

Composite PEO-Coatings as Defence Against Corrosion and Wear: A Review

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This paper reviews recent approaches to develop composite polymer-containing coatings by plasma electrolytic oxidation (PEO) using various low-molecular fractions of superdispersed polytetrafluoroethylene (SPTFE). The features of the unique approaches to form the composite polymer-containing coating on the surface of MA8 magnesium alloy were summarized. Improvement in the corrosion and tribological behavior of the polymer-containing coating can be attributed to the morphology and insulating properties of the surface layers and solid lubrication effect of the SPTFE particles. Such multifunctional coatings have high corrosion resistance ($R_p = 3.0 \times 10^7 \Omega \text{ cm}^2$) and low friction coefficient (0.13) under dry wear conditions. The effect of dispersity and ξ -potential of the nanoscale materials (ZrO_2 and SiO_2) used as electrolyte components for the plasma electrolytic oxidation on the composition and properties of the coatings was investigated. Improvement in the protective properties of the coatings with the incorporated nanoparticles was explained by the greater thickness of the protective layer, relatively low porosity, and the presence of narrow non-through pores. The impedance modulus measured at low frequency for the zirconia-containing layer ($|Z|_{f=0.01 \text{ Hz}} = 1.8 \times 10^6 \Omega \cdot \text{cm}^2$) was more than one order of magnitude higher than that of the PEO-coating formed in the nanoparticles-free electrolyte ($|Z|_{f=0.01 \text{ Hz}} = 5.4 \times 10^4 \Omega \cdot \text{cm}^2$).

Keywords: *Protective coating, Plasma electrolytic oxidation, Nanoparticles*

1. Introduction

The plasma electrolytic oxidation method is used for fabrication of coatings that improve the surface properties of various metals and alloys [1-11]. The porous coatings are produced by high voltage AC, DC or bipolar polarization of the substrate in appropriate electrolyte solutions. The plasma discharges occur at the electrode surface during the PEO process and lead to the formation of coatings similar to ceramic ones. The frictional, corrosion, electrical, and thermal properties of these coatings have generated interest in view of their possible use in mechanical, aerospace, aircraft, and automobile industry, engineering equipment components, and biomedical devices. This method can be used for the corrosion protection of Mg, Al, Ti alloys and steel [1-16]. The coatings obtained by the PEO method have an unopened porosity and are characterized by low corrosion currents (I_c) and high values of polarization resistance (R_p) and impedance modulus ($|Z|$) (especially in the range of low frequencies) [5]. The formation of coatings on the surface of metals and alloys by the PEO method enables one to expand substantially

the field of their practical application. However, in the case of a mechanical impact in the process of the article improper transportation or operation, there is the possibility of disruption of the surface layer, which inevitably results in deterioration of protective properties of the coating in whole [17]. In view of this, the development of the methods of deposition of coatings, which are not only corrosion-stable but also have antifriction and antiwear properties, is of extreme importance, since this would significantly reduce the probability of the articles mechanical damage in the exploitation process. PEO-coatings having good adhesion to the substrate and developed surface can serve as the basis for the creation of composite layers [12,18]. Moreover, one of the surface modification methods is the incorporation of polymer and/or inorganic nanoparticles in the electrolyte for the plasma electrolytic oxidation or in the surface layer of PEO pretreated sample [19-22]. It allows improving the practically important physical and chemical properties of PEO-coatings such as corrosion- and wear-resistance, hardness [21,22]. The main problem in the preparation of such suspensions for PEO is the achievement of their sufficiently high sedimentation and aggregative stability.

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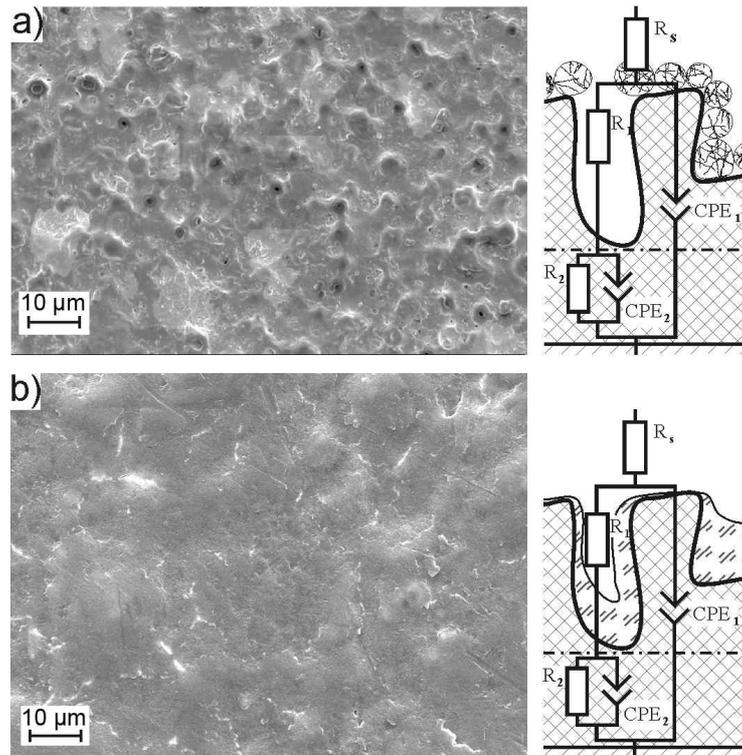


Fig. 1 SEM images and schematic structure of composite coatings with reduced sizes of pore inlet (a), with pores completely sealed with polymer (b) and respective EEC. R_s – the electrolyte resistance, R_1 – the electrolyte resistance in pores and defects, CPE_1 – porous outer layer capacitance, CPE_2 and R_2 , – capacitance and resistance of the barrier layer [21].

2. Formation of composite coating using polymer nanomaterials

The results of morphological studies demonstrate that the mesoporous cluster structure of coatings formed by PEO can serve as an appropriate substrate for deposition of nanosized polymer materials in order to improve inhibitive properties of protective coatings, increase their hydrophobicity, decrease their roughness, and abate negative influence of different defects [17,19,21]. Such composite coatings can be very efficient since they expand functional properties of metals and alloys. SPTFE possesses a significant advantage as a polymer material applicable to form composite layers [21].

A positive effect of the multiple layer deposition on protective properties of composite coatings on titanium was established earlier [19]. In the present review various methods of polymer deposition on porous PEO-treated surface of the material, which allow a purposeful formation of composite layers with specified inhibitive properties related to definite operation conditions, were developed (Fig. 1).

Structure and morphology of such coatings can be de-

scribed using electrochemical impedance data fitting by means of equivalent electrical circuits (EEC) application. These circuits can be applied for interface electrode/electrolyte description of different composite polymer-containing coatings formed on various metals and alloys. In the paper [21], the circuit's evolution is related to the process of the composite coating formation, notably, to the number of the SPTFE treatment steps. The schemes shown in Fig. 1 are applicable to coatings formed on different alloys and metals of certain functional purposes. For instance, the treatment method of surface layers on titanium, nitinol [23,24], steel [12] and MA8 magnesium alloy [21] (Fig. 1a) yielding the controlled narrowing of coating pores was developed. On the scanning electron microscopy (SEM) image, one can trace changes in the pore volume upon the polymer deposition. This surface treatment enables one to use pores of the coating formed on the implant surface as containers for drugs (antibiotics, immunity modulators, etc.) to provide their dosed release to the organism and time-controlled therapeutic effect. Another way of composite coating formation using PEO method was developed for additional corrosion protection of parts made of metals and alloys (especially magnesium alloys), which applied under moderate corrosion impact

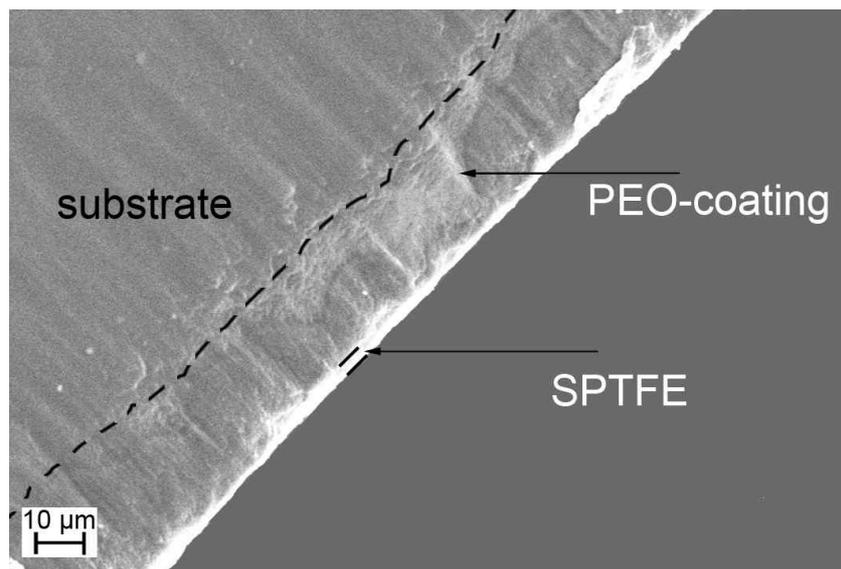


Fig. 2 SEM-images of the cross-section of the magnesium sample with PEO-coating after pore sealing with SPTFE. Cross-sections were prepared using Ar^+ etching [21].

Table 1 main electrochemical parameters of samples with different types of surface treatment [21]

Sample #	Type of sample surface	R_p ($\Omega \text{ cm}^2$)	I_c (A/cm^2)	E_c (V vs Ag/AgCl)	$ Z _{f=0.1, \text{Hz}}$ ($\Omega \text{ cm}^2$)
1	Without coating	4.9×10^2	5.3×10^{-5}	- 1.56	7.4×10^2
2	PEO-layer	3.3×10^5	7.8×10^{-8}	- 1.50	5.4×10^4
3	PEO-layer + SPTFE (single)	9.1×10^5	3.3×10^{-8}	- 1.46	1.4×10^6
4	PEO-layer + SPTFE (fivefold)	3.0×10^7	3.1×10^{-9}	- 1.27	2.7×10^7

conditions, in particular, in some heat exchangers [12]. A polymer plug strengthening protective properties of the composite coating is formed in PEO-layer pores.

For the application of electrochemically active materials, in particular, magnesium alloys, in harsh corrosion-active media (for example, in seawater), one more way of formation of composite coatings was developed (Fig. 1b). In this method, a maximal sealing of pores and cracks with a polymer is ensured. This approach provides blocking the diffusion routes of aggressive components to the substrate. As a result, the best possible protection of the material is provided. According to the analysis of SEM-images (Fig. 1b), the morphological structure of these composite coating is principally different from the surface state of coatings obtained using the above-described treatment method (Fig. 1a). The coating pores were filled with polymer and not discernible on the images. To implement each of the developed methods, following steps of superdispersed polytetrafluoroethylene treatment and special thermal mode were selected.

Onefold (Fig. 1a) and fivefold (Fig. 1b) SPTFE treatment at 265 °C for 1h were applied for obtaining the above-mentioned coatings [21].

The schemes shown in Fig. 1 are in good agreement with SEM-images of the cross-section. SEM-photos of the cross-section of the magnesium sample with PEO-coating after pore sealing with SPTFE (Fig. 2) illustrate one of the above-mentioned mechanism of the polymer deposition (Fig. 1b). Such composite layer could be obtained after fivefold SPTFE treatment.

Cross-section prepared by Ar^+ etching of the sample is shown in Fig. 2. The thickness of the obtained PEO-coating was found to be 20 μm . The SPTFE layer was uniform with the thickness of about 1–1.5 μm .

From the results of electrochemical measurements, the conclusions were made on a positive effect of PEO-layer treatment with superdispersed polytetrafluoroethylene on inhibitive properties of the formed composite coatings. The shape of polarization curves and values of electrochemical characteristics calculated from them (Table 1)

Table 2 Calculated EEC parameters for the MA8 alloy samples with different surface treatment [21]

Sample #	Type of sample surface	CPE_1		R_1 ($\Omega \text{ cm}^2$)	CPE_2		R_2 ($\Omega \text{ cm}^2$)
		Y_{o_2} ($\text{S cm}^{-2} \text{ s}^n$)	n		Y_{o_2} ($\text{S cm}^{-2} \text{ s}^n$)	n	
1	Without coating	–	–	–	3.3×10^{-5}	0.85	4.8×10^2
2	PEO-layer	9.8×10^{-8}	0.81	1.0×10^4	8.4×10^{-7}	0.68	6.2×10^4
3	PEO-layer + SPTFE (single)	9.2×10^{-9}	0.72	1.3×10^4	4.5×10^{-7}	0.84	5.4×10^5
4	PEO-layer + SPTFE (fivefold)	1.2×10^{-9}	0.73	3.9×10^5	1.2×10^{-8}	0.83	2.3×10^7

clearly indicate the improvement of protective properties of the samples with composite coatings, as compared to samples with and without base PEO-layer. Samples with composite coatings have nobler open circuit potentials in comparison with the abovementioned systems. Even a single treatment of the PEO-layer with SPTFE provides a certain improvement of protective properties of the formed coatings (Table 1). The fivefold SPTFE treatment provides the best protective characteristics of the sample among all the examined ones. For this composite layer, the corrosion current is by more than 4 orders of magnitude lower than that for the sample without coating and more than 25-fold lower than that for the base PEO-layer.

Graphs of the impedance modulus dependence on frequency corroborate the conclusion made on the basis of the analysis of polarization curves. Impedance modulus values measured at low frequency ($|Z|_f = 0.1 \text{ Hz}$, Table 1) for the samples with a polymer layer are by orders of magnitude higher than those for the base PEO-coating or the bare substrate itself. The impedance spectrum of a bare metal has one time constant, i.e., it can be described using one R_2 - CPE_2 -circuit (CPE - Constant Phase Element) (Fig. 1a). The spectrum of a PEO-coating contains two time constants. The first one characterizing the geometric capacitance of the whole oxide layer, with the phase angle maximum -70° , is located in the frequency range from 1×10^3 up to 1×10^5 Hz.

The less expressed second time constant responsible for the nonporous sublayer, with the phase angle maximum -50° , is located in the frequency range from 1 up to 2×10^3 Hz. This spectrum was fitted, with high accuracy ($\chi^2 = 1.2 \times 10^{-4}$), by an equivalent electrical circuit consisting of serial-parallel connection of two R - CPE -circuits, in which the R_1 - CPE_1 elements describe the porous part of the oxide layer, whereas the R_2 - CPE_2 elements are related to the poreless layer (Fig. 1a). The quantitative parameters characterizing the porous and nonporous parts of the composite layer formed as a result of treatment

of the PEO-coating with SPTFE can be also calculated from the experimental impedance spectra using the EEC with two R - CPE -circuits (Fig. 1b).

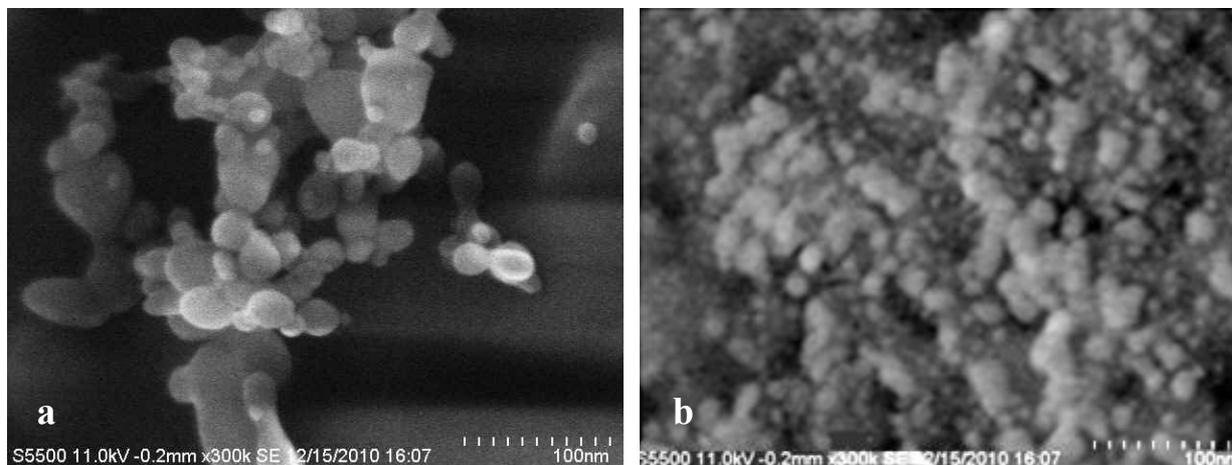
The calculated parameters of the EEC elements (Table 2) are in full agreement with the data of polarization measurements (see Table 1). The trend to the reduction of the parameter Y_o of CPE_1 and CPE_2 for composite coatings, as compared to the base PEO-layer, indicates that along with the geometric thickness increase of composite coating, the nonporous sublayer thickness increases as well.

It is possible due to SPTFE penetration into the pores and sealing them up. The increase of the value of the electrolyte resistance in pores (R_1) reflects the decrease of the inlet of pore channels, the pore narrowing and total decrease of the number of defects over the surface. Here total resistance of the composite coating ($R_1 + R_2$) obtained through fivefold SPTFE treatment is more than 320-fold higher than that of the initial coating formed by the PEO method.

Use of the CPE element in equivalent electrical circuit data is caused by the heterogeneity of the system under study. The CPE impedance is determined in accordance with the equation: $Z_{CPE} = 1/[Y_o(jw)^n]$, where w is an angular frequency ($w = 2\pi f$), j is an imaginary unit, n and Y_o are the exponential coefficient and the frequency independent constant, respectively. For integer values $n = 0$ and $n = 1$ the CPE is classic element such as conductor ($1/R$) or capacitor (C), respectively [6,12,17,19,21]. The deviation of n values from 1 in Table 2 reflects the degree of heterogeneity of the studied layers. The equivalent electrical circuits suggested in this work have a good correlation with results obtained by various scientific groups dealing with fitting of impedance spectra [21]. Generally, PEO-coatings formed on the surface of different metals and alloys are described by equivalent electrical circuits, containing R - CPE -circuits, impedance of Warburg finite or semi-infinite length of diffusion, corresponding to outer porous, inner poreless layers, and to the diffusion proc-

Table 3 The results of the tribological tests [21]

Type of sample surface	Load (N)	Friction coefficient	Rotation number	Time (min)	Distance (m)	Wear ($\text{mm}^3/\text{N m}$)
Without coating (MA8)	5	0.52 ± 0.07	320	16.5	10.0	3.75×10^{-3}
PEO-layer	10	0.43 ± 0.06	300	15.5	9.4	1.69×10^{-3}
PEO-layer + SPTFE	10	0.13 ± 0.05	84249	4110	2648.5	7.18×10^{-7}

**Fig. 3** SEM images of zirconia (a) and silica (b) nanopowders [22].

esses, which were realized on the coating/electrolyte interface.

As can be concluded from the above data, polymer sealing PEO-coating pores with subsequent thermal treatment enables one to create on magnesium alloy surface composite polymer-containing layers with high inhibitive characteristics in chloride-containing media.

The composite coating demonstrates the best tribological parameters due to the presence of superdispersed polytetrafluoroethylene on its surface. The friction coefficient here has the lowest values: 0.13, which is more than 3-fold lower than one for the base coating formed by PEO method. The composite coating with thoroughly sealed pores of the base PEO-layer provides the Mg alloy details not only with the maximal corrosion protection but also with the decrease of the friction coefficient. Low value of this parameter indicates a substantial increase of the coating antifriction properties. Here SPTFE serves as a lubricant.

The results of tribological tests (Table 3) testify the significant improvement of wear-resistance of the composite layers. The parameters were shown at the moment of rubbing the coatings down to the metal.

3. Formation of composite coating using inorganic nanomaterials

Analysis of electron micrographs of the investigated nanopowders ZrO_2 and SiO_2 enables one to estimate the size and shape of the powder particles in a dry state (Fig. 3).

For effective use of nanoparticles in electrolyte composition for plasma electrolytic oxidation, it is important to control their size and ξ -potential. Ordinary in aqueous medium the particles are associated in agglomerates. It is necessary to support the negative ξ -potential of the particles. It was found that as a result of addition of anionic surfactant in aqueous electrolyte the nanoparticles have the negative ξ -potential about -30 mV. In the electric field they move to the anode and incorporate into the coating [22].

Plasma electrolytic oxidation was carried out on MA8 magnesium alloy samples. The morphology structures of coatings formed using ZrO_2 and SiO_2 particles are significantly different (Fig. 4). PEO-coatings formed in the electrolyte with silica nanoparticles have the surface which more nodular and rough (Fig. 4a) as compared to the surface of coatings which contain zirconia nanoparticles (Fig. 4b).

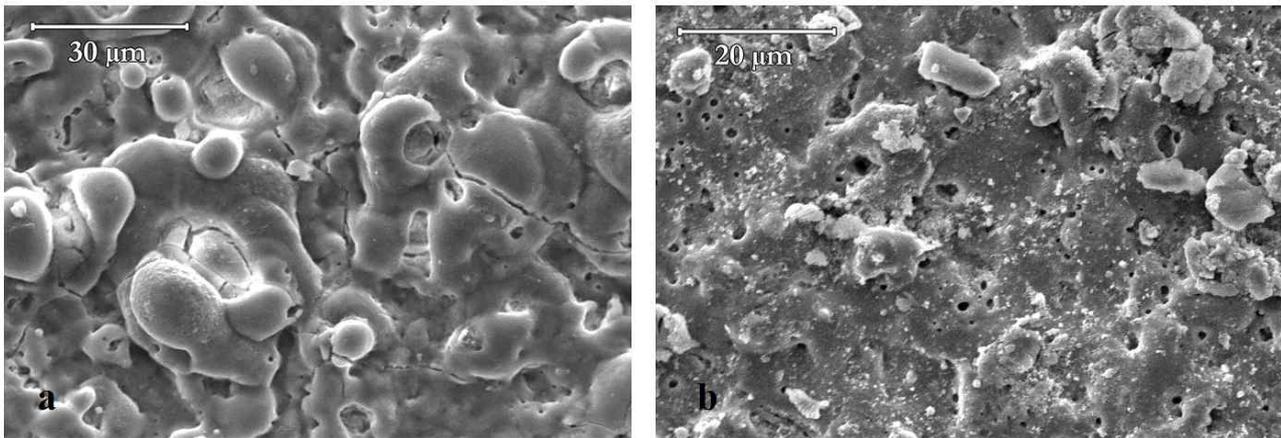


Fig. 4 SEM images of the coating surface with silica (a) and zirconia (b) nanoparticles.

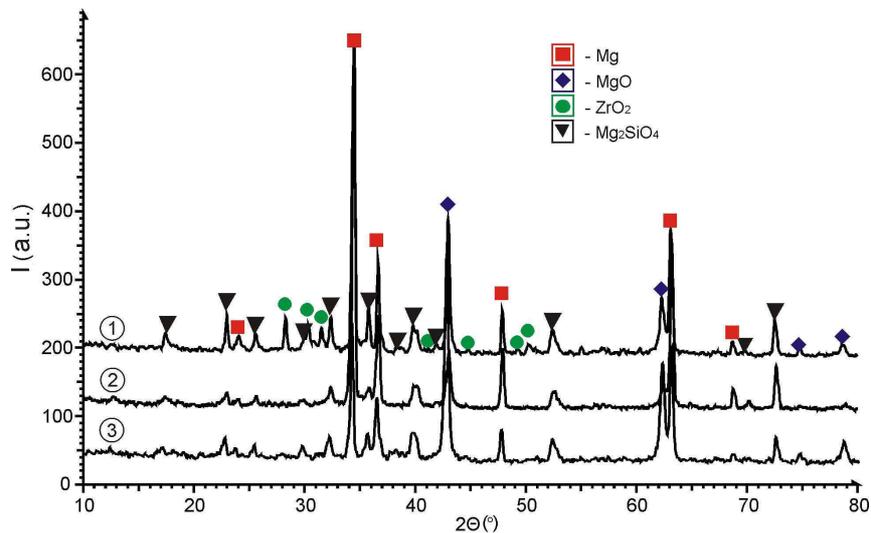


Fig. 5 X-ray patterns of the PEO-coatings produced in base electrolyte (3) and using electrolyte with ZrO_2 (1) and SiO_2 (2) nanopowders.

The analysis of X-ray patterns shown that the presence of the ZrO_2 nanoparticles in the electrolyte for plasma electrolytic oxidation results in the incorporation of particles into the surface layers in the initial chemical state (Fig. 5). Moreover, the nanoparticles were fused into the surface layer during the PEO process.

The SiO_2 nanoparticles used in this work are amorphous. Besides, the silicon incorporates into the coating from the silicate-containing electrolyte. So, it is quite difficult to set the intensity of the incorporation of the SiO_2 nanoparticles into the coating composition by X-ray method.

It was found by X-ray fluorescence analysis that coatings have a heterogeneous composition. The content of elements in the coatings varies in dependence on used electrolyte. The concentration of Si in the surface layers

has increased from 30.03 up to 44.45 mass % in comparison with PEO-coating obtained in the electrolyte without silica nanoparticles. While Zr concentration in the coating obtained in the electrolyte with zirconia nanopowders achieved only 2.7 mass %.

The study of electrochemical properties of the formed layers was conducted using potentiodynamic polarization and electrochemical impedance spectroscopy techniques. Experimental impedance data presented in Bode plot, i.e. dependences of impedance modulus $|Z|$ and phase angle Q on the frequency (Fig. 6.).

Impedance modulus measured at lowest frequency for coatings, which include zirconia, is almost by one order of magnitude higher than the PEO coatings obtained in the base electrolyte without nanoparticles and nearly by three orders of magnitude greater than for bare metal.

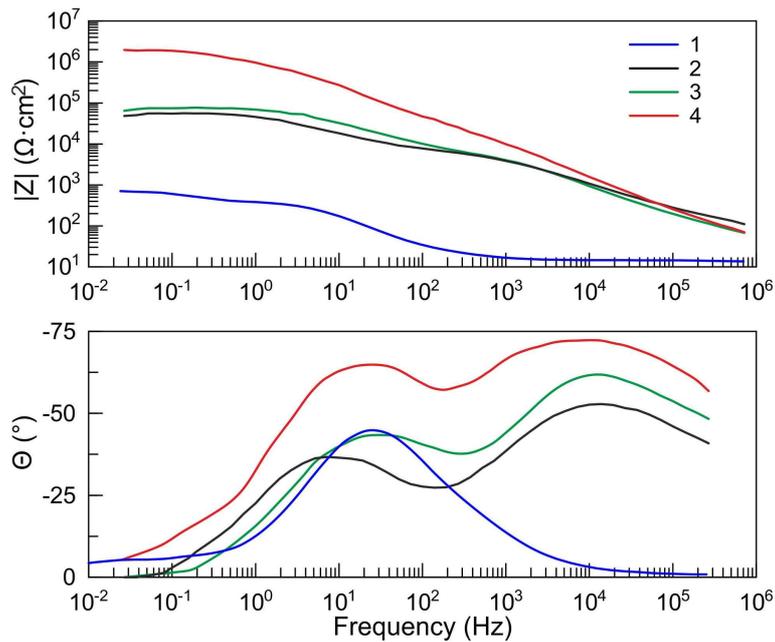


Fig. 6 Bode plots for magnesium alloy samples without coating (1) and with PEO coating, formed: in the electrolyte without nanoparticles (2), with silica (3) and zirconia (4) nanopowders.

Table 4 The main corrosion performances of MA8 magnesium alloy samples [22]

Type of sample surface	R_p ($\Omega\cdot\text{cm}^2$)	I_c (A/cm^2)	E_c (V)	$ Z _{f=0.01 \text{ Hz}}$ ($\Omega\cdot\text{cm}^2$)
Bare Mg	3.6×10^5	1.1×10^{-5}	- 1.56	8.1×10^2
PEO-layer	2.4×10^5	1.1×10^{-7}	- 1.52	5.4×10^4
PEO-layer + SiO_2 nanopowders	3.2×10^5	8.2×10^{-8}	- 1.42	5.6×10^4
PEO-layer + ZrO_2 nanopowders	4.9×10^5	5.3×10^{-8}	- 1.50	1.8×10^6

Data of potentiodynamic study testified significant protective properties of composite coatings formed in electrolytes comprising nanopowders. The coating with zirconia nanoparticles has the corrosion current density more than 2 times lower ($I_c = 5.3 \times 10^{-8} \text{ A}/\text{cm}^2$) in comparison with the PEO-coating formed without nanoparticles ($I_c = 1.1 \times 10^{-7} \text{ A}/\text{cm}^2$) (Table 4). Polarization resistance of the coating with zirconia nanoparticles ($R_p = 4.9 \times 10^5 \Omega\cdot\text{cm}^2$) increased almost by 1.5 times as compared to PEO-coatings obtained in the electrolyte with silica nanopowders ($R_p = 3.2 \times 10^5 \Omega\cdot\text{cm}^2$). Polarization resistance of the coating with silica powder, in turn, is almost 1.3 times higher than for the PEO-coating formed in the electrolyte without nanoparticles ($R_p = 2.4 \times 10^5 \Omega\cdot\text{cm}^2$).

Increase of protective properties of the coatings with nanoparticles can be explained by several factors. SiO_2 and ZrO_2 nanoparticles have high dielectric properties, which increase the polarization resistance of coatings and

reduce corrosion currents. In addition, the particles seal pores and cavities on the coating and thus prevent the ingress of the corrosive environments to the metal surface [25].

4. Conclusions

To sum up, the unique method of the composite polymer-containing coating formation on the surface of MA8 magnesium alloy has been established in this paper. Special treatment of plasma electrolytic oxidation coatings with superdispersed polytetrafluoroethylene enables one to improve significantly both protective and antifriction properties of the surface of magnesium alloys. Such multifunctional coatings have high corrosion resistance ($R_p = 3.0 \times 10^7 \Omega\cdot\text{cm}^2$, $|Z|_{f=0.1 \text{ Hz}} = 2.7 \times 10^7 \Omega\cdot\text{cm}^2$) and good friction coefficient (0.13) under dry wear conditions that extends the field of magnesium alloys application. According to electrochemical impedance spectroscopy da-

ta 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 poreless sublayer thickness also increases, as compared to the base PEO-layer. Protective properties of the composite coating obtained using fivefold SPTFE treatment were more than 25-fold higher than that of the base coating formed by the PEO method.

As a result of the performed investigation, the stable electrolytic systems of complex composition containing zirconia and silica nanopowders have been developed. These electrolytes were used to form by plasma electrolytic oxidation the protective nanostructured composite coatings on the MA8 magnesium alloy in order to improve their functional characteristics. It has been shown that coatings, which contain nanoparticles have a significant advantage in comparison with the surface layers obtained without their addition. It was established that coatings formed in the electrolyte containing zirconia nanoparticles have the best protection.

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