D. Murzynski

Koszalin University of Technology, Institute of Technology and Education, Sniadeckich 2, 75-453 Koszalin, Poland

ARTICLE INFO

Article history:

Received 16 April 2013

Accepted in revised form 4 September 2013

Available online 12 September 2013

Keywords:

Cathodic arc evaporation

MoN phases

Surface roughness

Substrate bias voltage

Adhesion

Wear

ABSTRACT

Among the many techniques for the deposition of Mo–N coatings, AC and DC magnetron sputtering, ion implantation and cathodic arc evaporation, the latter is the most comprehensive, owing to the high degree of particle ionisation in the plasma, high density and coating quality. The phase structure of Mo–N coatings strongly depends on the deposition technology, mainly on the pressure of nitrogen in the working chamber, and the substrate bias voltage. Coatings deposited at four nitrogen pressures: 0.6, 1.0, 1.8 and 3.0 Pa, and four negative substrate bias voltages U_B : 10, 70, 150 and 250 V, were widely tested. EDS and WDS were used to evaluate the chemical composition, XRD to determine the phase composition, scanning and an optical microscopy to assess the morphology and surface quality, the scratch test and Daimler-Benz test to estimate the coatings adhesion, and ball-on-disc test to define the specific wear rate.

The increase in the nitrogen pressure changes the phase structure of the body-centred cubic lattice of molybdenum Mo, through cubic γ -Mo₂N to the hexagonal δ -MoN. Due to the different structures of the crystal lattice, the given phases exhibit different physical properties. The substrate bias voltage rise initiates the resputtering of the coating, causing a reduction in nitrogen atoms in the coating. This affects the changes in the chemical composition and the coating morphology. It can be the cause of the cubic γ -Mo₂N phase existing in the deposition conditions of the hexagonal δ -MoN phase.

The relatively large amount of macroparticles on the coating surface depends on the nitrogen pressure and the substrate bias voltage. The surface roughness R_a of the coating deposited at substrate bias voltages of more than -70 V is relatively small and almost independent of the nitrogen pressure. The coatings deposited at low substrate bias voltages ($U_B = -10$ V) are characterised by more than twice the surface roughness R_a , decreasing as the partial pressure of nitrogen increases.

The mechanical parameters of the deposited coatings depend on their phase composition due to the different properties of Mo, Mo₂N and MoN.

© 2013 Published by Elsevier B.V.

1. Introduction

Owing to the good thermal and catalytic properties and good tribological features of molybdenum nitride, a low wear rate and friction coefficient, thin coatings can be used in a wide range of applications. The oxidation of molybdenum nitride for layered MoO₃ molybdenum oxide allows their usage as self-lubricating coatings in nanotribological contacts working at high temperatures [1,2].

The phase structure of the molybdenum nitride coatings is firmly coupled with the deposition process parameters, mainly on the nitrogen pressure. An increase in nitrogen pressure changes the phase structure of the space-centred cubic lattice of molybdenum Mo [3], through the tetragonal centred cubic phases: β -Mo₂N [4], β' -Mo₂N [5], β'' -Mo₂N [6] and cubic γ -Mo₂N [7] to the hexagonal δ -MoN [8]. The tetragonal phases β -Mo₂N are low-temperature variations of the γ -Mo₂N cubic

phase. There is also a MoN cubic phase marked B1 MoN [9]. Due to different crystallographic structures, the phases exhibit different physical properties.

The reactions on the surface of the coating depend on the particles' energy, and this is indirectly related to the substrate bias voltage during the coating formation process and the current arc discharge source. The collisions of the atom components in the plasma, and their mobility on the coating surface, affect the reactions in the forming phases [10]. Additionally, the energy of the bombarding ions and molecules affects the ions' interaction with the surface of the coating and the type of the phases formed [11].

Mo–N coatings are mainly obtained using the magnetron sputtering method [12]. To form the δ -MoN hexagonal phase, a higher plasma ionisation and/or a higher nitrogen pressure is required. Such conditions meet the arc evaporation method [11,13,14]. The plasma ionisation in this method is considerably higher than in magnetron sputtering. The arc evaporation method also allows for obtaining coatings of higher density and quality.

^{*} Corresponding author. Tel.: +48 943478410; fax: +48 943486652.

E-mail address: adam.gilewicz@tu.koszalin.pl (A. Gilewicz).

One disadvantage of such a deposition method is the large amount of macroparticles and craters, that can be classified as pinholes or craters, pure metallic droplets, or droplets partly embedded in the coating [14–16]. Such defects are due to the fact that the droplets and pinholes incorporated during the film deposition are generated as a result of the removal of weakly bonded macroparticles from the coating [17,18]. The defects of this kind can reduce the toughness of the coating and thereby lead to coating failures; therefore there are drawbacks in the coating application. Improved properties (including surface) of the coatings can be achieved by reducing (minimising) the surface density of macroparticles, for example by optimising the deposition parameters.

The paper presents the effect of two technological parameters: the nitrogen pressure (0.6, 1.0, 1.8, 3.0 Pa) and the negative substrate bias voltage (10, 70, 150, 250 V) on the phase composition, surface roughness, morphology and macroparticle statistics, adhesion and the wear behaviour of the Mo–N coatings formed when deposited on a HS6-5-2 steel substrate using cathodic arc evaporation.

2. Experimental

2.1. Coating deposition

The molybdenum nitride coatings were deposited by cathodic arc evaporation in a TINA 900 M system on 32 mm diameter HS6-5-2 steel substrates. The diameter of the pure molybdenum (99.99%) cathode was 100 mm.

Standard metallographic techniques, grinding and polishing of the surface of the substrates, were used to prepare them. The top surface of the substrate was a highly-polished finish with an R_a of 0.02 μm . Before placing the substrates in the PVD system, degreasing and ultrasonic cleaning in an alkaline bath was applied. Then the substrates were rinsed in distilled water and dried in a warm-air stream.

The prepared substrates were installed on a turntable at a distance of about 18 cm from the arc sources equipped with molybdenum cathodes. The working chamber was pumped down to a pressure of about 1×10^{-3} Pa and then filled by argon to a pressure of about 0.5 Pa. The next stage of cleaning, the so-called sputter etching to remove the surface oxide layer, was carried out using chromium (Cr^+) and argon (Ar^+) ion bombardment at a voltage of -600 V for 10 min. To improve the adhesion of the coatings, a thin chromium layer with a thickness of 0.1 μm was deposited on the substrate [19]. The coatings were deposited in a pure nitrogen atmosphere. For depositing Mo–N coatings an arc current of 140 A, four nitrogen pressures and substrate bias voltages U_B : 0.6, 1.0, 1.8, 3 Pa and -10 , -70 , -150 and -250 V were applied respectively. The deposition temperature was about 300 °C.

2.2. Coating characterisation

The Energy Dispersive X-ray Spectroscopy (EDS) and the Wavelength Dispersive Spectroscopy (WDS) methods were applied to analyse the chemical composition of the coatings. Oxford Link ISIS 300 and Noran Instruments IBEX systems were used respectively. An X-ray diffractometer using $\text{Co K}\alpha$ radiation was applied to identify the structure of the coatings. Interpretation of the results was performed using a JCPDS database. The morphology of the coatings surface was evaluated by use of a scanning electron microscope (SEM) (JEOL JSM 5500LV).

A Hommel Werke T8000 profilometer was used to assess the surface roughness of the coatings. The test was carried out five times. For the evaluation of the surface density of the macroparticles an optical microscope, Nikon Eclipse Imaging MK200, equipped with Imaging Software NIS-Elements software was used to automatically collect data for quantitative and dimensional analysis. All coatings were evaluated using the same sharpness, contrast, threshold of sensitivity, magnification ($400\times$) and a scan area of $131 \times 174 \mu\text{m}^2$. Measurements were taken for each sample at five points, located in a line at an equal distance from each other.

The adhesion of the coating was specified using a Revetest scratch tester (CSEM) and the Daimler-Benz Rockwell C hardness test [20]. In the Daimler-Benz test, the amount and type of damage to the coating in contact with the Rockwell indenter determines the adhesion, and is specified in a 6-point scale. HF1 to HF4 marks indicate small cracks or coating delamination, suggesting a good adhesion to the substrate. Poor adhesion to the substrate, resulting from significant cracks or delamination of the coating, is marked HF5 and HF6. Each sample was subjected to five tests. The adhesion of the coatings to the substrate was also determined using a scratch test on a CSEM Revetest® Scratch Tester equipped with a diamond indenter Rockwell type C with a radius of 200 μm . The indenter was moved with a sliding speed of 10 mm/min by linearly changing at the same time the normal load from 0 to 200 N at a loading rate of 200 N/min. The load causing the failure of the coating is called the critical load L_c . It was defined on the basis of an acoustic emission recorded during the test and microscopic observation of the scratch. Critical load L_{c2} was defined as the force at which total detachment of the coating from the substrate was observed in the microscopic observations for at least 3 measurements.

The wear rate estimation was made by analysing the results obtained in the pin-on-disc (T-01 M) test conducted at room temperature (22 °C) and with an air humidity level of 45%, without lubrication. The counterpart was a 10 mm diameter alumina ball with a hardness of 15 GPa and a roughness $R_a < 0.03 \mu\text{m}$. Test parameters were as follows: normal load of 20 N, sliding speed of 0.2 m/s, and sliding distance of 1500 m. For each sample, at least five profiles of the wear track using a Hommel Werke T80000 surface profilometer were determined. From the obtained profiles, the wear area and then the wear volume were defined. Wear rate was defined as the wear volume divided by the normal load and the sliding distance [21].

Coating stresses of the Mo–N coatings were calculated using Stoney's formula after measuring the radius of curvature with the surface roughness analyser (Hommel Werke Profilometer T8000) [22]:

$$\sigma = \frac{E}{1-\nu} \frac{t_f^2}{6t_f} \left(\frac{1}{R} - \frac{1}{R_s} \right) \quad (1)$$

where: E – Young's modulus of the substrate, ν – Poisson's ratio of the substrate, t_f – thickness of a layer, R – radius of the substrate curvature together with the coating, and R_s – radius of the substrate curvature. The stress was measured using a silicon substrate of 0.3 mm thickness, 30 mm long and 4 mm width.

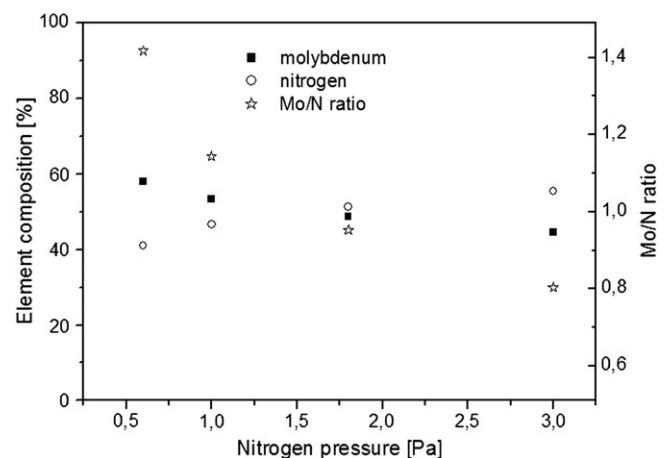


Fig. 1. Chemical composition and Mo/N ratio of Mo–N coatings deposited at various substrate bias voltages, nitrogen pressure: 1.8 Pa.

Download English Version:

<https://daneshyari.com/en/article/8028899>

Download Persian Version:

<https://daneshyari.com/article/8028899>

[Daneshyari.com](https://daneshyari.com)