Corrosion properties of composite coatings on AMg3 alloy surface

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Abstract. Method of the composite polymer-containing coatings formation on the AMg3 aluminum alloy by plasma electrolytic oxidation (PEO) with the subsequent application of a polymer from the suspension of superdispersed polytetrafluoroethylene is presented. The optimal parameters such as a multiplicity of the application, the temperature and the time of heat treatment were determinate in order to obtain coatings with the highest protective properties. Composite layers significantly improve the anticorrosion properties of aluminum alloy, reducing corrosion current density by 2 orders of magnitude in comparison with the base PEO-coating. This makes it possible to significantly reduce the possibility of corrosion damage of the protective coating during operation, and, consequently, improve its reliability.

1. Introduction

Aluminum alloys as structural and functional metals have a number of technical and economic advantages, providing expediency of their use in aircraft, automotive and electronics industries [1–2]. The mechanical properties of a number of aluminum alloys are not inferior to the strength of steels, which makes it possible to reduce the metal consumption of the structure, facilitates the transportation of equipment, installation and repair work, etc.

However, aluminum alloys have a low corrosion resistance in some aggressive media [3–4]. One of the most promising methods of aluminum alloys protection is the application of coatings on their surface by plasma electrolytic oxidation (PEO), which allows to form anticorrosive coatings on the surfaces of metals and alloys [5–7]. Moreover, the convoluted and rough surface of the PEO-coating allows to form the composite polymer-containing layers in order to provide additional protection to products [8, 9]. Particular interest such polymer component of composite coatings (CC) are fluoropolymer compounds due to their unique resistance to various aggressive media.

Earlier, we developed methods of introducing polymers into the porous part of the PEO-coating, which made it possible to purposefully form composite protective layers using the suspensions of superdispersed polytetrafluoroethylene on a magnesium alloy [10, 11]. The use of the PEO-method and fluoropolymer materials with directed formation of composite coatings provides a number of advantages in comparison with other approaches. This expands the range of practical application of metals and alloys. In particular, improving of the electrochemical characteristics of the surface layers of the material is extremely useful for aluminum alloys.
In this paper, original methods for the formation of protective composite polymer-containing layers on the AMg3 aluminum alloy are presented.

2. Materials and methods
For the formation and investigation of CC the AMg3 aluminum alloy samples were used. Samples were in the form of rectangular plates with the size of 15 mm × 30 mm × 1 mm. Prior to oxidation all samples were mechanically treated with grinding paper with a sequential reduction of grain size down to 14 μm in order to remove burrs, outgrowths, and various defects from the metal surface, washed with distilled water and degreased with ethanol. This is necessary for standardizing the surface of the samples. As an electrolyte for PEO was used following aqueous solution: 0.6 g l⁻¹ NaF, 5 g l⁻¹ C₆H₇O₆K₂·0.5H₂O, 10 g l⁻¹ Na₂MoO₄·2H₂O, 10 g l⁻¹ Na₃BaO₂·10H₂O, and 10 g l⁻¹ Na₃PO₄·12H₂O. A 15% suspension of superdispersed polytetrafluoroethylene (SPTFE) in isopropanol was used to prepare a composite polymer-containing coating.

Formation of the PEO-coatings was carried out in a bipolar mode, including galvanostatic and potentiodynamic stages. During the PEO process, in the cathodic part at all stages the current density was equal to −0.1 A cm⁻². The anodic component was potentiostatically stabilized at a value of 30 V at the first stage. At the second stage, the anodic voltage was increased from 30 to 420 V. Then, at the third stage, the anodic component decreased from 420 to 230 V. The oxidation time was equal to 45 min. The PEO-layers were coated with a polymer by immersion in a suspension of SPTFE followed by heat treatment. The polymer was applied one- (CC-1x), two- (CC-2x), and threefold (CC-3x). Most homogeneous layer was obtained by the slow immersion, exposure to the solution for 10–15 s, and rapid withdrawal. An applied layer was predried at air for 20 min at 25 °C. Next step was a heat treatment at 350 °C during 15 min.

The surface morphology of formed coatings was investigated with the use of an Evex Mini-SEM scanning electron microscope (SEM) (Evex Analytical Instruments, USA).

The electrochemical properties of the coatings were studied using the VersaSTAT MC electrochemical system (Princeton Applied Research, USA). The measurements were carried out in a three-electrode cell at room temperature in a 3 wt. % NaCl solution. The niobium mesh covered with platinum was used as a counter electrode. The saturated calomel electrode (SCE) was used as a reference electrode. The exposed area of the sample was equal to 1 cm². The samples were kept in a solution for 30 min prior the start of the electrochemical tests to achieve steady state. The potentiodynamic polarization measurements were carried out at a scan rate of 1 mV s⁻¹.

To describe the experimental dependence of the current density I on the potential E, the Levenberg-Marquardt method was used (1) [12]:

\[ I = I_C \left( \frac{E - E_C}{\beta_a} + 10^{\frac{E - E_C}{\beta_c}} \right) \]  \hspace{1cm} (1)

This approach allows one to obtain the most precise calculated values of such parameters as corrosion potential \( E_C \), corrosion current density \( I_C \), the slope of the cathodic polarization curve \( \beta_c \), and the slope of the anodic polarization curve \( \beta_a \).

The polarization resistance \( R_p \) was determined in a separate experiment by potentiodynamic polarization of the sample in the potential range \( \Delta E = E_C \pm 20 \text{ mV} \) at a scan rate of 0.167 mV s⁻¹, in which the linear dependence \( I = f(E) \) is observed.

\( R_p \) values was calculated according to the equation (2):

\[ R_p = \frac{\Delta E}{\Delta I} \]  \hspace{1cm} (2)
3. Results and Discussion

The analysis of the SEM data indicates the developed morphology of the base PEO-layer (figure 1a). Pores and microdefects, which are a consequence of the sharp cooling of the microdischarge zone after its attenuation, are presented on the surface of the sample. After a single application of SPTFE, particles of this material appear on the surface of the PEO-coating; however, no significant changes in the morphology of the surface layer are observed (figure 1b). With an increase in the multiplicity of the treatment with organofluorine material up to two and three times, pores and defects are sealed, and a formation of the uniform polymer film is observed (figure 1c, d). After a twofold treatment with organofluorine material, an increasing of the thickness of the polymer-containing coating is observed (from 19 to 31 μm). It should be noted that there is no significant difference in morphological structure between polymer-containing layers with double and triple application of SPTFE.

![Figure 1 SEM-images of PEO-coating (a) and composite coatings with different multiplicities of treatment: CC-1x (b), CC-2x (c), CC-3x (d).](image-url)

Analysis of the experimental data obtained by the potentiodynamic polarization (table 1) indicates an increase in the protective characteristics of the formed polymer-containing layers in comparison with the base PEO-coating and the uncoated material. At a single treatment of the PEO-layer with a fluoropolymer material, the corrosion current density \( I_c \) is reduced by more than 28 times (table 1). Further, with increasing of the treatment multiplicity up to two, the corrosion current density \( I_c \) is reduced, and the polarization resistance \( R_p \) is increased by one order of magnitude (table 1). The highest protective characteristics is observed for CC-3x: for this coating the \( I_c \) values decreased by more than 4 and 2 orders of magnitude in comparison with the uncoated and PEO-coated materials, respectively.
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### Table 1. Corrosion properties of studied samples

| Sample                  | $E_C$ (V vs. SCE) | $I_C$ (A cm$^{-2}$) | $R_p$ (Ω cm$^2$) |
|-------------------------|-------------------|---------------------|------------------|
| Without coating         | −0.76             | 8.3×10$^{-6}$       | 0.5×10$^5$       |
| With PEO-coating        | −0.63             | 5.4×10$^{-8}$       | 1.0×10$^4$       |
| CC-1x                   | −0.64             | 1.9×10$^{-9}$       | 2.5×10$^7$       |
| CC-2x                   | −0.64             | 1.4×10$^{-10}$      | 3.2×10$^8$       |
| CC-3x                   | −0.61             | 2.3×10$^{-11}$      | 1.6×10$^9$       |

Such improvement in the protective properties of composite layers is associated with sealing of the pores and blocking of the defects in the PEO-coating with a polymer, as well as forming a uniform PTFE layer on the sample surface (figure 1). The higher protective characteristics of CC-3x in comparison with CC-2x results a more complete penetration of the polymer into the pores of the coating and increase of the thickness of composite layer from 31 to 35 μm with an increase in the number of the fluoropolymer material applied.

### 4. Conclusion

The method of composite polymer-containing coating formation on the AMg3 aluminum alloy by PEO and subsequent treatment with polymer have been developed. The protective properties of composite coatings are significantly higher than those of the base PEO-layer: the corrosion current density is decreased by more than 2 orders of magnitude. The presence of the chemically stable PTFE in the composition of polymer-containing coating increases the samples resistance to corrosion. The formed composite coatings have prospects for using in automobile and aircraft manufacture, electronics, and medicine.