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

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Abstract: The paper reveals the changes in corrosion properties of the samples with composite coating subjected to atmospheric corrosion test for 6 months. Composite coating (CC) was formed by treatment of oxide layer obtained by plasma electrolytic oxidation (PEO) with suspension of superdispersed polytetrafluoroethylene microparticles (SPTFE) in polyvinylidenefluoride (PVDF). The corrosion current density was compared for the composite coatings, PEO-coated and untreated samples. It is shown that corrosion current density for the sample with CC tested for 6 months ($2.9 \cdot 10^{-11}$ A·cm^{-2}) is more than 3 orders of magnitude lower in comparison with the sample with PEO-layer ($3.5 \cdot 10^{-8}$ A·cm^{-2}) and almost 6 orders of magnitude less than for uncoated aluminium alloy ($1.7 \cdot 10^{-5}$ A·cm^{-2}).

Keywords: aluminum, protective coating, plasma electrolytic oxidation, composite coating, electrochemistry

Изменение барьерных свойств защитных композиционных покрытий на алюминиевом сплаве при климатических испытаниях

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Аннотация. В работе представлены данные, характеризующие динамику изменения коррозионных свойств образцов с композиционным покрытием, подвергнутых атмосферной коррозии в течение 6 мес. Композиционное покрытие (КП) формировали обработкой оксидного слоя, полученного плазменно-электролитическим оксидированием (ПЭО), суспензией микрочастиц ультрадисперсного политетрафторэтилена (УПТФЭ)

в поливинилиденфториде (ПВДФ). Проведено сопоставление полученных значений тока коррозии после 3 и 6 месяцев испытаний с соответствующими значениями для необработанного образца и образца с ПЭО-покрытием. Установлено, что барьерные свойства образца с КП более чем на 3 порядка выше по сравнению с образцом с ПЭО-слоем и почти на 6 порядков выше, чем у сплава без покрытия.

Ключевые слова: алюминий, защитное покрытие, плазменное электролитическое оксидирование, композиционное покрытие, электрохимия

Introduction

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 AMg3 aluminum alloy [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. For this purpose, as the most suitable for testing and evaluating the influence of these factors on the anti-corrosion properties of composite coatings the estimation of protective properties assessed via electrochemical study of samples subjected to atmospheric corrosion test for 3 and 6 months was performed.

Materials and Methods

Plasma electrolytic oxidation of AMg3 aluminum alloy samples with size of $30 \times 30 \times 2$ (mm)^3 was carried out in bipolar mode for 15 minutes. The voltage during the anodic period was increased from 30 to 540 V at a rate of 3.4 V/s. During the cathodic period current density was maintained at 0.12 A·cm^{-2}. The duty cycle was equal to 1. The silicate electrolyte (20 g/L Na$_2$SiO$_3$·5H$_2$O, 10 g/L Na$_2$B$_4$O$_7$·10H$_2$O, 2 g/L NaF and 2 g/L KOH) and polarization 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 [1]. Then the samples were dip-coated and dried at 65 ℃ for 3 h.

To study the dynamics of changes in electrochemical properties during the atmospheric corrosion, the samples were installed at the Marine Corrosion Test Station of the Institute of Chemistry of FEB RAS, located on Russkiy Island, Rynda Bay [5]. This water area has a salinity of seawater close to the average oceanic (34‰) and classifies according to ISO 9223:2012 as category C3, i.e. a marine environment with medium atmospheric corrosivity. Samples with size of $30 \times 30 \times 2$ (mm)^3 were exposed at an angle of 45 to the horizon on racks located about 20 m away from the coastline. The witness samples were taken after 3 and 6 months of field testing.

The morphology of the composite coatings was investigated by scanning electron microscopy (SEM) using Carl Zeiss EVO 40 microscope with an acceleration voltage of 20 kV.

Electrochemical properties were investigated using ModuLab XM ECS (Solartron analytical, Farnborough, UK). Measurements were carried out in a three-electrode cell in a 3 wt.% NaCl. Platinum mesh was used as a counter electrode, and saturated calomel electrode was used as a reference electrode. The exposed area of samples was equal to 1 cm². The samples were kept

in a solution for 60 minutes prior to electrochemical tests to achieve a steady state. To record the impedance spectrum, a sinusoidal signal with an amplitude of 10 mV (rms) was used. The experiments were carried out in the frequency range from 0.1 MHz to 0.01 Hz at a logarithmic sweep of 10 points per decade. The potentiodynamic polarization measurements were carried out at a scan rate of 1 mV·s^{-1} in the range from E_c −0.25 V to E_c +2 V, where E_c is the corrosion potential. The values of polarization resistance R_p were determined in separate experiments from the linear potential current density plot in range of $E_c \pm 20$ mV as the $R_p = \Delta E/\Delta j$.

Results and Discussion

Analysis of the SEM-images in Fig. 1 indicates that PEO-layer formed in the established oxidation mode and electrolyte, have a complex morphology. Application of PVDF solution with SPTFE microparticles atop the PEO-layer leads to a shielding of microdefects and pores and covers surface with uniformly distributed particles. PVDF solution embeds microparticles and provides adhesion to the PEO-coating.

Moreover, the microparticles form large agglomerates, which probably better cover the porous part of the PEO-layer and increase its anti-corrosion parameters [1].

SEM image of the CC surface after 6 months of the atmospheric exposure is presented in Fig. 2. Composite coating has high strength and resistance to temperature changes, as well as resistance to ultraviolet radiation and atmospheric precipitation. The SPTFE particles sealed the pores and defects, preventing pitting corrosion. At the same time, there are no defects in the PEO-coating, which, during 6 months of atmospheric corrosion, remained completely covered with a PVDF/SPTFE-layer.

In the investigated range of potentials, the potentiodynamic curve for an uncoated aluminum alloy is the typical for this material. After the cathodic part of the curve (Fig. 3), a breakdown of the natural oxide-hydroxide film occurs with a corresponding sharp increase in the current density during the development of the corrosion process. The potentiodynamic curves obtained for the coated samples are located in the zone of significantly lower currents compared to the curve for the uncoated alloy and demonstrate a significant inhibition of the corrosion process.
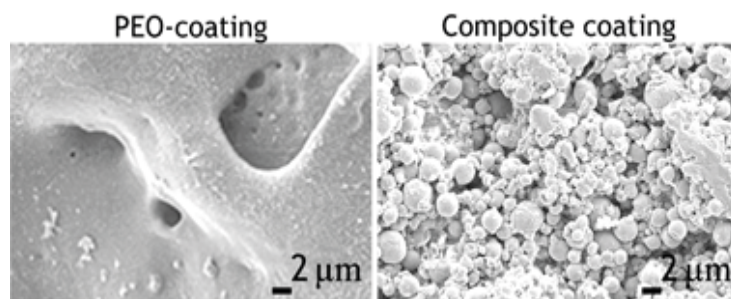

Fig. 1. SEM-images of the PEO and composite coatings
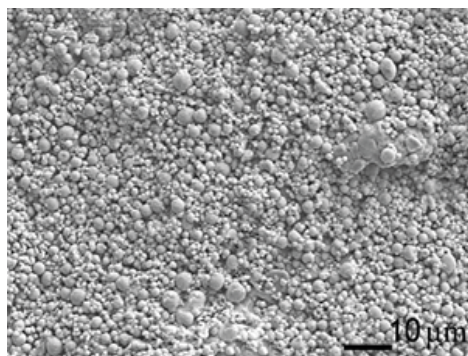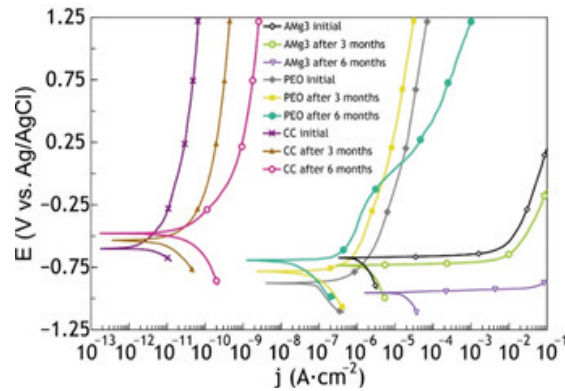formed on the AMg3 aluminum alloy

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

Fig. 3. Evolution of the electrochemical properties for uncoated, PEO-coated
and composite polymer contained AMg3 aluminum alloy during atmospheric exposure

Electrochemical studies of the samples found that the formed protective layers significantly reduce the corrosion current density.

Thus, for a sample with a composite coating, the corrosion current density is equal to $7.5 \cdot 10^{-12}$ A·cm^{-2}, which is more than 4 and 5 orders of magnitude lower than this parameter for the PEO-coated ($I_c = 8.4 \cdot 10^{-8}$ A·cm^{-2}) and for the uncoated AMg3 aluminum alloy ($I_c = 1.1 \cdot 10^{-6}$ A·cm^{-2}), respectively.

The composite coating has the highest barrier properties among the studied layers due to its multimodal textured surface (Fig. 1). According to the results of [6], the area of direct contact of such coatings with an aggressive medium, calculated using the Cassie-Baxter equation, is no more than 3% of the total area of the sample immersed in a chloride-containing media. The stable state of the entrapped air in the irregularities of the multimodal surface, which prevents the formation of a wetting film between the liquid and the developed surface of the coating, provides high anti-corrosion properties [6]. Therefore, a sample with a composite coating, having a multilevel relief formed by agglomerates of SPTFE microparticles, has a higher value of polarization resistance ($R_p = 3.9 \cdot 10^{10}$ Ω·cm^2) compared to samples without a coating ($R_p = 1.9 \cdot 10^5$ Ω·cm^2) and with a PEO-coating ($R_p = 2.4 \cdot 10^4$ Ω·cm^2).

The results of electrochemical studies of samples after atmospheric corrosion are presented in Table 1 and Fig. 3. For sample with PEO-coating, the corrosion current density during 6 months exposition is reduced by 2.5 times due to the sealing of its pores with corrosion products. Similarly, the polarization resistance increases for it (in 3 times). Also, the corrosion current density for the sample with CC tested for 6 months ($I_c = 2.9 \cdot 10^{-11}$ A·cm^{-2}) is 3 orders of magnitude lower in comparison with the sample with PEO-layer ($I_c = 3.5 \cdot 10^{-8}$ A·cm^{-2}) and almost 6 orders of

Table 1

Electrochemical parameters calculated for the samples without coating, with PEO-layer and composite coating before and after atmospheric corrosion test for 0, 3 and 6 months

Samples	β_a, mV	β_c, mV	E_c, V vs. SCE	I_c, A·cm^{-2}	R_p, Ω·cm^2
AMg3	17.5	154.8	−0.67	$1.1 \cdot 10^{-6}$	$2.4 \cdot 10^4$
AMg3 after 3 months	7.6	207.9	−0.73	$1.6 \cdot 10^{-6}$	$2.5 \cdot 10^3$
AMg3 after 6 months	11.2	179.3	−0.95	$1.7 \cdot 10^{-5}$	$3.8 \cdot 10^2$
PEO	39.0	429.5	−0.87	$8.4 \cdot 10^{-8}$	$1.9 \cdot 10^5$
PEO after 3 months	86.3	334.3	−0.79	$6.9 \cdot 10^{-8}$	$4.3 \cdot 10^5$
PEO after 6 months	78.3	422.1	−0.69	$3.5 \cdot 10^{-8}$	$5.7 \cdot 10^5$
CC	488.8	243.2	−0.59	$7.5 \cdot 10^{-12}$	$3.9 \cdot 10^{10}$
CC after 3 months	279.3	416.4	−0.53	$1.5 \cdot 10^{-11}$	$4.9 \cdot 10^9$
CC after 6 months	305.0	302.3	−0.48	$2.9 \cdot 10^{-11}$	$2.3 \cdot 10^9$

magnitude less than for uncoated AMg3 aluminum alloy ($I_c = 1.7 \cdot 10^{-5}$ A·cm^{-2}). The polarization resistance for this sample over the same period showed the value $2.3 \cdot 10^9$ Ω·cm^2, which is more than 3 orders of magnitude higher than one for sample with a PEO-layer ($R_p = 5.7 \cdot 10^5$ Ω·cm^2) and almost 7 orders of magnitude greater than for uncoated AMg3 aluminum alloy ($R_p = 3.8 \cdot 10^2$ Ω·cm^2).

Comparison of the corrosion current values obtained as a result of field tests (Table 1) with the literature data showed that after six months of exposure, both PEO ($I_c = 3.5 \cdot 10^{-8}$ A·cm^{-2}) and composite coating ($I_c = 2.9 \cdot 10^{-11}$ A·cm^{-2}) have higher barrier properties compared to other PEO coatings ($I_c = 3.9 \cdot 10^{-8}$ A·cm^{-2}) [5], ($I_c = 1.5 - 4.5 \cdot 10^{-6}$ A·cm^{-2}) [7], as well as composite coatings ($I_c = 7.6 \cdot 10^{-10}$ A·cm^{-2}) [7]. The initial values of corrosion current density for Alodine 1200s and PreCoat A32 chromium (VI) containing conversion coatings ($I_c = 8.0\text{-}9.5 \cdot 10^{-7}$ A·cm^{-2}) in the work [8] an order of magnitude higher compared to the values registered for the PEO-layer ($I_c = 8.4 \cdot 10^{-8}$ A·cm^{-2}) and 5 orders of magnitude higher than for the composite coating ($I_c = 7.5 \cdot 10^{-12}$ A·cm^{-2}). Even after 6 months of exposure the CC shows higher level of barrier properties ($I_c = 2.9 \cdot 10^{-11}$ A·cm^{-2}) in comparison with PTFE-containing IFKhANAL-3 conversion coating ($I_c = 1.0 - 2.0 \cdot 10^{-6}$ A·cm^{-2}) [9]. It can also be noted that the corrosion current density for the presented composite coating is one order of magnitude lower than estimated for the superhydrophobic coating formed by treatment of laser-processed aluminum alloy with fluorosilane ($I_c = 10^{-10} - 10^{-11}$ A·cm^{-2}) presented in [10].

Conclusion

It has been established that composite coating 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 both the polymeric materials and the PEO-coating used as the matrix. The increase in protective parameters for the PEO-coating is explained by the sealing of its pores with corrosion products.

Acknowledgments

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