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Influence of SPTFE on corrosion behavior of composite coatings during salt-spray test

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Abstract: Plasma electrolytic oxidation has been used to create a sublayer on aluminum alloy to form a composite coating to improve the corrosion properties of the processed material. The evolution of protective characteristics of the resulting coatings were examined by potentiodynamic polarization during the exposure in a salt spray chamber. The absence of pittings after a 10-day test for the entire series of composite coatings on aluminum alloy confirms the high level of barrier properties of the coated samples.

Keywords: plasma electrolytic oxidation (PEO), composite coating (CC), potentiodynamic polarization, salt spray testing

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Влияние УПТФЭ на коррозионное поведение композиционных покрытий при испытаниях в солевом тумане

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Аннотация. Плазменное электролитическое оксидирование использовали для создания подслоя на сплаве алюминия для формирования композиционного покрытия для улучшения коррозионных свойств обрабатываемого материала. Изменение защитных характеристик сформированных покрытий оценивали методом потенциодинамической поляризации в ходе проведения испытаний в камере соляного тумана. Отсутствие точечной коррозии после 10-дневного испытания для всей серии композиционных покрытий на сплаве алюминия подтверждает высокий уровень защиты, обеспечиваемый образцами с покрытиями.

Ключевые слова: плазменно-электролитическое оксидирование (ПЭО), композитное покрытие (КП), потенциодинамическая поляризация, испытания в камере соляного тумана

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Introduction

In order to provide protection against long-term corrosion, aluminum parts are coated by various protection methods: anodizing, painting, and others. Another modern method of corrosion protection is plasma electrolytic oxidation (PEO) [1,2]. However, such oxide layers possess a porous structure. Pores could be the pathway for corrosive media to the substrate. In order to overcome this drawback, a composite coating comprising a combination of paint applied to a PEO-coating could be formed. Additionally, the paint itself could be modified by different fillers aimed at providing new functional characteristics. Examples include biofouling coatings, which advance mainly in two directions: hydrophobic fouling-release and biocide-free coatings based on siloxanes and fluoropolymers that reduce the attachment of organisms, and antifouling systems, in particular, new environmentally friendly biocides with reduced toxicity and regulated leaching rates. To modify the paint, we have used the unique fluoropolymer material, superdispersed polytetrafluoroethylene (SPTFE) [3,4,5], which is a micropackage of nanofilms. Such coatings should possess high level of corrosion protection. Salt spray testing is an accelerated corrosion test that produces a corrosive attack to coated samples in order to evaluate the suitability of the coating. This paper reports on the evolution of electrochemical properties of a composite coating formed by spray coating of the PEO layer with the paint modified by SPTFE during salt spray testing.

Materials and Methods

Rectangular plates of the $AlMg_3$ aluminum alloy with size of the 50 mm×50 mm×2 mm were used for the experiments. all samples were subsequently ground with SiC sand papers from 120 to 1200 grit, washed with distilled water, air dried and degreased with alcohol.

Plasma electrolytic oxidation (PEO) is an electrochemical surface treatment process for generating oxide coatings on valve metals. Process of PEO was carried out in the electrolyte, containing 20 g/L $Na_2SiO_3 \cdot 5H_2O$, 10 g/L $Na_2B_4O_7 \cdot 10H_2O$, 2 g/L NaF, and 2 g/L KOH, dissolved in deionized water. All samples were processed in two stages in bipolar mode, with periodic alternation of cathodic and anodic pulses. At the first stage, the voltage in the anodic period increased from 30 to 540 V with a sweep rate of 3.4 V/s, and then the voltage value was fixed at 540 V for 750 s. In the cathodic period, the current was held at 6.5 A for 900 s. The duty cycle was equal to 1. The presented electrolyte composition and mode parameters allowed us to obtain thick surface layers with a developed surface [1].

On the formed PEO coating, 5 types of paints were applied by spraying. Jotun SeaForce 30 was chosen for modification. SPTFE was added to this paint in different concentrations from 0 to 20 wt.%. As a result, 5 composite coatings were obtained for further study.

Morphology of surface was investigated by a field emission scanning electron microscope (SEM) Sigma 300 VP (Carl Zeiss, Germany).

The electrochemical properties of the coatings were investigated 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% NaCl solution. A platinum-coated niobium mesh was used as a counter electrode, and a calomel electrode was used as a reference electrode. The working area of the sample was 1 cm^2. To establish the corrosion potential E_C the samples were kept in a solution for 30 min. Potentiodynamic measurements were carried out with a sweep rate of 1 mV/s.

Salt spray tests [5, 6, 7] were carried out in a salt spray chamber according to GOST 30630.2.5-2013. 5% solution NaCl was sprayed for 15 min every 45 min. The temperature in the S120 salt spray chamber (Ascott Analytical Equipment Ltd, UK) was maintained at 27 ± 2 ºC. The duration of the test was 10 days with an intermediate analysis after 4 days of exposure. Coatings were rinsed by deionized water and dried at room temperature for 120 min.

Results and Discussion

The morphology of the PEO coating and composite coatings is shown in Fig. 1.

Analysis of the surface morphology of the coatings (Fig. 1), the following can be noted: PEO coating has porous and convoluted morphology, which ensure stable adhesion with paint, sprayed paint without the addition of SPTFE and with 5% SPTFE has the same morphology, subsequent increase in the concentration of SPTFE leads to appearance of a large number of depressions, which, when the concentration of SPTFE is brought to 15%, begin to combine.

The formed PEO coating has a thickness of 45±5 μm (Fig. 2). The application of a paint on a PEO coating resulted in an increase in the coating thickness to 120±12 μm. Fig. 2 shows that paint fills the pores of the formed PEO coating.

The electrochemical characteristics of the studied samples were evaluated by potentiodynamic polarization. The polarization curves taken for the samples under study are presented in Fig. 3.

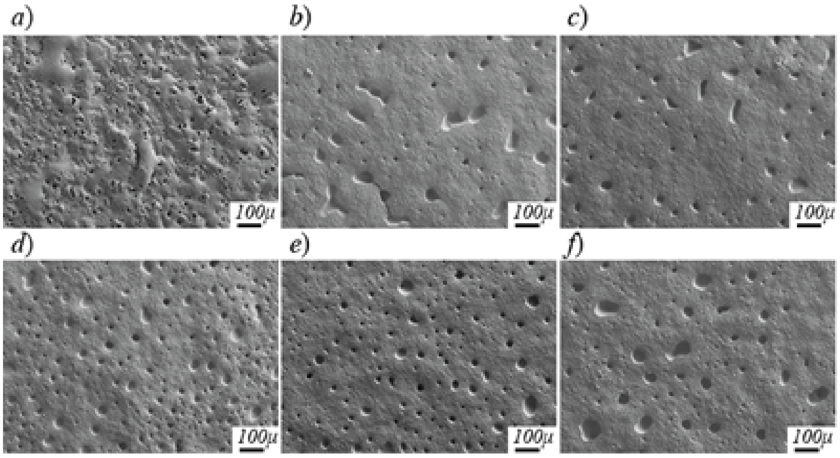

Fig. 1. Morphology of the studied coatings: PEO-coating (*a*), CC without SPTFE (*b*), CC with 5% SPTFE (*c*), CC with 10% SPTFE (*d*), CC with 15% SPTFE (*e*), CC with 20% SPTFE (*f*)

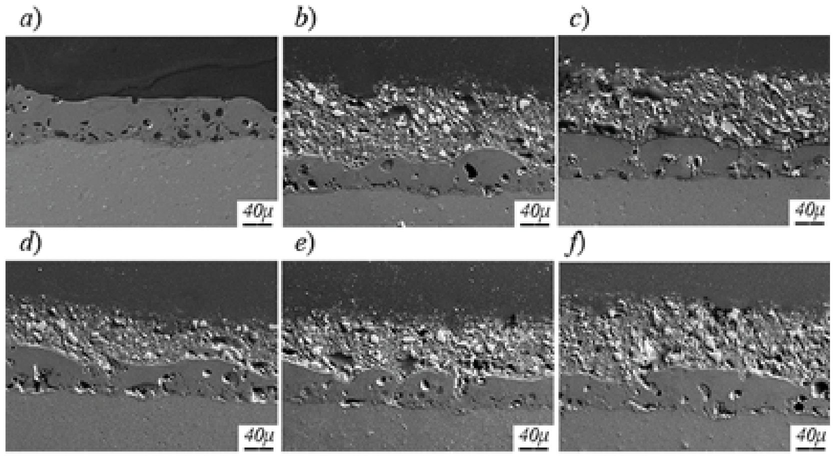

Fig. 2. Morphology of the studied coatings (sections): PEO-coating (*a*), CC without SPTFE (*b*), CC with 5% SPTFE (*c*), CC with 10% SPTFE (*d*), CC with 15% SPTFE (*e*), CC with 20% SPTFE(*f*)

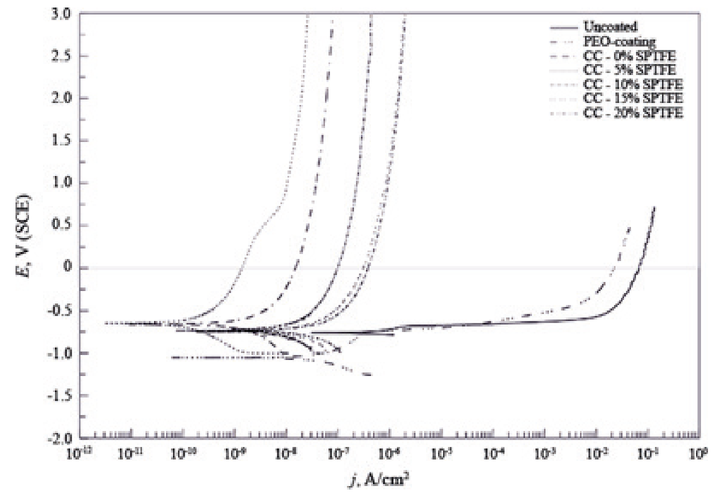

Fig. 3. Potentiodynamic polarization curves for the studied samples taken in 3% NaCl

Analysis of the data in Fig. 3 showed that all protective coatings have a lower corrosion current density compared to pure aluminum $AlMg_3$ ($3.47 \cdot 10^{-7}$). Composite coatings also showed increased barrier properties compared to PEO coatings ($4.80 \cdot 10^{-8}$). The lovest value of corrosion current density was demonstrated by the CC with the addition of 5% SPTFE to the paint ($1.88 \cdot 10^{-10}$). Relative to this CC, in both directions there is an increase in *y* by an order of magnitude without SPTFE in the coating ($1.56 \cdot 10^{-9}$) and with 10% SPTFE in the coating ($2.79 \cdot 10^{-9}$). A further increase in the concentration of SPTFE leads to another increase in the corrosion current density by one order of magnitude ($1.19 \cdot 10^{-8}$ for 15%, $1.95 \cdot 10^{-8}$ for 20%).

The appearance of the samples during testing changed as the aluminum alloy became covered with a corrosive film, the PEO coating became darker (initially light gray) due to water uptake but without visible corrosion damage, and the composite coatings remained unchanged.

Fig. 4 shows the bar graph with a change in the corrosion current density depending on the exposure time in the salt spray chamber.

It follows from analysis of the obtained electrochemical parameters that the sample with a composite coating with 5% SPTFE has the best characteristics. Fig. 4 shows that the corrosion current density did not change significantly over 10 days for this sample. The same changes are observed in the sample with a composite coating without SPTFE, but this coating initially has an order of magnitude higher corrosion current density (see Fig. 3). The remaining composite coatings have, on average, an increase in the corrosion current density by one order of magnitude (for a concentration of 10% SPTFE, it is slightly less, for a concentration of 20% SPTFE, more than one order of magnitude). We can assume from analyzing Fig. 4 that the barrier properties of the paint, with and without the addition of SPTFE, decrease with increasing exposure time in the salt spray chamber. However, due to the unchanged morphology with the addition of 5% SPTFE, it could be assumed that this coating will have better characteristics among the presented coatings and will be capable of withstanding approximately 30 days of exposure.

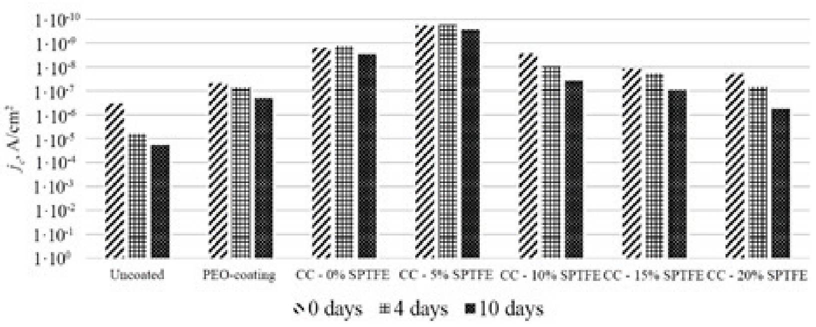

Fig. 4. Corrosion current density vs. exposure time in the salt spray chamber

Conclusion

As a result of the performed study, it was found that adding 5% of SPTFE to paint leads to a significant increase of the protective properties. Thus, the value of corrosion current density for this sample is more than three, two, and one order of magnitude lower compared to the uncoated sample, PEO-coating, and unmodified CC, accordingly. Despite the fact that appearance of the CCs remained unchanged, application of potentiodynamic polarization allowed to unveil the difference in the dynamics of changes in the electrochemical parameters of coatings during exposure. These data are explained by the fact that adding a small concentration (5% SPTFE) does not lead to a change in the morphology of the coating. According to the results of microscopic study, the number of pores increases with increased concentration, at the same time the values of corrosion current increase. We can thus conclude that an increase in concentration leads to a change in the structure (appearance of defects and pores) through which the saline solution penetrates more easily into the substrate.

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