Surface modification of aluminum alloy AMg6 by ethanol solutions of alkyl phosphates

A.M. Semiletov,[1]* A.A. Kudelina,[1] E.S. Khudoleeva[2] and Yu.I. Kuznetsov[1]

[1]A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninsky pr. 31, 119071 Moscow, Russian Federation
[2]LDC SPA "NIIPAV", Khimikov st. 62, 347366 Volgodonsk, Rostov region, Russian Federation
**E-mail: semal1990@mail.ru*

Abstract

The paper considers the possibility of obtaining superhydrophobic (SHP) protective films from ethanol solutions of phosphoric acid esters (monododecyl phosphate and didodecyl phosphate) on the surface of aluminum alloy AMg6 after its pre-etching with 10% NaOH solution at $t = 60°C$ in order to obtain polymodal roughness. It is shown that the alloy treatment in alkyl phosphate solutions leads to superhydrophobization of the surface. The stability of obtained coatings in alkylphosphate solutions is compared with similar alloy surface treatment in dodecylphosphonic and dodecanoic acid solutions. The protective ability of the coatings obtained was evaluated by polarization measurements and corrosion tests in a temperature-humidity chamber. It was established that the best anti-corrosion properties are shown by films formed from solution containing 10 mmol·L^{-1} of the monododecyl- and didodecylphosphate mixture.

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Introduction

Among numerous corrosion inhibitors (CIs), organic CIs capable of forming thin self-assembled films on metal surfaces attract particular attention of researchers [1−5]. Such inhibitors include, for example, higher carboxylic [6−9] and alkylphosphonic [10−13] acids and their salts, thiols [14−16], that due to the diphilic structure of molecules have high surface activity and ability to self-organization in the adsorption layer.

Due to the simplicity of obtaining such layers, they can be a very prospective and effective corrosion protection method, since organic CIs can firmly chemosorb on the metal surfaces and their oxides, forming thin protective layers. Self-assembly of organic molecules on the metal surface, can lead to hydrophobization and even superhydrophobization, which enhances corrosion resistance [2, 5, 13, 17, 18].

Despite the fact that aluminum alloys due to oxide film formation are characterized by a sufficiently high corrosion resistance in the atmosphere. Nevertheless, in humid atmosphere, when aggressive chloride anions get on the surface, the oxide layer can be locally destroyed, significantly reducing the lifetime of storage and operation of steel structures [19, p. 122]. Formerly, hexavalent chromium compounds were used to protect aluminum alloys. But due to the high toxicity of chromates, their usage is undesirable and being replaced by safer CIs [20].

Phosphonate complexes and metal complexonates, especially zinc, which are widely used in reagent water treatment to control salt deposition and corrosion, occupy a central place among phosphorus-containing CIs [21, p. 187−200]. The use of phosphoric acid esters (alkylphosphates) as CIs, which have been widely used as antistatic agents, emulsifiers, wetting agents and hydrotropes since the late 1950s, seems to be quite interesting. Their advantage is derived from mild and non-irritating properties, due to which they are used in personal care products, shampoos and oral compositions [22], that turns out to be important in terms of ecology.

Anion stability of mono- and disubstituted phosphoric acid esters, ability to complex and form hydrophobic passive films determines their efficiency as CIs [23−25]. Sodium dioctyl phosphate (DOPh) is the most studied alkylphosphate and has proven to be one of the best passivators for mild steel in neutral solutions [24]. It causes not only spontaneous steel passivation at relatively low concentrations and increases the value of its local depassivation potential, but is also capable of preventing the oxide film growth on steel up to the realization of the oxide-free passivation mechanism. The presence of a phosphate group in the DOPh molecule additionally provides its high adsorption capacity, which is confirmed by ellipsometric measurements in neutral borate buffer solution [24]. Passivation properties of DOPh are shown not only in relation to iron and steels, but also to other metals or alloys: as early as [22] observed the passivation facilitation of zinc and aluminum alloy D16 in aqueous chloride solution by the introduction of DOPh. Later in [25] the adsorption of DOPh on the D16 alloy surface was studied by the ellipsometric method and its chemisorption character was established.

Sodium dodecyl phosphate (DDPh, laurylphosphate) possesses adsorption activity on aluminum and its oxide [26, 27]. These studies were conducted due to the necessity to prevent corrosion of aluminum microparticles that are used as pigments in protective primers. Authors have concluded that the effective corrosion inhibition induced by alkyl phosphate anions may be derived from their chemisorption involving the formation of bridging bidentate complexes, as well as its ability to form stable complexes with aluminum.

Investigations on possibility of obtaining DDPh layers on surface of the aluminum alloy LY12 (Al-Cu-Mg system alloy) are noteworthy [28, 29]. In [28] it has been shown that alloy surface treatment in solution containing 2 mM DDPh leads to surface hydrophobization (value of contact angle, $\Theta_c = 105°$). Accelerated corrosion tests in aqueous solution containing 0.01 M NaCl and 0.01 M Na_2SO_4 showed that the alloy LY12 surface modified with DDPh remains without visible corrosion sites during 96 hours of exposure in this solution. The results of electrochemical impedance spectroscopy (EIS) analysis indicate that the value of charge transfer resistance for modified LY12 alloy surface was 100 times higher than the same electrode without DDPh coating.

Later, these authors [29] have investigated the pH effect of DDPh solutions used in surface modification of LY12 alloy. It is shown that the resulting self-organized DDPh layers from neutral solution exhibit higher value Θ_c=125° and greater thickness, compared to DDPh films obtained from acidic and alkaline solutions (values of Θ_c=101° and 114°, respectively). Corrosion tests in marine atmosphere also showed the advantage of DDPh films formed from neutral solution. The authors explain it that the pH value of solutions significantly affects the DDPh hydrolysis and oxide layer thickness, since the presence of a greater number of free OH-groups on aluminum surface can affect the self-assembly process.

In [30], it was studied that the possibility of increasing the protective ability of cerium conversion coating on galvanized steel by surface treatment in *n*-mono DDPh solution. It has been shown that surface hydrophobization occurs after surface modification and the value Θ_c reaches 115°. FTIR and XPS studies proved the formation of self-assembled alkylphosphate layer on the surface, that effectively prevents corrosion of steel samples. According to the action mechanism, DDPh layer behaves as an anodic inhibitor. And proposed protection technology is considered as an alternative to chromate coatings. DDPh is not restricted to laboratory studies as an effective CI, but is applied in practice. For example, DDPh potassium salt (trademark Tainolin MLP-K, Taiwan NJC Corporation) is used in metal corrosion protection compositions and as an emulsifier and hydrotrope.

Alkylphosphates can not only be effective CIs of aluminum alloys but also enhance the protective effect of other CIs. For example, M. Forsyth *et al.* observed [31, 32] that rare earth metals (REM) diphenyl phosphates provide greater corrosion protection for aluminum alloy 2024 in comparison to many similar carboxylate salts. They suppose that synergism of protection by such salts is due to the difference in their action mechanism. REM cations, primarily cerium, inhibit predominantly cathodic reaction, while organic anions inhibit anodic reaction.

The present paper deals with the possibility of obtaining superhydrophobic (SHP) protective films from ethanol solutions of phosphoric acid ester mixture (monododecyl phosphate and didodecyl phosphate) on the aluminum alloy AMg6 surface. The stability of obtained SHP coatings in alkyl phosphate solutions is compared with similar SHP treatment of the alloy surface in dodecylphosphonic and dodecanoic acid solutions.

Experimental

Aluminum alloy AMg6 (analogue of AA 5182) was used as the base metal containing (wt%): Al 91.1–93.68; Mg 5.8–6.8; Fe up to 0.4; Si up to 0.4; Mn 0.5–0.8; Be 0.0002–0.005; Ti 0.02–0.1; Cu≤0.1; Zn≤0.2. The samples represented by rectangular plates 30×40×1.2 mm in size were sanded with different grit sandpapers to a “mirror” shine.

A mixture of monododecyl (mono-DDPh; 40 wt%) and didodecyl (di-DDPh; 55 wt%) phosphates (mDDPh), dodecylphosphonic acid (DDPhA) and dodecanoic acid (DDA) were used as hydrophobizing (HP) agents (Figure 1). Etching in 10 wt% NaOH solution at varied temperature (20, 60 and 70°C) and treatment time τ_{etch} (30–120 s) was used to create roughness on the AMg6 surface. Further, the alloy surface was treated in ethanol solutions of HP agents at room temperature (t=20±2°C), then samples were dried for 60 min at 65°C.

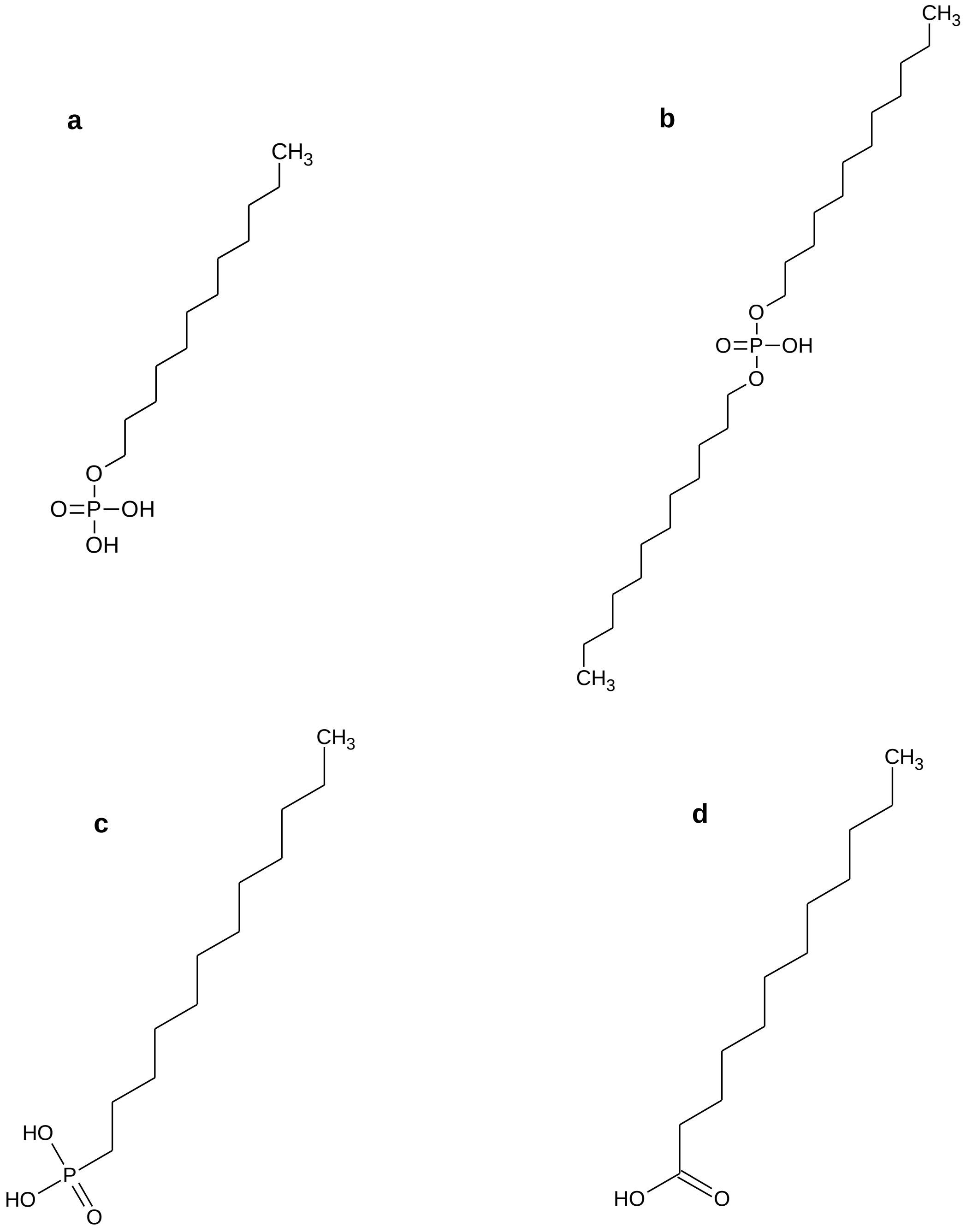


Figure 1. Structural formulas of studied compounds: monododecyl phosphate (a) and didodecyl phosphate (b), dodecyl phosphonic acid (c) and dodecanoic acid (d).

A Model-130 profilometer was used to estimate the surface roughness parameters. And the index was calculated the surface roughness by the system of mean lines. Principle of profilometer's operation consists in sequential tracing of the sample with a diamond needle, located perpendicular to the surface under study, and converting its vibrations into a digital signal with its further processing in a computer. The length of measurement trace was 12.5 mm, and at least 5 surface profile measurements were performed for each sample. Surface roughness grade was determined according to ISO 21920-1:2021 and average values of parameters were calculated: R_z, μm – height of profile roughness; R_a, μm – arithmetic means deviation; and roughness grade. Roughness parameters were determined for samples subjected to mechanical polishing and alkaline etching.

To measure the contact angle (Θ_c) values, video images of a 3–5 μL distilled water drop on the investigated surface were obtained using a camera LevenhukM 1000 Plus. The contact angles were determined from photo-image data using a graphic editor "Inkscape 1.3". In order to obtain a reliable characterization of coating wetting, the initial values of Θ_c were measured 5–10 sec after droplet landing on 5 different surface areas of each sample. The mean angle value Θ_c was measured for 10 consecutive droplet images.

Polarization curves of AMg6 alloy were taken in a Teflon cell using potentiostat IPC-Pro. The neutral borate buffer solution with pH 7.4 containing 0.01 M NaCl was used as a base solution. Electrode potentials (E) were measured relative to a saturated silver chloride electrode and converted to normal hydrogen scale. The counter electrode is platinum. Protective properties of SHP layers were evaluated by increase in local depassivation potential E_{pit} compared to the same value measured in the absence of SHP electrode treatment, $\Delta E_{\text{pit}} = E_{\text{pit}}^{\text{SHP}} - E_{\text{pit}}^{\text{bare}}$.

The protective ability of coatings was determined by testing samples in temperature humidity chamber. Protection efficiency criterion was the time until the first corrosion damage appeared on the samples. The chamber operated according to the mode: it was switched on at t=40°C for 8 h, the rest of the day its heating was switched off, which resulted in abundant condensation of moisture on the samples.

Results and Discussion

The hydrophobicity of organic compounds' neutral molecules, which is quantitatively characterized by the logarithm of substance partition coefficient in octanol–water immiscible liquid system (lg$P$), affects their adsorption capacity. The value of lg$P$ can be obtained both experimentally and computationally, using the f-constants of substituents' hydrophobicity [33]. The lg$P$ values calculated in the program ACDLABS 12.0 for studied organic compounds are shown in Table 1. According to the results, hydrophobicity increases in the series DDPhA < mono-DDPh < DDA < di-DDPh.

Table 1. The lg*P* values calculated using the program ACDLABS 12.0 for studied organic compounds.

Compound name	mono-DDPh	di-DDPh	DDPhA	DDA
lg*P*	4.25±0.21	10.70±0.58	3.83±0.58	5.03±0.18

After mechanical polishing and degreasing with ethanol, the AMg6 alloy surface is hydrophilic and has a small value of contact angle $\Theta_c=36°$. Post-treatment of the sample with DDPh ethanol solution at $C=1$ mmol·L^{-1} for $\tau_{tr}=1$ h leads to alloy surface hydrophobization. Meanwhile, the value of Θ_c increases and reaches 105°.

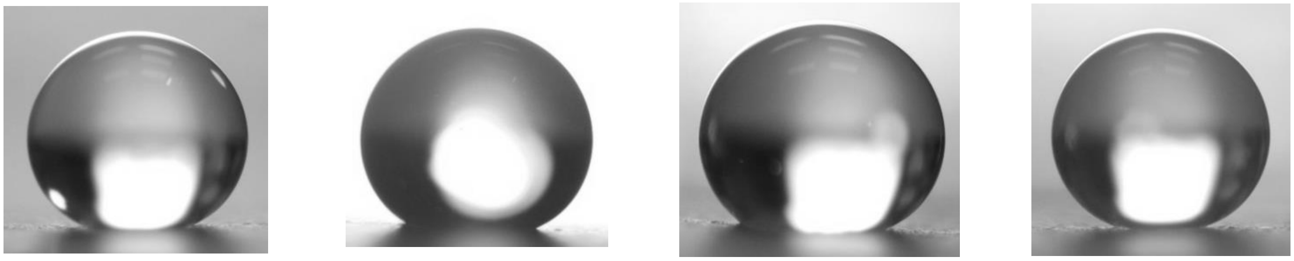
Nevertheless, surface roughness must be considered to obtain SHP coatings. To determine the most optimal etching mode of AMg6 alloy, roughness parameters were evaluated by profilometric measurements, and HP treatment of samples was carried out in mDDPh solution at $C=1$ mmol·L^{-1}. According to the results of profilometry and determination of Θ_c value, etching at $t=20$°C is found to be ineffective to achieve SHP surface condition (Table 2). However, increasing the temperature of alkaline solution leads to an increase in surface roughness, as evidenced by an increase in R_z values, and obtained mDDPh films are characterized by better hydrophobic properties. The maximum value of $\Theta_c=148°$ is observed for samples subjected to etching at $t=60$°C for $\tau_{etch}=90$ sec.

Table 2. Profilometer measurements results of AMg6 alloy samples without and after etching in 10 wt% NaOH solution and Θ_c values after surface hydrophobization in mDDPh ethanol solution ($C=1$ mmol·L^{-1}, $\tau_{tr}=1$ h).

Etching mode		**Measurement parameters**				**Θ_c, deg**
***t*, °C**	**τ, sec**	**R_z, µm**	**R_a, µm**	**R_{max}, µm**	**Surface roughness grade**	
After mechanical polishing		2.26	0.23	2.69	N5	105
20	30	2.02	0.22	2.55	N5	131
20	60	2.58	0.27	3.37	N5	133
20	90	2.91	0.42	3.29	N6	127
20	120	3.71	0.54	4.59	N6	123
60	30	2.16	0.23	3.59	N5	139
60	60	4.10	0.66	4.55	N6	138
60	90	6.49	0.82	7.34	N7	148
70	60	5.51	0.77	6.36	N7	122
70	90	6.33	0.78	7.08	N7	124

According to the data of profilometric measurements (Table 2), the profile roughness height R_z of mechanically polished samples does not exceed 2.26 μm, with the maximum profile height R_{max}=2.69 μm, which corresponds to N5 roughness grade. During alloy surface etching, the roughness increases, and the average size of roughness for selected optimal etching mode is R_z=6.49 μm, that corresponds to N7 roughness grade.

Among the studied compounds, DDPhA was the most effective in achieving SHP state on AMg6 alloy surface at C=1 mmol·L^{-1}, and Θ_c=153° (Figure 2). However, as DDPhA concentration increases, the Θ_c value decreases and surface retains only HP properties, which is probably caused by partial etching of alloy surface and disruption of multimodal roughness. Treatment with mDDPh ethanol solution at C=1 mmol·L^{-1} is slightly inferior to DDPhA, and the value of Θ_c=148°. With increasing mDDPh concentration, nevertheless, the surface acquires SHP properties and Θ_c value passes through a maximum of 153° at C=8 mmol·L^{-1}. DDA was less effective in achieving the SHP state, and Θ_c=143°. The contact angles obtained are slightly different from a number of calculated lg$P$ values, which is due to the different nature of anchor group interaction of these compounds with alloy surface and, apparently, different degree of alkyl tail molecules ordering in the protective SHP layer. With increasing the duration of alloy treatment in mDDPh solution C=10 mmol·L^{-1} up to 1.5 h, the value of contact angle is the largest, Θ_c=156°. Nevertheless, the value of Θ_c is not affected by duration of alloy surface treatment in solutions of other studied compounds.

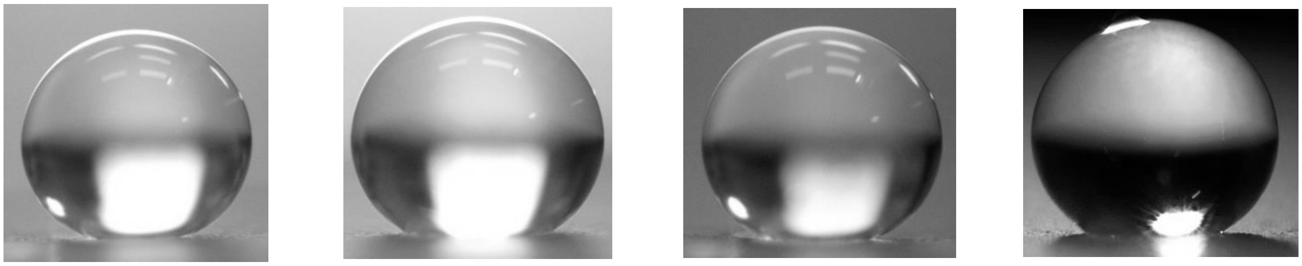


mDDPh 1 mmol·L^{-1} 148°

mDDPh 4 mmol·L^{-1} 148°

mDDPh 6 mmol·L^{-1} 148°

mDDPh 8 mmol·L^{-1} 153°



mDDPh 10 mmol·L^{-1} 151°

DDA 10 mmol·L^{-1} 143°

DDPhA 1 mmol·L^{-1} 153°

DDPhA 4 mmol·L^{-1} 144°

Figure 2. Photographic images of droplets obtained on AMg6 alloy samples pre-etched in 10 wt% NaOH solution and then modified in CIs ethanol solutions (τ_{tr} =1 h).

Polarization measurements allow to quickly assess the protective capacity and stability of formed layers. Anodic polarization curves of AMg6 alloy in neutral borate buffer solution containing 0.01 M NaCl are shown in Figure 3. The initial potential of AMg6 electrode when immersed in background solution is $E_{\text{in}}=-0.61$ V. A gradual increase in current i_a occurs with the imposition of anodic polarization, and further at $E_{\text{pt}}=-0.48$ V, a rapid increase in i_a is observed, indicating the formation of pitting on electrode surface.

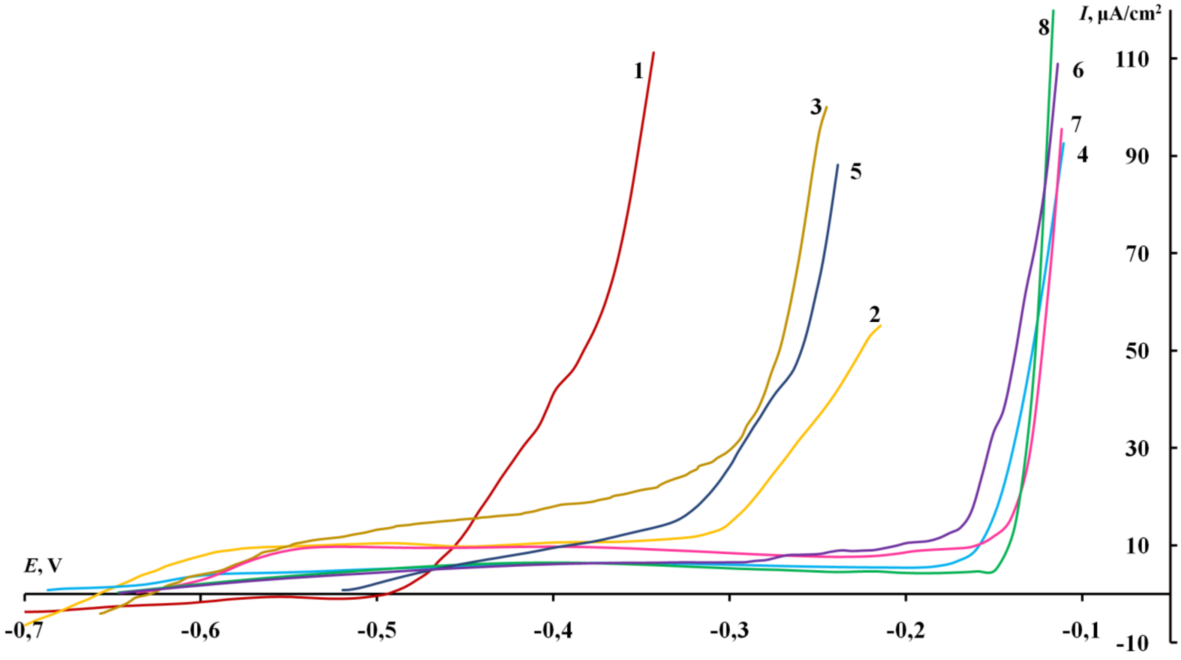


Figure 3. Anodic polarization curves of AMg6 alloy in neutral borate buffer solution containing 0.01 M NaCl, without (**1**) and after etching in 10 wt% NaOH solution (**2−8**) and then modified in ethanol solutions of HP agents: **3** – DDA, $C=10$ mmol·L^{-1}; **4** – DDPA, $C=1$ mmol·L^{-1}; **5** – mDDP, $C=1$ mmol·L^{-1}; **6** – mDDP, $C=6$ mmol·L^{-1}; **7** –mDDP, $C=8$ mmol·L^{-1}; **8** – mDDP, $C=10$ mmol·L^{-1}.

Etching of AMg6 alloy in alkali leads to a slight shift of E_{pt} value to anodic direction, E_{pt} value slightly increases, and $\Delta E_{\text{pt}}=0.19$ V. When the alloy was further treated for $\tau_{\text{tr}}=1$ h in ethanol solutions of DDA $C=10$ mmol·L^{-1} and DDPhA $C=1$ mmol·L^{-1}, shifts were $\Delta E_{\text{pt}}=0.19$ V and $\Delta E_{\text{pt}}=0.32$ V. In the case of alloy surface modification in a mDDPh solution $C=1$ mmol·L^{-1}, protective properties of resulting films are low, and $\Delta E_{\text{pt}}=0.18$ V. However, when mDDPh concentration in solution was increased to 8 and 10 mmol·L^{-1}, ΔE_{pt} values increased to 0.33 V and 0.34 V, respectively. Thus, according to the results of polarization measurements, surface treatment of AMg6 alloy in mDDPh solution $C=10$ mmol·L^{-1} provides the best protection of alloy in chloride-containing borate buffer solution, and is superior to modification in DDPhA solution, and ΔE_{pt} appears to be higher by 0.02 V.

The corrosion test results of AMg6 aluminum alloy samples under humid atmosphere conditions show its low corrosion resistance. First corrosion damages on samples previously subjected to etching in alkali were observed already after τ_1=1 day, and after τ_2=2 days the alloy surface was completely corroded (Figure 4). Surface treatment for 1.5 h in mDDPh solution C=1 mmol·L^{-1} does not affect the time of appearance of first corrosion damages, but slightly inhibits their development, and the value of τ_2=3 days. Increasing the mDDPh concentration to C=10 mmol·L^{-1} results in increased values of τ_1=15 days and τ_2=18 days. The same degree of protection is observed for layers formed from DDPhA solution at C=1 mmol·L^{-1}. Layers obtained from DDA solution C=10 mmol·L^{-1} are slightly inferior to mDDPh and DDPhA films in terms of protective properties, and the time of first corrosion damage appearance does not exceed 7 days.

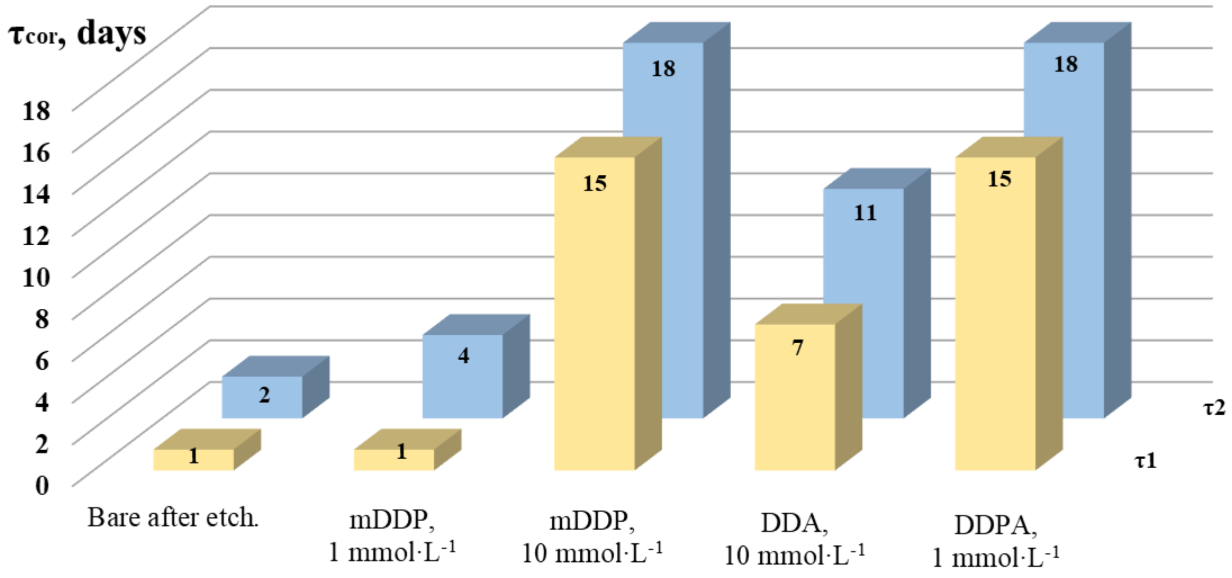


Figure 4. Values of corrosion parameters (τ_{cor1}, τ_{cor2}) for AMg6 alloy samples with SHP coatings CIs under temperature humidity chamber conditions.

Conclusions

1. The possibility of obtaining SHP films on aluminum alloy AMg6 surface by its preliminary alkaline etching and subsequent modification in ethanol solutions of monododecyl and didodecylphosphate mixture has been shown for the first time. The most optimal etching conditions were established by changing the value of contact angle: t=60°C and τ_{etch}=90 sec. According to profilometric measurements in this etching mode, roughness with an average size of 6.49 μm is formed on alloy surface.
2. Treatment of AMg6 alloy in ethanol solution of dodecyl phosphate mixture at C=10 mmol·L^{-1} for 1.5 h leads to the formation of protective film on the surface, for which value of contact angle is the highest Θ_c=156°.
3. Polarization measurements of AMg6 alloy samples with SHP films of CIs in neutral chloride-containing borate buffer solution showed that protective layers of studied

compounds effectively prevent alloy local depassivation. The best protective ability is possessed by dodecyl phosphate films formed at $C = 10\ \text{mmol}\cdot\text{L}^{-1}$. The high protective effectiveness of these SHP layers is also confirmed by corrosion tests in humid atmosphere conditions. And time to the appearance of first corrosion damages is 15 times higher than for samples without SHP coating, and is not inferior to films formed from dodecylphosphonic acid solution.

Acknowledgments

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