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# CORROSION AND TRIBOCORROSION INHIBITION OF ALUMINUM ALLOY IN CHLORIDE SOLUTION BY A SYNERGISTIC BIOPOLYMER-BASED COMPOSITION

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The corrosion and tribocorrosion behavior of aluminum alloy in a chloride-containing environment was studied using a synergistic inhibitor based on maltodextrin (MLD) and zinc gluconate (ZG). EIS, SEM/EDX, and tribocorrosion tests were employed to evaluate its performance. MLD alone was ineffective in 0.1% NaCl, whereas the addition of 0.06 g/L ZG produced a strong synergistic effect. The MLD+ZG composition achieved inhibition efficiency above 90%, with increased impedance and charge transfer resistance, indicating the formation of a dense protective film. SEM/EDX confirmed the reduction of corrosion products and the incorporation of zinc into the surface layer. Under tribocorrosion conditions, the inhibitor suppressed depassivation, shifted the corrosion potential to more positive values, reduced polarization current, and improved wear resistance by decreasing roughness and friction coefficient. The environmentally friendly MLD–ZG system provides effective protection for AA2024 against corrosion and tribocorrosion in chloride-containing environments.

**Keywords**: aluminum alloy, chloride solution, maltodextrin, zinc gluconate, corrosion, tribocorrosion inhibition.

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## *Introduction*

Aluminum alloys are extensively used across a wide range of industries, including aerospace, aviation, automotive manufacturing, and construction [1]. They are valued for their good machinability, high electrical conductivity, and favorable strength-to-weight ratio [2]. However, in aggressive environments, these materials are susceptible to localized corrosion. Corrosion leads to significant economic losses, material degradation, and poses challenges to the sustainable development of modern economies [3]. In recent years, environmentally friendly biopolymers have attracted considerable attention as corrosion inhibitors for aluminum alloys. These compounds can interact with metal surfaces via both physical adsorption and chemical bonding, thereby reducing corrosion rates [4–6].

The biopolymer maltodextrin is a product of partial starch hydrolysis, characterized by a relatively low degree of polymerization, predominantly short linear chains, and a well-controlled composition. As a result, it exhibits high solubility in aqueous media [7]. In the context of corrosion protection, these properties are of significant importance. Maltodextrin rapidly diffuses to the metal surface and adsorbs effectively due to its numerous hydroxyl groups, forming a protective adsorption layer. This promotes rapid surface passivation and reduces the rates of both anodic and cathodic processes. However, maltodextrin's effectiveness as a corrosion inhibitor depends strongly on the medium's composition. The most pronounced inhibiting effect is observed in acidic solutions, where protonation of functional groups occurs, enhancing adsorption on the metal surface [8]. In neutral chloride-containing environments, its protective action is significantly reduced, which is associated with the competition of chloride ions for active surface sites and the insufficient ability of the formed layer to effectively prevent localized corrosion.

Gluconic acid and its salts, in particular zinc gluconate, are known as corrosion inhibitors mainly for carbon steel in saline environments [9] and in cooling water systems [10]. One of the advantages of zinc gluconate is its environmental compatibility. However, effective inhibition of aluminum alloy corrosion by zinc gluconate in salt solutions has been observed only at relatively high concentrations, on the order of 1 g/L or higher, which is economically unfavorable [11]. Korniy et al. [12] demonstrated a significant enhancement of the protective effect of the natural polysaccharide dextrin in combination with microquantities of the organic salt zinc gluconate.

At the same time, aluminum alloy structures often operate under conditions of mechanical activation of their surface in a corrosive environment, i.e., under tribocorrosion conditions [13]. Tribocorrosion is a critical factor in the degradation of aluminum alloys in contact assemblies. Mechanical destruction of the passive film leads to local surface activation and the initiation of corrosion defects (pitting), which act as stress concentrators and accelerate the development of fatigue cracks. There is a need to apply corrosion-inhibiting compounds to protect aluminum structures against tribocorrosion.

In contrast to earlier studies [4–6], which mainly focused on other polysaccharides, relatively high concentrations of zinc salts, or corrosion conditions without metal surface mechanical activation, the present work investigates: (i) maltodextrin as a corrosion inhibitor for AA2024 aluminum alloy in a neutral chloride-containing environment; (ii) the synergistic effect between maltodextrin and a small amount of zinc gluconate, enabling high inhibition efficiency at significantly reduced zinc salt content; and (iii) the performance of the inhibitor system under tribocorrosion conditions involving continuous destruction and restoration of the passive film. These aspects represent the key novelty and distinguish the present study from previously reported biopolymer-based inhibitor systems.

In this context, the aim of this work was to investigate corrosion inhibition efficiency of maltodextrin-based compositions with a small addition of zinc gluconate on an aluminum alloy in a neutral chloride-containing environment under conditions of tribocorrosion of its surface.

***Materials and methods***

Corrosion of the AA2024 aluminum alloy was studied in an uninhibited 0.1 wt.% NaCl solution and in the presence of additions of the natural polysaccharide maltodextrin (1–3 g/L) and zinc gluconate (0.06 g/L).

The corrosion behavior of the aluminum alloy was studied using electrochemical impedance spectroscopy (EIS). A Gill AC potentiostat was employed, with a saturated silver/silver chloride (Ag/AgCl) reference electrode, a working electrode made of AA2024 aluminum alloy, and a platinum counter electrode. Impedance spectra were recorded at the open circuit potential over a frequency range of 10,000–0.01 Hz. The amplitude of the AC perturbation signal was 10 mV. The exposed surface area of the working electrode was 1 $cm^2$. Prior to immersion in the test solution, the alloy samples were sequentially ground using P400, P600, and P800 abrasive papers and degreased with acetone. The obtained impedance spectra were modeled using the ZSimWin 3.60 software, employing the equivalent electrical circuit $R_s(Q_f(R_f(Q_{dl}R_{ct})))$.

The inhibiting effectiveness (IE) of maltodextrin-based compositions was determined from impedance measurements using the following formula:

$$IE = \frac{R_{ct} - R_{ct0}}{R_{ct}} \cdot 100\%,$$

where $R_{ct}$ and $R_{ct0}$ are the charge-transfer resistances of the metal in the solution containing the biopolymer-based composition and in the uninhibited solution, respectively.

The chemical composition of the surface of AA2024 aluminum alloy specimens after exposure to corrosive media was investigated using a Zeiss EVO-40XVP scanning electron microscope (SEM) equipped with an AZtecLive (Oxford Instruments) energy-dispersive X-ray spectroscopy (EDX) system based on an Ultim Max 65 detector.

Tribocorrosion tests of AA2024 aluminum alloy were conducted in a corrosive environment under reciprocating sliding conditions using a ball-on-flat tribological configuration. The normal load applied to the counterbody was 2 N, the sliding speed was 1.6 $mm \cdot s^{-1}$, and the wear track length was 24 mm. The applied load was selected deliberately to ensure mechanical removal of the native oxide film and continuous exposure of the freshly formed aluminum surface during tribocorrosion, which was necessary for reliable electrochemical assessment of the inhibitor performance. Flat specimens (50×40×5 mm) of

AA2024 alloy were ground with SiC abrasive papers (P400, P800, and P1500) and polished with diamond pastes ACN 60/40, ACN 28/20, and ACN 14/10. Before each wear test, the ceramic ball and AA2024 specimens were cleaned in an ultrasonic bath with acetone for 10 min, and then air-dried. Using an MTech SPG-500fast potentiostat, a saturated Ag/AgCl reference electrode, and a platinum counter electrode, the corrosion potential of the aluminum alloy and its polarization current – obtained by applying the open-circuit potential – were recorded.

The morphology and surface topography characteristics of the wear track on the specimen in both inhibited and uninhibited solutions were investigated using a non-contact 3D interference profilometer, Micron-alpha.

***Results and discussion***

The effect of maltodextrin on the corrosion resistance of AA2024 aluminum alloy in a 0.1% NaCl solution was preliminarily investigated using electrochemical impedance spectroscopy (EIS). The impedance modulus $Z_{0.1}$ at a low frequency (0.1 Hz) was used as an indicator of protective performance [14]. The concentration of maltodextrin was varied from 1 to 3 g/L. It was found that the use of maltodextrin alone at concentrations of 1.0 and 1.5 g/L has virtually no effect on the impedance modulus and, consequently, on the corrosion resistance of the aluminum alloy. At concentrations of 2.0 g/L and higher, a decrease in this parameter was observed. Based on the experimental results, it can be concluded that maltodextrin is not an effective corrosion inhibitor for the aluminum alloy in a neutral chloride-containing environment. A positive corrosion inhibition effect of maltodextrin was observed only in an acidic medium [8].

However, upon introduction of a biopolymer MLD-based composition together with a micro-amount of the co-synergist ZG (0.06 g/L) into the 0.1% NaCl solution, the corrosion resistance of the AA2024 aluminum alloy significantly improved, as confirmed by electrochemical impedance spectroscopy (EIS) results (Fig. 1). It was established (Fig. 1) that the AA2024 aluminum alloy in a 0.1% NaCl solution inhibited with the composition of 2.5 g/L MLD+0.06 g/L ZG, after 24 h of exposure, exhibited the highest impedance modulus at a frequency of 0.1 Hz ($Z_{0.1}$), reaching $4.97 \cdot 10^4$ Ω·cm². At the same time, the $Z_{0.1}$ values for alloy samples in other media inhibited with MLD+ZG compositions were in the range of $3.23 \cdot 10^3$ to $3.32 \cdot 10^4$ Ω·cm².

Frequency dependences of the phase angle θ of the aluminum alloy after 24 h exposure in 0.1% NaCl with MLD+ZG compositions are shown in Fig. 1. For MLD+ZG compositions, an increase in the maximum phase angle and its shift toward higher frequencies (10–1000 Hz) were observed, indicating the formation of a dense protective film. The highest θ value ($60^0$) was obtained for 2.5 g/L MLD+0.06 g/L ZG, compared to ~$50^0$ in the uninhibited solution.

The obtained impedance spectra were modeled using the electrical equivalent circuit $R_s(Q_f(R_f(Q_{dl}R_{ct})))$ and the ZSimWin 3.60 software. Here, $Y_0(Q_{dl})$, $n(Q_{dl})$ are the admittance and the power exponent of the constant phase $Q_{dl}$ element, respectively; $Y_0(Q_f)$, $n(Q_f)$ are the admittance and the power exponent of the constant phase $Q_f$ element, respectively. The charge transfer resistance ($R_{ct}$) of the AA2024 aluminum alloy in the corrosion solution containing composition No. 5 after 24 h of exposure (Table 1) was

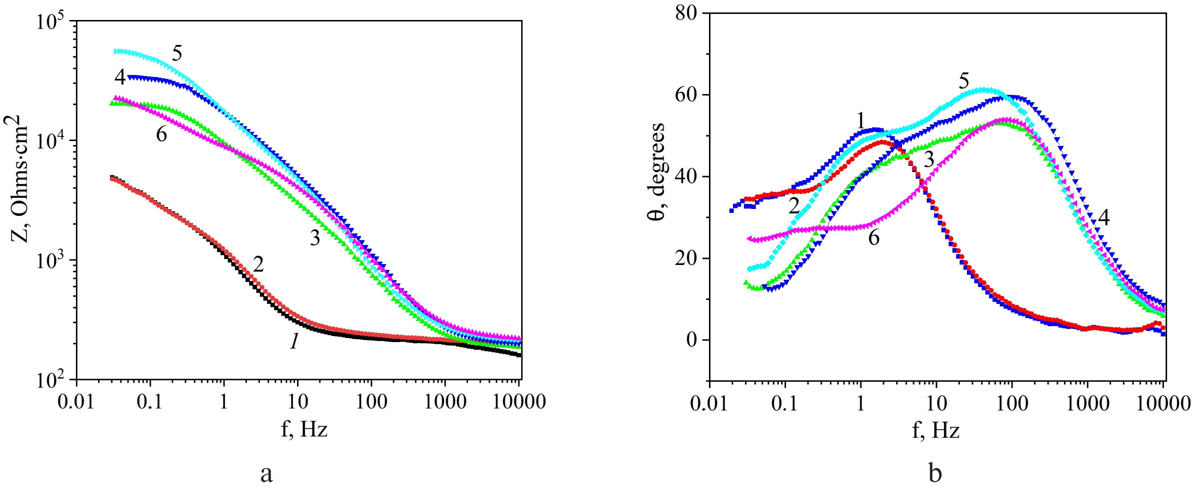


Fig. 1. Frequency dependences of impedance modulus (a) and phase angle (b) for AA2024 alloy after 24 hours of exposure to 0.1% NaCl solution (1) in the presence of 1 g/L MLD+0.06 g/L ZG (2); 1.5 g/L MLD+0.06 g/L ZG (3); 2.0 g/L MLD+0.06 g/L ZG (4); 2.5 g/L MLD+0.06 g/L ZG (5); 3.0 g/L MLD+0.06 g/L ZG (6)

$6.2 \cdot 10^4$ Ω·cm$^2$, which is approximately 10 times higher than in the uninhibited solution and 1.5–2.8 times higher than for other «MLD+ZG» compositions. It was established (Table 1) that after 24 h of exposure, the admittance $Y_0(Q_{dl})$ decreased by one to two orders of magnitude in all solutions inhibited with «MLD+ZG» compositions compared to the uninhibited solution, indicating the formation of a stable organic film on the surface. Notably, in the 0.1% NaCl solution, the admittance $Y_0(Q_{dl})$ increased to $9.59 \cdot 10^{-4}$ $S^n/(\Omega \cdot cm^2)$ due to corrosion degradation of the AA2024 alloy and the formation of oxidation products (Table 1). An increase in the maltodextrin content in the composition with ZG up to 3.0 g/L led to a deterioration of the inhibition performance. A similar trend was previously reported in ref. [15] for a corrosion inhibitor of aluminum alloys based on the biopolymer dextrin. This can likely be explained by changes in solution pH due to the biopolymer. The calculated inhibition efficiency for protecting AA2024 using the synergistic biopolymer-based composition (2.5 g/L MLD+0.06 g/L ZG) was the highest, exceeding 90% (Table 1).

The surface of AA2024 aluminum alloy after 24 hours of exposure in uninhibited and inhibited 0.1% NaCl solutions was analyzed by SEM/EDX. The elemental composition is presented in Table 2. In the uninhibited solution, a high oxygen content (58.41 wt.%) indicates intensive formation of corrosion products. The presence of Na and Cl confirms the incorporation of electrolyte components. In the presence of MLD, the oxygen content slightly decreases (51.97 wt.%), indicating partial corrosion inhibition. The increased carbon content (28.11 wt.%) reflects the adsorption of maltodextrin, forming an organic layer. The absence of Na and Cl suggests a limited barrier effect.

The strongest inhibition was observed for MLD+ZG. A significant decrease in oxygen (26.61 wt.%) and an increase in aluminum (37.04 wt.%) indicate reduced corrosion product formation and a thinner surface layer. The higher carbon content (32.32 wt.%) confirms the formation of organic film, while the presence of zinc (4.03 wt.%) suggests that zinc-containing species are incorporated into the surface layer and may contribute to its protective properties [13].

Figure 2 shows the evolution of the corrosion potential (E) of AA2024 in 0.1% NaCl under reciprocating sliding. In the uninhibited solution (curve 1), the potential initially stabilizes at ~−0.50 V, indicating a passive surface. When friction starts (~100 s), E shifts negatively to approximately −0.80...−0.85 V due to depassivation caused by destruction of oxide film. A quasi-steady state then forms (−0.85...−0.90 V), reflecting a balance between film breakdown and repassivation. After stopping friction (~900 s), E shifts positively to ~−0.65 V, indicating recovery of passivity. With the inhibitor (curve 2), the initial E is similar (~−0.50 V), but the negative shift during friction is much smaller (~−0.55...−0.60 V). The potential remains stable,

Table 1

**Characteristics of an equivalent electrical circuit $R_s(Q_f(R_f(Q_{dl}R_{ct})))$ calculated from the impedance spectra of aluminum alloy in control and inhibited solutions**

| Numbering of spectra according to Figs. 1 and 2 | $R_{ct}$, Ω·cm$^2$ | $Y_0(Q_{dl})$, $s^n/\Omega \cdot cm^2$ | $n(Q_{dl})$ | $R_f$, Ω·cm$^2$ | $Y_0(Q_f)$, $s^n/\Omega \cdot cm^2$ | $n(Q_f)$ | IE, % |
|---|---|---|---|---|---|---|---|
| 1 | 6449 | $9.59 \cdot 10^{-4}$ | 0.63 | 196 | $2.06 \cdot 10^{-4}$ | 0.79 | – |
| 2 | 6771 | $2.80 \cdot 10^{-5}$ | 0.68 | 205 | $2.59 \cdot 10^{-5}$ | 0.88 | 4 |
| 3 | 21931 | $2.13 \cdot 10^{-5}$ | 0.78 | 219 | $2.01 \cdot 10^{-5}$ | 0.91 | 71 |
| 4 | 36805 | $9.91 \cdot 10^{-6}$ | 0.74 | 230 | $4.99 \cdot 10^{-6}$ | 0.91 | 82 |
| 5 | 62030 | $1.01 \cdot 10^{-6}$ | 0.97 | 238 | $1.63 \cdot 10^{-6}$ | 0.92 | 90 |
| 6 | 24349 | $3.96 \cdot 10^{-5}$ | 0.81 | 225 | $4.85 \cdot 10^{-5}$ | 0.90 | 74 |

Table 2

**Elemental composition of aluminum alloy surface film after 24 hours of exposure**

| Solution | Content, wt.% | | | | | | |
|---|---|---|---|---|---|---|---|
| | C | O | Na | Al | Cl | Cu | Zn |
| 0.1% NaCl | 16.07 | 58.41 | 2.34 | 18.43 | 2.33 | 2.41 | – |
| 0.1% NaCl+MLD | 28.11 | 51.97 | – | 17.37 | – | 2.59 | – |
| 0.1% NaCl+MLD+ZG | 32.32 | 26.61 | – | 37.04 | – | – | 4.03 |

indicating suppressed depassivation and rapid film repair. After friction, E further shifts anodically (~−0.52 V), suggesting a more stable passive state. Thus, the inhibitor stabilizes the potential at more positive values, reduces depassivation, and enhances repassivation under tribocorrosion.

Figure 3 shows the evolution of polarization current of AA2024 under tribocorrosion in 0.1% NaCl. In the uninhibited solution (curve 1), the current rapidly increased in the first ~100 s due to oxide film destruction, then reached a quasi-steady state (~0.025–0.030 mA) with large fluctuations caused by cyclic depassivation–repassivation. This indicates progressive surface activation and wear. In the inhibited solution (curve 2, 2.5 g/L MLD+0.06 g/L ZG), the current remained significantly lower (~0.003–0.010 mA), reflecting more stable protection and limited anodic dissolution. Overall, the inhibitor markedly reduced polarization current, indicating suppression of the anodic process during tribocorrosion.

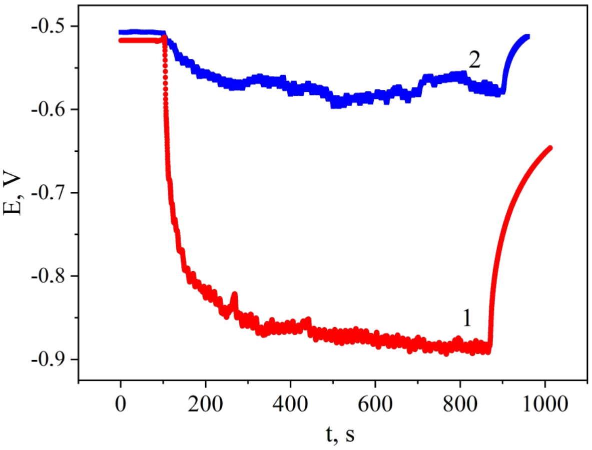


Fig. 2. Time dependences of the electrode potential of the aluminum alloy under tribocorrosion loading in: 1 – 0.1% NaCl; 2 – 0.1% NaCl+2.5 g/L MLD+0.06 g/L ZG

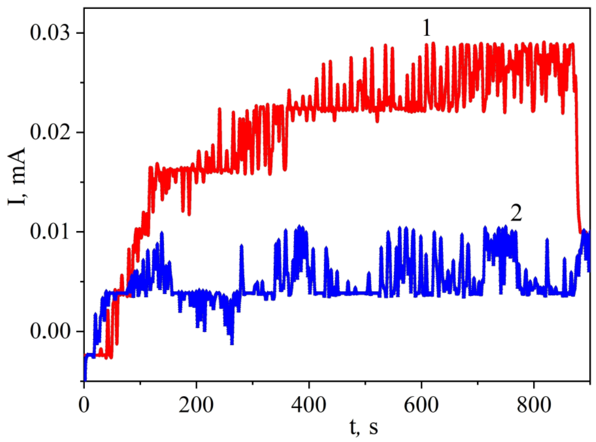


Fig. 3. Time dependences of the polarization current for the aluminum alloy under tribocorrosion conditions in: 1 – 0.1% NaCl; 2 – 0.1% NaCl+2.5 g/L MLD+0.06 g/L ZG

Based on 3D profilograms of AA2024 wear tracks in 0.1% NaCl and in a solution with maltodextrin-based composition, roughness parameters ($R_a$, $R_z$) were determined. In the uninhibited solution, high roughness values ($R_a$=0.972 μm, $R_z$=4.145 μm) indicate severe wear and corrosion. In contrast, the MLD+ZG composition leads to surface smoothing and reduced roughness ($R_a$=0.6655 μm, $R_z$=2.102 μm). The decrease in $R_a$ and $R_z$ by 1.4–2 times confirms the formation of a protective layer and the effective suppression of tribocorrosion.

It was found (Fig. 4) that the inhibitor composition reduces the coefficient of friction (μ) for the «aluminum alloy–ceramic ball» pair. The low scatter of μ in the inhibited solution indicates uniform wear without significant contact area growth, likely due to the formation of an adsorbed organic film (Fig. 4). In contrast, the uninhibited medium shows large μ fluctuations and severe surface damage. The adsorbed film presumably provides lubrication, resulting in an average friction coefficient 2.8 times lower than in 0.1% NaCl.

***Conclusions***

Maltodextrin alone does not provide effective corrosion inhibition for AA2024 aluminum alloy in a 0.1% NaCl solution. However, its combination with zinc gluconate exhibits a strong synergistic anticorrosion effect with inhibition efficiency above 90%. EIS results indicate increased charge-transfer resistance, confirming the formation of a dense protective film. SEM/EDX analysis revealed a reduction in corrosion products and the incorporation

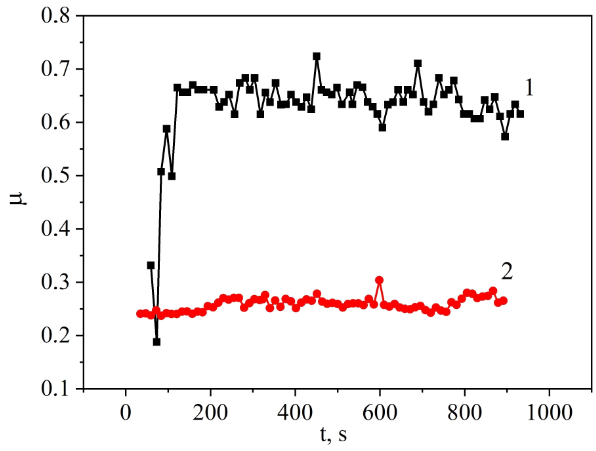


Fig. 4. Dependences of the coefficient of friction in the AA2024-T3 alloy+corund pair on time: 1 – 0.1% NaCl; 2 – 0.1% NaCl+2.5 g/L MLD+0.06 g/L ZG

of zinc-containing species into the surface layer, which may contribute to its protective properties. The composition also suppressed depassivation under tribocorrosion conditions, shifted the corrosion potential to more positive values, and reduced anodic currents. The use of the maltodextrin–zinc gluconate composition also substantially decreased wear intensity: surface roughness parameters ($R_a$, $R_z$) are reduced by 1.4–2 times, and the friction coefficient decreases by 2.8 times, indicating that the formed organic layer possesses certain lubricating properties. Thus, the developed environmentally safe inhibitory composition based on maltodextrin and zinc gluconate can be used for the protection of aluminum alloy against both corrosion and tribocorrosion in chloride-containing environments.

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### ІНГІБУВАННЯ КОРОЗІЇ ТА ТРИБОКОРОЗІЇ АЛЮМІНІЄВОГО СПЛАВУ В ХЛОРИДНОМУ РОЗЧИНІ СИНЕРГЕТИЧНОЮ КОМПОЗИЦІЄЮ НА ОСНОВІ БІОПОЛІМЕРІВ

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Досліджено корозійну та трибокорозійну поведінку алюмінієвого сплаву в хлоридовмісному середовищі з використанням синергічного інгібітора на основі мальтодекстрину (МЛД) та глюконату цинку (ЦГ). Для оцінювання його ефективності застосовано метод електрохімічної імпедансної спектроскопії (EIS), SEM/EDX-аналіз і трибокорозійні випробування. Встановлено, що сам по собі МЛД є неефективним у 0,1%-ому розчині NaCl, тоді як додавання 0,06 г/л ЦГ забезпечує виражений синергетичний ефект. Композиція МЛД+ЦГ досягала ефективності інгібування понад 90%, що супроводжувалося зростанням імпедансу та опору перенесенню заряду, вказуючи на формування щільної захисної плівки. За даними SEM/EDX підтверджено зменшення кількості продуктів корозії та включення цинку до поверхневого шару. В умовах трибокорозії інгібітор пригнічував депасивацію, зміщував корозійний потенціал у позитивнішу область, зменшував поляризаційний струм і підвищував зносостійкість завдяки зниженню шорсткості поверхні та коефіцієнта тертя. Екологічно безпечна система МЛД+ЦГ забезпечує ефективний захист сплаву АА2024 від корозії та трибокорозії в хлоридовмісних середовищах.

**Ключові слова**: алюмінієвий сплав; хлоридний розчин; мальтодекстрин; глюконат цинку; корозія; інгібування трибокорозії.

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