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TRIBOCORROSION OF ALUMINUM ALLOY IN A CHLORIDECONTAINING ENVIRONMENT INHIBITED BY A MALTODEXTRIN-BASED COMPOSITION

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Abstract: *The effect of an inhibitory composition based on the biopolymer maltodextrin (MLD) and zinc gluconate (ZG) on the tribo-corrosion of the AA2024-T3 aluminum alloy in a chloride-containing corrosion environment was studied. It was found that its inhibition efficiency is 90%. The application of the maltodextrin + zinc gluconate inhibitor composition contributes to a twofold reduction in the friction coefficient of the aluminum alloy/corundum pair and a decrease in the wear track width, indicating an effective reduction in tribo-corrosive impact. Under the influence of the synergistic composition, a slowdown in corrosion processes in the wear zone is observed, as confirmed by a sixfold decrease in the polarization current. Additionally, a reduction in roughness parameters Ra and Rz after frictional interaction in the inhibited environment was recorded, confirming the effectiveness of the applied inhibitor composition in reducing surface damage and improving the tribo-corrosion characteristics of the alloy.*

Keywords: *tribocorrosion, aluminium alloy, maltodextrin, zinc gluconate, friction coefficient, surface wear, metal polarization current*

1. INTRODUCTION

Aluminum alloys are widely used in the automotive, aviation, shipbuilding industries, and construction due to their high mechanical characteristics and low density. However, these materials are prone to local corrosion, especially in chloride-containing environments [1–3]. One of the promising approaches to protecting aluminum alloys is the use of environmentally safe corrosion inhibitors, in particular biopolymers [4–7]. However, the effectiveness of biopolymers in neutral chloride-containing environments remains insufficient. Previous studies have shown that the combination of biopolymers with carboxylic acid salts significantly improves the anticorrosion properties of the resulting compositions [6,7]. This opens up prospects for their use to protect aluminum alloys from tribocorrosion. Accordingly, the aim of this work is to study the effect of a composition based on the biopolymer maltodextrin and zinc gluconate on tribocorrosion processes in aluminum alloys in chloride-containing environments.

2. EXPERIMENTAL

2.1 Corrosion research

The corrosion of AA 2024-T3 alloy was investigated in a 0.1% NaCl solution, to which the natural polysaccharide maltodextrin (MLD) and zinc gluconate (ZG) were added as corrosion inhibitors. Both MLD (1–3 g/L) and its compositions with ZG (0.06 g/L) were introduced into the corrosive solution.

The anti-corrosion efficiency of the inhibitor composition was investigated by electrochemical impedance spectroscopy using a Gill AC potentiostat. Measurements were performed in the frequency range of 10,000–0.01 Hz at an open circuit potential. The working electrode was aluminum alloy AA2024-T3, the reference electrode was silver chloride (type EVL-1M1), and the auxiliary electrode was platinum. The amplitude of the applied signal was 10 mV, and the area of the working surface of the samples was 1 cm^2.

2.2 Tribocorrosion research

Tribocorrosion tests of 2000 series aluminium alloy AA 2024-T3 were performed on flat samples using a special self-made linear reciprocating tribometer (Fig. 1). A corundum ball with 9 mm diameter was used as an indenter. The set-up consists of a frame, a reciprocating stage and a support with the mounted indenter. The stage is moved by an electric motor through a worm gear. A flat alloy sample was secured on the stage and was also contained within a corrosion cell fastened to the sliding wear stage through a rubber seal. The friction couple was loaded by a weight placed on the top of the indenter. Strain sensors were fixed to the indenter support and recorded a moment of friction force. The friction coefficient between the ceramic ball and the aluminium alloy was calculated using values of this moment. The total loading on the ball was 2 N, the sliding speed of indenter was 1.6 mm·s-1 and the length of wear track was 24 mm. Flat samples (50x40x5 mm) of the AA2024 alloy were abraded with SiC paper (800 and 1500 grit) and polished with diamond pastes ACN 60/40, ACN 28/20, ACN 14/10. Before each wear test, the ceramic ball and AA2024 samples were ultrasonically cleaned in acetone within 10 min and then air dried.

The investigations were carried out in 0.1 % NaCl solution to which a composition based on maltodextrin (2.5 g/l) and zinc gluconate (0.06 g/l) was added. Polarization current of aluminium alloy in corrosive solutions at free corrosion potential was recorded during tribocorrosion tests using a MTech SPG-500fast potentiostat-galvanostat, a saturated Ag/AgCl reference electrode and a platinum auxiliary electrode. The morphology and characteristics of the topography of the friction surface of the sample in inhibited and uninhibited solutions were studied by a non-contact 3D interference profilometer "Micron-alpha".

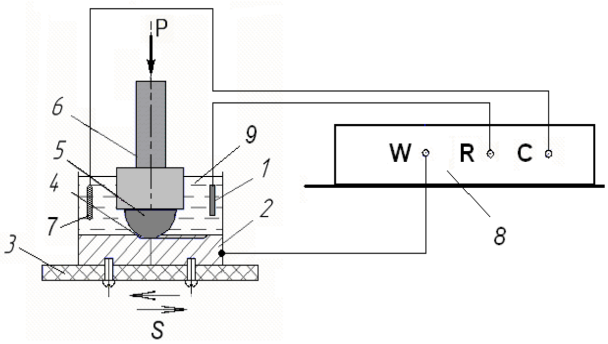

Figure 1. Scheme of corrosive wear test of aluminium alloy: 1) saturated Ag/AgCl reference electrode; 2) flat test sample; 3) reciprocating stage; 4) contact zone; 5) corundum ball, Ø=9 mm; 6) indenter support with strain sensors; 7) platinum electrode; 8) MTech SPG-500fast potentiostat-galvanostat; 9) 0.1% NaCl solution; P - loading; S - direction of stage movement

3. RESULTS AND DISCUSSION

The results of electrochemical impedance spectroscopy for AA2024-T3 alloy after 24 hours of exposure in 0.1% NaCl show that the addition of maltodextrin (MLD) at concentrations of 1.0 g/L, 1.5 g/L, 2.0 g/L, 2.5 g/L and 3.0 g/L (Fig. 2) leads to a slight decrease in the impedance modulus in the studied frequency range. This indicates a complete lack of protective effect of this inhibitor on the aluminum alloy.

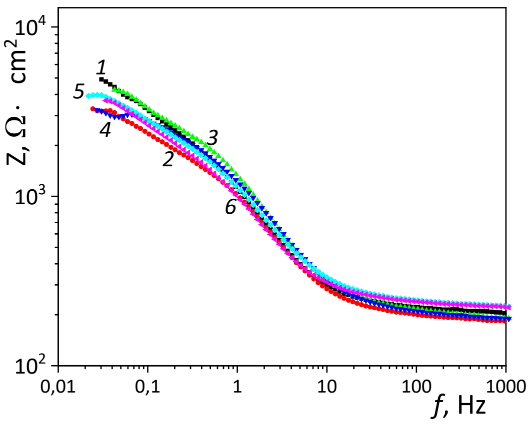

Figure 2. Frequency impedance dependences of AA2024-T3 alloy after 24 h of exposure to 0.1% NaCl solution in the presence of maltodextrin (MLD)*:* (*1*) 0.1% NaCl; (*2*) 1 g/l MLD; (*3*) 1.5 g/l MLD; (*4*) 2 g/l MLD; (*5*) 2.5 g/l MLD; (*6*) 3 g/l MLD

From the frequency impedance dependences of the aluminum alloy obtained after 24 hours of exposure in 0.1% NaCl (Fig.3), it is seen that in the uninhibited solution (curve 1) the alloy had the lowest values of the impedance modulus in the entire frequency range, which indicates its low corrosion resistance. Adding the MLD+ZG composition to the corrosion solution contributed to an increase in the impedance values (curves 2–6), which indicates the inhibition of corrosion processes. The maximum values of the impedance modulus were observed at concentrations of 2.0 g/l MLD + 0.06 g/l ZG (curve 5) and 2.5 g/l MLD + 0.06 g/l ZG (curve 6), which indicates the formation of the most effective protective layer on the metal surface.

The behavior of the phase angle of the aluminum alloy correlates with its impedance dependences (Fig. 4). For the sample in the solution without inhibitor (curve 1), the phase angle had lower values, probably due to the intensive corrosion process. The addition of the inhibitor in 0.1% NaCl (curves 2–6) caused an increase in the phase angle in the mid-frequency region, which indicates an improvement in the barrier properties of the protective film on the alloy surface. The maximum values of the phase angle were observed at concentrations of 2.0–2.5 g/l MLD + 0.06 g/l ZG (curves 4 and 5) in the range of 20–200 Hz, which indicates the formation of the most stable protective layer. Further increase in the MLD concentration in the inhibitor composition to 3 g/l (curve 6) led to a decrease in the maximum value of the phase angle, which may indicate a deterioration in the protective properties of the surface film.

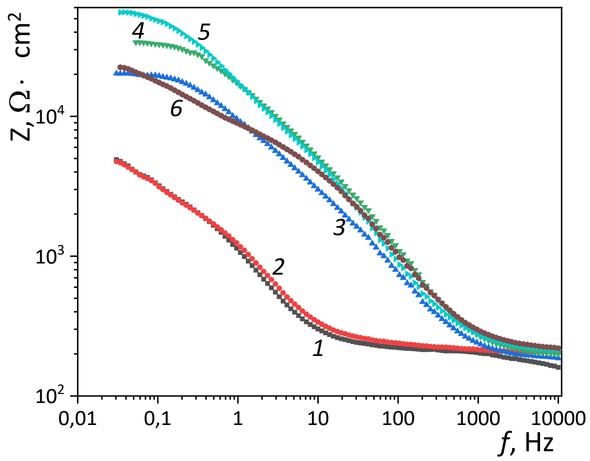

Figure 3. Frequency impedance dependences of AA2024-T3 alloy after 24 h of exposure to 0.1% NaCl solution in the presence of composition MLD+ZG *:* (*1*) 0.1% NaCl; (*2*) 1 g/l MLD+0.06 g/l ZG; (*3*) 1.5 g/l MLD+0.06 g/l ZG; (*4*) 2 g/l MLD+0.06 g/l ZG; (*5*) 2.5 g/l MLD+0.06 g/l ZG; (*6*) 3 g/l MLD+0.06 g/l ZG

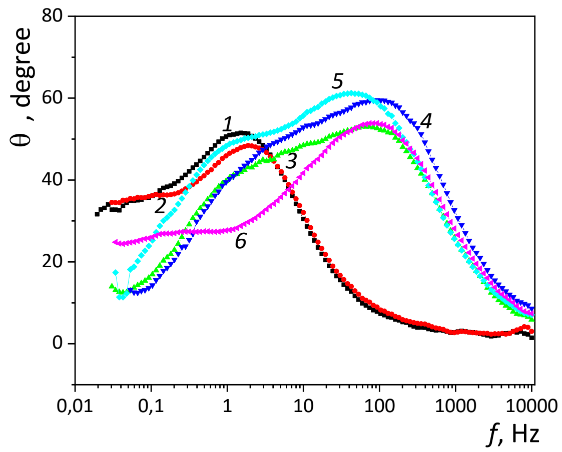

Figure 4. Dependencies of the phase angle of AA2024-T3 alloy after 24 h of exposure in 0,1% NaCl: (*1*) 0.1% NaCl; (*2*) 1 g/l MLD+0.06 g/l ZG; (*3*) 1.5 g/l MLD+0.06 g/l ZG; (*4*) 2 g/l MLD+0.06 g/l ZG; (*5*) 2.5 g/l MLD+0.06 g/l ZG; (*6*) 3 g/l MLD+0.06 g/l ZG.

The impedance dependences obtained for the AA2024-T3 alloy in the control environment and in environments inhibited by the MLD+ZG composition were simulated using the ZSimWin 360 computer program and the electrical equivalent circuit $R_s(Q_f(R_f(Q_{dl}R_{ct})))$. Here, R_s represents the resistance of the corrosive environment, R_{ct} is the charge transfer resistance of the metal, Q_{dl} is the capacitance of the electric double layer on the metal surface, and Q_f is the capacitance of the surface film. The capacitances Q_{dl} and Q_f are expressed in terms of constant phase elements [8].

The inhibition efficiency of maltodextrin-based compositions was determined by the formula:

$$\eta = \frac{R_{ct} - R_{ct0}}{R_{ct}} \cdot 100\ \%. \qquad (1)$$

where R_{ct}, R_{ct0} represent the charge transfer resistance of the metal in the corrosion solution containing the biopolymer-based composition and in the uninhibited 0.1% NaCl solution, respectively.

Table 1. Characteristics of equivalent circuit derived from modelling of EIS spectra of D16T alloy samples exposed to inhibited corrosion solutions

Spectra according to Fig. 3	R_{ct}, $\Omega\cdot cm^2$	Q_{dl}, $s^n/\Omega\cdot cm^2$	Q_f, $s^n/\Omega\cdot cm^2$	η, %
1	6449	$9{,}59\cdot10^{-4}$	$2{,}06\cdot10^{-4}$	-
2	6771	$2{,}80\cdot10^{-5}$	$2{,}59\cdot10^{-5}$	4
3	21931	$2{,}13\cdot10^{-5}$	$2{,}01\cdot10^{-5}$	71
4	36805	$9{,}91\cdot10^{-6}$	$4{,}99\cdot10^{-6}$	82
5	62030	$1{,}01\cdot10^{-6}$	$1{,}63\cdot10^{-6}$	90
6	24349	$3{,}96\cdot10^{-5}$	$4{,}85\cdot10^{-5}$	74

According to the data in Table 1, the presence of a 2.5 g/L MLD + 0.06 g/L ZG composition in the corrosion solution resulted in a 9.6-fold increase in the charge transfer resistance (R_{ct}) of the aluminum alloy after 24 hours compared to the uninhibited solution. Additionally, the capacitive element (Q_{dl}) decreased by approximately two orders of magnitude, indicating the formation of a protective film on the surface. This film effectively reduces metal ionization and the transition of its cations into the solution. The degree of metal protection *(η)* in the inhibited environment containing 2.5 g/L MLD + 0.06 g/L ZG was 90%, the highest value among all tested inhibited solutions. Based on these results, this composition was selected for further tribocorrosion studies, as it provides optimal anti-corrosion performance.

Figure 5 presents the dependence of the friction coefficient μ of the AA2024-T3/corundum ball pair on test time in two solutions: 0.1% NaCl (curve 1) and 2.5 g/L MLD + 0.06 g/L ZG (curve 2). Analysis of the results shows that in 0.1% NaCl, the friction coefficient increases rapidly within the first seconds of the test and stabilizes at ≈0.6–0.7. This indicates intensive wear of the alloy surface due to the absence of an effective protective layer. In contrast, in the solution containing 2.5 g/L MLD + 0.06 g/L ZG, the friction coefficient remains stable at ≈0.25–0.3, which is approximately half the value observed in the uninhibited solution. This suggests the formation of a protective film that reduces friction and slows down the wear of the alloy surface. Thus, the studied composition demonstrates effective anti-corrosion and anti-friction properties, significantly reducing the mechanical degradation of the AA2024-T3 alloy surface during tribocorrosion tests.

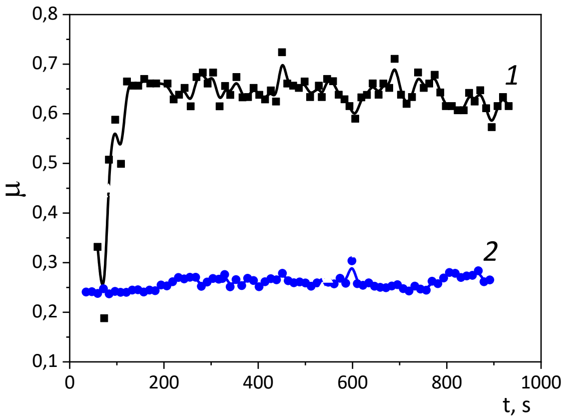

Figure 5. Dependences of the coefficient of friction in the AA2024-T3 alloy+corund pair on time: *1* – 0,1 % NaCl; *2* – 2.5 g/l MLD + 0.06 g/l ZG.

Figure 6 illustrates the reduction in the wear track width of the aluminum alloy in a 0.1% NaCl solution after the addition of the MLD and ZG inhibitor composition, confirming its effectiveness in protecting the metal from tribocorrosion.

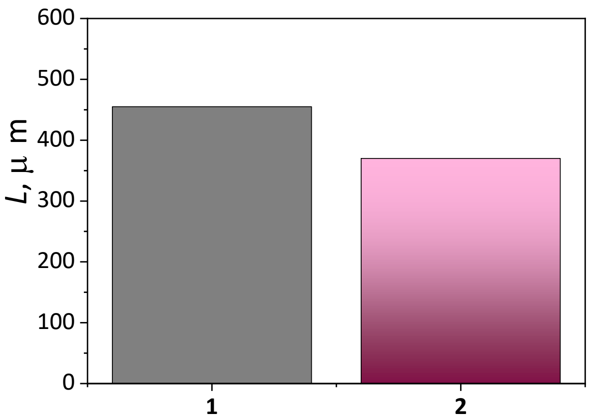

Figure 6. Wear track width of aluminum alloy in: 1 – 0.1% NaCl; 2 – 0.1% NaCl + 2.5 g/l MLD + 0.06 g/l ZG.

During tribo-corrosion loading of the AA 2024-T3 aluminum alloy in a 0.1% NaCl solution (**Fig. 7**), the polarization current (I) at the lapping stage (up to 170 s) sharply increased to 0.015 mA and then gradually rose to 0.03 mA over the entire period of frictional interaction. In the inhibited environment containing the MLD-based composition, significantly lower current values (~0.005 mA) and relative stability throughout the test were observed. This indicates the formation of a stable protective film that effectively prevents the tribo-corrosion of the alloy.

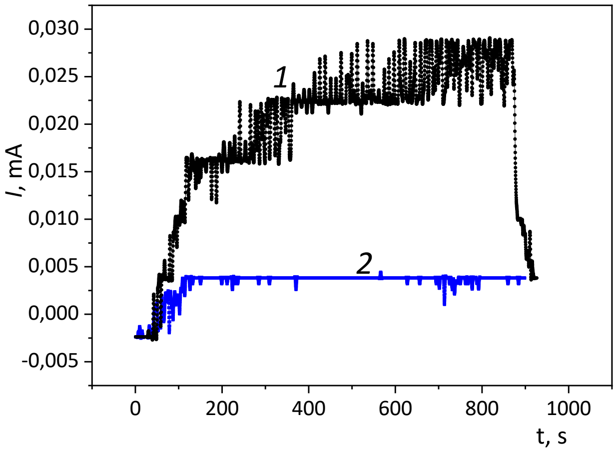

Figure 7. Change in polarization current during friction AA2024-T3 alloy: *1* – 0,1 % NaCl; *2* – 2.5 g/l MLD + 0.06 g/l ZG

In a 0.1% NaCl solution, the electrode potential of the AA2024-T3 aluminum alloy (Fig. 8, curve 1) at the onset of friction sharply shifted to the negative direction, reaching approximately -0.85 V. This indicates the rapid destruction of the oxide layer and an intensive progression of anodic corrosion processes on the wear track under mechanical loading. The potential remained consistently low throughout the entire tribo-corrosion loading, indicating the absence of effective protection for the metal surface.

In the environment of 0.1% NaCl + 2.5 g/L MLD + 0.06 g/L ZG (Fig. 8, curve 2), the potential of the AA2024-T3 aluminum alloy underwent a slight shift in the negative direction at the onset of friction, after which it stabilized at approximately -0.55 V. Throughout the entire tribo-corrosion loading period, the potential exhibited only minor fluctuations, indicating the effective formation and preservation of a protective layer on the metal surface.

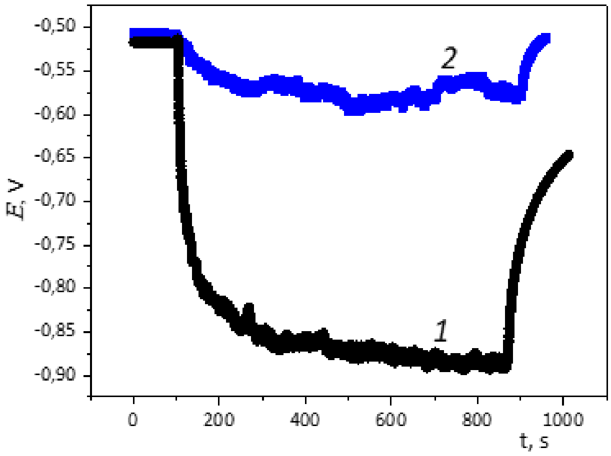

Figure 8. Potential change during friction AA2024-T3 alloy: *1* – 0,1 % NaCl; *2* – 2.5 g/l MLD + 0.06 g/l ZG.

The analysis of the surface topography of the friction tracks (Fig. 9) showed that after exposure to the uninhibited 0.1% NaCl solution, the surface of the aluminum alloy exhibited uneven areas with pronounced wear marks, scratches, and possibly zones of localized corrosion. This indicates an intense mechanical wear process aggravated by corrosive effects. In contrast, in the environment containing 2.5 g/L MLD and 0.06 g/L ZG, the alloy surface appeared significantly more uniform, with reduced roughness and less pronounced wear marks. This change in surface morphology confirms the effectiveness of the maltodextrin + zinc gluconate composition in reducing the tribo-corrosive wear of the AA2024-T3 alloy, thereby contributing to an increase in its operational durability.

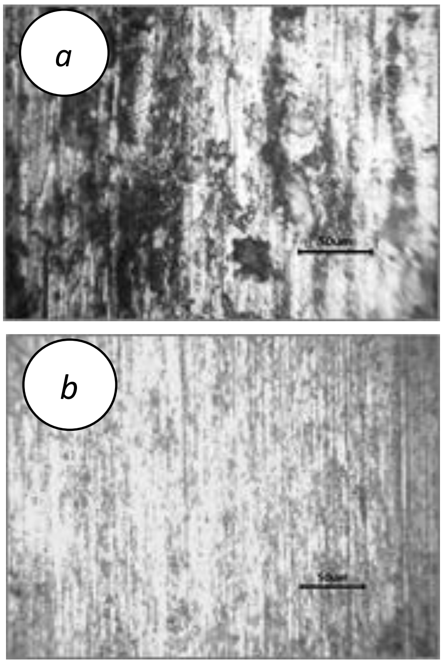

Figure 9. Topography of friction surface of AA2024-T3 alloy in: *a* – 0,1 % NaCl; *b* – 2.5 g/l MLD + 0.06 g/l ZG.

Based on the 3D profilograms of the wear tracks of the aluminum alloy in uninhibited and inhibited solutions, the average values of height roughness parameters were determined across five cross-sections (Fig. 10). It was found that in the uninhibited 0.1% NaCl solution, after tribo-corrosion, the arithmetic mean deviation of the profile (Ra) was 0.972 µm, and the roughness height (Rz) was 4.145 µm (Fig. 10a). In the environment inhibited with the maltodextrin + zinc gluconate composition, these parameters decreased to Ra = 0.6655 µm and Rz = 2.102 µm (Fig. 10b). Thus, the surface profilometry results confirm that the use of the studied inhibitor composition contributes to reducing surface roughness and promoting more uniform wear. This, in turn, improves the tribo-corrosion characteristics of the metal, which is consistent with the results of friction coefficient and polarization current measurements in the investigated corrosive environments.

The inhibitory efficiency of MLD is explained by its adsorption on the metal surface through hydroxyl groups, which form coordination bonds. A similar protection mechanism has been described in [10] for zinc in an acidic environment. However, in a neutral environment, maltodextrin alone exhibits insufficient inhibitory efficiency.

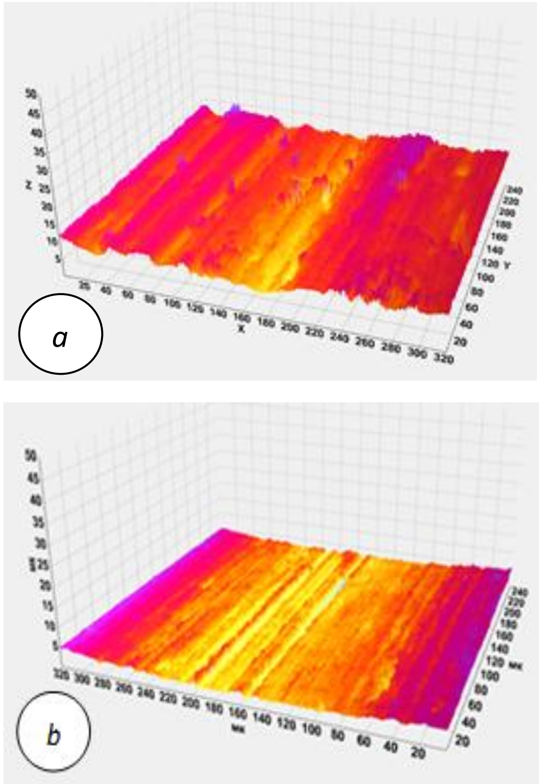

Figure 10. 3D profilograms of friction surface of AA2024-T3 alloy in: *a* – 0,1 % NaCl; *b* – 2.5 g/l MLD + 0.06 g/l ZG.

Combining it with zinc gluconate provides a high anti-corrosion effect for the aluminum alloy under tribo-corrosion conditions. This is confirmed by a decrease in the double electric layer capacitance, an increase in charge transfer resistance, and a reduction in the friction coefficient, indicating effective blocking of active corrosion sites on the aluminum alloy surface. It is likely that the combination of MLD with ZG contributes to the densification of the protective film due to Zn^{2+} cations, which further enhances its protective properties. In [11], the positive effect of zinc gluconate is explained by an increase in the blocked metal surface area due to the adsorption of gluconate molecules at active corrosion sites.

4. CONCLUSION

The effect of an inhibitory composition based on the biopolymer maltodextrin and zinc gluconate on the tribo-corrosion of the AA2024-T3 aluminum alloy in a chloride-containing corrosion environment was studied. It was found that its inhibition efficiency is 90%. The application of the maltodextrin + zinc gluconate inhibitor composition helps reduce the friction coefficient of the aluminum alloy/corundum pair by approximately half and narrows the wear track, indicating an effective reduction in tribo-corrosive impact. Under the influence of the synergistic composition 2.5 g/L MLD + 0.06 g/L ZG, corrosion processes in the wear zone slow down, as confirmed by the kinetics of the polarization current, which decreases sixfold. Additionally, a reduction in roughness parameters Ra and Rz by 32% and 48%, respectively, was recorded after frictional interaction in the inhibited environment. This confirms the effectiveness of the applied inhibitor composition in reducing surface damage and improving the tribo-corrosion characteristics of the alloy.

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