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# Adsorption of Anions of Higher Carboxylic Acids on Magnesium from Weakly Alkaline Aqueous Solutions

V. A. Ogorodnikova<sup>a</sup>, Yu. I. Kuznetsov<sup>a,\*</sup>, N. P. Andreeva<sup>a</sup>, A. Yu. Luchkin<sup>a</sup>, and A. A. Chirkunov<sup>a</sup>

<sup>a</sup>Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, 119071 Russia \*e-mail: kuznetsov@ipc.rssi.ru

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Abstract—The adsorption of sodium salts of higher carboxylates on oxidized magnesium is studied via in situ reflective ellipsometry. It is shown that the free energies of adsorption of sodium oleyl sarcosinate (OsS) and sodium linoleate (LiS) is >55 kJ/mol, indicating the chemisorption of carboxylates on oxidized magnesium surfaces. Electrochemical impedance spectra, voltammetry, and corrosion testing show that sodium oleate (OlS) has the best protective properties on pure and oxidized magnesium. The strong protective properties of OlS are confirmed by Mg plate testing under conditions of a wet atmosphere with daily condensation. Tentative passivation of chemically oxidized Mg in a 16 mmol/L OlS solution protects against corrosion for 92–96 h.

*Keywords:* adsorption, ellipsometry, corrosion, magnesium, corrosion inhibitors, electrochemical impedance spectroscopy, carboxylates

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## **INTRODUCTION**

Magnesium and its alloys are in high demand in industry, since they have unique combinations of physical and mechanical properties. Magnesium is the lightest metal, with a density of ~1.7 g/cm<sup>3</sup>. This is lower than that of Al (~2.7 g/cm<sup>3</sup>), Ti (~4.5 g/cm<sup>3</sup>), and Fe (~7.9 g/cm<sup>3</sup>) [1]. Magnesium is eighth among the elements of the Earth's crust, so its alloys are widely available. Their useful properties are high strength, rigidity, good damping capability, machinability, excellent casting characteristics, and low heat capacity. However, weak corrosion resistance hinders the broad use of Mg alloys in practice, so anticorrosion treatment of their surfaces is needed [2].

One of the most effective ways of protecting Mg alloys against corrosion is to create barrier coatings on their surfaces to mask the basic material from the environment. This is achieved by depositing either a conversion coating (CC), including those obtained via anodization and microarc oxidation (plasma electrolytic oxidation) (MAO, PEO), or by applying paint or lacquer. According to [3, 4], now there is a number of ways of producing chromate-free CCs for Mg alloys that have their own merits and demerits. An interesting strategy for developing new and more ecological CCs for Mg alloys is treating alloys with natural organic acids that form insoluble salts with magnesium. The authors of [4] considered vanillic acid (4hydroxy-3-methoxybenzoic acid  $C_8H_8O_4$ ) on alloy AZ31 as substitutes for toxic chromatizing. Such CCs formed on Mg surfaces have a number of advantages: environmental friendliness, inhibition of anodic metal dissolution, reduced corrosion current, and the ability to improve the adhesion and protective properties of polymer coatings.

The use of corrosion inhibitors (CIs) is a promising way of improving the corrosion resistance of Mg. For example, it is known [2] that sodium decanoate in a solution with neutral pH slows the rate of corrosion and ensures the passivation of Mg.

Surfactants predominate among organic CIs. The authors of [5] thus investigated the effect 151 organic compounds had on the corrosion behavior of nine Mg alloys. In this work, a number of new CIs were found that provided effective protection comparable to and even higher than that of chromate.

Controlling the corrosion of Mg alloys is worthy of special attention. It is achieved by dissolving their electropositive metal impurities, which settle on a surface to become cathodes. The ability of CIs to bind such cations (i.e. iron ions) in complexes is thus of interest [5, 6]. Sodium salts of derivatives of pyridinedicarboxylic and salicylic acids are the ones most effective and universal.

There is interest in passivating Mg alloys with aqueous solutions of organic CIs to form oxide films in air [7–9] or CCs obtained via PEO [10, 11]. Sodium salts of higher carboxylic acids, i.e. oleic (OIA), stearic (SA), tridecanoic (TDA), are used as CIs. Sodium oleate (OIS), sodium oleyl sarcosinate (OsS), and IFKhAN-25 are of special interest [7–9].

Not only is using alkyl carboxylates as CIs an effective way of reducing metal corrosion; it is relatively environmentally friendly. The aim of this work was to study the adsorption of higher aliphatic carboxylates on Mg to form passivating layers that are stable in an aggressive wet atmosphere.

#### EXPERIMENTAL

Our investigations were performed using technical magnesium Mg90 of the following composition: Mg, 99.9%; Fe, up to 0.04%; Mn, up to 0.03%; Al, up to 0.02%; Ni, up to 0.001%; Cu, up to 0.004%; Si, up to 0.009%; and Cl, up to 0.005%.

Sodium salts of carboxylic acids were used as CIs: oleate (OIS,  $(CH_3(CH_2)_7CH=CH(CH_2)_7COONa)$ , linoleate (LiS,  $CH_3(CH_2CH=CH)_3(CH_2)_7COONa)$ , stearate (SS,  $CH_3-(CH_2)_{16}COONa)$ , lauryl sarcosinate (LsS,  $C_{15}H_{28}NNaO_3)$ , and oleyl sarcosinate (OsS,  $CH_3(CH_2)_7CH=CH(CH_2)_7CON(CH_3)CH_2COONa)$ . Solutions of OsS, LiS, and SS were prepared by neutralizing the corresponding acids with equimolar amounts of NaOH. Solutions of OIS and LsS were prepared from commercially available reagents. All reagents were of pure grade.

Protective CI films were obtained by holding an electrode in aqueous solutions of CIs (OsS, OlS, LiS, and LsS) with concentration  $C_{in} = 16 \text{ mmol/L}$  at room temperature (t). The SS CI film was deposited from a water–alcohol solution at  $t = 55^{\circ}$ C.

Electrochemical investigations were performed using cylindrical electrodes machined from technical Mg, embedded in epoxy resin. The working surface area of the electrodes was  $0.75 \text{ cm}^2$ . Polarization curves for Mg90 were measured in a glass cell with separated electrode spaces using IPC-Pro MF potentiostat (Russia). Potential (*E*) of Mg90 electrode was measured vs. a silver chloride reference electrode, and recalculated to the standard hydrogen scale. The auxiliary electrode was Pt.

The electrode for electrochemical investigations was polished with abrasive papers with different grain sizes and degreased with acetone. Two series of experiments were performed. In the first, we obtained the anodic and cathodic polarization curves of Mg90 in borate buffer solutions with pH 9.2 that contained 1 mmol/L of NaCl with and without 8 or 16 mmol/L of added CI. The electrode was immersed in a borate buffer containing one inhibiting additive and held in it for 15 min to determine the free corrosion potential  $E_{\rm cor}$ . Finally, polarization with a scanning rate of 0.2 mV/s was switched on.

In the second, polarization curves were measured for the specimens with preliminarily formed adsorption CI films. The films were produced in two ways.

1. A polished and degreased electrode was held for 10 min in an CI solution and dried in air for 60 min.

2. An electrode was oxidized for 1.5 h in a 5.0 M NaOH solution, washed with distilled water, and dried in air for 60 min. The dried oxidized electrode was then held in an CI solution for 10 min and dried again in air.

After such preparation, each sample was immersed in a background solution and anodic polarization was immediately switched on with a scanning rate of 0.2 mV/s.

Potential  $E_{cd}$  of local depassivation was found from the polarization curves. The protective properties of the passive films were found using the difference  $\Delta E = E_{cd}^{in} - E_{cd}^{bg}$ , where  $E_{cd}^{bg}$  and  $E_{cd}^{in}$  are values  $E_{cd}$ , measured for the electrodes with and without CI treatment.

The adsorption of OsS and LiS on technical Mg was investigated in situ via reflective ellipsometry in a borate solution with pH 11.2 and 0.05 M of  $Na_2B_4O_7$ .  $10H_2O + 0.1$  M NaOH. Ellipsometric angles  $\Delta$  and  $\Psi$ were measured on a portable ellipsometer (Rudolph Research Co.) in a cell used for simultaneous electrochemical and ellipsometric investigations. The source of radiation was a helium-neon laser with wavelength  $\lambda = 640$  nm, the angle of incidence on the sample was 68.5°. To ensure a stable surface (the constancy of ellipsometric angles  $\Delta$  and  $\Psi$ ), magnesium electrode was subjected to special preliminary passivation. The stripped, polished, and degreased electrode was chemically oxidized in 5.0 M of NaOH solution for 1.5 h. The electrode was transferred to the working solution (a borate solution with pH 11.2), where it was held for another 17 h. The electrode's surface retained a high gloss after such treatment. After 17 h, a potentiostat was used to maintain the electrode potential 20 mV more negative than  $E_{\rm cor}$ . After angles  $\Delta$  and  $\Psi$ became stable, the concentrated inhibitor solution was added to the cell. For every concentration of CI  $(C_{in})$ , angle  $\Delta$  was measured over time until it became constant. For every change in  $C_{\rm in}$ , the angle was

$$\delta \Delta = \Delta - \Delta_0, \tag{1}$$

where  $\Delta$  is the current angle obtained after the inhibitor additive was introduced into the solution, with  $\Delta_0$ is the initial value. We obtained the experimental dependence of  $\delta\Delta$  on  $C_{in}$ ; i.e., isotherm  $\delta\Delta - f(C_{in})$ , which was reconstructed into isotherm of adsorption  $\Theta - f(\ln C)$ . This isotherm is described by the Temkin complete equation proposed in [12]:

$$\Theta = \frac{1}{f} \ln \frac{1 + n^{-1} B_{\max}(C - C_0)}{1 + n^{-1} B_{\min}(C - C_0)}.$$
 (2)

Here, *f* is the factor of energy surface inhomogeneity;  $B_{\text{max}}$  and  $B_{\text{min}}$  are constants of the adsorption equilibrium corresponding to the highest and the lowest energies of adsorption. In this equation, concentration *C* is an independent variable,  $C_0$  is the minimal concentration obtained via extrapolation  $\Theta \rightarrow 0$ , and *n* is



**Fig. 1.** Dependence of the change in (a) ellipsometric angle  $(-\delta\Delta)$  and (b) degree of filling ( $\theta$ ) on  $\ln C_{in}$  for (1) OsS and (2) LiS.

the normalization factor equal to the number of water moles in 1 L. The procedure for calculating f,  $B_{max}$ , and  $B_{min}$  from the results of ellipsometric measurements was given in [12]. Using  $B_i$ , we calculated the corresponding values of the standard free energy of adsorption using the relation

$$B_i = \exp(-\Delta G_{a,i}^0 / (RT)), \qquad (3)$$

where index  $i = \max$  or min.

The calculations for passivating films were performed according to the program at Internet resource http://www.ccn.yamanashi.ac.jp/~kondoh/ellips e.html.

Corrosion testing was done with periodic condensation of moisture on both unoxidized and chemically oxidized rectangular samples  $20 \times 30 \times 5$  mm in size. The plates for corrosion testing were prepared as in electrochemical investigations. Prepared samples were hung in glass cells filled with 40–50 mL of distilled water at  $t = 40-50^{\circ}$ C. The cells with samples were placed in a drying oven for 8 h at  $t = 40 \pm 2^{\circ}$ C. Heating was then switched off, ensuring the condensation of moisture on a sample's surface (State Standard 9.308-85).

The samples were examined hourly to fix the time of the first signs of corrosion. An IPC PRO-MF potentiostat and a FRA frequency response analyzer (Russia) were used for electrochemical impedance spectroscopy (EIS). A three-electrode cell with undivided electrode space was used in each experiment. The reference electrode was a two-key silver chloride electrode, the auxiliary electrode was Pt, and the electrolyte was a borate buffer solution with pH 9.2 and 1 mM of sodium chloride. Electrodes for electrochemical impedance spectroscopy were prepared as for the electrochemical and corrosion investigations. We placed each treated sample in an electrolytic cell, held it for 15 min to stabilize  $E_{cor}$ , fixed the potential, and obtained spectra in the 0.01–100000 Hz range of frequencies at a 0.01 V amplitude of potential oscillation.

In calculating the EIS parameters, an equivalent scheme was used to describe the impedance spectra of magnesium alloys [13]:



where  $R_s$  is the resistance of the bulk electrolyte solution between the auxiliary and operating electrodes;  $R_s$  does not affect electrode processes, and its value depends on the conductivity of the test medium and cell geometry;  $R_{sl}$  is the resistance of the film of the surface layers (both oxide and inhibitor); and  $R_{st}$  is the polarization resistance characteristic of the electrochemical kinetics of corrosion.

Instead of pure capacities, elements of constant phase Q were used in the equivalent scheme that were due to the degree of inhomogeneity of surface films and the electrochemical double layer [14].  $Q_{sl}$  is the element of the constant phase characteristic of the capacity of surface films (oxide and inhibitor).  $Q_{dl}$  is a component of the model that expresses the capacity of electrical double layer of film defects.

The results were processed and the data calculated using the Dummy Circuits Solver program (version 2.1). The correspondence between the experimental and calculated data was at least 97%. The degree of magnesium electrode protection was calculated according to the formula

$$Z = ((R_{\rm inh} - R_{\rm hg})/R_{\rm inh}) \times 100\%,$$

where  $R_{bg}$  and  $R_{inh}$  is the total resistance of the Mg90– electrolyte interphase interaction with the participation of  $R_{st}$  and  $R_{sl}$  before and after electrode passivation, respectively. All of the values given in this work are the results from averaging 5–10 independent experiments.

# **RESULTS AND DISCUSSION**

Measuring the adsorption of inhibitor from the background solution ellipsometrically allowed us to estimate the strength of its bond with the metal surface. Unfortunately, because of the high reactivity of



**Fig. 2.** Anodic and cathodic polarization curves for technical magnesium (without chemical oxidation pretreatment) in a borate buffer with pH 9.2 and 1 mM NaCl (I) without CI and after adding 8 mmol/L of CI: (2) OIS, (3) OsS, (4) LiS, and 16 mM of CI ( $2^*$ ) OIS, ( $3^*$ ) OsS, ( $4^*$ ) LiS.

Mg, measuring the adsorption of CIs ellipsometrically was possible only when the electrode's surface was in a stable passive state, which was attained via oxidation according to the procedure described above.

Figure 1a presents the experimental dependences  $(-\delta\Delta)$  on  $\ln C_{\rm in}$  for OsS and LiS in a borate solution with pH 11.2. The adsorption of carboxylates starts within the region of low  $C_{\rm in} = (2.2-5.5) \times 10^{-10} \text{ mol/L}$  and manifests as a change in angle  $\Delta$ . After reaching a certain  $C_{\rm in}$ ,  $\Delta$  becomes constant and a plateau can be distinguished in the curve that is responsible for the formation of a conventional inhibitor monolayer with a surface filling of  $\Theta = 1$ . However, angle  $\Delta$  changes as  $C_{\rm in}$  continues to grow, testifying to further adsorption of the inhibitor. According to the isotherm of OIS adsorption obtained in [15], the conventional monolayer in this case formed at  $C = (0.42-1.58) \times 10^{-6} \text{ mol/L}$ .

We constructed the  $\Theta - f(\ln C)$  isotherms of the adsorption of these inhibitors from the linear dependence of the changes observed experimentally in angle  $\Delta$  on degree  $\Theta$  of the filling of the electrode's surface with CI particles. They are shown in Fig. 1b.

Table 1 presents values  $(-\Delta G_{a,\min}^{\circ})$  and  $(-\Delta G_{a,\max}^{\circ})$ , coefficient *f*,  $B_{\max}$ , and  $B_{\min}$ , obtained using formulas (2), (3).

As is seen from Fig. 1a, OsS is absorbed earlier than LiS, so its free energy of adsorption is greater.

The thicknesses of the CI monolayers were found from the values of angles  $\Delta$  and  $\Psi$ . Because OsS monolayer thickness  $\delta = 1.2-1.5$  nm and molecule length  $l_m = 2.5$  nm, we may assume that each molecule is adsorbed obliquely on the surface at an angle 36.9°. A monolayer with  $\delta = 0.9$  nm forms on Mg90 oxidized LiS with  $l_m = 2.4$  nm, so the angle of its slope is probably 66°.

It was shown in [9, 15] that OIS is a promising CI for Mg alloys in neutral and weakly alkaline media. The curve of polarization in a borate buffer with pH 9.2 and 8 mM of OIS is shown in Fig. 2. Not only does this CI inhibit the cathodic reaction and raise  $E_{cor}$  by 0.15 V, it also provides a wide range of potentials in which Mg90 is in the passive state.

When OsS and LiS (8 mmol/L) were introduced into the borate buffer solution with pH 9.2,  $E_{cor}$  grew by 0.024 and 0.092 V, respectively, but only for the LiS solution can we note an increase in electrode polarizability, testifying to the inhibition of both electrochemical reactions. The protective effect grew when  $C_{in}$  was raised from 8 to 16 mM (Fig. 2), as is seen from the increase in  $E_{cor}$  and the polarizability of Mg90 in OsS and LiS solutions. In the anodic polarization curve with an additive of 16 mM of OIS, the passive

**Table 1.** Dependence of the logarithmic partition coefficients (log *P*), as well parameters f,  $(-\Delta G_{a,\min}^{\circ})$ ,  $(-\Delta G_{a,\max}^{\circ})$  on chemical structures of carboxylates. log *P* values were obtained using the ACDLABS program

Inhibitor	$\log P$	$B_{i,\max}$ , mol <sup>-1</sup>	$B_{i,\min}$ , mol <sup>-1</sup>	$-\Delta G^\circ_{ m a,min}$ , kJ/mol	$-\Delta G^\circ_{ m a,max},\  m kJ/mol$	f
OIS	7.70	$1.59 \times 10^{10}$	$3.65 \times 10^{9}$	53.65	57.22	1.47
OsS	7.00	$2.15 \times 10^{11}$	$3.57 \times 10^{10}$	59.20	63.58	1.8
LiS	6.50	$5.21 \times 10^{10}$	$1.36 \times 10^{10}$	56.86	60.12	1.31

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potential range is higher than when 8 mM of OIS was introduced into the solution.

The passivating action of CI aqueous solutions was studied at  $C_{in} = 16$  mM. The duration of the formation of adsorption layers on Mg90 with an oxide film formed in air (Fig. 3a) or via oxidation in alkali (Fig. 3b) was 10 min. The electrode treated in this way was placed in the borate buffer solution with pH 9.2 and immediately subjected to polarization.

The LiS film displayed a larger shift of initial potential  $E_n$  of the electrode (-0.92 V), than that of OIS. A region with low current density observed in the anodic polarization curve is shorter than the one with OIS in both the neutral buffer [9] and the BBS with pH 9.2. At the same time, the presence of LiS in the background electrolyte did not result in an emergence of passive potential range, as it is shown above. It is likely that the cross-linking the LiS molecules proceeds with the participation of double bonds during preliminary treatment and drying, but not when LiS is introduced into the solution.

The inhibition of intense anode dissolution was not observed in the anodic polarization curves when unoxidized Mg was treated in 16 mM solutions of LsS and SS, and  $E_n$  was shifted anodically by 50 and 159 mV, respectively.

OsS, another anionic surfactant that also contains one double bond and 17 carbon atoms in its hydrocarbon chain, is markedly inferior to OIS in inhibiting the anodic dissolution of Mg. One difference between these CIs is the higher hydrophobicity of OIS anions, relative to those of OsS. The hydrophobicity of the investigated compounds can be described by the logarithm of the partition coefficient in the octanol-water system,  $\log P$  [16]. It helps to calculate anion hydrophobicity  $\log D$ , allowing for  $pK_a$  of the corresponding acid [17] and the pH of the solution:

$$\log D = \log P - \log[1 + 10^{\text{pH} - pK_a}].$$

These values can be calculated with the resource ACD/I-Lab (https://ilab.acdlabs.com/). The logP values for oleic acid and oleyl sarcosine are 7.70 and 7.0;  $\log D$  at pH 7.4 is 5.10 and 3.61, respectively; at pH 9.2, it is 3.3 and 2.6, respectively. However, hydrophobicity does not play a key role in Mg protection. This is confirmed by the adsorption film of SS having the highest hydrophobicity among the studied carboxylates:  $\log P = 8.23$  and  $\log D = 5.62$  (pH 7.4) and 4.06 (pH 9.2). In protection effectiveness, it is markedly inferior to analogous films formed with OIS and differs little from OsS. The great effectiveness of Mg90 protection with OIS and LiS is likely due to the ability of their molecules to be cross-linked on a surface because of the presence of double bonds. There was virtually no protective effect after treating with the solution of the least hydrophobic LsS ( $\log P = 4.33$ ).



**Fig. 3.** Anodic and cathodic polarization curves for technical magnesium (a) with no and (b) after chemical oxidation in a borate buffer with pH 9.2 and 1 mM of NaCl (*1*) without tentative adsorption, and after holding in 16 mM of CI solution for 10 min: (*2*) OIS, (*3*) OsS, (*4*) LiS, (*5*) SS, (*6*) LsS.

Ex situ ellipsometry showed that when magnesium electrodes are preliminarily oxidized for 1.5 h in 5.0 M NaOH, an oxide-hydroxide film ≈80 nm thick forms on the surface. The picture changes somewhat after oxidized Mg90 is treated with CI solutions (Fig. 3b). The  $E_n$  value for the oxidized electrode is far more positive than that of the electrode not subjected to alkaline oxidation: 1.13 V instead of -1.57 V. This difference shows the protective action of the oxidehydroxide film. Subsequent treatment with the OIS solution affects the  $E_n$  value slightly, but the passive potential range becomes wider. This changes only when  $E_{\rm cd} \approx -0.69$  V, while OIS adsorption without oxidation yields  $E_{\rm cd} \approx -0.85$  V. The protective action of the LiS film is markedly improved, as is seen from the drop in current density in the passive potential range. The protective action of adsorption films of LsS, SS, and OsS declines, as is seen from the drop in  $E_{\rm n}$  to -1.42, -1.43, and -1.36 V, respectively. This was likely due to the partial dissolution of the oxidehydroxide layer when the films were supported from solutions.

Under conditions of the periodic condensation of moisture onto Mg samples with naturally formed

No.	Composition of passivati	pН	t, °C	τ, h	
1	Without treatment	Stripped	—	_	0.5-1
		Oxidized			17-20
2	16 mM OlS	Stripped	8	20	18-20
		Oxidized			92-96
3	16 mM OsS	Stripped	8	20	8
		Oxidized			43
4	16 mM LsS	Stripped		20	2
		Oxidized			33.5
5	16 mM LiS	Stripped	9.4	20	8
		Oxidized			25
6	16 mM SS	Stripped		55	8
	From water-alcohol solutions	Oxidized			20.5

 Table 2. Results from corrosion tests of Mg90 with periodic condensation of moisture

t is temperature of treatment;  $\tau$  is the time before the first attack.

oxide film, corrosion begins at  $\tau_{cor} = 30-60$  min. The least efficient CI on stripped Mg is LsS ( $\tau_{cor} = 2$  h). Films produced with OsS, SS, and LiS ( $\tau_{cor} = 8$  h) are four times more effective. Preliminary treatment of Mg with 16 mM OIS is most effective, providing protection up to  $\tau_{cor} = 18-20$  h (Table 2). The thickness of OIS after such Mg treatment in 16 mM aqueous solution without subsequent washing was  $\approx 60-62$  nm.

An oxide-hydroxide film of 80 nm thick formed in 5 M NaOH solution has a protective effect commensurable with the one for OIS on Mg90 ( $\tau_{cor} = 17-20$  h). In the subsequent treatment of oxidized Mg90 with a 16 mM SS water-alcohol solution, a nonuniform white deposit that was easily removed with filtering paper formed on the surface. The  $\tau_{cor}$  value for oxidized samples covered with the SS film was 20.5 h. LiS, LsS, and OsS films provided some enhanced pro-



Fig. 4. Nyquist plots for technical magnesium in a borate buffer with pH 9.2 and 1 mM of NaCl: (1) without treatment,  $(1^*)$  after preoxidation in 5 M NaOH, (2) after passivation of stripped Mg90 in 16 mM of OIS aqueous solution,  $(2^*)$  after passivation of preoxidized Mg90 in 16 mM of OIS aqueous solution.

the oxidized Mg90 with 16 mM OIS aqueous solution provided the greatest protection:  $\tau_{cor} = 94 \pm 2$  h. EIS is a well known means of surface investigation used to study magnesium and its alloys. It allows us to

used to study magnesium and its alloys. It allows us to study the mechanism and kinetics of electrode processes, along with the characteristics of passive films, with a minimal effect on films. EI spectra obtained for stripped and oxidized Mg90 samples are presented in Fig. 4, along with ones for samples passivated with OIS.

tection:  $\tau_{cor} = 25$ , 33, and 43 h, respectively. Treating

Mg90 samples after oxidation and/or passivation in OIS solutions have larger hodograph radii than ones that are not treated, testifying to their greater corrosion resistance. The calculated nominals are given in Table 3.  $R_{\rm ct}$  grows considerably for oxidized and/or extrapassivated samples, due to a drop in the rate of electrode processes.  $R_{\rm sl}$  also grows, which could indicate a thicker protective layer with improved stability in a solution.

The oxidation of electrodes results in a slight rise in  $R_{\rm ct}$  and a growth of 1.5 times in  $R_{\rm sl}$ . This indicates a drop in the rate of corrosion processes. A small reduction in  $Q_{\rm dl}$  was also observed, indicating a drop in the fraction of the electrochimically active surface of Mg. The small increase in  $Q_{\rm sl}$  is a consequence of a thicker layer of magnesium oxide in the alkaline oxidation process. The values of *n* allow us to assume that the corrosion rate of the stripped sample was due to diffusion of the reagents and products of corrosion to or from the surface. However, oxidation reduced the fraction of diffusive processes on the electrode's surface.

Treating pure and oxidized Mg90 electrodes with OlS raises  $R_{ct}$  hundreds of times. This demonstrates the strong inhibition of electrode processes. The  $Q_{dl}$  value falls relative to background by two orders of magnitude, testifying to the large drop in the area of the electrochimically active surface. The *n* values

Samples	$R_{\rm ct}, \Omega {\rm cm}^2$	CPE <sub>dl</sub> , T	$n_{\rm dl}, \Phi$	$R_{\rm sl}, \Omega  {\rm cm}^2$	CPE <sub>sl</sub> , T	$n_{\rm sl}, \Phi$	$R_{\rm r}, \Omega {\rm cm}^2$	$Z_1$	$Z_2$
Mg90 stripped	16.48	0.003	0.62516	200.83	$3.9 \times 10^{-5}$	0.875	36.635	_	_
Mg90 oxidized	23	$5.3  imes 10^{-4}$	0.90000	300.21	$5.2 \times 10^{-5}$	0.812	29.619	32.77	—
16 mM OlS on stripped Mg90	4803	$1.4 \times 10^{-5}$	0.57935	1391.00	$1.5 \times 10^{-6}$	0.963	43.382	96.49	—
16 mM OlS on oxidized Mg90	5741	$1.1 \times 10^{-5}$	1	6880.60	$1.8 \times 10^{-5}$	0.607	14.197	98.28	97.44

 Table 3. Calculated values for Mg90 electrodes in BBS with 1 mM NaCl pH 9.2

 $Z_1$  and  $Z_2$  are relative to stripped and oxidized Mg90, respectively.

allow us to assume that on electrodes passivated with OIS without preliminary surface oxidation, diffusive processes make a substantial contribution to the observed inhibition. This contribution is far less on preliminarily oxidized electrodes passivated with OIS.

When inhibiting films form, the  $R_{\rm sl}$  value falls substantially (which in this case characteristically describes surface oxide—inhibitor layers), so their values on preliminarily oxidized samples are far higher than on unoxidized ones. The  $Q_{\rm sl}$  values also fall somewhat. The protective effect the inhibitor film has on preliminarily formed oxide is thus more effective than protection with an inhibitor of Mg90 surface without oxidation.

The  $n_{st}$  value testifies to diffusion processes proceeding in surface layers. However, their contribution is far greater for inhibiting treatment of an oxidized surface than when magnesium is passivated without preliminary oxidation in an alkaline solution.

Our investigations showed that the best protective action was Mg90 passivation with preliminary oxidation of its surface in an alkaline solution, which correlates with the corrosion and voltammetry data.

#### CONCLUSIONS

The values of the free energy of OsS and LiS adsorption are  $-G_{a,max}^{\circ} > 55 \text{ kJ/mol}$ , so we may assume they are chemisorbed on an oxidized surface of Mg. Treating oxidized Mg90 with an aqueous 16 mM solution OIS effectively inhibits its anodic dissolution in a borate solution containing chloride ions and slows atmospheric corrosion even under conditions of daily condensation of moisture on samples. Preliminary oxidation of an Mg surface in an alkaline solution enhances the passivating action of CI aqueous solutions, particularly the one most effective, sodium oleate.

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## REFERENCES

- 1. K. U. Kainer, *Magnesium: Alloys and Technology* (Wiley, Chichester, 2003).
- 2. A. Mesbah, C. Juers, et al., Solid State Sci. 9, 322 (2007).
- X. B. Chen, M. A. Easton, and N. Birbilis, in *Corrosion* Prevention of Magnesium Alloys (Woodhead, Philadelphia, 2013), p. 282. https://doi.org/10.1533/9780857098962.2.282
- P. A. Guilherme, T. Alfredo, P. Nunes, et al., J. Alloys Compd. **738**, 224 (2018). https://doi.org/10.1016/j.jallcom.2017.12.115
- S. V. Lamaka, B. Vaghefinazari, Di Mei, et al., Corros. Sci. 128, 224 (2017). https://doi.org/10.1016/j.corsci.2017.07.011
- S. V. Lamaka, D. Höche, R. P. Petrauskas, et al., Electrochem. Commun. 62, 5 (2016). https://doi.org/10.1016/j.elecom.2015.10.023
- 7. Yu. I. Kuznetsov, Organic Inhibitors of Corrosion of Metals (Plenum, New York, 1996).
- 8. Yu. I. Kuznetsov, Korroz.: Mater., Zashch., No. 1, 1 (2017).
- 9. A. M. Semiletov, Yu. I. Kuznetsov, and A. A. Chirkunov, Korroz.: Mater., Zashch., No. 7, 25 (2016).
- S. V. Oleinik, V. C. Rudnev, Yu. A. Kuzenkov, et al., Korroz.: Mater., Zashch., No. 10, 39 (2015).
- 11. S. V. Oleinik, V. C. Rudnev, Yu. A. Kuzenkov, et al., Korroz.: Mater., Zashch., No. 12, 29 (2016).
- 12. M. O. Agafonkina, N. P. Andreeva, and Yu. I. Kuznetsov, Russ. J. Phys. Chem. A **91**, 195 (2017).
- L. M. Calado, M. G. Taryba, M. J. Carmezim, et al., Corros. Sci. 142, 12 (2018). https://doi.org/10.1016/j.corsci.2018.06.013
- L. J. Zhang, J. J. Fan, Z. Zhang, et al., Electrochim. Acta 52, 5325 (2007). https://doi.org/10.1016/j.electacta.2006.12.083
- 15. V. A. Ogorodnikova, Yu. I. Kuznetsov, and N. P. Andreeva, Korroz.: Mater., Zashch., No. 5, 27 (2018).
- 16. C. Hansch and A. Leo, *Correlation Analysis in Chemistry and Biology* (Wiley New York, 1981).
- 17. R. A. Scherrer and S. M. Howard, Med. Chem. **20**, 53 (1977).

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