

Changes in barrier properties of protective composite coatings on aluminum alloy during climatic testing

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Protection of aluminum and its alloys, which are prone to corrosion in halide-containing media, is an important scientific and sought after practical task [1]. The performed studies established a high level of protection provided by a composite coating (CC), where heterogeneous oxide layer is used as a matrix for the polymer layer on aluminum alloy AMg3 [2, 3]. However, the conditions of exploitation and electrochemical express-testing may vary significantly [4]. Therefore, it is necessary to verify the obtained parameters under appropriate exploitation conditions. In this regard, studies have been carried out on the evolution of electrochemical properties of the composite coatings during the 6 months of atmospheric testing.

Plasma electrolytic oxidation (PEO) of aluminum alloy AMg3 samples $(30 \times$ 30 × 2 mm) was carried out in bipolar mode for 15 minutes. The voltage during the anode period was equal to 540 V. During the cathodic period current density was maintained at $0.12 \,\text{A} \cdot \text{cm}^{-2}$. The duty cycle was equal to 1. The silicate electrolyte and mode led to formation of the layer with a complex morphology [1].

To form CC, superdispersed polythetrafluoroetylene (SPTFE) particles were added to the 6 % polyvinylidenefluoride (PVDF) solution in N-methyl-2-pyrrolidone in optimal proportions 1:5 [1]. Then the samples were dipcoated and dried at 65 °C for 3 h.

To study the dynamics of changes in electrochemical properties during testing for 6 months atmospheric corrosion, samples were installed at the Marine Corrosion Test Station of the Institute of Chemistry of FEB RAS, located on Russkiy Island, Rynda Bay. The morphology of the composite coatings was investigated by scanning electron microscopy (SEM) using equipment from Carl Zeiss Group. Electrochemical properties were investigated using ModuLab XM ECS.





Fig. 2. SEM-image of the composite coating after 6 months of the atmospheric exposure

SEM of the CC surface after 6 months of the atmospheric exposure is defects of the PEO-layer.

corrosion are presented on Table and Fig. 3. It is shown that the sample [1]. with CC has lowest corrosion current density $(2.9 \cdot 10^{-11} \text{ A} \cdot \text{cm}^{-2})$ compared to both samples bare AMg3 aluminum alloy substrate $(1.7 \cdot 10^{-5} \text{ A} \cdot \text{cm}^{-2})$ and with PEO-coating $(4.1 \cdot 10^{-9} \text{ A} \cdot \text{cm}^{-2})$. For sample with PEO-coating the corrosion current density during 6 months exposition is reduced by 20 times due to the sealing of its pores with corrosion products. Also, the corrosion current density for the sample with CC tested for 6 months is 2 orders of magnitude lower in comparison with the sample with PEO-layer and almost 6 orders of magnitude less than for bare AMg3 alloy.

Table. Electrochemical parametrs for the initial samples and after 3 and 6 months of the atmospheric exposure

Fig. 1. SEM-images of the composite coatings formed on the AMg3 aluminum alloy

Analysis of SEM-images of the PVDF composite coatings indicates that the covered of the polymer atop the PEO-layer leads to a significant increase in surface relief uniformity and a decrease in the number of microdefects and pores (Fig. 1). The study of the morphology of combined coatings allows us to conclude that an incorporation of fluoropolymer materials in a ratio of 1:1 does not lead to significant increase in surface uniformity. As the concentration of SPTFE microparticles in a PVDF solution increases, there is an increase in the uniformity of surface morphology and in the number of pores and microdefects filled with fluoropolymers. Moreover, when the proportion of PVDF and SPTFE reaches 1:3 and 1:4, the agglomeration of particles is observed, which leads to the formation of a multimodal surface presented in Fig. 2. It shows that SPTFE particles sealed the pores and roughness. However, when the ratio of PVDF to SPTFE reaches 1:5, the microparticles form large agglomerates, which probably better covers the The results of electrochemical studies of samples after atmospheric porous part of the PEO-layer and increases its anti-corrosion parameters



Sample	β _a [mV]	β _c [mV]	E _c [V vs. SCE]	l₀ [A·cm ⁻²]	R _P [Ω·cm ²]	Z f = 0.01 Hz [Ω·cm²]
AMg3 initial	17.5	154.8	-0.67	1.1.10-6	2.4·10 ⁴	2.9·10 ⁴
AMg3 after 3 mounth	7.6	207.9	-0.73	1.6·10 ⁻⁶	2.5·10 ³	2.0·10 ⁴
AMg3 after 6 mounth	11.2	179.3	-0.95	1.7·10 ⁻⁵	3.8·10 ²	7.3·10 ³
PEO initial	39.0	429.5	-0.87	8.4·10 ⁻⁸	1 .9 ∙10⁵	5.6·10 ⁶
PEO after 3 mounth	86.3	334.3	-0.79	6.9·10 ⁻⁸	4.3·10 ⁵	5.2·10 ⁶
PEO after 6 mounth	78.3	422.1	-0.69	4.2·10 ⁻⁹	6.8·10 ⁶	4.0·10 ⁶
CC initial	488.8	243.2	-0.59	7.5·10 ⁻¹²	3.9·10 ¹⁰	2.0·10 ¹⁰
CC after 3 mounth	279.3	416.4	-0.53	1.5·10 ⁻¹¹	4.9·10 ⁹	1.6·10 ¹⁰
CC after 6 mounth	305.0	302.3	-0.48	2.9·10 ⁻¹¹	2.3·10 ⁹	2.9·10 ⁹

Fig. 3. Evolution of the electrochemical properties for samples with polymer-containing coatings during atmospheric exposure

It has been established that CC provides reliable protection even after a long-term exposure, the difference in currents is half an order of magnitude. This result is ensured by the high stability of the polymeric materials used and the coating-matrix. The increase in protective parameters for the PEO-coating is explained by the sealing of its pores with corrosion products.

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