ENVIRONMENTALLY FRIENDLY ELECTRODEPOSITED Ni-Mo-B COATINGS FOR TRIBOCORROSION APPLICATIONS

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Corrosion-resistant Ni-Mo-B electrodeposited coatings were produced from a self-regulating suspension electrolyte, and the effect of deposition parameters on their composition, structure, and properties was examined. The coatings exhibit a fine-grained structure, contain 8–27 wt.% Mo and 1.30–3.39 wt.% B, and are free of pores and cracks. An increase in molybdenum content improves corrosion resistance in chloride media. Micromechanical properties were evaluated using scratch testing and nanoindentation, while tribological and tribocorrosion behavior was studied using a "plane–ball" scheme in air and in 3% NaCl solution. It was established that coatings with 8 wt.% Mo are more effective under dry friction, whereas coatings with 16 wt.% Mo perform better under tribocorrosion loading. Ni-Mo-B coatings are considered as an environmentally friendly alternative to hard chromium.

Keywords: electrodeposited Ni-Mo-B coatings, tribocorrosion, corrosion resistance, micromechanical properties

Introduction: One of the effective ways to protect materials from corrosion and wear is the application of electrodeposited coatings, which are characterized by technological simplicity and cost-efficiency [1]. Particular attention is paid to nickel-based coatings modified with composite additives (SiC, MoS_2, ZrO_2, etc.), which provide enhanced hardness, corrosion resistance, and wear resistance. However, studies of their behavior under tribocorrosion conditions remain limited due to the complex interaction of electrochemical and frictional factors. Although alloying can modify wear mechanisms and improve coating performance, excessive alloying may cause internal stresses and microcracks.

Ni-Mo-B coatings are of particular interest, as they combine high microhardness with resistance to aggressive environments [2]. Traditional chemical deposition methods, however, require toxic boron-containing reagents and are technologically inefficient. Therefore, electrodeposition using amorphous boron is promising, as it increases boron content in the coatings, improves performance, and reduces costs.

In this study, Ni-Mo-B electrodeposited coatings of various compositions obtained from a self-regulating suspension electrolyte [1] were investigated. The aim was to establish relationships between their structure, deposition conditions, and mechanical, tribological, and tribocorrosion properties.

Materials and methods. Ni–Mo–B coatings were electrodeposited onto steel 45 substrates from a self-regulating electrolyte with 50 g/L amorphous boron (pH 9.0, 60 ± 1 °C) at current densities of 0.5–5.0 A/dm², stirring at 300 rpm, for 1 h. The anode was a nickel plate. Micromechanical properties were studied using scratch testing and nanoindentation ("Micron-gamma"). Tribological and tribocorrosion tests (Al_2O_3 ball, Ø9 mm) were performed in air and 3% NaCl solution (load 10 N, stroke 16 mm).

Morphology and composition were analyzed using a Zeiss EVO-40XVP scanning electron microscope with an Oxford INCA ENERGY 350 EDS system. Boron content was determined by titration with 0.1 M NaOH.

Results and discussion. It was established that molybdenum content decreases with increasing current density, from ~27 wt.% at 0.5 A/dm² to ~8 wt.% at 5 A/dm², while boron content increases from ~1.30 wt.% to ~3.39 wt.% under the same conditions.

The coatings are characterized by uniform boron particle distribution and defect-free microstructure. Additional boron alloying promotes the formation of a fine-grained globular surface with evenly distributed boron particles. Coating thickness decreases with increasing Mo content, from 82 µm down to 3 µm, due to reduced cathodic current efficiency (fig.1 *a-d*).

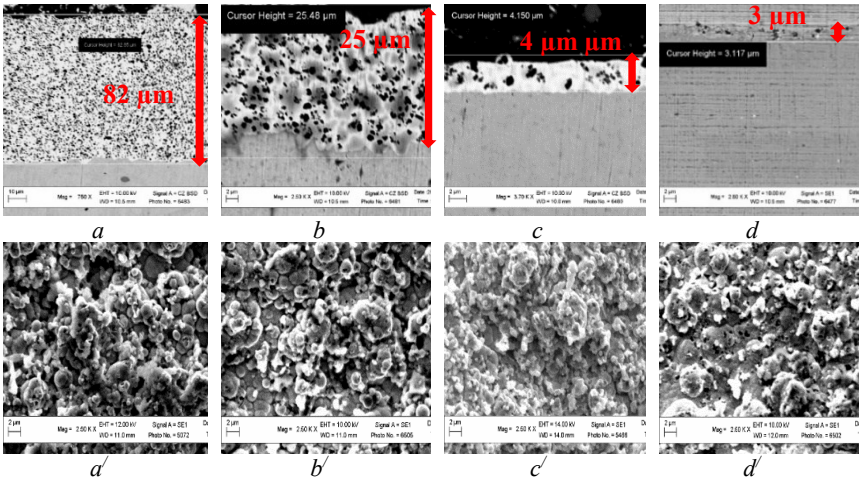

Fig. 1. Microstructure and corresponding SEM images of the surface of Ni-Mo-B coatings with different Mo contents (wt.%): *a* – 8; *b* – 16; *c* – 21; *d* – 27.

At Mo contents above 21 wt.%, thickness drops to 3–4 µm. Such thin layers were excluded from tribological and micromechanical tests as they lack functional wear resistance.

As a result of tribological tests (Fig. 2*a*, *b*), it was established that the evolution of the friction coefficient depends on the molybdenum content in Ni-Mo-B composite coatings. For the coating with 8 wt.% Mo, an initial running-in stage was observed at the beginning of testing, during which the friction coefficient decreased by approximately 0.25 units compared to its initial value. Subsequently, both samples demonstrated a gradual increase in the friction coefficient, followed by stabilization at a steady-state friction regime maintained throughout the entire test duration (up to 1200 s). The average friction coefficient values were 0.5 for the coating with 8 wt.% Mo and 0.6 for the coating with 16 wt.% Mo.

Analysis of the wear track topography revealed distinct boron particles embedded in the coating structure, as well as characteristic traces of plastic deformation in the contact zone (Fig. 2 *a*′, *b*′). This indicates the active role of boron in the friction process, acting as a solid phase that contributes to reducing the friction coefficient and localizing the applied load.

The results also revealed a correlation between microhardness, friction coefficient, and material loss. The coating with 8 wt.% Mo exhibited a more pronounced increase in wear resistance (~40%), whereas for 16 wt.% Mo the reduction in wear track width was only about 10%. This effect can be explained by the higher boron content in the coatings with lower molybdenum concentration, which promotes the formation of a more friction-resistant surface.

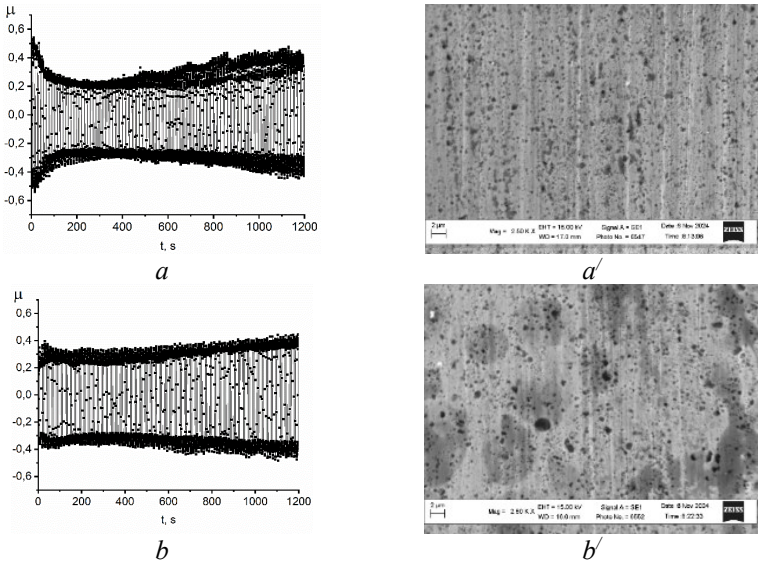

Fig. 2. Variation of the friction coefficient during testing in air for Ni-Mo-B composite electrochemical coatings with different molybdenum contents (wt.%): *a* – 8; *b* – 16, and the corresponding topography of the friction surface (*a*′ and *b*′).

Coatings with 8 wt.% Mo showed ~40% higher wear resistance, while those with 16 wt.% Mo showed ~10% improvement. This is attributed to higher boron content in the former, forming a more friction-resistant surface.

Tribocorrosion studies established that due to the lubricating properties of the aqueous chloride solution, the evolution of the friction coefficient differs significantly from that observed in air (Fig. 3 *a, b*). In particular, no characteristic running-in stage was detected for the investigated coatings. The average friction coefficient values in the electrolyte were practically the same as in air, remaining at ~0.4.

For coatings with 16 wt.% Mo, slightly lower material losses were observed—approximately 6% less compared to coatings containing 8 wt.% Mo which is attributed to the higher microhardness of the former. Analysis of the worn surface topography (Fig. 3 a´, *b*´) revealed leaching of amorphous boron from the friction zone under electrolyte exposure, which prevents the formation of an effective solid lubricating layer characteristic of dry sliding in air. This also explains the absence of a noticeable reduction in the friction coefficient.

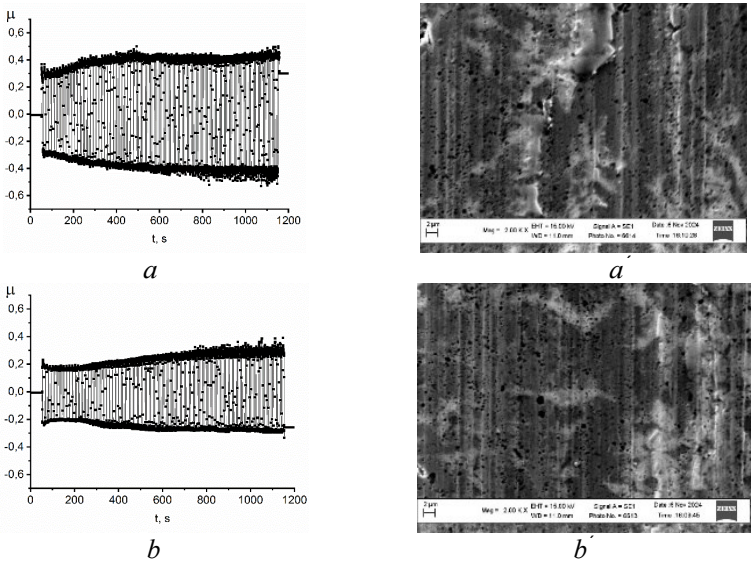

Fig. 3. Variation of the friction coefficient during testing in 3,0 % solution NaCl for Ni-Mo-B composite electrochemical coatings with different molybdenum contents (wt.%): *a* – 8; *b* – 16, and the corresponding topography of the friction surface (*a*´ and *b*´).

Additionally, stronger adhesive interactions under tribocorrosion conditions were evidenced by the dynamics of electrode potential variation during sliding, which confirms the active involvement of the surface in electrochemical processes. Figure 4 illustrates the change in electrode potential during

tribocorrosion tests of Ni-Mo-B composite coatings with different molybdenum contents. For both samples, a sharp potential drop was observed immediately after the onset of frictional interaction, indicating the breakdown of the passive film and activation of the corrosion process. Subsequently, the potential stabilized, forming a new equilibrium state. The coating containing 16 wt.% Mo exhibited more stable and slightly higher electrode potential values compared to the coating with 8 wt.% Mo, which indicates its superior resistance to tribocorrosion degradation.

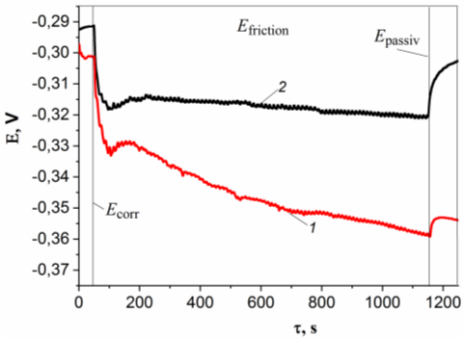

Fig. 4. Change in electrode potential during tribocorrosion tests of Ni-Mo-B coatings with different Mo contents (wt.%): 1 – 8%; 2 – 16%.

Thus, under corrosion–mechanical wear conditions, coatings containing 16 wt.% Mo can be applied to enhance resistance to tribocorrosion.

Conclusions: It was established that under dry friction conditions, coatings with 8 wt.% Mo are more effective due to their lower stiffness and higher amorphous boron content, which promotes the formation of a lubricating layer. In contrast, under tribocorrosion loading, coatings with 16 wt.% Mo are optimal, being characterized by higher hardness, lower material loss, and more stable electrode potential behavior during frictional interaction in the electrolyte. Thus, Ni-Mo-B coatings containing 8 and 16 wt.% Mo can serve as environmentally friendly and functionally viable alternatives to hard chromium for a wide range of applications.

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