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Evolution of tribological properties of the composite coatings on AMG3 aluminum alloy during the atmospheric exposure

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Abstract: The paper presents the results of an evaluation of the tribological characteristics of samples with composite coatings during 12 months of atmospheric corrosion. Composite coatings were obtained by treating oxide layer formed by plasma electrolytic oxidation (PEO) with fluoropolymers: superdispersed polytetrafluoroethylene (SPTFE) or polyvinylidene fluoride (PVDF), as well as a suspension of SPTFE in PVDF. It was found that the composite coatings formed in suspension with a ratio of PVDF to SPTFE 1:5 demonstrate the best tribological performance among the studied samples and characterizes by initial coefficient of friction 0.006–0.010. It is shown that samples with composite coatings have 1–1.5 orders of magnitude lower wear rate ($9.7 \cdot 10^{-5}$ – $4.4 \cdot 10^{-4}$ mm³/(N·m)), in comparison with the PEO-treated sample ($3.9 \cdot 10^{-3}$ mm³/(N·m)).

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

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Эволюция трибологических свойств композиционных покрытий на алюминиевом сплаве АМГЗ в процессе натуральных испытаний

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Аннотация. В работе представлены результаты оценки изменения трибологических характеристик образцов с композиционными покрытиями в течение 12 месяцев атмосферной коррозии. Композиционные покрытия формировали обработкой



оксидных слоев, получаемых методом плазменного электролитического оксидирования (ПЭО), фторполимерами: ультрадисперсным политетрафторэтиленом (УПТФЭ) или поливинилиденфторидом (ПВДФ), а также суспензией УПТФЭ в ПВДФ. Выявлено, что композиционные покрытия, формируемые в суспензии с соотношением ПВДФ и УПТФЭ 1:5 демонстрируют наилучшие трибологические показатели среди исследованных образцов, обладая начальным значением коэффициента трения равным 0,006–0,010. Установлено, что образцы с композиционными покрытиями характеризуются меньшей на 1–1,5 порядка величины ($9,7 \cdot 10^{-5} - 4,4 \cdot 10^{-4} \text{ мм}^3/(\text{Н} \cdot \text{м})$) скоростью износа в сравнении с ПЭО-покрытием ($3,9 \cdot 10^{-3} \text{ мм}^3/(\text{Н} \cdot \text{м})$).

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

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Introduction

The formation of wearproof protective surface layers on aluminum and its alloys is an important scientific and practical task. One of the possible ways to solve this problem is the creation of the composite polymer-containing coatings [1]. Plasma electrolytic oxidation (PEO) could be a suitable method to form the oxide matrix for such composite layers. The presence of CF_2 groups provides polytetrafluoroethylene with nonpolarity and both low surface energy and a low coefficient of friction [2, 3]. The performed research established the high level of protection provided by such coatings to aluminum alloy [4, 5]. For the layers formed using PVDF:SPTFE suspensions additional increase in barrier properties is provided by the multimodal surface relief formed by the SPTFE microparticles. This type of morphological structure is responsible for the appearance of a three-phase coating/air/electrolyte interface. This results in a low part of the surface (less than 3%) being in direct contact with corrosive medium [6]. However, it is necessary to verify the obtained parameters under appropriate exploitation conditions due to the fact that properties of the polymeric layers could be affected by the UV light. The paper presents the results of an evaluation of changes in the tribological characteristics of samples with composite coatings during 12 months of atmospheric corrosion. Composite coatings were formed by treating oxide layers obtained by plasma electrolytic oxidation (PEO) with fluoropolymers: superdispersed polytetrafluoroethylene (SPTFE) or polyvinylidene fluoride (PVDF), as well as a suspension of SPTFE in PVDF.

Materials and Methods

AMg3 aluminum alloy rectangular sheets with dimensions $50 \times 50 \times 2 \text{ mm}^3$ were used as samples to form the coatings.

For the formation of PEO-layers a two-stage bipolar mode was used. At the first stage the voltage during the anode period increased from 30 to 540 V at a rate of 3.4 V/s, and then during the second stage the voltage was maintained at 540 V for 750 s. In the cathodic period the current density was hold at 0.12 A/cm^2 for 900 s. The electrolyte contained 20 g/L $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$, 10 g/L $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, 2 g/L NaF and 2 g/L KOH. The presented electrolyte composition and mode polarization parameters allowed us to obtain thick surface layers with a developed surface.

In order to form composite coating on the sample with the PEO-layer by dip-coating method, the 15% suspension of SPTFE in isopropyl alcohol) was used (SPTFE sample). The samples were then

heat treated at 315 °C for 15 min to provide the best pores filling with a fluoropolymer material. The PVDF-layer was formed by immersing the sample in a 6% solution of polyvinylidene fluoride (PVDF sample) in N-methyl-2-pyrrolidone followed by drying at 70 °C for 2 h. To form PVDF/SPTFE-coating, SPTFE particles were added to the PVDF solution at a ratio 1:5 (PVDF:SPTFE 1:5 sample). Then the samples were dip-coated and dried at 65 °C for 3 h.

Thickness of the formed PEO and composite coatings was measured using a VT-201 eddy current thickness gauge (KID, Russia).

The atmospheric corrosion testing of the samples during one year exposure was carried out at the Marine Corrosion Test Station of the Institute of Chemistry of FEB RAS, located on Russkiy Island, Rynda Bay (Sea of Japan). 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. The samples were exposed at an angle of 45° to the horizon on racks located about 20 m away from the coastline. The samples were withdrawn from the test site after 3, 6 and 12 months of exposure.

Tribological tests were carried out using Tribometer (CSM Instruments, Switzerland) operated via InstrumX software. Tests were performed according to the “ball–disk” test scheme: Ø10 mm corundum ball at load of 10 N and a linear rotation speed of 50 mm/s was used as a counterbody. After tribological tests, the wear tracks were examined using the MetekSurtronic 25 profilometer and the wear rate was calculated using InstrumX software (CSM Instruments, Switzerland).

Results and Discussion

Fig. 1 shows the dependences of the coefficient of friction (COF) on the number of cycles for SPTFE-coated samples tested after atmospheric exposure. The data for uncoated aluminum alloy and PEO-coating are provided for comparison. For the AMg3 aluminum alloy, there is a sharp rise in the COF from 0.11–0.14 to 0.55–0.56, which was stable during the entire test at 100 cycles. The sample with 69 ± 6 μm thickness PEO-coating showed a slightly smoother rise in COF from 0.15–0.16 to 0.84 with a gradual decrease to 0.80 over 42,000 cycles at the moment of abrasion of the coating to the substrate, which is accompanied by a sharp drop in COF, tending to the level of the uncoated sample.

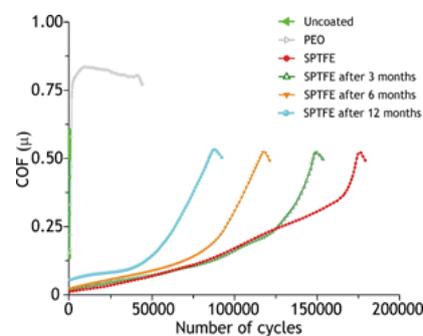


Fig. 1. Dependencies of the coefficient of friction on the number of cycles for uncoated samples, samples with PEO-coating and with SPTFE-coating during atmospheric corrosion

For samples with 70 ± 4 μm thickness PEO-coatings with SPTFE (Fig. 1), with 79 ± 3 μm thickness PEO-coatings with PVDF-film and with 82 ± 5 μm thickness with PVDF:SPTFE 1:5-layer (Fig. 2), there is a significant decrease in the coefficient of friction, in comparison with the sample with PEO-coating only. As both graphs show, in comparison with the PEO-layer, the composite coatings reduce the COF by 16–17 times. For samples with composite coatings before corrosion testing, the coefficient of friction was equal to 0.009 for SPTFE-layers, 0.019 for PVDF-layers and 0.006 for PVDF:SPTFE 1:5-coatings. As a result of exposure for 3–12 months the increase in the coefficient of friction is observed from 0.015 to 0.060 for SPTFE, from 0.03 to 0.04 for PVDF and from 0.007 to 0.010 for PVDF:SPTFE 1:5 samples.

The shape of the curves indicates that despite the tendency of tribological characteristics to decrease, the wear mechanism itself has not changed: it was uniform abrasion. However, after

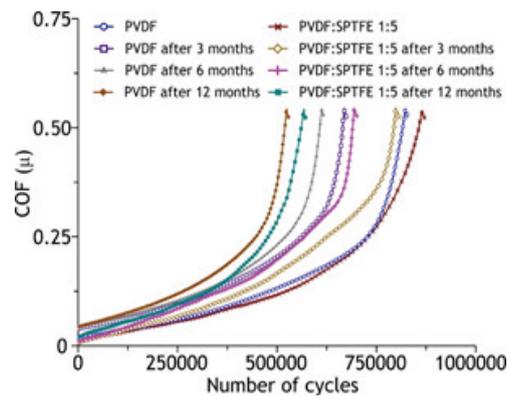


Fig. 2. Dependencies of the coefficient of friction on the number of cycles for PVDF and PVDF:SPTFE 1:5 samples during atmospheric corrosion test

12 months exposure to atmosphere, the smallest increase in the initial coefficient of friction from 0.01 to 0.02 was recorded only for the PVDF:SPTFE 1:5 sample (Fig. 2).

The results presented in Table 1 allow us to conclude that samples with composite coatings have 1 to 1.5 orders of magnitude lower wear rate ($9.7 \cdot 10^{-5} - 4.4 \cdot 10^{-4} \text{ mm}^3/(\text{N} \cdot \text{m})$), in comparison with PEO-treated ($3.9 \cdot 10^{-3} \text{ mm}^3/(\text{N} \cdot \text{m})$) and uncoated aluminum alloy samples ($5.8 \cdot 10^{-3} \text{ mm}^3/(\text{N} \cdot \text{m})$).

The SPTFE sample showed the highest wear ($4.4 \cdot 10^{-4} \text{ mm}^3/(\text{N} \cdot \text{m})$) among the samples with polymer layers, due to the peculiarities of its preparation and smaller thickness, in comparison with PVDF and PVDF:SPTFE 1:5 samples ($2.2 \cdot 10^{-4} \text{ mm}^3/(\text{N} \cdot \text{m})$ and $1.1 \cdot 10^{-4} \text{ mm}^3/(\text{N} \cdot \text{m})$), respectively.

Table 1

Number of cycles and wear rate for the samples under study after the atmospheric corrosion test for 0, 3, 6, 12 months

Samples	Number of cycles ($\times 10^3$)*				Wear rate, $\text{mm}^3/(\text{N} \cdot \text{m})$			
	0	3	6	12	0	3	6	12
Uncoated	0.1	—	—	—	$5.8 \cdot 10^{-3}$	—	—	—
PEO	42	—	—	—	$3.9 \cdot 10^{-3}$	—	—	—
SPTFE	174	149	117	86	$4.2 \cdot 10^{-4}$	$4.2 \cdot 10^{-4}$	$4.3 \cdot 10^{-4}$	$4.4 \cdot 10^{-4}$
PVDF	823	669	614	525	$1.2 \cdot 10^{-4}$	$1.8 \cdot 10^{-4}$	$1.9 \cdot 10^{-4}$	$2.2 \cdot 10^{-4}$
PVDF:SPTFE 1:5	864	802	694	565	$9.7 \cdot 10^{-5}$	$9.7 \cdot 10^{-5}$	$9.9 \cdot 10^{-5}$	$1.1 \cdot 10^{-4}$

Note. The number of cycles was fixed until the coating was abraded to the substrate.

Conclusion

Evolution of tribological properties of the composite coatings on AMg3 aluminum alloy during one year of atmospheric corrosion tests. The least increase of the rate wear is observed for the SPTFE sample (from $4.2 \cdot 10^{-4}$ to $4.4 \cdot 10^{-4} \text{ mm}^3/(\text{N} \cdot \text{m})$), which is associated with its lower thickness compared to PVDF and PVDF:SPTFE 1:5 samples. For the last two CCs, having similar thickness, the rate wear increased from $1.2 \cdot 10^{-4}$ to $2.2 \cdot 10^{-4} \text{ mm}^3/(\text{N} \cdot \text{m})$ and from $9.7 \cdot 10^{-5}$ to $1.1 \cdot 10^{-4} \text{ mm}^3/(\text{N} \cdot \text{m})$, respectively. Such a decrease in characteristics may be associated with some degradation of the polymer layer (due to exposure to solar radiation, temperature changes, penetration of a corrosive medium into coating microdefects). At the same time, it should be noted that the coating formed using SPTFE microparticles not only demonstrated the highest wearproof, but also the here smallest decrease.

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