COMPOSITE POLYMER-CONTAINING COATINGS ON MAGNESIUM ALLOYS FOR INDUSTRY APPLICATION

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Abstract: Modification of magnesium alloys for formation of composite coatings by plasma electrolytic oxidation (PEO) and subsequent treatment in suspension of the superdispersed polytetrafluoroethylene (SPTFE) or telomeric solution of tetrafluoroethylene (TFE) are discribed. Composite coatings have been obtained by dipping with subsequent heat treatment. Electrochemical properties and wettability of protective composite coatings have been investigated. Composite coatings formed on PEO-layer by fourfold treatment of samples in SPTFE suspension possess best protective properties. The obtained coatings increase impedance modulus $(1.9 \times 10^9 \ \Omega \ cm^2)$ by orders of magnitude in comparison with unprotected magnesium alloy and base PEO-coating. The highest value of contact angle (CA) have been obtained for coatings with triple application in telomeric solution. CA for such composite coatings attains to $171 \pm 2°$, as result of multimodal roughness of the composite coating's surface.

INTRODUCTION

Today magnesium alloys are used increasingly in industries such as aviation, automotive, producing of high-tech devices and in their components (1, 2). However, low corrosion and wear resistances substantially restrict the application field of these promising materials. Despite the presence of native oxide film at the Mg surface, protective properties of this film are not sufficient to decrease corrosion destruction during exploitation. One of the most effective ways to increase the corrosion and wear resistance of Mg and its alloys is to form a coating on the surface to protect the base metal from the aggressive environment (3). The work (3) describes the main methods of forming coatings (by electrochemical plating, producing conversion coatings, anodizing, etc.).

One of the possible ways to protect magnesium alloys from the negative impact is the fabrication of coatings by plasma electrolytic oxidation (PEO) (4–6). PEO is the method of coatings formation, which is based on electrochemical and plasma-chemical synthesis of the coating's material (4). The PEO-coatings are produced under the high voltage AC, DC or bipolar polarization of the substrate in different electrolytes. During PEO process components of electrolyte are transported in the plasma discharges channels to the substrate surface, interact with the material of substrate, as a result coating, containing electrolyte's and substrate's components, is formed. Coatings processed by PEO have a number of useful characteristics, such as corrosion and wear resistance, thermal stability, high adhesion to the substrate,

etc. (7–9). In addition, PEO-method allows forming on the magnesium alloy protective layers, which have a convolute and rough surface (7, 10, 11). Such structure can be serving as a basis for application the polymeric materials on the PEO pretreated surface in order to provide the additional protection for the processed alloys and metals (12, 13).

Various types of organofluorine materials are suitable to be used as component of composite polymer-containing coatings, for their chemical durability, low friction coefficient, high electroinsulating properties, and performance over wide ranges of low and high temperatures (14–17). In addition, some types of those materials are hydrophobic and can used to create surfaces with high hydrophobicity, i.e., with contact angles within the range 120°–150° or greater. However, problem of forming multifunctional (hydrophobic, corrosion resistant) composite layers using organofluorine materials on the magnesium alloys are not resolved, that is due to the complexity of formation of such composite systems.

In previous study, we consider composite coatings obtained by triboelectrical method using superdispersed polytetrafluoroethylene (16). These coatings showed higher protective properties in comparison with the base PEO-layers. This article presents the results of investigation of protective properties of composite coatings (CC) obtained on magnesium alloys using of various organofluorine materials: superdispersed polytetrafluoroethylene (SPTFE) and tetrafluoroethylene (TFE) telomeres by dip-coating with subsequent heat treatment. Furthermore, in the article we investigate a new composite coating obtained using solution of TFE telomeres that has significant perspective as protective layer as well as composite coatings obtained using new developed SPTFE suspension.

MATERIALS AND METHODS

Samples

Rectangular plates (30 mm × 15 mm × 1 mm) prepared from MA8 magnesium alloy (belongs to system Mg-Mn-Ce: 1.30 wt. % Mn; 0.15 wt. % Ce; balance – Mg) were used as samples. The base coating was formed by PEO method in the water solution containing 15 g l^{-1} sodium orthosilicate and 5 g l^{-1} sodium fluoride. The process of coating formation was realized using the tyristor rectifier as a power supply. Coatings were fabricated in a bipolar PEO mode. During this mode the coatings formation process was performed using the bipolar pulse packets with periodically alternated anodic and cathodic signals. According to preliminary results and our previous study (18), the application of cathodic component allows obtaining microdischarge with high power and as result the formation of a thicker coating. In the first step of the bipolar mode, the anodic current density was specified of 0.61 A cm^{-2} (under increasing voltage up to 270 V). Cathodic component was maintained potentiostatically at –40 V. In the second step, the voltage was gradually decreased down to 200 V in the anodic part and up to –10 V in the cathodic one. The duration of the first and second phases of the PEO was equal to 200 s and 600 s, respectively.

TFE telomeric solution (trademark Cherflon®) (19) and suspension of SPTFE (trademark Forum®) (20) were used as fluoropolymer materials for formation of composite coatings. The polymer was deposited by dipping of the sample with PEO-coating in different suspensions for 10–15 s. After application, the samples were dried for 20 min at 25 °C in the ambient conditions. Next step was a heat treatment at 275 °C for coatings, which were obtained by application of telomeric solution

(hereinafter CC-1). This temperature was chosen as an optimal one for obtaining multimodal roughness of the surface. According to previous our work (21) such kind of the surfaces have superhydrophobic properties, that in turn increases protective characteristics of coatings. The optimal multiplicity of the processing was chosen empirically and it was equal to three. For composite coatings, which were obtained with application of SPTFE, the temperature of heat treatment was equal to 315 °C and the multiplicity of the processing was fourfold (hereinafter CC-2).

The cross-section of the composite coatings were studied using a scanning electron microscope (SEM) EVO 40 (Carl Zeiss, Germany).

At least three samples have been used for each measurement. In addition, all the results were statistically processed; the standard deviation does not exceed 5 %.

Electrochemical Measurements

Electrochemical properties of coatings were investigated using electrochemical system VersaSTAT MC (Princeton Applied Research, USA). Measurements were carried out in a three-electrode cell in a 3 % sodium chloride solution at room temperature (25±1 °C). Faraday cage was used during electrochemical measurements to minimize noises. Platinum gauze was used as a counter electrode. The saturated calomel electrode was used as a reference electrode. The exposed area of samples was 1 cm^2. Before experiment, the sample was kept for 30 min in electrolyte for stabilization of the free corrosion potential to achieve the steady state. Then the last open circuit potential value was maintained potentiostatically for electrochemical impedance spectroscopy (EIS) measurements Therefore, samples were in a steady state during recording of the EIS spectra. During the impedance measurements, the sinusoidal signal with amplitude of 10 mV (rms) was used. A spectrum was recorded in the frequency range from 0.01 Hz to 0.1 MHz.

Wettability Investigations

The wettability of the obtained coatings was evaluated by sessile drop method on drop shape analyser DSA100 (KRÜSS, Germany). The sessile drop method is an optical contact angle (CA) technique used to estimate wetting properties of a localized region on a solid surface. The angle between the baseline of the drop and the tangent at the drop boundary were measured (22). Solution of 3 % sodium chloride in bidistilled water was used for contact angle measurements. For calculation of CA the Young-Laplace method taking account of gravitational distortions liquid drops form under its own weight was used (21, 22, 23).

Thermal Analysis

Thermal stability of TFE telomeres was studied using the differential thermal analysis and thermogravimetry methods. Investigations were carried out on a DTG–60H derivatograph (Shimadzu, Japan) at the heating rate of 2.5 deg min^{-1} in corundum crucible in an air. The thermal stability of SPTFE was estimated in our previous paper (24).

RESULTS AND DISCUSSION

Morphology and Composition of Coatings

Based on our previous work (16) and analysis of cross-section images (Fig.1) it can be concluded that particles of organofluorine materials as a single phase incorporate into the outer porous part of PEO-layer, sealed the pores and microdefects in base PEO-coating.
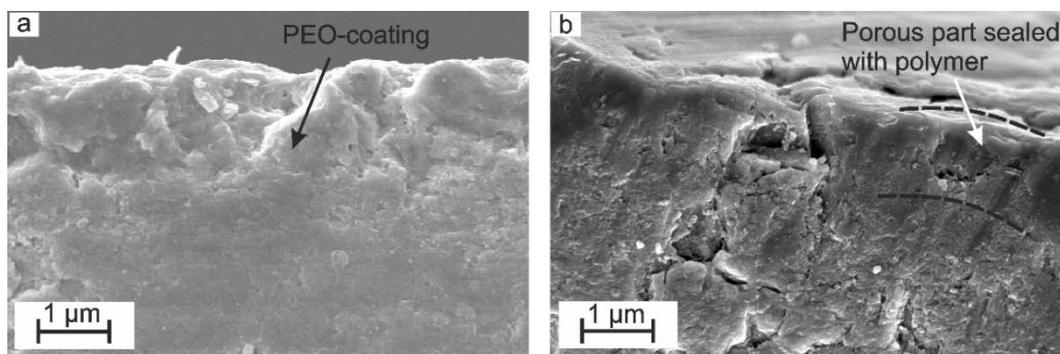

Figure 1. Cross-sectional SEM-images of PEO-coating (a) and composite coating obtained with fourfold application of SPTFE (b).

As a result of this operation, the composite fluoropolymeric coating was formed, in which the base PEO-layer is the matrix filled with organofluorine material. The thickness of CC (Fig.1b) increased insignificantly as compared to the base PEO-coating (Fig.1a) due to predominant embedding of polymer in the outer porous part of PEO-layer. Only the thin polymeric film (about 0.1-0.2 µm) was formed atop of the PEO-layer. Presented cross-sections show only porous part of base PEO-coating (Fig.1a) and outer part of composite coating sealed with fluoropolymer (Fig.1b). For this reason nonporous sublayer of base PEO-coating and Mg substrate are not presented in these SEM-images.

Electrochemical Properties of Coatings

Analysis of EIS data revealed a significant difference in the electrochemical properties of the composite coatings depending on the conditions of the heat treatment, the multiplicity of polymer application and type of the organofluorine material. Observed transformation of the position and amplitude of the phase angle on the Bode plots (Fig.2b) indicates a change in the surface state: porosity, homogeneous of composite layers. In order to describe the charge transfer mechanism at the coating/electrolyte interface, three kinds of equivalent electrical circuits (EEC) were used (Fig.3). The Bode plot for uncoated sample is characterised by a negative values of phase angle at high and intermediate frequencies and a positive values at low frequencies (Fig.2b).
The negative values of phase angle are associated with presence of parallel charge transfer resistance and double layer capacitance at the electrode/electrolyte interface. The positive values of phase angle at low frequencies is a consequence of adsorption of intermediate products during the pitting corrosion process (25). The electrochemical behaviour at low frequencies was not reproducible, possibly, due to corrosion damage. Therefore, the frequency range for analysis and fit of experimental data was deliberately limited. It is a common practice in impedance measurements (25). Thus, the spectrum of the sample without coating could be fitted using the simplified equivalent electrical circuit (EEC) with one R_2-CPE_2-circuit, where R_2 is the charge transfer resistance, and CPE_2 is the double layer capacitance (Fig.3a).
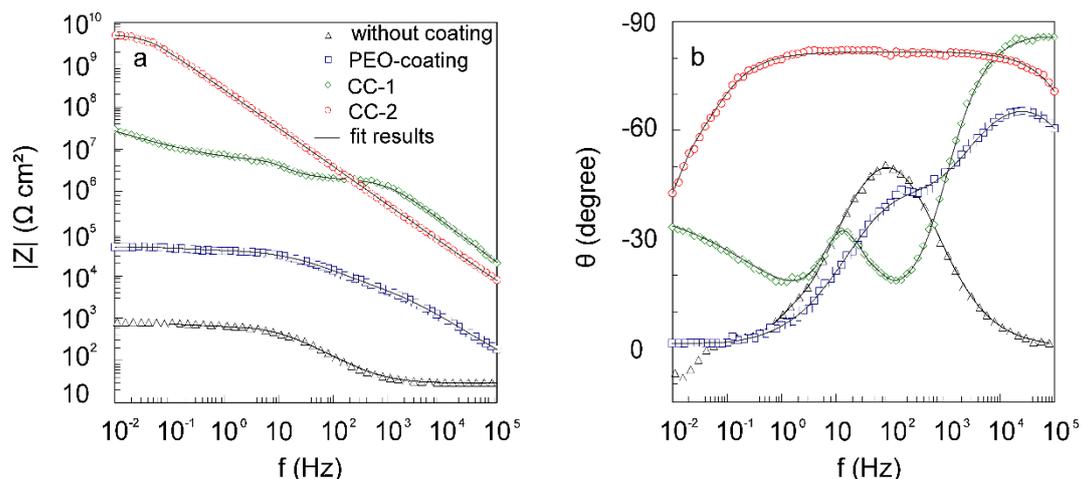
Figure 2. Bode plots (dependence of the impedance modulus |Z| (a) and the phase angle θ (b) on the frequency f) for the studied samples made of magnesium alloy MA8 without coating, with PEO-coating, with composite coatings.

For samples with coatings, two kinds of EEC were used: two-*R-CPE*-chain circuit (base PEO-coating) (Fig.3b), and three-*R-CPE*-chain circuit (composite coatings) (Fig.3c). Bode plot for base PEO-coating has two bends. This is result of two-layer structure of PEO-coating: outer porous layer and inner barrier sublayer (26). The use of three-*R-CPE*-chain circuit associated with the appearance of the third time constant on the spectrum (Fig.2b). This is a consequence of the sealing air by polymeric plug in the pores of PEO-layer at composite coating formation. Note, that the dependence of the phase angle θ on the frequency f for CC-2 (Fig.2b) is capacitive, that suggests a high uniformity of the obtained coating. This impedance spectrum may be fit using both EEC with one and three time constants. However, according to the mechanism of composite coatings formation (sealing air by polymeric film in the pores and microdefects of base PEO-coating and lesser value of chi-squared (χ^2) for three time constant in comparison with one time constant) we used EEC with three time constant.
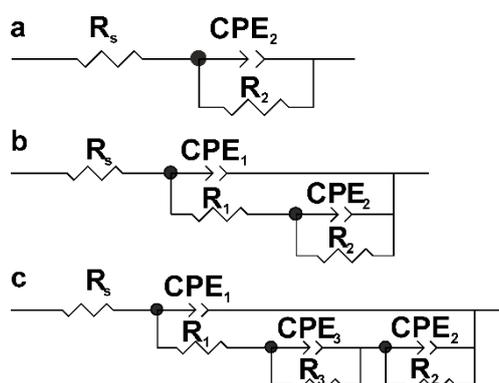

Figure 3. Equivalent electrical circuits used to fit the experimental impedance spectra: one-*R-CPE*-chain (a); two-*R-CPE*-chain (b); three-*R-CPE*-chain (c).

In Figure 2 experimental data marked with the symbol, and theoretical spectra, which were obtained by fitting using of appropriate EECs, shown as lines. Calculated parameters (Table 1) provide a high goodness of fitting (χ^2 values are in the range $(1.0–1.5)\times10^{-4}$). From the analysis of EEC parameters (Table 1) it can be concluded

about increasing R_1 and decreasing Q_1 (parameters, which characterize the porous layer of composite coatings) for composite coatings in comparison with the base PEO-coating as result of increasing thickness of composite layer. Lesser value Q_1 for CC-1 in comparison with CC-2 corroborates the bigger general thickness for CC-1 than CC-2. Moreover, as for nonporous inner sublayer, that analysis of calculated parameters of the R_2-CPE_2-circuit for composite layers revealed the increasing of R_2 and reducing of Q_2 in comparison with ones for a base PEO-coating. Because the R_2-CPE_2-element characterizes the nonporous layer, it can be concluded that some amount of the organoflurine material penetrates to the bottom of pores. This increases the nonporous sublayer thickness. The higher value of R_3 and lower value of Q_3 for CC-2 in comparison with ones for CC-1 testify the more uniformity of the CC-2.

The results of experiments enable one to conclude that multiple treatment of the PEO-coated sample with telomeric solution increases the impedance modulus $|Z|_{f \rightarrow 0\,Hz}$ up to $10^7\,\Omega\,cm^2$, and in the case of the treatment with SPTFE suspension up to $10^9\,\Omega\,cm^2$. These values are almost by 3 and 5 orders of magnitude higher than one for the PEO-coating. Apparently, all above-mentioned reasons of improving the characteristics of CC associated with the sealing of the pores and defects, which are presented in the base PEO-coating.

Hydrophobic Properties of Coatings

Results of wettability investigations for samples revealed the high hydrophobic properties of composite coatings. The highest values of the CA (171°) were obtained for the CC-1. Values of the CA greater than 150° indicate that this sample has superhydrophobic properties. In accordance with the results of previous studies, a superhydrophobicity is caused by multimodal roughness of the surface (21). Apparently, in the case of using of the TFE telomeric solution such structure is formed as a result of the partial destruction of the organofluorine compounds and subsequent aggregation during heat treatment. This conclusion is confirmed by thermal analysis of TFE telomere presented in Fig.4.
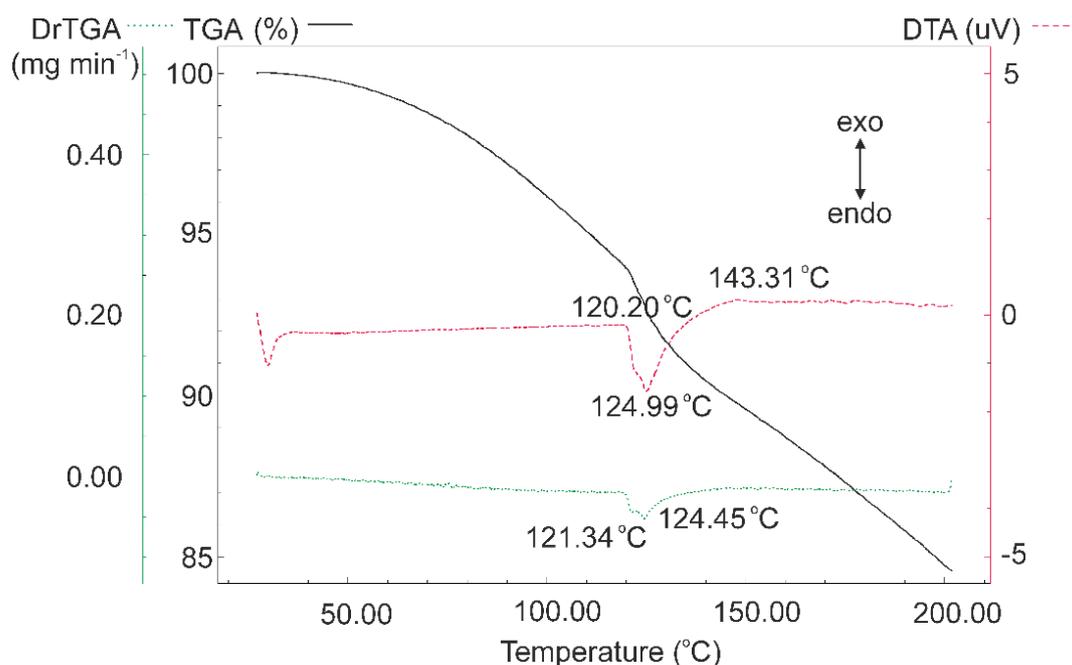
Figure 4. Thermal analysis of TFE telomeres.

A pronounced endothermic effect associated with the beginning of melting is presented on the graph. Since the treatment temperature was more than 200 °C, such heat treatment causes a partial degradation of the organofluoric material. As a result, these processes led to formation of the multimodal surface roughness.

CONCLUSION

A new method for the formation of the protective composite layers by PEO and subsequent treatment with fluoropolymer materials has been developed. The optimal conditions of composite polymer-containing layer formation for used different organofluorine materials have been found. Comparative analysis of the properties of formed composite coatings was held. The best protective properties have been shown by composite coating obtained using SPTFE in comparison with the coating formed using TFE telomeric solution. The obtained polymer-containing coatings increase the impedance modulus by 5 and 3 orders of magnitude in comparison with PEO treated alloy. The highest value of contact angle and superhydrophobic properties have been found for composite layer obtained using TFE telomeric solution. Values of the contact angle attain to 171°.

ACKNOWLEDGEMENTS

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Table 1 Calculated parameters of equivalent electrical circuits for investigated samples

Type of coating	R_1 (Ω cm^2)	CPE$_1$ Q_1 (Ω^{-1} cm^{-2} s^n)	n_1	R_2 (Ω cm^2)	CPE$_2$ Q_2 (Ω^{-1} cm^{-2} s^n)	n_2	R_3 (Ω cm^2)	CPE$_3$ Q_3 (Ω^{-1} cm^{-2} s^n)	n_3
Without coating	–	–	–	0.7×10^3	6.0×10^{-5}	0.85	–	–	–
Base PEO	6.8×10^3	1.3×10^{-7}	0.80	3.5×10^4	9.7×10^{-7}	0.66	–	–	–
CC-1	1.5×10^6	1.0×10^{-10}	0.98	8.7×10^7	1.6×10^{-8}	0.74	4.9×10^6	8.2×10^{-8}	0.55
CC-2	3.7×10^9	7.3×10^{-10}	0.92	2.2×10^9	6.2×10^{-9}	0.90	3.7×10^9	5.9×10^{-7}	0.90