Anticorrosion and wear-resistant composite coatings at the surface of magnesium alloys

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Summary

The results of surface modification of magnesium alloys by plasma electrolytic oxidation (PEO) and subsequent treatment in suspension of superdispersed polytetrafluoroethylene (SPTFE) and telomeric solution of tetrafluoroethylene (TFE) have been presented. Electrochemical, tribological properties and wetting ability of obtained protective composite coatings were investigated. The fabricated coatings decrease the density of corrosion current and wear by orders of magnitude as compared to unprotected magnesium alloy and base PEO-coating.

Such multifunctional coatings have high corrosion resistance ($R_p = 4.9 \cdot 10^8$ Ohm·cm^2, $|Z|_{f=0.1\text{Hz}} = 1.9 \cdot 10^9$ Ohm·cm^2) and good friction coefficient (0.1) under dry wear conditions that extends the application magnesium alloys area. According to electrochemical impedance spectroscopy data and calculated parameters of the elements of equivalent electrical circuits, the SPTFE-treatment of the PEO-coating results in the increase of the geometric thickness of the composite coating. Moreover, the nonporous sublayer thickness also increases, as compared to the base PEO-layer. Protective properties of the composite coating obtained through SPTFE treatment by four orders of magnitude higher than that of the initial coating formed by the PEO method.

New approaches to the formation of composite polymer-containing PEO-pretreated coatings by tetrafluoroethylene telomer dispersion have been developed. Composite coatings decrease of corrosion current density and wear by three orders of magnitude in comparison with base PEO-coating. Moreover, coatings obtained by means of PEO and TFE telomer dispersion dipping possess hydrophobic and superhydrophobic properties. Telomer dispersion composition and a temperature of the following heating treatment are very important as well.

1 Introduction

Development of highly efficient methods for protection of metals and alloys against corrosion is a complex research and engineering problem. The solution of this task depends on the comprehensiveness of the gained information about the mechanisms of these processes, how the effect can be reduced, and how to decrease the intensity of corrosion.

Today magnesium alloys are increasingly being used in industries such as aviation, automotive, producing of high-tech devices and in their components. But low corrosion and wear resistance substantially restrict the application scope of this material.

One of the possible ways to protect magnesium alloys from the negative impact is the formation coatings by plasma electrolytic oxidation (PEO) [1–8]. PEO-method is widely used in both scientific and engineering fields for producing the oxide multifunctional coatings at the surface of the valve metals [1–8]. During the PEO-process the oxidation of the metal or alloy is occurred under the high values of the voltage in comparison with conventional anodizing. In such conditions on the electrode in the plasma discharge channel the high temperature up to 10000 K, pressure up to 100 MPa, intensive ion and electron transfer realized under the critical values of the electric field strength (up to 10^6–10^7 V/cm). This process promotes the electrochemical and plasmachemical synthesis with participation of the anode material and electrolyte components [1–8]. After such high-energy influence with the subsequent attenuation of the plasmic channel, the sharp cooling of the discharge zone down to electrolyte temperature is realized. This effect has an influence on the physicochemical properties of the formed surface layers. Variation of the electrolyte composition and regime of the coating formation enable one to regulate the chemical composition and, therefore, purposefully to change the surface layers properties.

PEO-method allows forming on the magnesium alloy protective layers, which have a convolute, rough surface. Such structure can be served as a basis for application at the PEO-surface polymeric materials in order to provide additional protection for this product [8]. In this regard fluoropolymers due to their chemical stability represent a particular interest. This paper describes the results of investigation of protective properties of composite coatings (CC) on magnesium alloys with various organofluorine materials.

2 Methods

Rectangular plates of magnesium alloy MA8 (system Mg-Mn-Ce) were used as samples. Silicate-fluoride solution was used as electrolyte for PEO [3, 6-8]. The process of coating formation was realized using the tyristor rectifier as a power supply. Coatings were formed in bipolar PEO-mode. In the first step the anodic current density was specified of 0.61 $A \cdot cm^{-2}$ (under incresing voltage up to 270 V), cathodic component was kept potentiostatically at a level of –40 V. In the second step voltage was gradually decreased down to 200 V in the anodic part and down to –10 V in the cathodic. The duration of the first and second phases of the PEO was 200 s and 600 s, respectively.

Solution of telomers of TFE (trademark Cherflon®) [9] and aqueus suspension of SPTFE (trademark Forum®) [10] were used as fluoropolymer materials for formation of CC. The polymer was deposited by immersing the sample with PEO-coating in different suspensions with subsequent heat treatment. Time of the immersion in suspensions was not more than 10-15 s. After application, the samples were air dried for 20 minutes at 25°C. Next step was heat treatment at 250°C for coatings, which were obtained by application of telomeric solution (the number of applications was 3) (hereinafter CC-1) and at 315°C for coatings, which were obtained by application of SPTFE (the number of applications was 4) (hereinafter CC-2).

Electrochemical properties of coatings were investigated using electrochemical system VersaSTAT MC (Princeton Applied Research, USA). Measurements were made in a three-electrode cell at room temperature in a 3 % NaCl solution. Platinum gauze was used as a counter electrode. Calomel electrode was used as a reference electrode. The exposed area of the sample was 1 cm^2. Potentiodynamic measurements were made at sweep rate of 5 $mV\,s^{-1}$ from $E_c - 0.15$ V up to $E_c + 0.5$ V. During the impedance measurements sinusoidal signal with amplitude of 10 mV was used. A spectrum was recorded at the open curcuit potential in the frequency range from 0.01 Hz to 0.1 MHz.

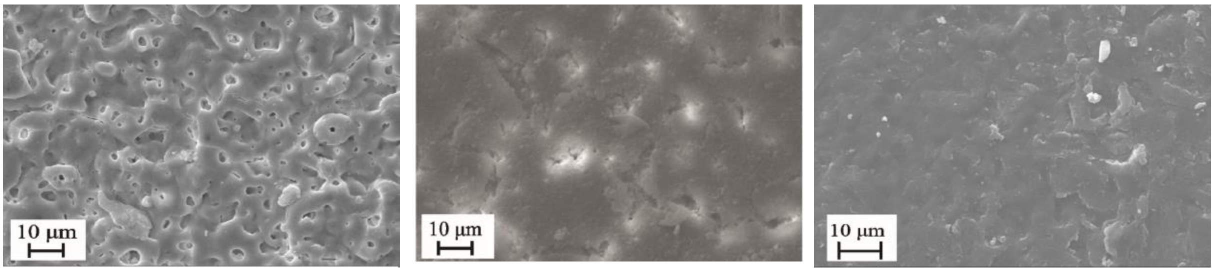
The wettability of the obtained CC was evaluated by sessile drop method on drop shape analyser DSA100 (KRÜSS, Germany). Solution of 3 % NaCl in bidistilled water was used for contact angle measurements.

Wear of CC was tested by "ball-on-disk" method on tribometer Revetest-RST (CSM Instruments, Switzerland) using Al_2O_3 ball of 10 mm in diameter at a line speed of 50 $mm \cdot s^{-1}$ and load of 10 N.

The surface morphology of the obtained CC was studied with using a scanning electron microscope (SEM) EVO 40 (Carl Zeiss, Germany).

3 Results and discussions

Data analysis of SEM-images identified the influence of the multiplicity of applying organofluoric material and subsequent heat treatment on the surface morphology of the formed layers (Fig. 1). At surface treatment of the base PEO-coating (Fig. 1a) with the telomeric solution the number of pores and defects on the surface decreases and the surface becomes more uniform (Fig. 1b). In the case of applying SPTFE (Fig. 1c) a uniform film was formed with no visible defects.



(a) (b) (c)

Figure 1: SEM-image of PEO-coating (a) and composite coatings obtained using telomeric solution (b) and using suspension of SPTFE (c)

Interpretation of the potentiodynamic polarization data presented in Fig. 2, and analysis of the data presented in Table enable one to conclude that application of organofluorine material at the surface of the base PEO-coating has a positive effect on the protective properties of composite layers.

In the case of applying at the surface the telomer of TFE, the corrosion current density I_c reduces, and the polarization resistance R_p increases by 4 orders of magnitude as compared to the uncoated bare material and by 2 orders of magnitude as compared to the PEO-coating (see Table).

Formed coatings, which were obtained using SPTFE suspension, have even higher protective properties. For such CC I_c reduces and R_p increases by 6 and 4 orders of magnitude as compared to the uncoated alloy and PEO-coating, respectively (see Table). Moreover, for both types of composite layers the ennoblement of of OCP (value of E_o increases at least 0.5 V as compared to one for the PEO-coating) has been observed. The conclusion can be done that CC-1 has lower values of R_p, and a higher I_c as compared to CC-2 (see Table). Apparently, this is due to the greater uniformity of the film obtained using a suspension SPTFE (Fig. 1c) as compared to the film obtained using telomeric solution (Fig. 1b).

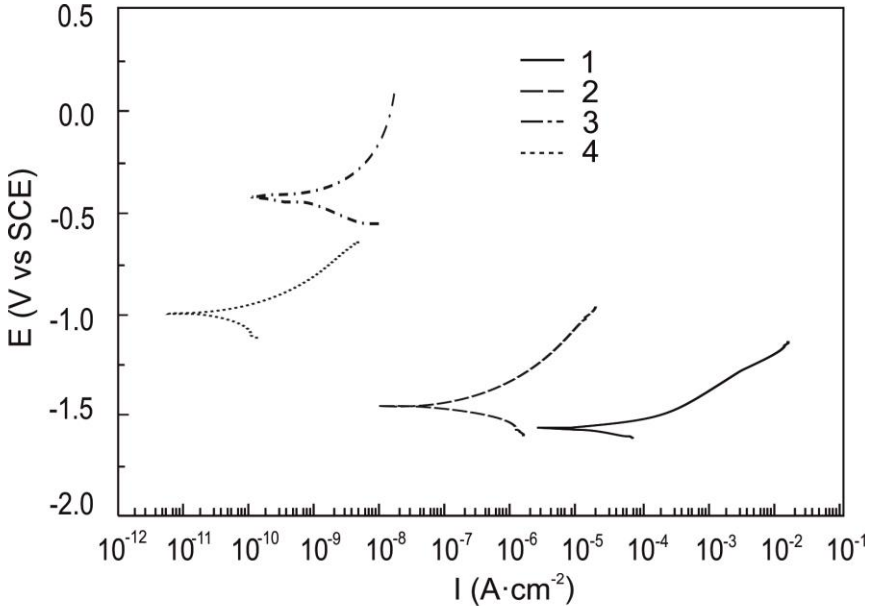


Figure 2: Polarization curves for samples with a different surface treatment: 1 – without coating; 2 – PEO-coating; 3 – CC-1; 4 – CC-2

Table: Corrosion and tribological properties and wettability of investigated samples

Type of coating	E_c (V)	I_c (A·cm^{-2})	R_p (Ω·cm^2)	$\lvert Z\rvert_{f\to 0\,Hz}$, ($\Omega$·cm^2)	Contact angle (°)	Wear (mm^3 (N m)$^{-1}$)
Mg alloy without coating	–1.61	$5.3\cdot10^{-5}$	$0.5\cdot10^{3}$	$0.8\cdot10^{3}$	38±1	$3.8\cdot10^{-3}$
Base PEO	–1.48	$2.4\cdot10^{-7}$	$1.0\cdot10^{5}$	$4.3\cdot10^{4}$	49±2	$1.7\cdot10^{-3}$
CC-1	–0.39	$1.4\cdot10^{-9}$	$4.6\cdot10^{7}$	$5.1\cdot10^{7}$	168±2	$5.7\cdot10^{-6}$
CC-2	–0.95	$5.4\cdot10^{-11}$	$4.9\cdot10^{8}$	$1.9\cdot10^{9}$	140±2	$7.6\cdot10^{-7}$

Data analysis of electrochemical impedance spectroscopy revealed a significant difference in the morphology of the CCs depending of the conditions of the heat treatment, the multiplicity of application and type of organofluorine material. Observed transformation of the position and amplitude of the time constants in the plot of the phase angle θ versus the frequency f (Fig. 3b), which is indicating 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. For the uncoated sample the one-*R*-*CPE*-chain circuit was applied (Fig. 4a). For samples with coatings two kinds of EEC were used: two-*R*-*CPE*-chain circuit (base PEO-coating) (Fig. 4b) and three-*R*-*CPE*-chain circuit (composite coatings) (Fig. 4c).

The using three-*R*-*CPE*-chain circuit associated with the appearance of the third time constant on the spectra (Fig. 3b). This is a consequence of the sealing air by polymeric plug in the pores of PEO-layer. It should be noted that the dependence of the phase angle θ on the frequency f for CC-2 (Fig. 3b) is capacitive, which suggests a high uniformity of the obtained coating.

According to fitting of experimental impedance spectra by a presented EES it was established that SPTFE- and TFE-treatment of the PEO-coating results in the increase of the thickness of the inner porousless sublayer and the geometric thickness of the coating as well.

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

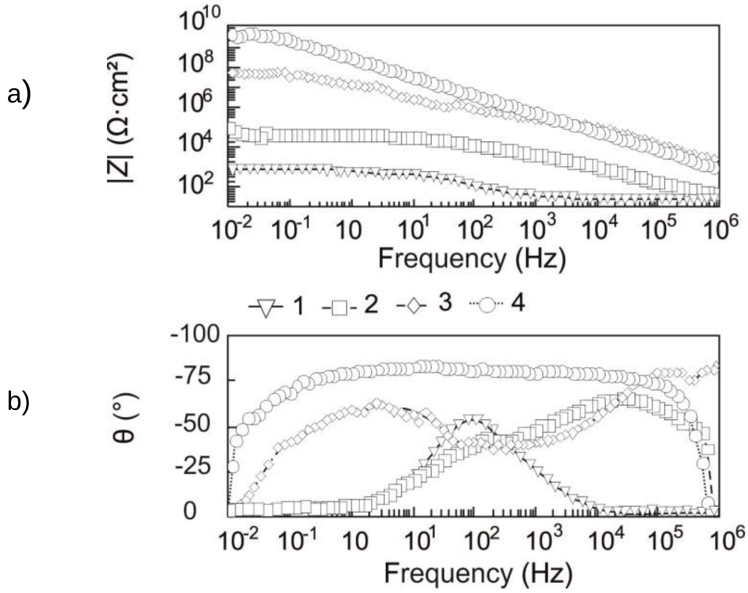
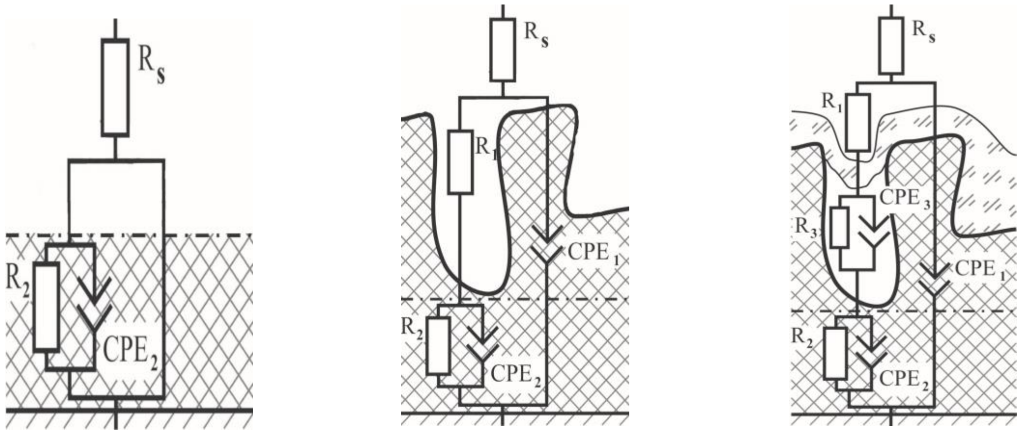


Figure 3: Bode plots (dependence of the impedance modulus $|Z|_{f \rightarrow 0\ Hz}$ (a) and the phase angle θ (b) on the frequency *f*) for samples with a different surface treatment: 1 – without coating; 2 – PEO-coating; 3 – CC-1; 4 – CC-2



(a) (b) (c)

Figure 4: Models of the composite coatings structure with the equivalent electrical circuits used for the fit of the experimental impedance spectra: a – one-*R*-*CPE*-chain EEC; b – two-*R*-*CPE*-chain EEC; c – three-*CPE*-*R*-chain EEC

Results of wettability investigations for samples revealed the high hydrophobic properties of CCs (see Table). The highest values of the contact angle (168°) were obtained for the CC-1. Contact angle values of greater than 150° indicate that this sample possesses the superhydrophobic properties. In accordance with the results of previous studies [4, 5, 7] a superhydrophobicity is caused by multimodal roughness of surface. 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.

As a result of data analysis about changing the friction coefficient (Fig. 5) there are at least 2 stages of the wear for composite polymer containing coatings. The first stage is an abrasion of fluoropolymer film. In this stage the friction coefficient *μ* varies from 0.10 to 0.15 (Fig. 5) in dependence on the forming method of the composite layer. The second stage (abrasion of the PEO-layer) is characterized by a sharp increase of the friction coefficient (Fig. 5).

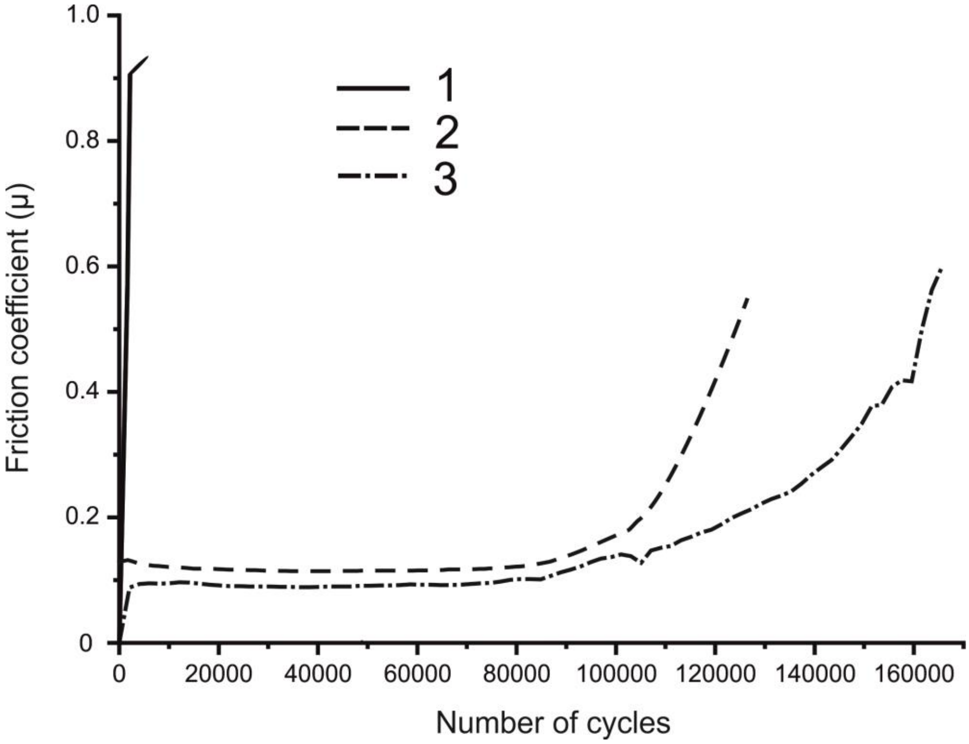


Figure 5: Dependence of the friction coefficient on the number of cycles for samples with a different surface treatment: 1 – without coating; 2 – PEO-coating; 3 – CC-1; 4 – CC-2

At full abrasion of the coating in the contact zone the friction coefficient attains of 0.55 and more. Analysis of tribological data revealed a positive impact of incorporation of fluoropolymer particles into the PEO-coating to improve the wear resistance of composite layers (Tab.). Thus, the applying of TFE telomeric solution in composite coating reduces wear by 3 orders of magnitude as compared to the base PEO-coating. For composite coating, obtained using SPTFE suspension the wear was decreased by 4 orders of magnitude in comparison with the base PEO-layer. Such increasing of the wear resistance is associated with the formation of the polymer-containing layer in the outer part of the PEO-coating, which has a low friction coefficient. Formed polymer-containing film has a low friction coefficient and used as a dry lubricant.

4 Conclusion

New method for the formation of the protective composite layers by PEO and subsequent treatment with fluoropolymer materials was developed. The obtained polymer-containing coatings decrease the corrosion current densities and the wear by 6 and 4 orders of magnitude, respectively, as compared to unprotected alloy. Values of the contact angle attain up to 168°.

According to electrochemical impedance spectroscopy data and calculated parameters of the elements of equivalent electrical circuits, the SPTFE- and TFE-treatment of the PEO-coating results in the increase of the thickness of the inner porousles sublayer and the composite coating in whole.

Acknowledgments

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5 References

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