Multifunctional coatings formed using organic and inorganic nanomaterials

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Abstract. The method of forming composite coatings by the plasma electrolytic oxidation (PEO) using organic and inorganic nanoscale materials is presented. The effect of the incorporated components on the protective properties of the obtained surface layers was studied. It is established that the presence of nanomaterials in the composition of composite coatings makes it possible to reduce the corrosion current density by 4 orders of magnitude in comparison with the base PEO layer. The data of tribological studies confirm a significant increase in the wear resistance of coatings (by 2-4 orders of magnitude). The presence of hydrophobic substances in the composition of composite coatings in combination with the formation technique allows to impart high hydrophobic properties to composite coatings.

1. Introduction
At present, in various industries alloys of such non-ferrous metal as magnesium are increasingly used as structural and functional materials (aircraft manufacturing, automotive industry, medicine, as well as the energy industry) [1]. Due to the combination of ease of processing, low specific density, acceptable strength characteristics, alloys of this non-ferrous metal have several advantages over many structural and functional materials [2]. Such advantages are the reduction in the cost of the final product (due to the ease of processing), the possibility of reducing the mass of the final product (due to the low specific density), etc.

However, magnesium and its alloys also have a number of drawbacks that significantly limited their scope of application. Due to the low stability of the natural oxide film on the surface, magnesium and its alloys are easily destroyed in a corrosive environment [3]. Additionally, magnesium alloys are highly susceptible to wear during the friction due to their low hardness [4].

Today there is an extensive set of protection methods against the effects of negative destructive factors. Thus, in most cases, to reduce corrosion losses in industry, reagent methods for treating a corrosive medium are used, for example, by adding inhibitors [5]. The formation of surface layers, as a way of protecting metals and alloys, has high efficiency, simplicity and versatility, eliminates the use of inhibitors and other reagents for treatment of aggressive environments [6, 7].

Among modern effective methods for producing protective coatings, plasma electrolytic oxidation (PEO) can be distinguished. The surface layers formed by the PEO method on valve metals such as magnesium, aluminum, and titanium, as well as their alloys, increase the protective properties of the material, such as corrosion resistance, wear resistance, and thermal stability [8, 9]. One of the
significant advantages of this method is that the electrolytes used to form coatings are environmentally friendly, thereby significantly reducing the risk of environmental pollution. An additional advantage of PEO layers is the presence of pores in the outer part of the coating and the developed surface structure, which allows them to be used as the basis for creating composite coatings (CC), for example, as a result of incorporation into the pores of the surface layer and application of various nanopowders (TiO₂, TiN, SiO₂, ZrO₂, etc.) and polymers to the rough heteroxide surface [10–16]. Such hybrid coatings have enhanced protective characteristics and versatility compared to the base PEO layers [17]. Composite coatings give the surface of materials such functional properties as low wettability, self-cleaning, anti-friction and anti-icing properties.

This work is a compilation of our studies of formation of composite layers using nanomaterials. It presents the results of studies on the formation of composite coatings by the PEO method with the use of various nanoscale substances, as well as the results of tests of coatings for anticorrosion properties, wear resistance and wettability.

2. Materials and methods

2.1. Samples

The MA8 magnesium alloy (Mg–Mn–Ce system, 1.30 wt. % Mn; 0.15 wt. % Ce; balance: Mg) was used as material for the manufacture of the studied samples. The samples for the experiments were rectangular plates with the size of 15 mm × 30 mm × 1 mm. Before oxidation, all samples were grinded sequentially with sand papers with a decrease in grain size to 14 μm, washed with distilled water and degreased with alcohol.

2.2. Coatings formation

In this work, nanoparticles of silicon dioxide (SiO₂) and zirconium dioxide (ZrO₂) were used as inorganic nanomaterials for the formation of composite coatings.

Organofluorine materials such as superdispersed polytetrafluoroethylene (SPTFE) and telomers of tetrafluoroethylene (TFE) were used to form composite layers with organic components.

Depending on the applied nanomaterials, the methods for incorporating them into the base PEO layer were changed. Thus, inorganic substances were embedded directly in the process of plasma synthesis from specially developed electrolytic systems. Upon obtaining of polymer-containing coatings, organofluorine materials were incorporated at the second stage of coatings formation by dip-coating of samples in special dispersed systems with subsequent heat treatment. Heat treatment was carried out at 300 °C for CC obtained using TFE telomers and 315 °C for CC obtained using SPTFE. The aim of the heat treatment is to study the incorporation of the molten polymer deeper into the pores and strong connection of polymer with walls of pores of the base PEO layer, and, thus, to form a composite coating.

Base PEO coating was obtained using an aqueous solution of sodium silicate and sodium fluoride (15 g/l Na₂SiO₄ and 5 g/l NaF) in two stages in the bipolar mode, in which the anodic pulses periodically alternate with cathodic ones. The control over the PEO process was carried out using an automatic system coupled with a computer with the appropriate software. A reversing thyristor rectifier was used as a power supply. At the first stage, the anodic part voltage was increased from 30 to 240 V at a sweep rate of 1.05 V/s; the cathodic component was fixed in the potentiostatic mode at a value of –40 V. At the second stage, the voltage was changed in the anodic component from 240 down to 200 V at a sweep rate of 0.07 V/s, in the cathodic one from –40 up to –10 V at a sweep rate of 0.05 V/s. The duration of the first stage of the PEO process was equal to 200 s, while for the second one it was equal to 600 s. The duration ratio of the anodic and cathodic pulses was equal to 1, i.e. the duty cycle was 50%. The polarization frequency was 300 Hz. During the oxidation process, the electrolyte temperature (8±1 °C) was controlled using a ChillerSmart H150-3000 cooling unit (LabTech Group, UK).
2.3. Coatings analysis

The surface morphology of the samples were studied using an Evex Mini-SEM scanning electron microscope (SEM) (Evex Analytical Instruments, USA).

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 cm². To establish the corrosion potential $E_C$ before starting the electrochemical measurements, the samples were kept in solution for 30 min. Potentiodynamic measurements were carried out with a sweep rate of 1 mV/s.

The wear resistance of the protective coatings was studied on the TRB-S-DE tribometer (CSM Instruments, Switzerland) using an Al₂O₃ corundum ball with a diameter of 10 mm at constant sliding speed and load (50 mm/s and 10 N, respectively) with the subsequent determination of the depth of the wear track and the calculation of the degree of wear of the surface layers. The diameter of the track was 10 mm.

The wettability of the obtained coatings was evaluated by measuring and analyzing the contact angle of the drop applied to the test surface using a microsyringe on a DSA100 analyzer (KRÜSS, Germany). A 3% NaCl solution was used as a test fluid for measuring the contact angle. To calculate the contact angle, the Young-Laplace method was used, which allows one to take into account the gravitational distortions of the drop contour formed under its own weight [18].

3. Results and discussion

An analysis of the data of scanning electron microscopy clearly demonstrates the significant influence of the embedded nanomaterials on the structural features of the coatings (Figure 1).

The formed PEO coatings are characterized by a developed surface morphology, the presence of pores and microdefects, which is a consequence of the sharp cooling of the breakdown zone after attenuation of the plasma discharge and gas evolution during oxidation (Figure 1(a)).

The incorporation of ZrO₂ and SiO₂ nanoparticles into the composite layer significantly reduced the number of such defects (Figure 1(b),(c)) as result of the filling of pores in the coating with nanoparticles (Figure 1(b),(c)).

Application of TFE telomeres on the surface of the sample led to a similar result. However, the surface layer formed as a result of the use of telomeres has a significantly more uniform surface, both in comparison with the base PEO coating and with composite coatings obtained using inorganic nanoparticles (Figure1(a–d)).

Note that the introduction of superdispersed polytetrafluoroethylene into the composition of composite coatings made it possible to obtain a practically defect-free coating with a uniform surface structure (Figure1(e)).

The corrosion properties of the samples were investigated by the potentiodynamic polarization method (Table 1). Note that the formation of a PEO coating on the surface of a magnesium alloy reduced the corrosion current density $I_C$ and increased the polarization resistance $R_P$ (Table 1), which can significantly reduce the corrosion of the processed material. Evaluation of the data of electrochemical tests indicates a positive effect of the incorporation of ZrO₂ and SiO₂ nanoparticles into the composition of the composite coating (Table 1). The formed coatings reduced the corrosion current density and increased the polarization resistance by more than 3 times in comparison with the base PEO layer (Table 1). According to the presented data, CC with TFE telomeres reduced the corrosion current density by more than 39 times in comparison with PEO coating (Table 1). The highest protective properties were obtained by the samples, in composition of which was SPTFE. For these polymer-containing layers, the corrosion current density decreased and the polarization resistance increased by more than 6 orders of magnitude compared with uncoated magnesium alloy and by more than 4 orders of magnitude compared with the base PEO coating (Table 1). An increase in the protective properties of samples is a consequence of a lower porosity of composite coatings in
comparison with base PEO layers due to the embedding of nanomaterials in their composition (Figure 1).

![SEM images of a PEO coating (a) and composite coatings obtained using ZrO₂ (b) and SiO₂ (c) nanoparticles, TFE telomeres (d) and SPTFE (e).](image)

**Figure 1.** SEM images of a PEO coating (a) and composite coatings obtained using ZrO₂ (b) and SiO₂ (c) nanoparticles, TFE telomeres (d) and SPTFE (e).

According to the analysis of the data presented in Table 2, applying a PEO layer on a magnesium alloy can reduce wear by 2 times. The formation of composite coatings using inorganic nanopowders significantly increased the wear resistance of the samples (by more than 2 orders of magnitude in comparison with PEO coating). This increase in wear resistance is due to the presence of hard ZrO₂ or SiO₂ nanoparticles in the composition of composite coatings (Figure 1(b),(c)), which increase the wearproof of the coatings. The application of polymer-containing layers to the base PEO coating also positively affects the wearproof of the samples. Thus, the incorporation of TFE telomeres into the coating allowed reducing wear by more than an order of magnitude (Table 2). The highest wear resistance was demonstrated by the layers obtained using SPTFE. These coatings reduced wear by more than 3 orders of magnitude compared to the base PEO layer (Table 2).
Table 1. Corrosion properties of the studied samples.

| Coating type                        | $E_C$ (V vs. SCE) | $I_C$ (A/cm$^2$) | $R_P$ (Ω·cm$^2$) |
|-------------------------------------|------------------|------------------|------------------|
| Without coating                     | $-1.61$          | $5.3 \times 10^{-5}$ | $0.7 \times 10^3$ |
| PEO coating                         | $-1.51$          | $2.5 \times 10^{-7}$ | $1.1 \times 10^5$ |
| CC with ZrO$_2$ nanoparticles       | $-1.42$          | $5.3 \times 10^{-8}$ | $4.9 \times 10^5$ |
| CC with SiO$_2$ nanoparticles       | $-1.50$          | $8.2 \times 10^{-8}$ | $3.2 \times 10^5$ |
| CC with TFE telomeres               | $-1.37$          | $6.3 \times 10^{-9}$ | $8.7 \times 10^5$ |
| CC with SPTFE                       | $-0.95$          | $5.4 \times 10^{-11}$ | $1.7 \times 10^9$ |

In the case of using organofluorine materials, an increase in wearproof is a consequence of the embedding of fluoropolymers into the coating composition (Figure 1(d),(e)), which have their own low coefficient of friction and give antifriction properties to the surface.

Table 2. Wearproof and wettability of the studied samples.

| Coating type                        | Wear $(\text{mm}^3 \times (\text{N} \times \text{m})^{-1})$ | Contact angle (°) |
|-------------------------------------|---------------------------------------------------------|-------------------|
| Without coating                     | $3.8 \times 10^{-3}$                                   | $38 \pm 1$        |
| PEO coating                         | $1.7 \times 10^{-3}$                                   | $49 \pm 2$        |
| CC with ZrO$_2$ nanoparticles       | $2.9 \times 10^{-5}$                                   | $52 \pm 2$        |
| CC with SiO$_2$ nanoparticles       | $3.5 \times 10^{-5}$                                   | $47 \pm 2$        |
| CC with TFE telomeres               | $1.5 \times 10^{-4}$                                   | $138 \pm 2$       |
| CC with SPTFE                       | $7.6 \times 10^{-7}$                                   | $140 \pm 1$       |

Evaluation of the wettability of the samples revealed that the formation of CC using nanopowders does not significantly affect the contact angle (CA) of the coating (Table 2). However, polymer-containing layers demonstrated an increase in CA by more than 89° in comparison with the base PEO layer, and showed high hydrophobic properties (Table 2). This is due to the presence of a fluoropolymer in the composition of the composite coatings (Figure 1(d),(e)), which has a low surface energy and, thereby, reduces wettability.

4. Conclusions
Multifunctional composite coatings were formed on MA8 magnesium alloy by plasma electrolytic oxidation using inorganic and organic nanomaterials.

The coatings obtained using SPTFE reduced the corrosion current density by more than 4 orders of magnitude compared to the base PEO layer and by more than 6 orders of magnitude compared to an uncoated magnesium alloy.

Composite coatings obtained using SPTFE reduced wear by more than 4 orders of magnitude compared to the base PEO coating.

Composite coatings obtained using organofluorine substances have hydrophobic properties that are close to superhydrophobic: the contact angle attained to 138 for CC obtained using TFE telomers and 140° for CC obtained using SPTFE.

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