Corrosion inhibition of Mg90 alloy by mixtures based on sodium oleate. Influence of oxide film thickness

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Abstract

The effect of the thickness of the oxide layer formed on commercial magnesium Mg90 on the efficiency of its anticorrosive protection with sodium oleate (SOI) and formulations based on it was studied. It was shown that in the absence of treatment with the corrosion inhibitor (CI), an increase in the thickness of the oxide-hydroxide film increases the corrosion resistance of Mg90. The longest protection is provided by a film formed in 10 minutes of degreasing in an alkaline phosphate solution, which is associated with incorporation of the inorganic inhibitor into the coating. Treatment of Mg90 samples coated with different oxide-hydroxide films in aqueous solutions of the CI improves the corrosion resistance. The protection efficiency was estimated in three ways: based on anodic polarization curves recorded in a borate buffer (pH 9.2) containing 1.0 mM NaCl; from EIS results obtained in the same solution but at the free corrosion potential, and by accelerated corrosion tests at 100% relative air humidity with forced daily moisture condensation on the samples. According to the EIS data, the formulation of 12 mM SOI + 4 mM vinyltrimethoxysilane (VS) was the best mixed CI, in whose solution a one-hour exposure of Mg90 samples chemically preoxidized in 5 M NaOH provided a high degree of protection, $Z=99.89\%$. The mixture of 12 mM IFKhAN 25F+4 mM VS was slightly less efficient ($Z=99.83$), but it proved to be the best CI in accelerated corrosion tests. FTIR analysis of the Mg90 surface confirmed the presence of CI components on it, and in the case of 12 mM IFKhAN 25F+4 mM VS, a band corresponding to the stretching vibrations of the Si–O–Si bonds was found in the range of $1000\text{--}1100\text{ cm}^{-1}$, indicating the formation of a network of siloxane bonds. This fact, together with the existence a band with a maximum at 3280 cm^{-1} due to the stretching vibrations of the silanol groups, supports our earlier assumption that an increase in the passivation efficiency upon incorporation of VS into the mixture is due to the ability of such a network to prevent the desorption of the main CI.

Keywords: *magnesium, mixed corrosion inhibitors, sodium oleate, vinyltrimethoxysilane, electrochemical impedance spectroscopy, FTIR spectroscopy.*

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Introduction

Magnesium alloys are promising structural materials that remain the main competitors of aluminum alloys in areas where weight characteristics are important. Due to the high reactivity of Mg, it instantly reacts with atmospheric oxygen in the absence of water to form an oxide [1, 2]. However, as a rule, after interaction with water vapor from the air or with water in a solution, there is a film on the Mg surface, which consists of a MgO inner layer and an outer porous layer of $\text{Mg}(\text{OH})_2$ [3–5]. Due to the solubility of magnesium oxide and hydroxide, such films is not stable toward neutral and acidic aqueous solutions. As a result, they have insufficient protective properties; therefore, magnesium alloys cannot be used without additional protection.

The effect of pH on the corrosion behavior of Mg and its alloys is the subject of many studies. Regardless of the composition of the studied medium, a general trend is observed: the anodic dissolution of Mg slows down with an increase in the electrolyte pH [6–10]. However, it is reported [5] that even high purity Mg is not passive but is active under all experimental conditions, with the exception of a chromic acid solution. The rate of Mg dissolution increases continuously as the potential increases.

Improvement of the corrosion resistance can be achieved in different ways, for example, by reducing the concentration of impurities [11]. According to [5], a decrease in the content of impurities in Mg favorably affects its corrosion resistance and reaches a maximum at 99.85 wt.% Mg.

Alloying Mg with rare earth metals is another method of increasing its corrosion resistance [1, 5]. The protection of Mg against corrosion is also achieved by applying conversion [12–17], anodic-oxide or sol-gel [18–20] and other coatings.

It was shown [21] that some pretreatments used in industry, including heat treatment, surface grinding and polishing, etching and sandblasting, also affect the corrosion characteristics of AZ31 magnesium alloy sheet. For example, surface grinding and acid etching enhance the corrosion resistance of Mg, whereas sandblasting degrades it. The authors attribute this to the removal of Fe impurities during the first two types of treatment and incorporation of new contaminants and formation of microstresses in the sandblasting process.

The usage of corrosion inhibitors (CI) is one of the ways to increase the corrosion resistance of Mg and its alloys. CI can improve the protective effectiveness of the above mentioned coatings [22–25] or may be used by themselves [25, 26] for the protection during storage between operations. It has been shown earlier [27, 28] that sodium oleate (SOL) and some formulations based on it increase the corrosion resistance of commercially pure Mg with an oxide film formed in air. In this regard, it was of interest to study the effect of the thickness of the oxide layer on commercial Mg surface on the effectiveness of its protection against corrosion by formulations based on SOL.

Experimental

An alloy of commercially pure Mg (Mg90) with 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%, Cl – up to 0.005% was chosen as the main object of research. The samples were preliminarily ground on emery papers from P240 to 1000 grit and degreased with acetone. Then a system of coatings consisting of an oxide-hydroxide sublayer and an CI film was formed.

The hydroxide layer was formed in two ways:

1. Magnesium samples were degreased for 10 min in an alkaline solution of 45 g/L NaOH and 10 g/L $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ [29] at 60°C, then washed with water and dried in air for 60 min (Ox/Phos).
2. Magnesium samples were chemically oxidized in 5 M NaOH for 90 min, then washed with distilled water and dried in air for 60 min (Ox).

Two- and three-component mixtures of SOI with sodium flufenamate (SFF), sodium salts of alkenylsuccinic acids (SAS), and vinyltrimethoxysilane (VS), $\text{H}_2\text{C}=\text{CHSi}(\text{--OCH}_3)_3$ were used as potential CIs. SFF and SAS solutions were prepared by neutralizing the corresponding acids with NaOH. Since VS is unstable in water, its concentrate was prepared as a 100 mM solution in isopropyl alcohol.

Samples of Mg90 with an oxide film were kept in solutions with the compositions shown in Table 1 and then dried in air.

Table 1. Compositions of passivating solutions and treatment modes.

No.	Solution composition, mM	pH	Exposure time in solution (<i>t</i>), min	
			10	60
1	16 mM SOI	8	+	+
2	12 mM SOI + 4 mM VS	8.2	+	+
3	8 mM SOI + 8 mM SFF (16 mM IFKhAN 25F)	7.5	+	+
4	6 mM SOI + 6 mM SFF (12 mM IFKhAN 25F) + 4 mM VS	7.7	+	+
5	12 mM SOI + 4 mM SAS	7.8	+	+
6	9 mM SOI + 3 mM SAS + 4 mM VS	7.76	+	+

The protective aftereffect of the resulting films was evaluated by recording anodic polarization curves and electrochemical impedance spectra (EIS) and by direct corrosion tests with periodic moisture condensation.

Anodic polarization curves were recorded in a three-electrode glass cell with divided spaces using an IPC-Pro MF potentiostat (RF). The potentials (E) of Mg90 were measured relative to a silver chloride reference electrode and recalculated to the standard hydrogen scale. A platinum auxiliary electrode was used. Polarization curves were recorded on an electrode without and with a CI adsorption film already formed in solutions (Table 1). After drying for 1 hour at room temperature, samples treated for t minutes were lowered into the cell and anodic polarization was started immediately, *i.e.*, from the initial potential (E_{in}).

EIS studies were carried out in a three-electrode glass cell with divided spaces using a “Solartron Schlumberger” computerized electrochemical set (United Kingdom) comprising a 1286 potentiostat and a 1250 frequency response analyzer (FRA). Samples were prepared in the same way as for electrochemical studies. EI spectra were obtained in the frequency range ω from 60 kHz to 0.1 Hz with an alternating voltage amplitude of 10 mV. The working ($S_w = 0.72 \text{ cm}^2$) and auxiliary electrodes (a platinum grid with an area of $S_{Pt} = 20 \text{ cm}^2$) were placed coaxially in the electrochemical cell. The potentials of the Mg electrodes were measured relative to a silver/silver chloride electrode. The studies were carried out in borate buffer solution (pH 9.2) containing 1 mM NaCl with natural aeration.

The working electrode was kept for 15 min in the borate buffer at the free corrosion potential, then the resulting E value was recorded, polarization was turned on, and the EIS measurement was started. The results were processed using the ZView program.

The hodograph of Mg in the working solution was described using the known equivalent electric circuit (EEC) of a coated electrode (Figure 1) [30–33]. It includes: resistance of the bulk electrolyte between the auxiliary and working electrodes – R_s , resistance of surface layers – oxide-hydroxide and/or adsorption layer – R_f , polarization resistance characterizing the electrochemical kinetics of the corrosion process – R_t , constant phase element characterizing the capacitance of the surface layers and/or adsorption film – Q_f , and the capacitance of the electric double layer in the film defects expressed as a constant phase element – Q_{dl} .

Figure 1. EEC of a coated electrode.

The degree of protection of a magnesium electrode was calculated by the following equation:

$$Z = \frac{R_{\text{Ox+Cl}} - R_{\text{Ox}}}{R} \cdot 100\% \quad (1)$$

where R_{Ox} and $R_{\text{Ox+Cl}}$ are the total resistances of the metal-electrolyte interface interaction, including R_f and R_{dl} , of an electrode with an oxide-hydroxide layer before and after treatment in Cl solutions, respectively.

The results of calculating the EEC parameters, R and Z are presented in Tables 2 and 3.

Corrosion tests were carried out with periodic moisture condensation on rectangular specimens of 20×30×5 mm size prepared in the same manner as those used in the electrochemical studies. The prepared samples were suspended in glass cells above 40–50 ml of distilled water at $t=40\text{--}50^\circ\text{C}$. The cells with the samples were placed in a drying oven where $t=40\pm2^\circ\text{C}$ was maintained for 8 h, then heating was turned off, thus providing moisture condensation on the surface of the samples (GOST 9.308-85). The samples were examined every hour. The times when the first corrosion damage appeared (τ) were recorded.

The thicknesses of the hydroxide films were estimated using *ex-situ* ellipsometry. For this purpose, the ellipsometric angles (Δ and Ψ) of the surface were measured before and after treatment. The calculation of the thicknesses of the passivating films was performed using the program available at http://www.ccn.yamanashi.ac.jp/~kondoh/ellips_e.html.

The chemical composition of both surface oxide layers and inhibitor films was studied by FTIR spectroscopy using a Nicolet 380 device (Thermo Electron Corp., USA) in diffuse reflection mode in the range of 400–4000 cm^{-1} . The number of scans ranged from 64 to 364. Mg90 plates with a size of 10×10×2 mm were used as the samples. Before measuring the spectra, the samples were grounded with sandpaper with grain size from 240 to 2000 grit and polished on felt with diamond paste. The diamond paste was removed and the samples were degreased for 5 min in an ultrasonic bath with acetone, then dried for 5 min in air. The prepared samples were further oxidized in different ways. Some of them were left in the air. Samples of the second group were kept for 10 min in a phosphate-alkaline solution [29] at 60°C, washed with water, and dried in air. Samples of the third group were chemically oxidized for 90 min in a 5 M NaOH solution, washed with distilled water, and dried in air.

After drying, the plates were kept for 10 min in solutions of inhibitor formulations, then dried in air for 60 min. Before FTIR measurements, the Cl were adsorbed only on chemically oxidized Mg surfaces.

The FTIR spectra of the films were recorded in a similar mode, using a plate of oxidized Mg90 as the reference sample. The resulting spectra were transformed by the Kubelka–Munk function using OMNIC 9 software.

Results and Discussion

Studies on the protective aftereffect of the films formed on Mg90 showed that the air-formed oxide-hydroxide film (Air/Ox) has weak protective properties. When the electrode is immersed in a solution and polarization is turned on, a rapid increase in the anodic current density is observed due to the active dissolution of Mg [27, 28].

According to ellipsometric measurements, after 10 minutes of degreasing in an alkaline phosphate solution, an oxide-hydroxide layer with a thickness of $\delta = 13 \pm 1$ nm is formed on Mg surface. The anodic curves obtained on such samples have a less negative initial potential, $E_{in} = -1.39$ V, than on samples with an oxide formed in air, $E_{in} = -1.57$ V, while the shape of the curves does not change. It is logical to associate the slight increase in E_{in} with the inhibition of the anodic process.

Chemical oxidation of Mg90 in an alkali solution (Figures 2, 3) allows achieving stronger inhibition of the anodic dissolution of Mg. In this case, the thickness of the oxide film was 80 nm [34]. Thus, with an increase in the thickness of the surface oxide-hydroxide layer, a slowdown of the anodic process is observed, and hence, an increase in the protection efficiency.

As shown earlier, treatment of Mg90 with an Air/Ox film in a 16 mM solution of SOI for 10 min not only increases E_{in} but also significantly reduces the anodic current density [34]. Exposure of Mg in a solution of this carboxylate insignificantly affects E_{in} but slows down the anodic dissolution of Mg. A sharp rise in the anodic polarization curve is observed only at $E \approx -0.69$ V, although in the absence of oxidation, SOI adsorption provided $E = -0.85$ V [34]. Earlier [28], the efficiency of protection of commercially pure Mg by films formed by mixtures of SOI with trialkoxysilanes in a neutral buffer solution and in a humid atmosphere was shown.

It was expected that the protective ability of CI adsorption films will gradually improve with an increase in the thickness of the oxide layer. According to electrochemical measurements, a 10-minute exposure of chemically degreased samples in solutions of 16 mM SOI and its mixture with silane ennobles E_{in} (by 80 and 128 mV, respectively) relative to a similar background (Figure 2a). However, such preparation is not efficient enough in comparison with the adsorption of the aforementioned CIs even on a natural oxide, and even more so on an oxide formed upon 90-minute treatment of Mg in alkali. This is probably due to the fact that the phosphate anions contained in the degreasing solution are included in the composition of the oxide-hydroxide film and impede the subsequent adsorption of CI anions on the surface.

It was shown in [27] that addition of 8 mM of an equimolar mixture of SOI with SFF to a borate solution with pH 9.2 containing 1 mM NaCl provides the longest region with low current densities (2.4 V). In addition, the adsorption film of this CI favors a greater increase in E_{in} than in the case of SOI itself. However, the region of potentials with low current densities was less extended in this case. Addition of SFF enhances the protection efficiency of Mg90 with an air-formed oxide film and under conditions of periodic moisture condensation [27]. In [28], we showed the possibility of enhancing the action of this mixture by adding trialkoxysilanes to it, while an increase in the treatment duration increases the efficiency of protection.

As one can see from Figure 2b (curves 2 and 3), exposure of Mg90 with an oxide film with $\delta = 13$ –14 nm in solutions of 8 mM SOI + 8 mM SFF and 6 mM SOI + 6 mM SFF + 4 mM VS for 10 min ennobles E_{in} by 80 and 70 mV, respectively (relative to the

corresponding background). Thus, it can be seen that the protective effect of the oxide-hydroxide Mg film is enhanced by the CI adsorption layers. Like in the case of SOL, this shift for its mixture with SFF is significantly smaller than for similar treatments of Mg90 with an air-formed oxide film, and the current densities suddenly increase in the region of potentials close to E_{in} for chemically oxidized Mg without CI films.

The film formed in a solution of a 16 mM equimolar mixture of SOL with SFF on a surface chemically pre-oxidized in 5 M NaOH favors the displacement of E_{in} of the electrode in cathodic direction (Figure 2b) relative to a similar background. This is probably due to the partial dissolution of the hydroxide film upon exposure to the CI. Replacing a fraction (4 mM) of the mixture with VS has practically no effect on the character of the anodic polarization curve of Mg90 in a weakly alkaline borate solution containing 1 mM NaCl.

It was shown [27, 35] that a combination of SOL and SAS in a ratio of 3:1 can provide effective protection of not only aluminum but also magnesium. An increase in the coating drying temperature from 20 to 65°C significantly enhanced the protective effect on Mg90.

Here, we investigated the properties of an adsorption film of SOL with SAS formed on oxide films with various thicknesses dried at 20°C. Despite the fact that this composition is inferior to SOL in inhibition of the anodic dissolution of Mg90 with an air-formed oxide, incorporation of the silane into it significantly increases E_{in} (by 0.63 V), which indicates an increase in the protective effect (Figure 2c). Exposure for 10 min in solutions of 12 mM SOL + 4 mM SAS and 9 mM SOL + 3 mM SAS + 4 mM VS favors a decrease in the E_{in} of the electrode (by 0.12 and 0.16 V, respectively). However, the anodic polarization curves demonstrate inhibition of anodic dissolution. A sharp increase in the anodic current densities on the curve obtained in a solution of 12 mM SOL + 4 mM SAS is observed at higher potentials than in the case of SOL ($E \sim -0.5$ V).

Increasing the time of electrode exposure in CI solutions from 10 to 60 min has a positive effect on the inhibition of the anodic dissolution of all the CIs studied (Figure 3a,b,c). This is manifested in a greater displacement of E_{in} in anodic direction. However, on some anodic curves, there are regions with negative current density values (cathodic loops) due to the cathodic reaction of hydrogen evolution. The addition of silane enhances the inhibition of the anodic process by CI films in most cases. This is especially pronounced in the anodic curves of Mg90 with films obtained from solutions of 8 mM SOL + 8 mM SFF and 6 mM SOL + 6 mM SFF + 4 mM VS. Replacement of 4 mM mixed CI by VS favors the formation of films, which either significantly ennoble the E_{in} of the electrode or inhibit the anodic dissolution to a greater extent.

Interestingly, the anodic curves of samples with films obtained from solutions of the SOL + SAS mixtures without and with addition of VS combined with 60 minutes of treatment (Figure 3c) demonstrated a correlation between the improvement of the protective properties and the increase in the thickness of the oxide-hydroxide layer. Among all treatment variants, the maximum protection of Mg90 was provided by the film of 9 mM SOL + 3 mM SAS + 4 mM VS formed in 60 min on a chemically pre-oxidized surface ($\delta = 80$ nm).

Figure 2. Anodic polarization curves of Mg90 in borate buffer (pH 9.2) + 1 mM NaCl without – 1 and after 10 min passivation in Cl solutions: a: 2 – 16 mM SOI; 3 – 12 mM SOI + 4 mM BC; b: 2 – 16 mM IFKhAN 25F; 3 – 12 mM IFKhAN 25F + 4 mM VS; c: 2 – 12 mM SAS; 3 – 12 mM SAS + 3 mM SAS + 4 mM VS. Curves with numbers without an asterisk – Mg90 after degreasing in the alkaline phosphate solution; * – after chemical oxidation in 5 M NaOH.

Figure 3. Anodic polarization curves of Mg90 in borate buffer (pH 9.2) + 1 mM NaCl without – 1 and after 60 min passivation in CI solutions: a: 2 – 16 mM SOI; 3 – 12 mM SOI + 4 mM VS; b: 2 – 16 mM IFKhAN 25F; 3 – 12 mM IFKhAN 25F + 4 mM VS; c: 2 – 12 SOI + 4 mM SAS; 3 – 12 mM SOI + 3 mM SAS + 4 mM VS. Curves with numbers without an asterisk – Mg90 after degreasing in an alkaline phosphate solution; * – after chemical oxidation in 5 M NaOH.

EIS is another electrochemical method that makes it possible to assess the corrosion resistance of coatings. Figures 4 and 5 show the Nyquist plots of Mg90 samples in a borate solution containing 1 mM NaCl with various thicknesses of the oxide-hydroxide layer, without and with CI films.

Figure 4. Nyquist plots obtained on Mg90 in borate buffer (pH 9.2) + 1 mM NaCl without – (a) and after 10 min passivation in CI solutions – (b, c, d): b: 2–16 mM SOL; 3 – 12 mM SOL + 4 mM VS; c: 2 – 16 mM IFKhaN 25F; 3 - 12 mM IFKhaN 25F + 4 mM VS; d: 2–12 SOL + 4 mM SAS; 3 – 12 mM SOL + 3 mM SAS + 4 mM VS. Semicircles with numbers without an asterisk – Mg90 with an air-formed oxide film; * – Mg90 after degreasing in the alkaline phosphate solution; ** – after chemical oxidation in 5 M NaOH.

Figure 5. Nyquist plots obtained on Mg90 in borate buffer (pH 9.2) + 1 mM NaCl after 60 min passivation in CI solutions: a: 2–16 mM SOL; 3 – 12 mM SOL + 4 mM VS; b: 2 – 16 mM IFKhAN 25F; 3 – 12 mM IFKhAN 25F + 4 mM VS; c: 2 – 12 SOL + 4 mM SAS; 3 – 12 mM SOL + 3 mM SAS + 4 mM VS. Semicircles with numbers without an asterisk – Mg90 with an air-formed oxide film; * – Mg90 after degreasing in the alkaline phosphate solution; ** – after chemical oxidation in 5 M NaOH.

As seen from Figure 4a, a layer with a low total resistance $R = 147 \Omega \cdot \text{cm}^2$ is formed on the air-oxidized surface. The formation of an oxide-hydroxide layer from a phosphate or pure hydroxide solution increases the R value by a factor of 2–3, but it remains much lower than $1 \text{ k}\Omega \cdot \text{cm}^2$ and the layer is not protective.

Let us consider how a 10-minute CI surface treatment affects the spectrum. It can be seen from Figure 4b (curve 2) that its adsorption from a 16 mM SOL solution on an air-oxidized surface of sample significantly (36-fold) increases the resistance of the coating formed in this case. Pretreatment of the surface in a degreasing phosphate solution (semicircles 2*) results in a slightly smaller increase in R after the adsorption of SOL, which is consistent with the measurements of E under anodic polarization. The best results are obtained upon adsorption of the CI on a relatively thick oxide-hydroxide layer formed in 5 M NaOH in 90 min (semicircles 2**). The addition of silane to the CI solution increases R only for oxidized magnesium (semicircles 3**), which can be associated with the greater thickness of the oxide-hydroxide layer formed in this case.

The use of a mixture of SOL with SFF (IFKhAN-25F) as the CI gave a greater scatter of results and lower absolute values than with SOL alone (Figure 4c). The R value changes with an increase in the thickness of the oxide-hydroxide layer from $260 \Omega \cdot \text{cm}^2$ for an air-oxidized surface (semicircles 2) and $2.25 \text{ k}\Omega \cdot \text{cm}^2$ for a phosphate-treated surface (semicircles 2*) to $10.2 \text{ k}\Omega \cdot \text{cm}^2$ for an oxidized surface. (semicircles 2**). The addition of VS to the CI formulation with the corresponding decrease in the concentrations of the other components gives a positive effect for the first two types of surface pretreatment, but decreases the R value of the coating on the electrode oxidized in the alkaline solution (C 3**).

The formulation of SOI with SAS (Figure 4d) shows good results on an air-oxidized surface (semicircles 2), but with other types of treatment, the resistance of the coating decreases relative to the above data. At the same time, significant progress is observed compared to surfaces not treated with a CI. The use of silane for this mixture shows a positive but not very significant effect.

One-hour treatment in a solution of 16 mM SOI (Figure 5a) shows itself equally well on an air-oxidized surface (semicircles 2), after phosphate treatment (semicircles 2*), and especially on an oxidized electrode (semicircles 2**). The effect of silane upon one-hour treatment is beneficial and quite significant in all cases (semicircles 3, 3*, 3**). Apparently, in 1 hour, in contrast to the 10-minute treatment, the silane manages to polymerize in the pores of the oxide-hydroxide coating, thereby enhancing its protective properties. For the formulation of 12 mM SOI + 4 mM BC, a high level of protection is observed on the oxidized surface: $Z = 99.89\%$, $Z_f = 99.76\%$.

One-hour treatment with a solution of 16 mM IFKhAN-25F significantly increases the R value in comparison with a 10-minute treatment by any of the methods (Figure 5b). The addition of VS to a CI solution gives a small effect for air-oxidized Mg surfaces degreased in the phosphate solution, but a more significant effect for oxidized magnesium: $Z = 99.83\%$, $Z_f = 99.63\%$.

One-hour treatment of the Mg with the SOI + SAS composition (Figure 5c), as in other cases, leads to an increase in R as the thickness of the oxide-hydroxide layer increases. For an oxidized surface where CI shows the best protection $Z_f = 99.62\%$. The introduction of silane into the composition of CI in all cases improves its protective properties, as evidenced by an increase in its resistance.

One-hour treatment of Mg90 by CI solutions gives a more stable coating, at least as shown by the EIS method, and the use of VS is more justified than in the case of a 10-minute treatment. The best results were shown by the following formulations: 12 mM SOI + 4 mM VS and 12 mM IFKhAN 25F + 4 mM VS if oxidized Mg was treated.

It may be noted that in the case of an air-oxidized Mg surface, in most cases, the power-law coefficient is $n_{dl} > 0.8$, and for an oxidized one, $n_{dl} < 0.5$. For a surface formed upon degreasing in the phosphate-alkaline solution, $n_{dl} = 0.5–0.7$. This suggests that an increase in the thickness of the oxide-hydroxide layer favors an increase in the heterogeneity of the coating, depending on the selected type of treatment.

Electrochemical methods are express methods for diagnosing the protective properties of coatings, but the results of accelerated corrosion tests can give a more accurate picture. In these tests, the accelerating factors include not only the constant high humidity of the atmosphere but also the regular condensation of moisture on the samples. The results of such tests under conditions of periodic moisture condensation of Mg90 with various types of oxide-hydroxide films without and after treatment in CI solutions are presented in Table 4. It follows from their analysis that the films formed on the air-formed oxide in solutions of the 8 mM SOI + 8 mM SFF and 12 mM SOI + 4 mM SAS formulations protect Mg90 from the first corrosion damage better than the film of SOI itself. However, the situation changes

if the adsorption of CI was carried out on Mg90 previously oxidized in 5 M NaOH. In this case, the inhibitors can be arranged in the following series: SOI < SOI + SFF < SOI + SAS.

Table 2. Calculated parameters of Mg90 electrodes in borate buffer containing 1 mM NaCl with pH 9.2, without and with CI films formed in 10 min.

CI	Oxide type	Q_f $\mu\text{S}\cdot\text{s}^n/\text{cm}^2$	n_f	R_f , $\Omega\cdot\text{cm}^2$	Q_{dl} $\mu\text{S}\cdot\text{s}^n/\text{cm}^2$	n_{dl}	R_t , $\Omega\cdot\text{cm}^2$	$R = R_f + R_t$, $\Omega\cdot\text{cm}^2$	Z, %	Z_f , %
Without CI	Air/Ox	1.35	0.89	38.6	21.35	0.85	267	147	–	–
	Ox/Phos	730	0.84	58.7	13.55	0.83	742	384	61.83	–
	Ox	1.06	0.95	116.7	16.08	0.85	533	312	52.96	–
SOI	Air/Ox	0.92	0.91	7157	225	0.90	4070	5389	97.28	97.28
	Ox/Phos	5.65	0.63	160.8	21.97	0.66	7315	5311	97.24	92.77
	Ox	0.88	0.79	5558	15.56	0.46	75334	38828	99.62	99.20
SOI + VS	Air/Ox	0.50	0.88	36.42	0.71	0.89	4338	2100	93.01	93.01
	Ox/Phos	1.60	0.80	199.1	25.80	0.54	6620	4910	97.01	92.18
	Ox	1.62	0.73	14306	13.51	0.38	79418	44988	99.67	99.31
IFKhAN 25F	Air/Ox	0.81	0.82	69.46	0.91	0.86	472	260	43.56	43.56
	Ox/Phos	2.21	0.79	108	12.64	0.84	2653	2250	93.48	82.93
	Ox	1.33	0.73	11418	6.14	0.89	9923	10244	98.57	96.95
IFKhAN 25F + VS	Air/Ox	1.35	0.73	86.52	0.30	0.98	2339	1746	91.60	91.60
	Ox/Phos	9.93	0.67	474	7.89	0.78	6309	4884	97.00	92.14
	Ox	2.55	0.69	0.1	16.77	0.30	3877	1861	92.12	83.23
SOI + SAS	Air/Ox	1.80	0.86	11285	6.88	0.68	15856	19542	99.25	99.25
	Ox/Phos	14.7	0.64	534	8.70	0.83	7070	5475	97.32	92.99
	Ox	8.13	0.70	2161	1.91	0.71	7719	4742	96.91	93.42
SOI + SAS + VS	Air/Ox	1.76	0.87	7700	22.68	0.84	14308	10564	98.61	98.61
	Ox/Phos				21.28	0.72	8580	4118	96.44	90.68
	Ox	1.73	0.73	8114	31.44	0.41	118580	60813	99.76	99.49

Z – degree of protection against air-oxidized surface

Z_f – degree of protection in relation to the type of surface preparation; for air-oxidized surface, $Z_f = Z$.

Replacement of 4 mM SOI and its compositions with VS increases the corrosion resistance of Mg90 (as compared to the initial solutions). The longest complete protection under conditions of periodic moisture condensation (118–120 h) is provided by a coating system consisting of a chemically formed oxide-hydroxide layer ($\delta = 80$ nm) and an

adsorption film formed in a solution of a three-component mixture of 6 mM SOI + 6 mM SFF + 4 mM VS. While in the case of EIS, increasing the time of exposure in CI solutions stabilized the coating, this parameter either did not have any effect or worsened the protective properties of the coatings in corrosion tests. The films of SOI + SAS and SOI + SAS + VS are the only exceptions.

Table 3. Calculated parameters of Mg90 electrodes in borate buffer containing 1 mM NaCl with pH 9.2, without and with CI films formed in 60 min.

CI	Oxide type	Q_f $\mu\text{S}\cdot\text{s}^n/\text{cm}^2$	n_f	R_f , $\Omega\cdot\text{cm}^2$	Q_{dl} $\mu\text{S}\cdot\text{s}^n/\text{cm}^2$	n_{dl}	R_t , $\Omega\cdot\text{cm}^2$	$R = R_f + R_t$, $\Omega\cdot\text{cm}^2$	Z, %	Z _f , %
SOI	Air/Ox	0.042	0.98	46.6	2.17	0.88	7330	5311	97.24	97.24
	Ox/Phos	0.60	0.84	15.0	31.84	0.52	8152	3920	96.26	90.20
	Ox	0.91	0.86	0.1	13.35	0.32	55630	26702	99.45	98.83
SOI + VS	Air/Ox				1.59	0.84	11885	8557	98.29	98.29
	Ox/Phos	2.1	0.80	7357	10.47	0.63	18900	18905	99.22	97.97
	Ox	0.50	0.90	9486	8.58	0.43	170430	129540	99.89	99.76
IFKhAN 25F	Air/Ox	0.32	0.84	56.6	2.29	0.82	5507	4006	96.34	96.34
	Ox/Phos	0.68	0.79	75.6	5.49	0.73	7724	5616	97.39	93.16
	Ox	0.91	0.81	17400	1.16	0.79	39557	27339	99.46	98.86
IFKhAN 25F + VS	Air/Ox	0.21	0.88	56.7	0.85	0.90	7807	5662	97.41	97.41
	Ox/Phos	0.46	0.81	25.35	15.12	0.61	9690	4663	96.85	91.77
	Ox	0.99	0.88	15428	8.39	0.41	160000	84205	99.83	99.63
SOI + SAS	Air/Ox	1.00	0.75	80.22	0.50	0.90	7931	3845	96.19	96.19
	Ox/Phos	4.35	0.73	2172	14.21	0.63	11420	6524	97.75	94.11
	Ox	1.02	0.85	3015	6.00	0.34	111100	82163	99.82	99.62
SOI + SAS + VS	Air/Ox	2.73	0.65	16.85	0.60	0.96	8607	4139	96.46	96.46
	Ox/Phos	0.56	0.90	0.1	13.28	0.46	56331	40558	99.64	99.05
	Ox	0.21	0.86	16054	19.23	0.58	74578	43503	99.66	99.28

In most cases, the addition of the alkoxysilane increases the protective properties of the CI. This can be attributed to the ability of silanes to be hydrolyzed to silanols in water. The subsequent condensation of silanols gives a siloxane network on the metal surface, which probably prevents the desorption of a CI from it.

Some differences in the results of the two methods are due to different test conditions. In the case of electrochemical tests, the medium has a slightly alkaline pH and corrosive NaCl is present in it, whereas in direct corrosion tests there is a thin film of water containing

a large amount of oxygen on Mg90 (conditions typical of atmospheric corrosion) but no corrosive ions.

Table 4. Results of corrosion tests of Mg90 with periodic moisture condensation.

No.	The composition of the passivating solution and the type of oxide-hydroxide sublayer	τ , h	
		After 10 min of treatment	After 60 min of treatment
	Without CI	Air/Ox	0.5–1
		Ox/Phos	23
		Ox	17–20
1	16 mM SOL	Air/Ox	18–20
		Ox/Phos	25.5
		Ox	92–96
2	12 mM SOL + 4 mM VS	Air/Ox	26
		Ox/Phos	48.5
		Ox	103
3	16 mM IFKhAN 25F	Air/Ox	23
		Ox/Phos	27.5
		Ox	58
4	12 mM IFKhAN + 4 mM VS	Air/Ox	23–24
		Ox/Phos	22–24
		Ox	118–120
5	12 mM SOL + 4 mM SAS	Air/Ox	21
		Ox/Phos	26.5
		Ox	54.5
6	9 mM SOL + 3 mM SAS + 4 mM VS	Air/Ox	33
		Ox/Phos	48
		Ox	63

Fourier Transform Infrared (FTIR) spectroscopy was used to confirm the presence of components of inhibiting solutions on the Mg90 surface. For this purpose, FTIR spectra were obtained for oxide and inhibiting films. Figure 6a shows the spectrum of magnesium with a natural oxide-hydroxide layer. The wide intense band in the range from 3200 to 3900 cm^{-1} corresponds to the stretching vibrations of hydroxy groups in the surface layer. The spectrum of Mg subjected to chemical degreasing (Figure 6b) differs from the background one

(Figure 6a). It can be seen in the figure that a band with a maximum at 1217 cm^{-1} appeared in the range of $\sim 1100\text{--}1500\text{ cm}^{-1}$. This is probably due to the incorporation of the phosphate anion into the oxide-hydroxide film during chemical degreasing.

Figure 6. FTIR spectra of Mg90 samples with oxide films: a – Mg90 with an air-formed oxide-hydroxide film; b – Mg90 after degreasing in the alkaline phosphate solution; c – Mg90 after chemical oxidation in 5 M NaOH.

The spectrum of Mg90 pre-oxidized in 5 M NaOH (Figure 6c) is identical to that recorded for samples without treatment. However, the intensity of the absorption bands in the spectrum of the oxidized sample is slightly higher. This indicates a greater layer thickness, while its composition is identical for both types of samples.

Figures 7 and 8 show the FTIR spectra of pre-oxidized Mg90 samples with adsorption layers of the studied CIs. Since all solutions contain SOI, all the spectra should contain the characteristic peaks of this compound. According to [36], a group of high-intensity bands in the region of $2850\text{--}2960\text{ cm}^{-1}$ corresponds to the stretching vibrations of the C–H bond in the $-\text{CH}_3$ and $=\text{CH}_2$ groups of the hydrocarbon chain. They are present in all the spectra shown in Figures 7 and 8. In Figure 7a, the maxima of these peaks are observed at 2954, 2922, and 2851 cm^{-1} . In this case, the first band corresponds to the CH_3 -group, while the

other two, to CH_2 . The broad bands observed in all the spectra in the region of $3010\text{--}3500\text{ cm}^{-1}$ characterize the stretching vibrations of the hydroxy groups. The bands belonging to the R-COO^- group are recorded in several wavenumber ranges. In particular, the carbonyl group of fatty monocarboxylic acids (including unsaturated ones in which the double bond is not in the α - or β -position) is characterized by an intense band in the region of $1705\text{--}1725\text{ cm}^{-1}$ [36, 37]. In the range of $1550\text{--}1650\text{ cm}^{-1}$, there is a band of asymmetric stretching vibrations in the COO^- group [38]. Finally, the band in the range of $1440\text{--}1395\text{ cm}^{-1}$ refers to the stretching vibrations of the C-O bonds and the in-plane bending vibrations of O-H , which are closely related to the former.

From the data shown in Figure 7a, it can be seen that in the case of SOL, the bands corresponding to the carboxy group have rather a low intensity. In our opinion, this is primarily due to the small thickness of the adsorption layer and, accordingly, the small number of such groups. In addition, impurities in the reagent and, as a consequence, in the composition of the adsorption layer can have a certain effect.

Figure 7. FTIR spectra of pre-oxidized Mg90 samples with adsorption layers of corrosion inhibitors: a – 16 mM SOL; b – 16 mM IFKhAN 25F; c – 12 mM SOL + 4 mM SAS. The inset in Figure b shows an enlarged section of the spectrum.

While one symmetric band with a maximum at 1562 cm^{-1} is recorded in the spectrum of the SOL film in the range $1500\text{--}1640\text{ cm}^{-1}$, the shape of the band changes in the spectrum of the adsorption layer formed from a solution of its mixture with SFF (Figure 7b). Obviously, this is due to its partial overlap with the bands of the stretching vibrations of the C=C group in the benzene ring and bending vibrations of the N–H group in secondary amines. According to [39], both types of vibrations are observed in the range of $1550\text{--}1650\text{ cm}^{-1}$. An additional confirmation of the inclusion of SFF in the adsorption layer is the change in the band shape in the range of $3300\text{--}3500\text{ cm}^{-1}$, which is characteristic of the stretching vibrations of the N–H group in secondary amines [38].

In turn, the inclusion of SAS into the adsorption layer is evidenced by a significant increase in the relative intensity of the absorption band in the range of $1504\text{--}1649\text{ cm}^{-1}$ that corresponds to the vibrations of carboxyl groups, which may be due to an increase in the number of these groups in the layer. Indeed, in contrast to SOL, SAS is a mixture of sodium salts of dicarboxylic acids.

Figure 8. FTIR spectra of pre-oxidized Mg90 samples with films of corrosion inhibitors: a – 12 mM SOL + 4 mM VS; b – 12 mM IFKhAN 25F + 4 mM VS; c – 9 mM SOL + 3 mM SAS + 4 mM VS.

Addition of VS to the system leads to additional changes in the FTIR spectra (Figure 8) of the samples obtained. It can be seen, in particular, that the spectra of all the three systems exhibit a broad band with a maximum near 3280 cm^{-1} caused by the stretching vibrations of silanol groups [40]. It is most intense in the spectrum of the sample with the composition 12 mM IFKhAN 25F + 4 mM VS (Figure 8b). The same sample is characterized by the presence of one more band in the range of $1000\text{--}1100\text{ cm}^{-1}$, which corresponds to the stretching vibrations of the Si–O–Si bonds. Obviously, in this case, hydrolysis and condensation of VS during the formation of the mixed adsorption layer take place, which leads to the formation of a network of siloxane bonds. The intensity of this band is very low, which can be due either to a small layer thickness or to a loose structure of the siloxane network. In our opinion, both of these processes occur in the remaining adsorption layers, but at a noticeably lower rate. Taking into account the close pH values for all the three systems, we assume that the main reason for the observed difference in rates lies in the composition of the reaction medium. Confirming this hypothesis will be one of our tasks at the next stage of our work.

Conclusion

1. An increase in the thickness of the oxide film favors an increase in the corrosion resistance of Mg90 without CI films. According to the corrosion tests and EIS data, the hydroxide layer obtained by degreasing in an alkaline phosphate solution has the best protective properties. This is due to the inclusion of phosphate, which itself is a CI of magnesium, into the composition of $\text{Mg}(\text{OH})_2$.
2. Polarization curves of Mg90 electrodes, previously kept for 10 min in solutions of 16 mM SOL or a CI based on it, in a borate buffer containing 1.0 mM NaCl (pH 9.2) indicate the greatest inhibition of the anodic dissolution of Mg, particularly oxidized in 5.0 M NaOH and treated in a solution of 12 mM SOL + 4 mM SAS. Increasing the exposure time of the electrode in the CI solution from 10 to 60 min enhances the protective effect, but the best CIs are 12 mM IFKhAN 25F + 4 mM VS and 12 mM SOL + 3 mM SAS + 4 mM VS.
3. EIS measurements carried out in a similar buffer solution but at the free corrosion potential confirm that treatment of Mg90 in a CI solution increases its protection with oxide films. An increase in the duration of such treatment in all cases increases the protective properties of the coatings. The formulation of 12 mM SOL + 4 mM VS was shown to be the best mixed CI, in the solution of which a one-hour exposure of Mg90 samples chemically oxidized in 5 M NaOH provides a high degree of protection, *i.e.*, $Z \sim 99.9\%$. The slightly less efficient formulations include 12 mM IFKhAN 25F + 4 mM VS and 12 mM SOL + 4 mM SAS ($Z \sim 99.8$).
4. According to the results of corrosion tests, an increase in the exposure time in a CI solution from 10 to 60 min either does not affect or worsens the protective properties of the coatings. The small discrepancies between electrochemical and corrosion data are due to differences in the experimental conditions. The longest protection under conditions of periodic moisture condensation is provided by films formed in 10 min on chemically

oxidized Mg90 from solutions of 12 mM SOI + 4 mM VS and 12 mM IFKhAN 25F + 4 mM VS.

5. Information about the composition of the oxide-hydroxide layer and CI adsorption films on Mg90 surfaces was obtained using IR spectroscopy with Fourier transform (FTIR). The FTIR spectra confirmed the adsorption of SOI on the surfaces of Mg90 studied, while in the case of mixed CI, the adsorption of not only SOI but also SFF or SAS was shown. When VS is added to them, a band with a maximum at 3280 cm^{-1} , which is due to the stretching vibrations of silanol groups in the case of adsorption layers formed by CI formulations of 12 mM IFKhAN 25F + 4 mM VS, becomes the most intense in the FTIR spectra. In this case, a band appeared in the range $1000\text{--}1100\text{ cm}^{-1}$ corresponding to the stretching vibrations of the Si–O–Si bonds, indicating the formation of a network of siloxane bonds. This is in favor of the previous assumption that such a network is capable of preventing the desorption of the main CI. The study of this phenomenon will be continued in our future works.

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