Proceedings of BALTTRIB'2024 edited by prof. J. Padgurskas
eISSN 2424-5089 (Online)

DOI: 10.15544/balttrib.2024.14

EFFECT OF INHIBITORY COMPOSITION BASED ON DEXTRIN AND ZINC GLUCONATE ON TRIBOCORROSION OF ALUMINIUM ALLOY

S. Korniy*, M. Tymus*[1], I. Zin*, **, N. Rats'ka*, B. Datsko*
* Karpenko Physico-Mechanical Institute of National Academy of Sciences of Ukraine, Lviv, Ukraine
** Lviv Polytechnic National University, Lviv, Ukraine

Abstract: The effect of an environmentally safe inhibitory composition based on dextrin and zinc gluconate on corrosion and tribocorrosion of an aluminium alloy in a chloride-containing solution was studied. Charge transfer resistance of the aluminium alloy in the solution inhibited by the composition with optimal component ratio increases significantly and electric double layer capacitance decreases compared to uninhibited 0.1% NaCl, which indicates a significant improvement of metal corrosion resistance. The frequency dependence of phase angle indicates the formation of an organic protective film on the surface of the aluminium alloy in the chloride solution inhibited by the composition. A decrease in the coefficient of friction of the aluminium alloy/corundum pair in an inhibited chloride-containing solution was established. The inhibitor composition significantly reduces the polarization current of the aluminium alloy under conditions of tribocorrosion. Optical 3D profilometry revealed more uniform and less surface wear of the aluminium alloy in the inhibited solution.

Keywords: tribocorrosion, aluminium alloy, surface wear, corrosion inhibitors.

1. INTRODUCTION

Aluminium alloys are widely used in different industries due to their low specific gravity and high strength. However, they are predisposed to localised corrosion due to the presence in their structure of intermetallic phases [1]. In some applications, aluminium is subject to simultaneous corrosion and mechanical wear [2]. The oxide film on the surface of aluminium alloy under such conditions is more rapidly destroyed due to the influence of mechanical abrasion and consequently, the metal corrosion is significantly accelerated. The synergy between these two processes, described in the paper [3], is known as tribocorrosion, and can cause significant economic losses due to early failure of process equipment and structures.

Corrosion inhibitors are widely used to protect aluminium alloys from aggressive environments. Biopolymers, particularly polysaccharides, show promise as corrosion inhibitors for aluminium alloys [4, 5]. They are environmentally friendly, cost-effective, modifiable, and possess good adsorption and inhibitory properties. These qualities make them a safer alternative to toxic synthetic corrosion inhibitors. Dextrin, a polysaccharide, is a low-molecular-weight carbohydrate produced by starch hydrolysis, containing D-glucose units linked by α-(1→4) or α-(1→6) glycosidic bonds. It primarily inhibits metal corrosion in acidic environments but is ineffective against aluminium alloy corrosion in neutral, chloride-containing solutions [6, 7]. However, the anti-corrosion effectiveness of polysaccharides can increase significantly when combined with carboxylic acid salts [8, 9]. Currently, there is no data on the protective properties of similar inhibitor compositions under the tribocorrosion conditions of aluminium alloys.

Gluconic acid and zinc gluconate are known corrosion inhibitors for aluminium alloys [10, 11]. Zinc gluconate has low toxicity to humans, animals, and plants, making it preferable for applications with

---

[1] Author for contacts: PhD. Marjana Tymus
E–mail: marjana.tymus@gmail.com

environmental exposure. However, achieving high corrosion inhibition efficiency for aluminium alloys requires large concentrations of zinc gluconate, which is economically inefficient. The synergistic protective effect of a plant extract containing anti-corrosion organic compounds combined with zinc salts on aluminium alloy corrosion in a 0.05 M NaCl solution has been documented [12]. The presented study investigates the possibility of enhancing the anti-corrosion protection of AA2024 aluminium alloy with dextrin in a chloride-containing solution by adding small amounts of zinc gluconate under both normal corrosion and tribocorrosion conditions.

2. METHODS AND MATERIALS

The corrosion inhibition effectiveness of the AA2024 alloy was evaluated using electrochemical impedance spectroscopy at an open circuit potential within a frequency range of 10,000 to 0.01 Hz on a Gill AC potentiostat in a 0.1% NaCl solution with added dextrin, zinc gluconate, and their mixtures at varying concentrations. The amplitude of the applied signal was 10 mV. Impedance data for the aluminium alloy, obtained after 24 hours of exposure in both the control solution and the dextrin + zinc gluconate (Dx+ZnGl) inhibited solutions, were modelled using the EIS Spectrum Analyzer software with an electrical equivalent circuit (Fig. 1).

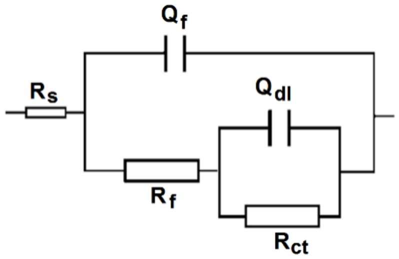


Fig. 1. Electric equivalent circuit simulating the corrosion of an aluminium alloy in a 0,1% NaCl solution, where R_s, R_f, R_{ct} – resistance of corrosion solution, resistance of electrolyte in pores of protective film, and metal charge transfer resistance, respectively; Q_f, Q_{dl} are surface film capacitance and electric double layer capacitance of the metal expressed through the constant phase element.

The inhibitory efficiency (IE%) of the Dx+ZnGl composition was evaluated using the polarization resistance R_p (sum of R_{ct} and R_f):

$$IE = ((R_p - R_{p0}/ R_p) \cdot 100\%$$

where Rp and Rp0 are the polarization resistance with and without an inhibitor, respectively.

Tribocorrosion tests of aluminium alloy AA 2024-T3 were performed on flat samples using a special self-made linear reciprocating tribometer (Fig. 2) in 0.1% NaCl solution without and with the addition of the composition Dx (1.5 g/l) + ZnGl (0.06 g/l). 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.

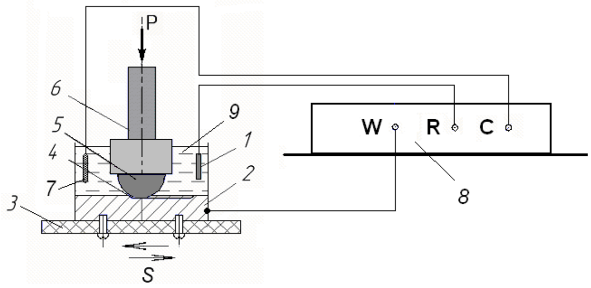


Fig.2. Scheme of corrosive wear test of aluminium alloy: 1) saturated Ag/AgCl reference electrode; 2) flat test sample; 3) reciprocating stage; 4) contact zone; 5) corundum ball, Ø=9 mm; 6) indenter support with strain sensors; 7) platinum electrode; 8) MTech SPG-500fast potentiostat-galvanostat; 9)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

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. Corrosion potential and polarization current at free corrosion potential of aluminium alloy in corrosion solutions 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".

3. RESULTS AND DISCUSSION

Previous studies [13] established that dextrin alone is ineffective as an inhibitor of aluminium alloy corrosion in a neutral chloride-containing environment. However, the addition of a 0.1% NaCl solution with dextrin and a critically small amount (0.06 g/l) of zinc gluconate significantly increased the corrosion resistance of the AA2024 alloy, as evidenced by electrochemical impedance spectroscopy data (Fig. 3). This effect is likely due to the synergistic enhancement of dextrin's protective properties by zinc gluconate. The highest metal impedance modulus at a frequency of 0.1 Hz ($Z_{0.1}$), measuring $3.24\cdot10^5$ Ω·cm², was observed in the corrosion solution inhibited by a mixture of 1.5 g/l dextrin and 0.06 g/l zinc gluconate. This value is approximately an order of magnitude higher than that obtained using only 1.56 g/l of zinc gluconate. Compositions with dextrin concentrations of 1 g/l and 2 g/l combined with 0.06 g/l zinc gluconate, as well as zinc gluconate alone, exhibited significantly lower inhibitory efficiency, as seen from the impedance data (Fig. 3a). Their $Z_{0.1}$ values range from $3.24\cdot10^4$ to $5.65\cdot10^4$ Ω·cm².

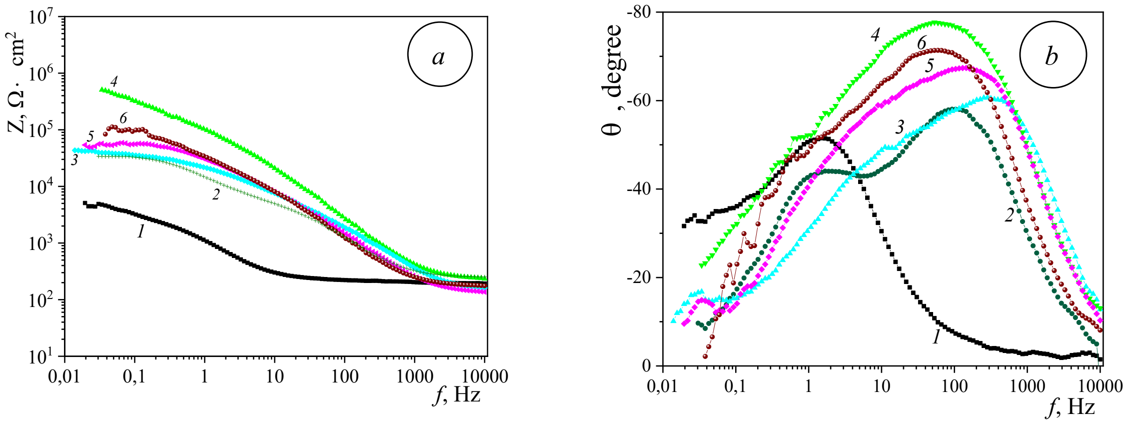


Fig. 3. Frequency dependences of impedance modulus (a) and phase angle (b) after 24 h of exposure in: 1) 0.1% NaCl; 2) 0.1% NaCl + 0.06 g/l ZnGl; 3) 0.1% NaCl + 1 g/l Dx + 0.06 g/l ZnGl; 4) 0.1% NaCl + 1.5 g/l Dx + 0.06 g/l ZnGl; 5) 0.1% NaCl + 2 g/l Dx + 0.06 g/l ZnGl; 6) 0.1% NaCl + 1.56 g/l ZnGl.

The maxima of the phase angle θ (Fig. 3b) of the AA2024 aluminium alloy after 24 hours of exposure in a 0.1% NaCl solution inhibited by Dx+ZnGl compositions and zinc gluconate shift to higher frequencies, approximately within the range of 10–200 Hz. This shift indicates the formation of adsorption protective films on the aluminium alloy surface. In the solution inhibited by the composition of 1.5 g/l Dx + 0.06 g/l ZnGl, the phase angle θ reaches its highest value of 80°, compared to 70° with ZnGl alone and 50° in the non-inhibited 0.1% NaCl solution. As Dx can acidify the environment, increasing its concentration to 2 g/l reduces the protective effectiveness of the inhibitory composition. Accordingly, the inhibition efficiency (IE) is highest at 99% for the 1.5 g/l Dx + 0.06 g/l ZnGl composition, compared to 94% for 1.56 g/l ZnGl alone (Table 1). For other compositions of Dx with ZnGl at 0.06 g/l, the IE ranges from 87% to 90%.

Table 1. Characteristics of an equivalent electric circuit (Fig. 1) calculated based on impedance spectra of an aluminium alloy in control and inhibited 0.1 % NaCl solutions

Curve number	R_{ct}, $\Omega \cdot cm^2$	$Q_{dl}(Y_0)$, $s^n/\ \Omega \cdot cm^2$	$Q_{dl}(n)$	R_f, $\Omega \cdot cm^2$	$Q_f(Y_0)$, $s^n/\ \Omega \cdot cm^2$	$Q_f(n)$	*IE*, %
24 h of exposure							
1	5500	$9.61 \cdot 10^{-4}$	0.63	197	$2.81 \cdot 10^{-4}$	0.72	–
2	34395	$1.02 \cdot 10^{-5}$	0.64	185	$3.45 \cdot 10^{-6}$	0.79	84
3	42135	$1.05 \cdot 10^{-5}$	0.57	233	$9.48 \cdot 10^{-6}$	0.92	87
4	523615	$3.55 \cdot 10^{-6}$	0.55	270	$1.93 \cdot 10^{-6}$	0.81	99
5	56116	$6.06 \cdot 10^{-6}$	0.62	198	$1.91 \cdot 10^{-6}$	0.90	90
6	96950	$7.21 \cdot 10^{-6}$	0.54	210	$1.09 \cdot 10^{-6}$	0.98	94

*1) control 0.1 % NaCl solution; 0.1 % NaCl with addition of: 2) 0.06 g/l ZnGl; 3) 1 g/l Dx + 0.06 g/l ZnGl; 4) 1.5 g/l Dx + 0.06 g/l ZnGl; 5) 2 g/l Dx + 0.06 g/l ZnGl; 6) 1.56 g/l ZnGl.

In the presence of the composition 1.5 g/l Dx + 0.06 g/l ZnGl (Table 1), the charge transfer resistance (Rct) of AA2024 alloy was $5.24 \cdot 10^5\ \Omega \cdot cm^2$. In comparison, in a 0.1% NaCl solution and the same solution inhibited by 1.56 g/l ZnGl alone, the Rct values were $5.50 \cdot 10^3\ \Omega \cdot cm^2$ and $9.70 \cdot 10^4\ \Omega \cdot cm^2$, respectively. In solutions with other inhibitor compositions, the R_{ct} values ranged from $3.44 \cdot 10^4$ to $9.70 \cdot 10^4\ \Omega \cdot cm^2$. The conductivity of the constant phase element Q_{dl} of AA2024 alloy in a chloride solution inhibited by 1.5 g/l Dx + 0.06 g/l ZnGl was $3.55 \cdot 10^{-6}$ sn/$\Omega \cdot cm^2$, which is approximately 37 times lower than the Y_0 of the metal sample in an uninhibited environment (Table 1). This decrease in Y_0 for the constant phase element Qdl of the alloy in the inhibited solution with Dx + ZnGl likely indicates the formation of a protective organic film on the alloy surface. Conversely, in the uninhibited 0.1% NaCl solution, the conductivity Y_0 of the constant phase element Qdl of the aluminium alloy increased due to the onset of local corrosion.

The increase and shift of the maximum frequency dependence of the phase angle of the aluminium alloy towards higher current frequencies in the corrosion solution inhibited by the Dx+ZnGl composition can be explained by the formation of a stable adsorption film on the metal surface. This film creates a physical barrier to the movement of ions or molecules to and from the metal surface, thereby inhibiting corrosion reactions. Thomas [14] noted that a similar effect occurs when the inhibitor molecule has a long hydrocarbon chain, which is characteristic of dextrin. In [15], the formation of a protective film is attributed to the ability of hydroxyl groups in the dextrin molecule to form coordination bonds with the metal surface. However, the adsorption film formed by the biopolymer on the metal surface may differ from that of low molecular weight compounds. Literature sources [16, 17] indicate that a polymer molecule adsorbed on a solid surface forms folds or loops that extend into the polymer solution. As a result, the adsorption film becomes thicker but also porous and loose. This is likely why dextrin alone does not sufficiently protect the aluminium alloy from corrosion in a neutral chloride solution.

As shown by electrochemical impedance spectroscopy data (Fig. 3), the combined use of dextrin and zinc gluconate in a chloride-containing corrosion environment promotes the formation of a more stable organic film on the aluminium alloy. Presumably, gluconate anions further compact the polysaccharide film by forming poorly soluble complex compounds with Al^{3+} ions, which are present in the solution as a result of electrochemical corrosion reactions of the aluminium alloy. The possibility of forming such complexes has been confirmed by other researchers [10, 11]. Zn^{2+} cations are also recognized as effective inhibitors, as they form a layer of sparingly soluble $Zn(OH)_2$ hydroxides on the cathodic areas of the corroding metal [12].

Since the 1.5 g/L Dx + 0.06 g/L ZnGl composition proved to be the most effective during electrochemical corrosion testing, its protective properties were further investigated under tribocorrosion conditions on the aluminium alloy. Tribocorrosion studies of the AA2024 alloy in a 0.1% NaCl solution without and with the addition of an inhibitory composition based on dextrin and zinc gluconate showed that the characteristic changes of the friction coefficient were similar (Fig. 4*a*). On the dependences of the coefficient of friction on time, there are areas of running-in when initially its values increase, and then became stabilized after about 200 s. Next, the friction coefficient changes with a slight spread of ± 0.05. It was established that in the inhibited solution the average values of the friction coefficient are ~1.3 times lower than in the uninhibited 0.1% NaCl solution.

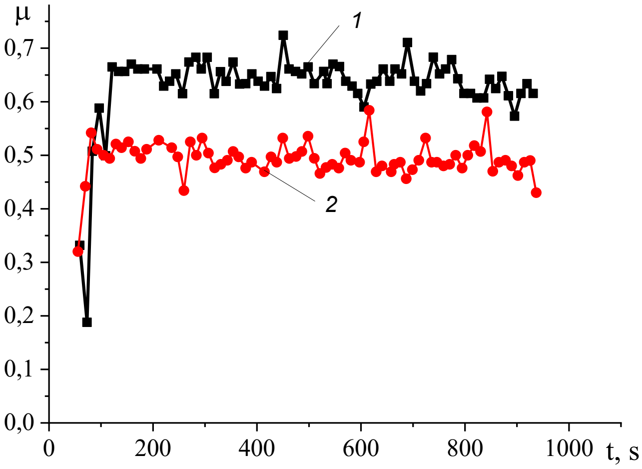


Fig. 4. Dependence of the friction coefficient on the sliding time of the aluminum alloy/corundum pair in 0.1% NaCl: 1) uninhibited; 2) with the addition of 1.5 g/l Dx + 0.06 g/l ZnGl.

At the beginning of the tribocorrosion test, a drop in the electrode potential of the aluminium alloy samples was observed, reaching –0.85 V in the uninhibited and –0.70 V in the inhibited sodium chloride solutions (Fig. 5a). During the next 200–900 s of tribocorrosion, the electrode potentials of the samples shifted slightly further in the negative direction, likely due to the gradual degradation of the protective film on the aluminium alloy in the track area by the corundum ball. Notably, with the addition of the inhibitor composition to the corrosion solution, the electrode potential of the alloy during tribocorrosion remained more positive than in the control environment. After the tribocorrosion load was removed, the electrode potentials of the aluminium alloy samples in both environments quickly returned to their initial values characteristic of free corrosion conditions, due to the restoration of the oxide surface film.

The polarization current of the aluminium alloy in the uninhibited 0.1% NaCl solution increased to 0.015 mA in the first 100 s after the tribocorrosion loading (Fig. 5b). Addition of the Dx + ZnGl inhibitor composition to the corrosion solution reduced this initial current spike to 0.01 mA.

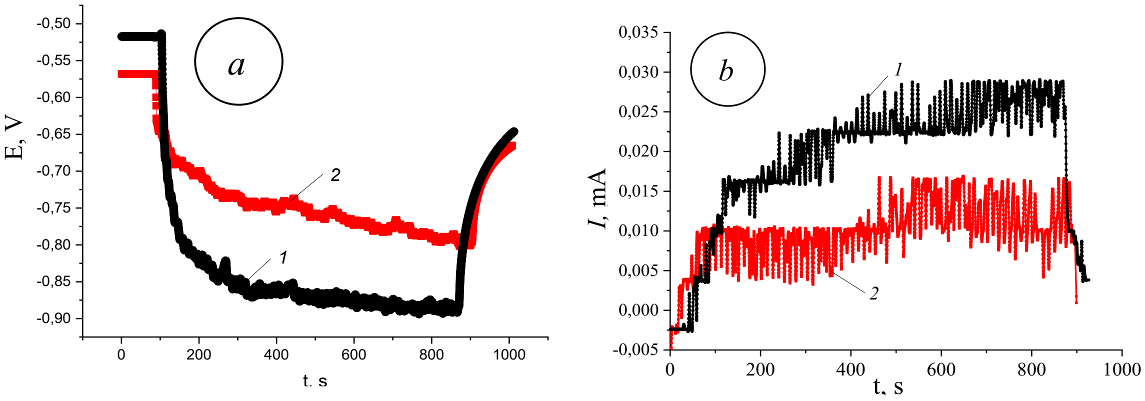
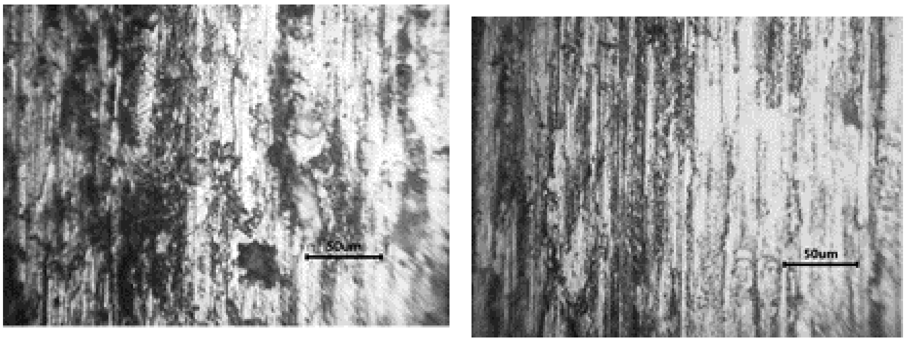


Fig. 5. Change in electrode potential (*a*) and polarization current (*b*) during friction of AA2024 alloy in 0.1 % NaCl: 1) uninhibited; 2) with addition of 1.5 g/l Dx + 0.06 g/l ZnGl.

A decrease in the values of the polarization current of the alloy in the inhibited solution indicates a slowing down of the dissolution of the alloy due to the compaction of the oxide film of the aluminium alloy by the inhibitor on the surface of the fracture track. The kinetics of the polarization current indicates that corrosion processes in the aluminium alloy's wear track slow down due to the protective effect of the inhibitory composition.

The analysis of the topography of the surfaces of the friction tracks of the samples and their optical 3D profilograms proved that in the environment inhibited by the "dextrin+gluconate" composition, the AA2024 alloy wears more evenly, and the friction surface is less rough (Fig. 6, 7).



a) *b*)

Fig. 6. Topography of friction surface of AA2024 alloy in 0.1 % NaCl (*a*) and in the solution, inhibited by composition "1.5 g/l Dx+0.06 g/l ZnGl" (*b*).

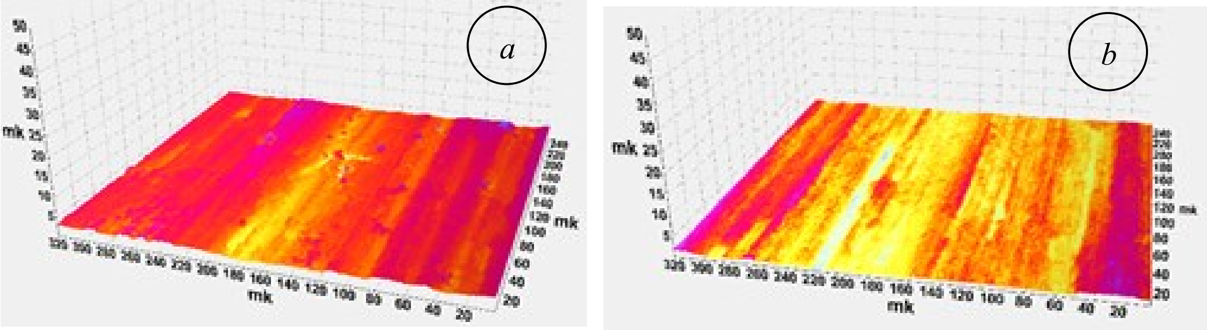


Fig. 7. 3D profilograms of friction surface of AA2024 alloy in 0.1 % NaCl (*a*) and in the solution, inhibited by composition "1.5 g/l Dx+0.06 g/l ZnGl" (*b*).

The quantitative characteristics of the roughness of the friction surface of the AA2024 alloy were evaluated and the average values of the height parameters of the roughness of the friction surface profile in its five sections were determined. It was established that after friction of the alloy in a 0.1% NaCl solution, the average profile deviation Ra is 0.972 µm, and the height of irregularities Rz is 4.145 µm. At the same time, after frictional interaction in an inhibited medium, the Ra and Rz parameters decreased by 20 and 10%, respectively. The profilometry data of the friction surface of the AA2024 alloy confirm the effectiveness of using the "dextrin+gluconate" inhibitor composition to improve the tribocorrosion characteristics of the AA2024 alloy in a 0.1% NaCl solution and correlate with the results of measuring the friction coefficient and polarization current during friction in the medium.

4. CONCLUSIONS

The effect of an inhibitory composition based on dextrin and zinc gluconate on the corrosion and tribocorrosion of an aluminum alloy in a chloride-containing solution was investigated. With the optimal component ratio in this composition, the charge transfer resistance (R_{ct}) of the aluminum alloy in the inhibited solution increased by 95 times, and the conductivity (Y_0) of the constant phase element (Q_{dl}) decreased by 270 times compared to the control 0.1% NaCl solution, indicating a significant increase in the metal's corrosion resistance. The frequency dependence of the phase angle suggests the formation of an organic protective film on the surface of the aluminum alloy in the chloride solution inhibited by the composition.

A decrease in the coefficient of friction of the aluminum alloy/corundum pair in the corrosive environment was observed under the influence of the inhibitory composition, reducing it by approximately 1.3 times. The kinetics of the polarization current indicate a slowdown of corrosion processes in the wear track of the aluminum alloy due to the protective effect of the inhibitor composition. 3D profilometry revealed more uniform and reduced wear on the aluminum alloy surface in the inhibited solution.

REFERENCES

[1] D. de la Fuente. Corrosion of aluminum, aluminum alloys, and composites. Editor(s): Francisca G. Caballero. Encyclopedia of Materials: Metals and Alloys, Elsevier 2022:160-169.

[2] A.C. Vieira, L.A. Rocha, N. Papageorgiou, S. Mischler. Mechanical and electrochemical deterioration mechanisms in the tribocorrosion of Al alloys in NaCl and in NaNO3 solutions. Corrosion Science 2012; 54: 26-35.

[3] S.W. Watson, F.J. Friedersdorf, B.W. Madsen, S.D. Cramer. Methods of measuring wear-corrosion synergism. Wear 1995;181–183:2:476-484.

[4] S.A. Umoren, U.M. Eduok. Application of carbohydrate polymers as corrosion inhibitors for metal substrates in different media - review. Carbohydrate Polymers 2016;140:314-341.

[5] S.A. Korniy, I.M. Zin, M.-O.M. Danyliak, Yu.Ya. Rizun. Eco-friendly metal corrosion inhibitors based on natural polymers - review). Material Science 2023;58 (5):567 – 578.

[6] S. A. Umoren, M. M. Solomon, V. S. Saji. Chapter 13 - Other natural polymers: gelatin, dextrin, and dextran. Editor(s): Saviour A. Umoren, M. M. Solomon, Viswanathan S. Saji. Polymeric Materials in Corrosion Inhibition, Elsevier 2022:303-322.

[7] B.P. Charitha, R. Padmalatha. Carbohydrate biopolymer for corrosion control of 6061 Al-alloy and 6061Aluminum-15%(v) SiC(P) composite – Green approach. Carbohydrate Polymers 2017;168:337-345.

[8] M.B.Tymus, I.M. Zin, O.P.Khlopyk, V.I. Pokhmurskii, M.Y.Holovchuk, S.A. Korniy. Corrosion inhibition of aluminum alloy by a composition of guar gum and tartrate. Materials Science 2022;57:679 – 687.

[9] S.A. Korniy, I.M. Zin, M.B.Tymus, O.P.Khlopyk, M.Y.Holovchuk. Steel corrosion inhibition by microbial polysaccharide and tartrate mixture. Journal of Bio- and Tribo-Corrosion 2022;8 (1):6.

[10] M.A. Amin, M.S. Refat. Study of complex formation in Al(III) – Gluconic acid system and the influence of UV light on the dissolution and passive behavior of Al. Arabian Journal of Chemistry 2013;6:2: 165–172.

[11] O.Sanni, C.A. Loto, A.P.I. Popoola. Inhibitive behaviour of zinc gluconate on aluminium alloy in 3.5 % NaCl. Solution. Silicon. 2016;8:195–200.

[12] J. Wang, J. Zhao, M. Tabish, L. Peng, Q. Cheng, F. Shi. Long-term corrosion inhibition for AA5052 aluminum alloy by an eco-friendly hybrid inhibitor: Synergism inhibition between rosemary extract and zinc chloride in 0.05 M NaCl solution. Journal of Industrial and Engineering Chemistry 2023;120:302-315.

[13] M.B. Tymus, I.M. Zin, S.A. Korniy. Inhibition of aluminum alloy corrosion in a neutral chloride-containing environment by a composition based on dextrin and sodium isoascorbate. Physico-Chemical Mechanics of Materials 2024;60:4:129-137.

[14] J.G.N. Thomas. 17.3 - The Mechanism of corrosion prevention by inhibitors, Editor(s): L.L. Shreir, R.A. Jarman, G.T. Burstein, Corrosion (Third Edition). Butterworth-Heinemann 1994:17:40-17:65.

[15] M. Liu, D. Xia, A. Singh, Y. Lin. Analysis of the anti-corrosion performance of dextrin and its graft copolymer on J55 steel in acid solution. Processes 2021;9:1642:2-16.

[16] Yu.S. Lipatov, L.M. Sergeeva. Adsorption of polymers. K.: Naukova dumka 1972:196.

[17] J. Gregory, S. Barany. Adsorption and flocculation by polymers and polymer mixtures. Advances in Colloid and Interface Science 2011; 169:1:1-12.