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CORROSION PROPERTIES OF OXIDE CERAMIC COATINGS BASED ON ALLOYS OF THE Al–Cu–Mg AND Al–Mg SYSTEMS

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By the methods of electrochemical impedance spectroscopy and potentiodynamic methods, we estimate the corrosion resistance of oxide ceramic coatings obtained on Al–Cu–Mg and Al–Mg alloys in the course of ozone bubbling. The results are compared with the data on the corrosion resistance of materials produced by using standard methods. The capacitance of all obtained oxide-ceramic coatings after 90 days is stabilized and becomes equal to 1–4 pF/cm^2. Their corrosion resistance of the D16 alloy is twice higher than for the AMg5 alloy. All developed coatings are characterized by the elevated protective properties and their resistance in a 3% aqueous solution of sodium chloride is $1–4\ \text{G}\Omega\cdot\text{cm}^2$.

Keywords: corrosion, plasma-electrolyte oxidation, aluminum oxides, oxide ceramic coatings, X-ray diffraction analysis, alloy.

Introduction

Aluminum alloys are now extensively used in the industry. However, their application is restricted by low corrosion resistance caused by the presence of intermetallic inclusions. Therefore, it is necessary to develop new reliable coatings for the purposes of protection and hardening. The procedure of plasma-electrolytic oxidation (PEO) is an efficient relatively new type of surface treatment and hardening of metal products, which is frequently used for the formation of oxide-ceramic coatings. However, the potentialities of this method are insufficiently studied.

These coatings have high microhardness, dielectric properties, and wear- and corrosion resistances. They are used in the automotive industry, instrument-making, and radioelectronics. The procedure of synthesis, phase compositions, and properties of these coatings were studied in detail in [1–3]. However, this process is quite energy-consuming. The optimal current density for the synthesis of coatings of this kind is equal to 20–25 A/dm^2 for a rather low rate of their formation (2 μm/min) [4].

The models of synthesis were described in [5–7]. These models are based on the idea that, in the course of PEO in spark channels, we observe not only the reactions of oxidation of aluminum but also the reactions of oxidation of all alloying elements present in the input alloy. In [8], the yield of aluminum oxide Al_2O_3 was determined both as a result of the direct reaction and as a result of its possible formation with participation of intermediate compounds, such as AlO, Al_2O, Al_2O_2, and AlO_2.

It was established [9] that the inner sections of oxide-ceramic coatings contain the excess amounts of aluminum. As one of the methods used to increase the growth rate of the coating, we can mention the possibility of

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increasing the amount of oxygen in the discharge channel by adding hydrogen peroxide H_2O_2 to the electrolytes [10].

Interesting results about the influence of H_2O_2 on the phase composition, corrosion resistance, porosity, and wear resistance of the coatings were obtained in [11, 12]. As a disadvantage of this electrolyte, we can mention its relatively rapid exhaustion. It is also possible to increase the amount of oxygen in the electrolyte by the procedure of air bubbling performed by using air enriched with ozone O_3 that dissolves in water 15 times faster than oxygen and is a strong oxidizer. These electrolytes have elevated serviceability. The rate of formation of the coatings is also affected by water glass (Na_2SiO_3). Penetrating into the coating, SiO_3^{2+} anions weaken the etching influence of alkali upon the base [13].

At present, electrolytes containing 2–60 g/liter of water glass or 2–8 g/liter of an aqueous solution of potassium hydroxide (KOH) are used most extensively. The chemical composition of electrolytes determines the quality of the coatings in the course of PEO, guarantees its functional characteristics, and significantly affects its composition and structure. It is known that oxide-ceramic coatings have improved physicomechanical and operating characteristics. However, they are porous. Therefore, it is necessary to additionally study their corrosion resistance.

In what follows, we evaluate the influence of ozone on the corrosion properties of coatings of the Al–Cu–Mg and Al–Mg systems in a 3% NaCl aqueous solution and in the same solution saturated with hydrogen sulfide.

Materials and Methods of Investigations

Oxide-ceramic coatings were synthesized on specimens 20 × 15 × 3 mm in size made of the aluminum alloys D16 (94.7% Al, 3.8–4.9 Cu, 1.2–1.8 Mg, 0.3–0.9% Mn) and AMg5 (94.7% Al, 5.6–6.8 Mg, 0.5–0.8 Mn, 0.02–0.05 Ti, 0.0002–0.0005% Be). They were preliminarily polished and washed in distilled water and ethyl alcohol. The coatings were formed by the method of alternating application of anodic and cathodic pulses. The anodic and cathodic current densities were equal, respectively, to $J_a = 10$ A/dm^2 and $J_c = 10$ A/dm^2. The duration of synthesis was 60 min. As electrolytes, we used aqueous solutions of two types: EL-1 with 3 g/liter KOH + 2 g/liter Na_2SiO_3 and EL-2 with 3 g/liter KOH + 6 g/liter $Na_2SiO_3 + O_3$. The phase compositions of the coatings were determined in a DRON-3 diffractometer (in the CuK_α-radiation) with the use of the FullProf software. The thicknesses of the coatings were measured by using a CHY TG-5 device.

The polarization curves were recorded in a PI-2MK-10A potentiostat in a three-electrode cell at a temperature of 25°C and a sweep rate of 1 mV/sec by introducing auxiliary graphite and silver-chloride reference electrodes. As a corrosion medium, we used a 3% aqueous solution of NaCl naturally aerated or saturated with hydrogen sulfide. We extrapolated the linear sections or plateaus of the polarization curves to determine the corrosion rate in the initial stages. We prepared solutions saturated with hydrogen sulfide by blowing it through the working solution for 2 h.

Protective properties of the coatings were studied by the method of electrochemical impedance spectroscopy at AC frequencies of 0.1, 0.2, 1, 10, 50, and 100 kHz. Alternating currents have a much weaker destructive influence upon the metal–coating electrochemical system than direct currents; moreover, it becomes possible to efficiently measure the resistance and capacitance at high frequencies (of about 100 Hz–100 kHz). The resistance and capacitance of the coatings were measured at room temperature in a specially produced electrochemical cell on an R-5083 automatic AC bridge. The role of working surfaces (electrodes) was played by sections of the coatings 0.65 cm^2 in size. These sections were chosen depending on the size of cylindrical cells. As an auxiliary electrode, we used a platinum spiral.

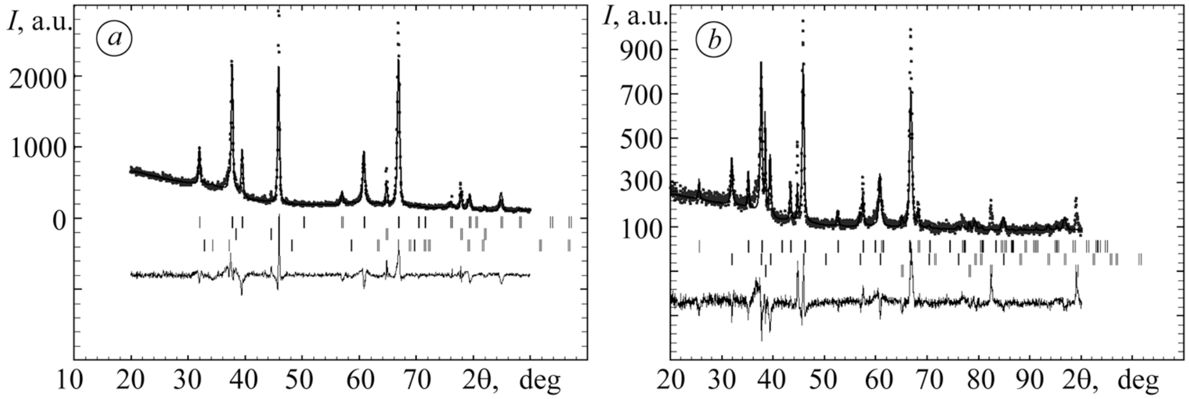

Fig. 1. X-ray diffractograms of oxide-ceramic coatings obtained on AMg5 (a) and D16 (b) alloys formed in the EL-1 electrolyte.

Table 1
Composition and Thicknesses of Oxide-Ceramic Coatings

Alloy	Electrolyte	t, min	J_c/J_a, A/dm^2	L, µm	P, %
D16	EL-2: 3 g/liter KOH + 2 g/liter Na_2SiO_3	60	10/10	58–67	2.9
D16	EL-1: 3 g/liter KOH + 6 g/liter Na_2SiO_3 + O_3	60	10/10	122–145	6.0
AMg5	EL-2: 3 g/liter KOH + 2 g/liter Na_2SiO_3	60	10/10	70–85	2.3
AMg5	EL-1: 3 g/liter KOH + 6 g/liter) Na_2SiO_3 + O_3	60	10/10	108–140	5.5

Results and Discussion

The oxide-ceramic coatings were applied to AMg5 and D16 alloys both by the standard method and in the course of ozone bubbling (Table 1, where t is the duration of synthesis of the coating, L is the thickness of the coating, and P is its porosity). It was discovered that if the concentration of water glass increases and the electrolyte is blown with ozone, then the thickness of coatings becomes almost twice larger.

By the method of X-ray phase diffraction analysis, we established the phase composition of the coatings (Table 2). The diffractograms of the coatings applied to AMg5 and D16 alloys in an electrolyte containing 3 g/liter KOH + 6 g/liter Na_2SiO_3 under the conditions of blowing with an ozone-air mixture at a rate of 5 mg of ozone in 1 liter/min are presented in Fig. 1.

It was shown (Fig. 2) that the plateau in the cathodic curves of the alloys placed in a 3% NaCl solution corresponds to oxygen depolarization. In this case, the rate of anodic processes is much higher than the rate of cathodic processes. Therefore, the corrosion rates of AMg5 and D16 alloys depend on the rates of cathodic processes and are equal to $4.6 \cdot 10^{-3}$ and $4.0 \cdot 10^{-3}$ mA/cm^2, respectively. If a 3% NaCl solution is saturated with hydrogen sulfide, then these corrosion rates become 2.6 and 3 times higher, respectively. This is clear because, under the indicated conditions, the pH value of the medium decreases from 7 to 4 [14], which accelerates the anodic process. The oxygen depolarization (Figs. 2a, b, curves 1) is replaced by the hydrogen depolarization (Figs. 2c, d, curves 2 and 3) as a result of the increase in the content of H^+ ions, which intensifies the rate of cathodic processes.

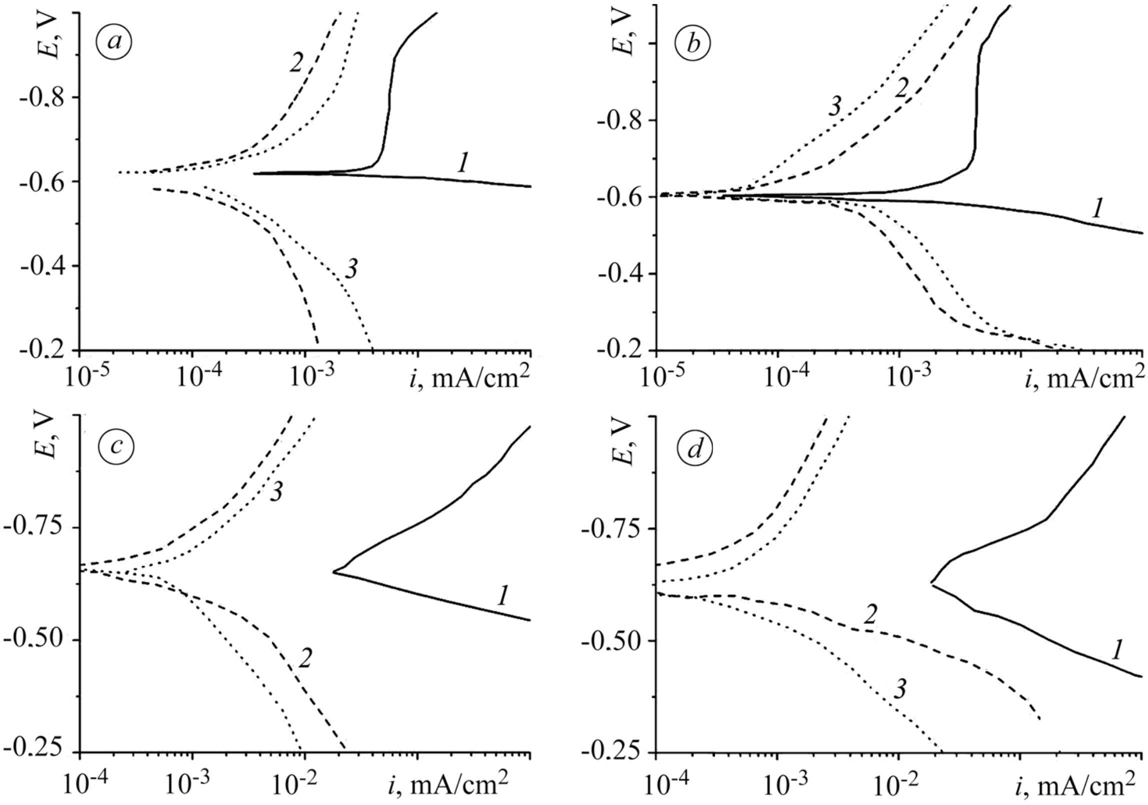

Fig. 2. Polarization curves of the as-received AMg5 and D16 alloys in a 3% NaCl solution without coating [(a, b): curve 1] and in a 3% NaCl solution saturated with hydrogen sulfide without coating [(c, d): curve (1)] and with coatings formed in electrolytes: (2) EL-1, (3) EL-2.

Table 2

Phase Compositions of the Coatings on AMg5 and D16 Alloys

AMg5		D16	
Composition	Content, wt.%	Composition	Content, wt.%
γ-Al_2O_3	42.00	α-Al_2O_3	17.48
Al	56.31	γ-Al_2O_3	73.29
Mg	1.69	Al	9.23

The corrosion rate of the specimens with PEO coatings decelerates due to a decrease in the contact area of the alloy with the medium, which is explained by their dielectric properties and through porosity. The corrosion potentials of specimens with and without coatings are practically identical, which confirms the same nature of corrosion processes (Table 3). Hence, the corrosion losses of the material of the specimens with coatings are lower by about two orders of magnitude than for the specimens without coatings, and the corrosion processes run in the pores.

The impedance studies reveal that the resistance of specimens with coatings increases after 20 days of holding in a 3% NaCl solution and remains constant for 150 days (Figs. 3a, c). This is caused by the closure of through

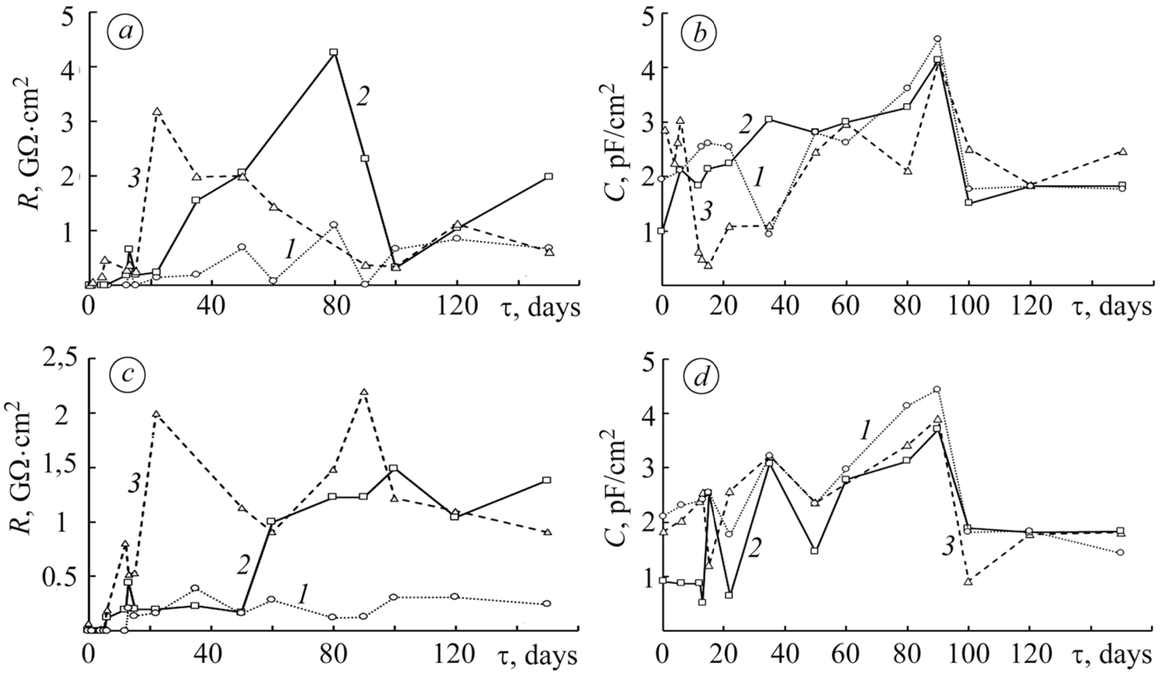

Fig. 3. Time dependences of the resistance and capacitance for the D16 (a, b) and AMg5 (c, d) alloys (3% NaCl solution) ($F = 1$ kHz): (1) as-received alloy; alloys with coatings formed in electrolytes: (2) EL-1, (3) EL-2.

Table 3

Potentials and Corrosion Currents for As-Received AMg5 and D16 Alloys and for the Corresponding Coatings Obtained in a 3% NaCl Solution Saturated with Hydrogen Sulfide

Alloy	E_{corr}, V	$I \cdot 10^3$, mA/cm^2
AMg5 – initial	– 0.620	4.571
AMg5, EL-1	– 0.624	0.110
AMg5, EL-2	– 0.622	0.126
D16 – initial	– 0.603	3.981
D16, EL-1	– 0.606	0.050
D16, EL-2	– 0.604	0.030
AMg5, H_2S(sat)	– 0.653	12.023
AMg5, EL-1 + H_2S(sat)	– 0.655	0.229
AMg5, EL-2 + H_2S(sat)	– 0.652	0.457
D16, H_2S(sat)	– 0.623	12.023
D16, EL-1 + H_2S(sat)	– 0.624	0.163
D16, EL-2 + H_2S(sat)	– 0.625	0.188

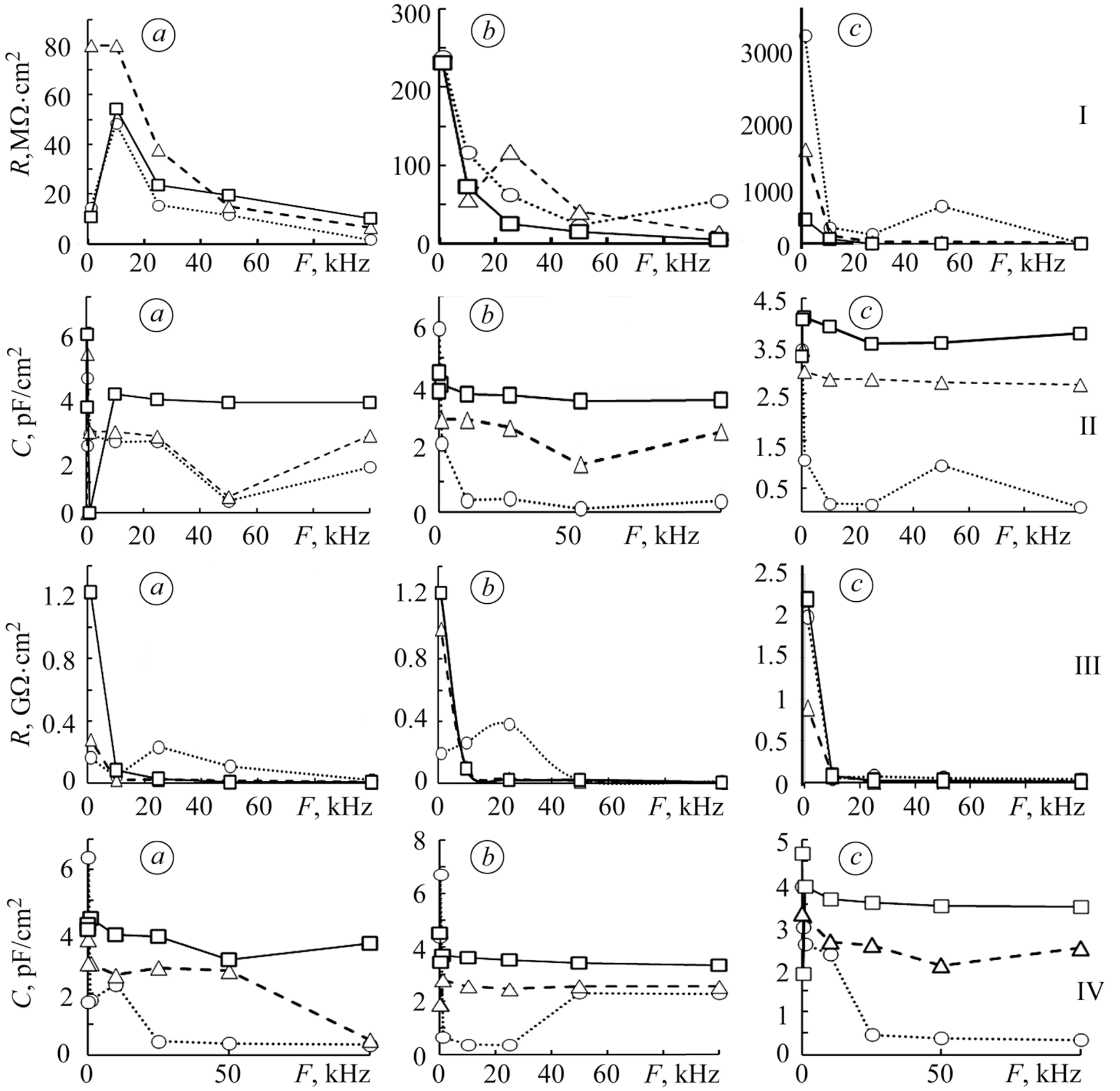

Fig. 4. Frequency dependences of the resistance and capacitance of the coatings on D16 (I, II) and AMg5 (III, IV) alloys in the course of holding in a 3% NaCl solution: (○) 20 days, (△) 60, (□) 90 days, respectively: (a) as-received alloy, (b, c) coatings formed in the EL-1 and EL-2 electrolytes, respectively.

pores by corrosion products according to the following mechanism [15–17]:

$$\mathrm{Al} + m\mathrm{H_2O} \rightarrow [\mathrm{Al(H_2O)}m]_{\mathrm{ads}}.$$

All coatings have almost identical protective properties and their resistance in a 3% NaCl solution is equal to 1–4 $\mathrm{G\Omega \cdot cm^2}$. Somewhat better impedance parameters are exhibited by D16 alloy. In the course of subsequent long-term holding of the coatings, we observe the inverse process.

If the resistance increases, the protective properties of the coatings are improved, and the protection of both alloys against corrosion is guaranteed. Due to the small area of pores ($0.5–1.5 \cdot 10^2$ μm²), the presence of corrosion products blocks the access to the base of alloys for the medium, thus improving the protective properties of the coatings. It is worth noting that the capacitance of continuous defectless protective coatings in the medium correlates with the degree of absorption of the aqueous medium by this coating and its destruction.

High protective characteristics of the proposed oxide-ceramic coatings on aluminum alloys ($F = 1$ kHz) are confirmed by comparing the dependences of capacitance of the time of holding in a 3% NaCl solution (Figs. 3b, d). The coatings synthesized in the EL-1 electrolyte after long-term holding (~ 150 days) have the lowest capacitance, which reflects their insignificant degradation and is in good correlation with high porosity. After a certain time, the capacitances of all oxide-ceramic coatings are stabilized and become equal to 1–4 pF/cm^2.

It was discovered that the capacitances of all coatings after the holding for different times in a 3% NaCl solution are practically independent of the AC frequency. It is clear that their barrier properties play an important role in this case. The high protective characteristics for the alloys were recorded after holdings for 20, 60, and 90 days (Fig. 4), which is confirmed by the linear dependences of the capacitance on the AC frequency. As the AC frequency increases, the resistances of coatings decrease, which reflects their improved protective properties.

In all cases (after holding for 20, 60, and 90 days), the resistances of the coatings insignificantly depend on the duration of the tests (Fig. 4), which correlates with the constant values of capacitance and shows that these coatings are quite promising for commercial applications.

CONCLUSIONS

By using the method of plasma-electrolytic oxidation, we synthesized oxide ceramic coatings on alloys of the Al–Cu–Mg and Al–Mg systems in electrolytes containing aqueous solutions of potassium hydroxide with an addition of water glass under the conditions of intense bubbling with ozone. The corrosion resistances of the coatings in a 3% NaCl solution and in the same solution saturated with hydrogen sulfide are determined. It is shown that the corrosion resistances of the alloys with coatings are higher by two orders of magnitude, and the corrosion processes run in the pores. The proposed coatings significantly increase the corrosion resistance of aluminum alloys. The results of impedance investigations confirm that their resistance increases after holding for 20 days in corrosive media and remain high for 150 days. This is caused by the phenomenon of closing of pores by corrosion products. All coatings have high resistances in a 3% NaCl solution. At the same time, their capacitance is stabilized and becomes equal to 1–5 pF/cm^2, which reflects high protective properties of the coatings.

In addition, it was discovered that the capacitance of the coatings is independent of the AC frequency for the durations of holding of 20, 60, and 90 days. It was established that the resistance decreases as the AC frequency increases. The oxide-ceramic coatings applied in electrolytes enriched with ozone have somewhat worse protective properties due to their higher porosity.

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