Research Article

Fabrication of Coatings on the Surface of Magnesium Alloy by Plasma Electrolytic Oxidation Using ZrO_2 and SiO_2 Nanoparticles

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Results of investigation of the incorporation of zirconia and silica nanoparticles into the coatings formed on magnesium alloy by plasma electrolytic oxidation are presented. Comprehensive research of electrochemical and mechanical properties of obtained coatings was carried out. It was established that the polarization resistance of the samples with a coating containing zirconia nanoparticles is two times higher than that for the sample with base PEO layer. One of the important reasons for improving the protective properties of coatings formed in electrolytes containing nanoparticles consists in enhanced morphological characteristics, in particular, the porosity decrease and increase of thickness and resistivity (up to two orders of magnitude for ZrO_2 -containing coating) of porousless sublayer in comparison with base PEO layer. Incorporation of silica and zirconia particles into the coating increases the mechanical performances. The layers containing nanoparticles have greater hardness and are more wear resistant in comparison with the coatings formed in the base electrolyte.

1. Introduction

Recently, magnesium and its alloys have been considered as promising functional and construction materials in industry. In comparison with other materials, Mg alloys are characterized with a number of practically important advantages including small specific gravity, high mechanical stability, easiness in processing, and low cost. Magnesium alloys are presently applied in aerospace and automobile industry and household electronics. The main disadvantages limiting the application of magnesium alloys are their high corrosion activity and low wear resistance. The method of plasma electrolytic oxidation (PEO), which is under intensive development and industrial application in many countries [1–4], allows substantial expansion of the field of practical use of metals and alloys through modification of their surface properties. In the recent decades, it has been established that the treatment of alloys (aluminum, titanium, magnesium, etc.)

in electrolytes by electric discharges facilitates the formation of surface similar to ceramic structures of stable chemical compositions. The process of producing oxide layers is controlled by high-temperature plasma-chemical reactions of interaction of substrate and solution components initiated by electric discharges at the electrode/electrolyte interface [4–6].

The possible solution of the problem of enhancing anti-corrosion characteristics and increasing wear resistance of magnesium alloys consists in application of the PEO method, which enables one to deposit protective films of a thickness of a few dozens of microns, thus improving the characteristics of the treated material without virtually any changes in the oxidized details size [6–9]. The composition of the electrolyte used in PEO is determining for the properties of coatings formed by this method. Recently, suspensions, in addition to true solutions, have been used as electrolytes for this method. Introduction of nanosized particles, which become embedded into the coating without changing its properties,

into the electrolyte composition appears to be promising direction of the PEO method development [4, 6–11].

Nanosized materials have been applied as components of composite systems for not a very long time, mainly since the 1990s. The range of nanomaterials and their fields of practical application kept extending significantly, and many new methods of nanoparticles formation have been developed [12–17]. At present, particles of a size of less than 100 nm of various chemical compositions are used in fabrication of catalysts, composites, extra durable ceramic articles, in microelectronics, and in medicine, pharmacy, metallurgy, and paint and varnish industry [13, 15, 18–22]. However, extra small sizes and the affinity to agglomeration in aqueous media impose limitations on nanomaterials usage.

Characteristics of nanoparticles differ from those of substances in a regular “macro” state. Modification of the surface using nanosized materials enables one to change the quality of the treated surface layers and impart them with a complex of practically important physical-chemical properties (anticorrosion, antifriction, antiwear, and magnetic) [2, 4, 6, 10]. One of the directions of nanomaterials application developed presently by many research groups consists in coatings formation on the surface of different metals and alloys by plasma electrolytic oxidation (PEO) [7, 8, 10, 23].

The present work describes the results of studies of electrochemical and mechanical properties of PEO coatings formed in electrolytes containing nanosized oxides of zirconium and silicon.

2. Experimental

2.1. Materials. PEO coatings were deposited on rectangular plates of a size of 15 mm × 20 mm × 2 mm made of deformable magnesium alloy MA8 (1.5–2.5 wt.% Mn; 0.15–0.35 wt.% Ce; Mg; balance). To standardize the surface prior to oxidation, the sample underwent mechanical treatment by sandpaper of different grain sizes (600, 800, and 1200). Thereafter, the samples were washed in distilled water and ethanol.

In the present work, to fabricate a composite coating, nanopowders of zirconia and silica of a particle size of up to 100 nm were used. Nanoparticles were obtained by the method of plasma-chemical synthesis [24]. The used nanomaterials are promising for modification of the surface of metals and alloys and improvement of their surface properties and working parameters as a whole [3, 25]. The zirconium dioxide particles are present in the used nanopowder in monoclinic and cubic crystal modifications and are distinguished by high mechanical strength, good antiwear properties, corrosion resistance, and hardness. In the initial state, silicon dioxide nanoparticles are X-ray amorphous.

2.2. Coatings Formation. Based on positive results of the earlier performed studies [6], the electrolyte containing sodium fluoride and sodium silicate was selected for the samples treatment in the present work. To obtain the working electrolyte, 100 mL of suspension of ZrO_2 or SiO_2 nanoparticles ($c = 40 \text{ g/L}$) was added to 900 mL of silicate-fluoride electrolyte. The concentrations of sodium silicate and sodium

fluoride in the final electrolyte were equal to 15 and 5 g/L, respectively. To reduce the effect of nanoparticle aggregation in the liquid media, the ultrasonic treatment (UST) carried out using a Bandelin HD 3200 ultrasonic homogenizer (Bandelin Electronics, Germany) equipped with a titanium probe was applied. The homogenizer working frequency was 20 kHz; the output power was 140 W. A VS70T titanium probe of a diameter of 12.7 mm was placed into a RZ3 rosette-like cell of a volume of 100 mL filled with the suspension. For the sake of suspension intensive circulation, dispersing was carried out in the pulse mode: 1 s of ultrasonic treatment alternating with 2 s pause. The pulse mode of ultrasonic dispersing allows changing the suspension portion under contact with the probe. After each stage of duration of 2 minutes, a pause of at least 30 minutes was made. The following liquids were used as dispersing media: water, ethanol, and base PEO electrolyte.

The size and electrokinetic or ζ -potential of particles in suspensions treated as shown above were measured on a Zetasizer Nano ZS (Malvern Instruments, Great Britain). The anionic surfactant sodium dodecyl sulfate was used for dispersion stabilization.

The process of coatings formation was carried out on a plasma electrolytic oxidation installation equipped with an automatic control system connected to PC with relevant software [6, 7, 26]. A conventional reversible thyristor rectifier was used as a power supply. The polarization frequency was 300 Hz. The duty cycles were 50%. All the samples were processed in the two-stage bipolar PEO mode. At the first stage, the anode component was fixed in the galvanostatic mode at a current density of 0.5 A/cm^2 , whereas the cathode phase was set in the potentiostatic mode at -30 V . The duration of the first PEO stage was 200 s. During the second stage, the anode component decreased in potentiodynamic mode from 270 down to 200 V. The cathode component was abated from -30 to -10 V . The duration of the PEO second stage was 600 s.

2.3. Coatings Characterization. For qualitative and quantitative estimation of the intensity of nanoparticle embedding to the coating composition, after PEO the samples were investigated by a complex of the methods: X-ray diffraction (XRD), energy dispersive X-ray fluorescence spectroscopy (EDXRF), and energy dispersive analysis (EDS). The X-ray diffraction analysis of surface layers on magnesium alloys was carried out using a D8 Advance automatic X-ray diffractometer with CuK_α radiation (Bruker, Germany). During measurements, a classic focusing according to the Bragg-Brentano geometry in the angle range (2θ) from 10° up to 80° with a scanning increment of 0.02° and an exposure time of 1 s in each point was used. The element composition of surface layers was determined using the energy dispersive X-ray fluorescence analysis on an EDX-800HS spectrometer (Shimadzu, Japan). The chemical elements distribution over the sample surface was studied on an S-5500 electron microscope (Hitachi, Japan) equipped EDS at an accelerating voltage of kV and a probe current of $20 \cdot 10^{-12} \text{ A}$.

2.4. Electrochemical Measurements. Electrochemical properties of the surface layers formed on magnesium alloy were

FIGURE 1: SEM images of ZrO_2 (a) and SiO_2 (b) powders.

carried out by potentiodynamic polarization and electrochemical impedance spectroscopy methods. Measurements were performed on a VersaSTAT MC device (Princeton Applied Research, USA). Aqueous solution of 3% NaCl was used as electrolyte. Exposed area of the sample was 1 cm^2 . Before electrochemical measurements, the sample was kept in electrolyte for 30 min. Potentiodynamic measurements were carried out at a sweep rate of 1 mV/s from $E_c - 0.25$ to 0.5 V . At impedance measurements, a sinusoidal signal of amplitude of 10 mV (rms) was used. The spectrum was recorded at the open circuit potential in the frequency range from 0.7 MHz to 0.01 Hz .

2.5. Mechanical Properties. Studies of the mechanical properties, in particular, determination of the material microhardness and elasticity modulus, were carried out on a DUH-W201 dynamic ultra microhardness tester (Shimadzu, Japan). Measurements were carried out on a cross section using a Berkovich indenter with a tip angle 115° and a load of 50 mN . The values obtained over 10 points were averaged and an error was calculated. Evaluation and comparative analysis of the coatings elastoplastic properties were performed using the Shimadzu DUH analysis Application v. 2.10 software.

Adhesion properties of surface layers were studied by the method of scratch testing on a Revetest Scratch Tester (CSM Instruments, Switzerland). Experiments were carried out at a preset trace length of 5 mm chosen empirically and a gradual load increase from 1 to 20 N at a loading rate of 9.5 N/min . For scratch testing, a Rockwell diamond indenter with an angle of 120° and a radius of $200\text{ }\mu\text{m}$ was used. The study was carried out by measuring the friction force and the friction coefficient, recording the acoustic emission, and fixing critical loads, at which characteristic destruction traces emerged. For each type of coating, the following parameters were determined: L_{c1} , the load at which the first cracking occurs; L_{c2} , the load at which the extent of fracture events increases; L_{c3} , loads, at which coating scratching down to metal occurred.

Tribological tests were carried out on a CSM Tribometer (CSM Instruments, Switzerland) according to the “ball-disc” test scheme. A ball of a diameter of 10 mm made of $\alpha\text{-Al}_2\text{O}_3$ (corundum) was used as a counterbody. All the studies were

performed at dry friction in air at a temperature of 25°C and a load of 10 N , and the sliding rate was equal to 10 mm/s . The experiment was stopped at the moment of coating wear down to metal substrate. The wear tracks were examined with a contact profilometer MetekSurtronic 25 (Taylor Hobson, USA) following the wear tests.

3. Results and Discussion

3.1. Peculiarities of Electrolytes Containing Nanoparticles. Figure 1 shows SEM images of ZrO_2 and SiO_2 nanopowders used in the present work. The average sizes of individual particles measured from these images are equal to 80 and 7 nm for zirconia and silica, respectively.

Since the nanoparticle-containing electrolytes can be attributed to disperse systems (suspensions), the main concern in using such systems consists in achievement of sufficient sedimentation and aggregation resistance of the aqueous suspension. Dispersing is one of the possible solutions of such a problem, which allows separation of nanoparticles agglomerates. Different dispersing methods require energy consumption for overcoming the intermolecular interaction forces and increasing the free surface energy of the formed particles. At the same time, not all the methods acceptable for macroobjects can be used for nanosized objects. The main reasons for nanoparticles agglomeration are related to various weak forces (intermolecular, electrostatic), which, in general, tend to decrease total nanoparticles surface area and, therefore, their surface energy. That is why the preliminary ultrasonic dispersing of the used nanoparticles in the liquid was selected to overcome the abovementioned forces. Collapse of the vapor bubbles occurred under effect of acoustic cavitation that leads to deaggregation of particles. At this moment, the gas pressure (P) and temperature (T) attain significant values, according to some data, P up to 100 MPa and $T > 5200\text{ K}$ [6], respectively. Upon the cavity collapse, in the surrounding liquid one observes a quickly attenuated spherical shock wave producing the disruption of forces linking the particles. After dispersing, the obtained system is very unstable and returns to the initial state with the formation of large nanoparticle aggregates within a short period (from a few minutes to a few hours).

TABLE 1: Characterization of nanopowder suspensions.

Nanoparticles under study	Stabilizer	UST stages number	Hydrodynamic diameter, nm	Electrokinetic potential, mV
ZrO ₂	—	1	231 ± 45	−16.8 ± 2.9
ZrO ₂	—	3	212 ± 41	−17.2 ± 2.1
ZrO ₂	Surfactant	1	224 ± 35	−18.3 ± 2.1
ZrO ₂	Surfactant	3	180 ± 26	−25.1 ± 2.6
SiO ₂	—	1	210 ± 40	5.4 ± 2.2
SiO ₂	—	3	196 ± 37	4.2 ± 2.8
SiO ₂	Surfactant	1	221 ± 39	−28.9 ± 2.3
SiO ₂	Surfactant	3	185 ± 27	−31.8 ± 3.2

FIGURE 2: Electrokinetic potential (a) and hydrodynamic diameter (b) distribution for aqueous dispersion of zirconia without (1) and with (2) anionic surfactant.

For the sake of preliminary estimation of dispersity parameters and ζ -potential of particle, aqueous suspensions with the particle content $c = 0.1$ g/L were prepared: they were used in working out the UST conditions. The consecutive decreasing of the particles aggregate sizes was shown to occur during the increase of the number of UST stages up to three; further treatment did not change the particle size (Table 1).

The dispersity of the formed suspensions (i.e., prevention of the repeated particle aggregation) can be controlled by addition of surfactants, which can significantly decrease the particles surface energy and, as a result, prevent their agglomeration. Besides, the use of anionic or cationic surfactants yields changes in the electrokinetic potential of a particle in the suspension, thus increasing the electrostatic particle adsorption on the charged surface. The Rebinder effect accompanying the impact of surfactants is manifested in the decrease of the interfacial energy. This results in nanoparticles deaggregation and stabilization of the formed electrolytic system over time.

Since during plasma electrolytic oxidation the coating growth occurs, as a rule, at the sample anode polarization, an anionic surfactant was used in the present work as a dispersion stabilizer. Studies of the particle size and electrokinetic potential enabled us to establish that addition of an anionic surfactant into an aqueous electrolyte imparts suspension particles with negative values of the electrokinetic potential and decreases the scatter of particles hydrodynamic diameter and ζ -potential (Table 1, Figure 2).

One of the main parameters affecting the ζ -potential is the pH of medium. To estimate its impact, the electrolytic systems containing nanoparticles were titrated using an MRT-2 automatic titration unit. One should mention the general trend to hydrodynamic diameter and electrokinetic potential (absolute values) of nanoparticle aggregates in electrolytic systems with the pH values increase.

In suspensions containing ZrO₂ and SiO₂ in acidic media (pH ranging from 2 to 5), all nanoparticles are included into aggregates of a size not exceeding 380 nm (Figure 3). Here, in the case of ZrO₂ (as compared to SiO₂), one observes the increase of the hydrodynamic diameter along with the pH increase over the whole pH range under study. In the case of SiO₂ particles (unlike those of ZrO₂) in alkaline media, aggregates are present in two fractions (dimension types): the first one close to the size of individual particles (≈ 300 nm) and the second one with the average size about 1100 nm (Figure 4). The zirconium oxide-containing electrolyte consists exclusively of aggregates of nanoparticles of a size 300–410 nm (Figure 3(a)). The electrokinetic potential for two types of particles under study is negative over the whole pH range.

The isoelectric point is absent on the ζ -potential dependence on pH. The latter must be caused by the use of the anionic surfactant. The values of ZrO₂ ζ -potential in the alkaline medium (at pH = 11) are twofold lower in absolute values (-36.8 ± 1.1 mV) than for SiO₂ aggregates (-78.6 ± 6.4 mV). These values indicate favorable conditions for particle suspension stabilization in the electrolyte. In the acidic medium,

FIGURE 3: Dependence of the particle electrokinetic potential and hydrodynamic diameter on pH of electrolytes containing ZrO_2 (a) and SiO_2 (b) nanoparticles.

FIGURE 4: Distribution of hydrodynamic diameter of aggregates of ZrO_2 (1) and SiO_2 (2) nanoparticles in the electrolyte alkaline medium for PEO (pH = 9).

the ζ -potential values are insufficient for the system stable conditions, which results in fast particles sedimentation.

3.2. Characterization of Fabricated Coatings. The process of plasma electrolytic oxidation was carried out in electrolytes with different nanopowder concentrations. Particles did not affect significantly the PEO process characteristics and the obtained coatings quality at the nanopowder concentrations in the electrolyte less than 4 g/L. At the nanopowder concentration equal to 4 g/L, the coatings obtained under earlier developed conditions [6] peeled off and destructed as early as prior to the process completion. As a result, at the nanopowder concentration in the electrolyte of 4 g/L and higher the process was carried out in the two-stage bipolar mode. This mode ensures an acceptable quality of the fabricated coatings.

According to the data obtained using scanning electron microscopy (Figure 5), the morphology of surface layers obtained in the base electrolyte and in those with ZrO_2 and SiO_2 particles differs substantially. The surface of the

coating containing zirconia nanoparticles (Figure 5(c)) is smoother in comparison with the convolute surface of the coating obtained in the base electrolyte without nanoparticles (Figure 5(a)) and in the silica-containing electrolyte (Figure 5(b)). Analysis of the obtained SEM images performed using the *ImageJ* software allowed estimating the formed layers porosity. The coatings fabricated in the base electrolyte had the maximal porosity –2.89%. The PEO layers formed in electrolytes containing ZrO_2 and SiO_2 particles had porosities equal to 2.17 and 1.61%, respectively. At the lowest porosity, the coating with SiO_2 nanoparticles has, due to higher surface roughness (presence of juts), the largest roughness value ($R_a = 1.70 \mu\text{m}$), as compared to the base PEO coating ($R_a = 1.23 \mu\text{m}$) and that containing ZrO_2 particles ($R_a = 1.21 \mu\text{m}$).

From the analysis of X-ray diffractograms, introduction of ZrO_2 nanoparticles into the electrolyte composition during plasma electrolytic oxidation of magnesium alloy MA8 results in formation of surface layers containing particles in the initial state (Figure 6). Most probably, due to PEO, nanoparticles from the suspension were melted into the heterolayer surface.

SiO_2 nanoparticles introduced into the electrolyte for oxidation are X-ray amorphous. Since silicon is present in the composition of the base electrolyte, it appears to be complicated to establish the intensity of embedding of silicon dioxide nanoparticles into the coating composition using the method of X-ray diffraction analysis.

The element composition of coatings was determined using the EDXRF analysis (Table 2). As compared to the base electrolyte, the silicon concentration in surface layers increased from 18.5 up to 27.9 wt.% for the PEO coating obtained in the electrolyte with silica nanoparticles. Similar trend to the silicon quantity increase on the surface is corroborated by the data obtained using the EDS method (Figure 7). The data on silicon distribution over the coating thickness demonstrated that nanoparticles included only the surface layers.

The zirconium concentration in the coating fabricated in the electrolyte with zirconia nanopowder attained just 1.7 wt.%.

TABLE 2: The elemental concentration of coatings.

Type of sample surface	Element, wt. %						
	Mg	O	Si	Zr	Na	Mn	Others
PEO layer	37.7	38.4	18.5	—	1.2	3.0	1.2
PEO layer with ZrO ₂ nanopowder	36.7	36.5	19.1	1.7	1.9	3.5	0.6
PEO layer with SiO ₂ nanopowder	28.2	37.2	27.9	—	2.5	2.9	1.3

FIGURE 5: SEM images of the surface morphology of PEO coatings formed in the different electrolytes: without nanoparticles (a), with zirconia (b), and silica (c) nanopowders.

FIGURE 6: X-ray diffractograms of the coating, produced by PEO in the electrolyte with ZrO₂ nanopowder (1) and with SiO₂ nanopowder (2) and in base electrolyte without nanoparticles (3).

3.3. Coatings Properties. To evaluate the corrosion resistance of the obtained coatings, their electrochemical properties were investigated. Analysis of polarization curves (Figure 8) enable one to conclude on a substantial positive effect of nanosized zirconia and silica in the composition of the forming electrolyte on anticorrosion properties of the fabricated coatings. Corrosion currents (I_c) of the samples with coatings formed in electrolytes containing nanoparticles

TABLE 3: Corrosion performances of MA8 magnesium alloy samples.

Type of sample surface	R_p ($\Omega \cdot \text{cm}^2$)	I_c (A/cm ²)	E_c (V)
Bare alloy	3.6×10^3	1.1×10^{-5}	-1.56
PEO layer	2.4×10^5	1.1×10^{-7}	-1.52
PEO layer with ZrO ₂ nanopowder	4.9×10^5	5.3×10^{-8}	-1.42
PEO layer with SiO ₂ nanopowder	3.2×10^5	8.2×10^{-8}	-1.50

are significantly lower in comparison with the sample with initial PEO layer (Table 3). One of the important reasons for improving the protective properties of coatings formed in electrolytes containing nanoparticles consists in enhanced morphological characteristics, in particular, the porosity decrease. Besides, the coatings obtained using nanoparticles contain chemical compounds (ZrO₂, SiO₂) having much higher chemical stability as compared to that of the main components of the base PEO layer.

Evaluation of the effect of nanosized materials present in the coatings on their electrochemical properties and the state of the composite layer/electrolyte interface was carried out by electrochemical impedance spectroscopy (Figure 9). The experimental data are presented as Bode diagrams, in which changes in the impedance modulus $|Z|$ and the phase angle θ are shown versus to the frequency f . The impedance spectra (Figure 9) obtained for different layers demonstrate significant differences in the external appearance, thus reflecting

FIGURE 7: Microphotographs of the cross section of coatings obtained in electrolytes of different compositions: without nanoparticles (a) and with ZrO_2 (b) and SiO_2 (c) nanoparticles. Below SEM images one can see EDS data on the distribution of main elements over the coating thickness.

TABLE 4: Calculated parameters of the elements of equivalent electrical circuits ($|Z|_{f=0.03 \text{ Hz}}$, R , $\Omega\cdot\text{cm}^2$; Q , $\text{S}\cdot\text{cm}^{-2}\cdot\text{s}^n$) for the samples.

Type of sample surface	$ Z _{f=0.03 \text{ Hz}}$	R_1	CPE ₁		R_2	CPE ₂	
			Q_1	n		Q_2	n
Bare Mg	1.8×10^3	—	—	—	4.8×10^2	3.3×10^{-5}	0.85
PEO layer	5.4×10^4	8.37×10^3	4.64×10^{-7}	0.68	5.21×10^4	2.63×10^{-6}	0.75
PEO layer with ZrO ₂ nanopowder	1.8×10^6	5.94×10^4	6.66×10^{-8}	0.83	1.45×10^6	5.92×10^{-8}	0.83
PEO layer with SiO ₂ nanopowder	5.6×10^4	8.50×10^3	2.37×10^{-7}	0.76	6.85×10^4	9.88×10^{-7}	0.76

FIGURE 8: Polarization curves of the samples of magnesium alloy MA8 without coating (1) and with PEO coatings obtained in the silicate-fluoride electrolyte without addition of nanoparticles (2) and with using ZrO₂ (3) and SiO₂ (4) nanopowders.

the difference in electrochemical properties of composite coatings at large.

The electrochemical simulation of the electrode/electrolyte interface based on experimental data of electrochemical impedance spectroscopy was based on a systematic approach, in which the studied object was considered as an equivalent electrical circuit including elements characterizing the electrode/electrolyte interface. Analysis of the obtained impedance spectra allows conclusion that the experimental data can be adequately simulated by an equivalent electrical circuit (EEC) with two R -CPE chains (Figure 10) [27]. In this circuit, the constant phase element (CPE) is used instead of the electrical capacitance: as a rule, it is used for description of nonideal capacitance (heterogeneous surface layers with heterogeneous composition and thickness, complex morphology, and gradient of charge carriers within the oxide layer).

The impedance of the CPE is defined by

$$Z_{\text{CPE}} = \frac{1}{Q(j\omega)^n}, \quad (1)$$

where Q is preexponential factor, which is a frequency-independent parameter, n is the exponent determining the character of the frequency dependence, ω is the angular frequency, and j is the imaginary unit. The constant phase

element is widely used in advanced electrochemical simulation of various complex objects, including the description of processes occurring at the anode oxide layers interfaces.

The value R_e comprises the electrolyte resistance (in this study it is equal to $29\text{--}32 \Omega\cdot\text{cm}^2$). The CPE₁ element is the coating geometric capacity. The R_1 element parallel to CPE₁ is responsible for the electrical resistivity of pores to ionic current. The elements of the parallel circuit CPE₂- R_2 characterize the nonporous coating layer. High values of the exponent n (close to 1, Table 4) for both constant phase elements indicate the capacitive character of CPE. The values of parameter calculated through fitting experimental impedance spectra to the theoretical model (EEC) are shown in Table 2.

Embedding of nanoparticles into the coating (Figure 10, curves 2 and 3) increases the value of the impedance modulus $|Z|_{f \rightarrow 0 \text{ Hz}}$ from 5.6×10^4 (for SiO₂-containing coatings) up to $1.8 \times 10^6 \Omega\cdot\text{cm}^2$ (for ZrO₂-containing coatings), as compared to that of the base PEO layer ($5.4 \times 10^4 \Omega\cdot\text{cm}^2$). From the analysis of the data shown in Table 4, the preexponent factor Q_1 in CPE₁, an analog of the geometric capacity, decreases for the coatings containing nanosized materials, which can be explained by the increase of the thickness of the heterooxide layer. The increase of the R_1 value characterizing the electrolyte resistance in pores for coatings containing ZrO₂ and SiO₂ nanoparticles, as compared to the base PEO layer, shows that the bulk porosity of composite coatings decreases. One should mention that embedding of ZrO₂ and SiO₂ nanoparticles into coatings results in the increase of the thickness of the nonporous layer, which is indicated by the decrease of Q_2 in CPE₂. For ZrO₂-containing coatings, this increase is almost 2 orders of magnitude.

One should mention that the impedance modulus at high frequencies for the samples with coatings, unlike that for bare alloy (Figure 9), does not attain the electrolyte resistance ($29\text{--}32 \Omega\cdot\text{cm}^2$), which can be explained by the complex morphological structure of surface layers formed by the PEO method (Figure 5).

Evaluation of the mechanical properties of the fabricated coatings was carried out using the method of microhardness testing. From the analysis of the results of dynamic microhardness tests (Figure 11, Table 5), the layers containing nanoparticles are harder in comparison with the coatings formed in the base electrolyte ($H_\mu = 2.8 \text{ GPa}$). The best microhardness parameters are characteristic of the coatings containing ZrO₂ nanoparticles, 4.7 GPa . SiO₂ nanoparticles provide somewhat lower microhardness value, 3.8 GPa . Such an increase is, probably, related to the composition of the embedded nanoparticles and the surface layer morphology.

FIGURE 9: Bode diagrams for samples of magnesium alloy MA8 without coating (1) and with PEO coating, formed in the different electrolyte, without nanoparticles (2) and with zirconia (3) and silica (4) nanopowders.

FIGURE 10: Equivalent electrical circuit used to fitting experimental impedance spectra of the MA8 magnesium alloys samples with PEO coatings. CPE_1 , R_1 and CPE_2 , R_2 , the constant phase elements and the resistances of the outer porous layer and the inner nonporous layer, respectively. R_e , the electrolyte resistance.

The surface part of nanoparticle-containing coatings has much lower porosity and higher density than for the coatings obtained in electrolytes without use of nanoparticles.

Adhesion properties were evaluated using the scratch testing. Figure 12 shows the data for the coating formed in the electrolyte with ZrO_2 nanoparticles that manifested the best performance. During the tests, several parameters were registered simultaneously: applied load (curve 3), indenter penetration depth (curve 2), acoustic emission (curve 4), and friction force of indenter on the sample under load (curve 5). To determine the coating material elastoplastic properties, the repeated registration of the indenter trace profile was carried out after unloading (curve 1). The value of the load corresponding to the first cracks (L_{c1}) for all types of the studied coatings is the same -5.0 ± 0.3 N. The load, at which the coating is worn down to metal (L_{c3}), varies from 13.8 to 14.3 N for the coatings under study (Table 6).

Tribological tests were performed to evaluate wearproof of samples under study. Figure 13 shows the dependencies of the friction coefficient μ on the number of cycles. Tests were

TABLE 5: Microhardness and Young's modulus for the magnesium alloy MA8.

Type of sample surface	Microhardness (GPa)	Young's modulus (GPa)
PEO layer	2.8 ± 0.6	7.3 ± 1.6
PEO layer with ZrO_2 nanopowder	4.7 ± 0.8	12 ± 5
PEO layer with SiO_2 nanopowder	3.8 ± 0.2	10 ± 5

TABLE 6: Mechanical characteristics of coatings determined using the method of scratch testing.

Type of sample surface	L_{c2} (N)	L_{c3} (N)
PEO layer	8.4 ± 0.5	13.8 ± 0.2
PEO layer with ZrO_2 nanopowder	9.4 ± 0.7	14.3 ± 0.7
PEO layer with SiO_2 nanopowder	9.3 ± 0.4	13.9 ± 0.7

carried out until the coating wear down to metal. In general, the trend to positive effect of embedded nanomaterials into the coatings composition on their mechanical properties is preserved (Figure 13, Table 7). Wear of coatings containing nanoparticles is lower than for the sample without them. The coatings with SiO_2 and ZrO_2 nanoparticles have higher microhardness in comparison with that of the base PEO coating (Table 5) and, as a result, sustain a 1.2–1.4-fold larger number of load cycles, as compared to the base PEO layer. One should mention that the slope angle of the curve of friction coefficient for the coatings obtained in electrolytes with nanoparticles is smaller than that for the base PEO coating. This fact is related to differences in the morphology and chemical composition of the coatings under study.

FIGURE 11: Dynamic load-unload dependence of changes in the depth of penetration of the indenter into the coating on the applied load: 1: coating formed in the base electrolyte, 2: coating containing ZrO_2 nanoparticles, and 3: coating containing SiO_2 nanoparticles.

FIGURE 12: Scratch testing data for the sample with PEO coating containing ZrO_2 nanoparticles and image of the scratch after the experiment: lines correspond to the values of loads, at which scaling of coatings parts (a) and its plastic abrasion down to metal (L_{c3}) (b) occur. 1: applied load, 2: depth of indenter penetration at load, 3: acoustic emission, 4: friction force, and 5: residual depth of indenter penetration after unloading.

The coatings wear (Table 7) was calculated using the normalization of the sample volume loss during tests ΔV_{sample} on the values of run (N) and applied load (P): $I = \Delta V_{\text{sample}} / (NP)$. The sample volume loss is as follows: $\Delta V_{\text{sample}} = S \cdot l$, where l is the trace length and S is the area of cross section of the wear trace.

TABLE 7: Wear of coatings.

Type of sample surface	Wear rate ($\text{mm}^3 / (\text{N} \cdot \text{m})$)	Cycles
Without coatings	$5.8 \cdot 10^{-3}$	150
PEO layer	$4.1 \cdot 10^{-5}$	2560
PEO layer with ZrO_2 nanopowder	$2.9 \cdot 10^{-5}$	3540
PEO layer with SiO_2 nanopowder	$3.5 \cdot 10^{-5}$	2970

FIGURE 13: Dependence of the friction coefficient of the corundum ball/sample for samples made of magnesium alloy MA8: with PEO coating obtained in the base electrolyte (1) and with PEO coating obtained using ZrO_2 (2) and SiO_2 (3) nanopowders.

4. Conclusions

As a result of the performed studies, electrolytic systems of complex composition containing nanopowders of zirconia and silica have been developed. The analysis of electrokinetic potential and hydrodynamic diameter values for the electrolytic systems containing nanoparticles has been performed. These systems were used for plasma electrolytic oxidation of MA8 magnesium alloy to create nanostructure similar to ceramic protective coatings having good prospects in practical terms. Application of the developed electrolytic systems enabled us to ensure intensive embedding of nano-sized oxide powders to the coating material.

It has been established that nanoparticle-containing coatings have significant advantages as compared to the base surface layer without nanoparticles. Embedding of ZrO_2 and SiO_2 nanoparticles into coatings results in the increase of the thickness of the nonporous layer, which is indicated by the decrease of Q_2 in CPE_2 . For ZrO_2 -containing coatings, resistivity of porousless sublayer increase is almost 2 orders of magnitude as compared to this sublayer in base PEO coating. Experimental data obtained enable one to conclude that the best corrosion inhibition and mechanical properties characterize the coatings formed in the electrolyte containing zirconium dioxide nanoparticles.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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