Influence of Ni on electrochemical resistance of tribo-adaptive Ti-Al-Mo-N coatings

V S Sergevnin, A P Demirov, D S Belov and A V Chernogor
National University of Science and Technology "MISIS", Leninskiy prospekt 4, 119049, Moscow, Russia
E-mail: v.s.sergevnin@gmail.com

Abstract. Electrochemical behavior of Ti-Al-Mo-N coatings before and after addition of Ni in amount of 1 and 2 at. % was investigated in alkaline and acidic media. Ni resulted in decrease in the corrosion current an alkaline media and reduction of oxygen concentration in the coating material after electrochemical test. It was found that addition of Ni to Ti-Al-Mo-N coatings with high molybdenum content increases the resistance to dissolution in alkaline media, but does not have a significant positive effect on their resistance in acidic environments.

1. Introduction
Multilayered arc-PVD Ti-Al-Mo-N coatings, characterized by alternating layers based on complex (Ti,Al)N nitride and molybdenum nitride, demonstrate high wear resistance due to hardness of ~ 40 GPa, and a low friction coefficient of up to 0.3. High tribological properties of the coatings are achieved due to the adaptation phenomenon of the coatings under intense friction through the MoO$_3$ Magneli phase formation in the friction zone, which acts as a solid lubricant due to low shear strength [1, 2]. The introduction of nickel into coating composition leads to a noticeable decrease in the modulation period and refinement of the grain structure of the coating from 35 to 12 nm, which leads to increase in the coating hardness up to 45 GPa with a simultaneous increase in the fracture toughness and resistance to abrasive and impact loading. Ni also has a positive effect on the heat resistance of the coating, increasing its maximum operating temperature to 700 °C and expanding its possible field of application [3]. However, the possible limits of applications are determined, among other things, by the resistance of the coating to aggressive acid and alkaline environments. The present work is devoted to the study of the effect of nickel addition on the electrochemical stability of Ti-Al-Mo-N coatings.

2. Materials and methods
Coatings were deposited on WC-Co carbide substrates using the arc-PVD method. Sputtering was performed in a nitrogen atmosphere at P(N$_2$) = 0.5 Pa using a two-cathode system with Ti-5%Al and Mo cathodes to deposit Ti-Al-Mo-N coating. The current of the evaporating arcs (I) at both cathodes was 135 A. The negative bias voltage (U$_b$) applied to the substrate was −140 V. In the case of obtaining the Ni-containing coating, a three-cathode system was used with an additional Ni-50%Ti cathode, which was evaporated with an evaporating arc current of 120 A.

The electrochemical behavior of coatings was studied in acidic and alkaline media using an IPC-ProMF potentiostat. A solution of 0.12 g/l NaOH (pH ≈ 12.7) was used as a model alkaline solution, and 100 cm$^3$ (20 g FeCl$_3$ 6H$_2$O + 5% HNO$_3$) + 19 H$_2$O g/cm$^3$ (pH ≈ 0) was used as an acidic solution.
The anode polarization curves were recorded after the stationary potentials were reached. After testing, the element concentration profiles over the coating thickness were obtained using XPS analysis during layer-by-layer etching with Ar+ ions.

3. Results and discussion

Figure 1 shows the potentiodynamic curves taken for three test samples: Ti-Al-Mo-N (1), Ti-Al-Mo-Ni-N with 1 at. % Ni (2), Ti-Al-Mo-Ni-N with 2 at. % Ni (3) in alkaline and acidic medium, respectively. The addition of Ni to Ti-Al-Mo-N coatings slightly changes the curve, increasing the corrosion potential (E_{corr}) and the corrosion current (i_{corr}) (figure 1).

![Figure 1. Potentiodynamic curves of the Ti-Al-Mo-N (1), Ti-Al-Mo-Ni-N with 1 at. % Ni (2), Ti-Al-Mo-Ni-N with 2 at. % Ni (3) coating taken in alkaline (a) and in acidic medium (b).](image)

In alkaline media, a sharp decrease in the corrosion current (table 1) with an increase in the Ni content indicates a noticeable decrease in the self-dissolution rate of coatings in alkaline environment. An increase in the corrosion potential may be due to the disinhibition of the anode process.

| Medium  | Coating | E_{corr}, mV | i_{corr}, mA/cm² |
|---------|---------|--------------|------------------|
| alkaline| 1       | -600         | 0.14             |
|         | 2       | -580         | 0.002            |
|         | 3       | -350         | 0.0007           |
| acidic  | 1       | 490          | 0.02             |
|         | 2       | -95          | 0.08             |
|         | 3       | 260          | 0.08             |

In an acidic solution, the addition of Ni does not significantly affect the appearance of the potentiodynamic curve (figure 1b). Coatings 2 and 3 have a higher self-dissolution rate compared to the coating 1. This is due to the weak resistance of Ni to oxidative acids (HNO₃) and to FeCl₃. The difference in the values of the corrosion potential is due to the different content of molybdenum in the coatings. As the molybdenum content increases, the corrosion potential increases. Thus, coating 2 contained 20 at. % Mo, and the E_{corr} was −95 mV (figure 1b, curve 2), and the coating 1 had a Mo content of 30 at. %, and it was characterized by a corrosion potential of 260 mV (figure 1b, curve 3). The resulting molybdenum oxides can dissolve in an acidic environment, increasing its pH, and thus, making it more neutral [4].
Figure 2. Series 1 coating concentration profiles obtained during electrochemical tests in alkaline (a) and acidic (b) media.

Figure 3. Series 2 coating concentration profiles obtained during electrochemical tests in alkaline (a) and acidic (b) media.

The concentration profiles of the tested coatings are shown in figures 2–4. They show a fundamental difference in the distribution of aluminum in the surface layers of Ti-Al-Mo-N and Ti-Al-Mo-Ni-N coatings after electrochemical tests. In series 1 coatings, after electrochemical tests, there is an increased content of aluminum on the surface relative to the volume (figure 2). After tests in alkaline and acidic environments, about 15 at. % and 10 at. % of aluminum on the surface of the coating, respectively, and about 1 at. % in the coating volume. The observed effect of upward diffusion can be caused by a gradient of thermodynamic potentials. As the coating comes into contact with an aggressive medium, Mo$_2$N at the coating/surface interface is dissolved, and Al$^{3+}$ cations diffuse from the near-surface layer of the coating (10–20 nm) to the coating/solution interface. These cations interact with oxygen ions to yield Al$_2$O$_3$. As a result, an aluminum concentration gradient is generated in the solution and diffusion of Al from the coating bulk towards the surface takes place. This effect is not observed in coatings 2 and 3 (figure 3, 4), which can be explained by the formation of thermodynamically stable Al-Ni intermetallic compounds under these conditions.

The obtained values of the binding energies of the photoelectron spectra Ti, Al, Mo, Ni, and N after etching for 10 minutes allowed us to determine the phase composition of coatings at a depth of 300 nm (for series 1) and 100 nm (for series 2 and 3) by comparing the obtained values with reference values.
In series 1 coatings at a depth of 300 nm, the values of the XPS peaks of the Mo3p3/2 spectra of series 1 coatings after electrochemical tests were $394.3 \pm 0.2$ eV in alkaline media and $394.4 \pm 0.2$ eV in acidic media, which corresponds to the value of the molybdenum binding energy in the Mo$_2$N. The Ti2p spectra of these coatings had a complex shape with several doublets, the energy of which was: $455.3 \pm 0.2$; $457.0 \pm 0.2$; $458.5 \pm 0.2$; $459.5 \pm 0.2$ eV in alkaline and in acidic environment. The minimum binding energy value corresponds to TiN, and the rest to titanium oxides. The energy value of the Al2p spectrum in alkaline and acidic media was $75.5 \pm 0.2$, which corresponds to the binding energy of aluminum in Al$_2$O$_3$. In series 2 coatings, the Ti2p3/2 peak located at $454.8 \pm 0.2$ eV, corresponding to the TiN phase, the Mo3d5/2 peak had a value of $228.0 \pm 0.2$ eV and can be attributed to Mo$_2$N. Series 3 coating also contained only titanium and molybdenum nitrides at a depth of 100 nm.

![Figure 4](image)

**Figure 4.** Series 3 coating concentration profiles obtained during electrochemical tests in alkaline (a) and acidic (b) media.

### 4. Conclusions

Electrochemical behavior of adaptive Ti-Al-Mo-N coatings before and after addition of Ni in amount of 1 and 2 at. % was investigated. Addition of Ni inhibits the Al upwards diffusion to the coating surface, but concentration of oxygen after experiments in the alkaline media and values of corrosion current showed that addition Ni increases the resistance to coating dissolution in alkaline media. However, Ni does not have a significant positive effect on their resistance in acidic environments.

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### References

[1] Sergevnin V S, Blinkov I V, Volkhonksii A O, Belov D S, Kuznetsov D V, Gorshenkov M V and Skryleva E A 2016 *Applied Surface Science* **388** 13–23

[2] Sergevnin V S, Blinkov I V, Belov D S, Smirnov N I, Volkhonksii A O and Kuptsov K A 2018 *The International Journal of Advanced Manufacturing Technology* **98** 593–601

[3] Sergevnin V S, Blinkov I V, Volkhonksii A O and Belov D S 2020 *Russian Journal of Non-Ferrous Metals* **61** 466–74

[4] Tomaszewski L, Gulbinski W, Urbanowicz A, Suszko T, Lewandowski A and Gulbinski W 2015 *Vacuum* **121** 223–9