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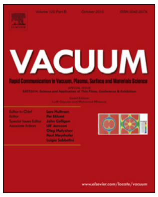

Protective composite coatings obtained by plasma electrolytic oxidation on magnesium alloy MA8

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ABSTRACT

Earlier developed approaches to the formation of composite polymer-containing coatings by plasma electrolytic oxidation (PEO) using various low-molecular fractions of superdispersed polytetrafluoroethylene (SPTFE) have been summarized and a unique method for the formation of composite polymer-containing coatings at the surface of magnesium alloy MA8 has been suggested. The improvement in the corrosion and tribological behavior of the polymer-containing coating can be attributed to the morphology and insulating properties of surface layers and the solid lubrication effect of 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 dispersion and ξ-potential of the nanoparticles (ZrO_2 and SiO_2) used as an electrolyte component for PEO on the composition and properties of the coatings has been investigated. Improvement of the protective properties for coatings with the incorporated nanoparticles has been explained by the greater thickness of the protective layer, relatively low porosity and the presence of narrow non-through pores. The layer with zirconia has an impedance modulus measured at low frequency ($|Z|_{f\to 0\text{Hz}} = 1.8 \times 10^6\ \Omega\ \text{cm}^2$) more than one order of magnitude higher than the PEO-coating formed in the electrolyte without nanoparticles ($|Z|_{f\to 0\text{Hz}} = 5.4 \times 10^4\ \Omega\ \text{cm}^2$).

1. Introduction

The plasma electrolytic oxidation method is used for fabrication of coatings that improve the surface properties of various metals and alloys [1–12]. 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, corrosive, electrical, and thermal properties of these coatings have generated interest in view of their possible use in mechanical, aerospace, aircraft, the automobile industry, engineering equipment components, and biomedical devices. This method can be used for corrosion protection of Mg alloys [6,13–38].

In Refs. [5,13–38] the results of the targeted synthesis of a protective coating on the surface of the magnesium alloy MA8 by plasma electrolytic oxidation were reported. The coatings obtained by the PEO method have 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 at 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's 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 as a whole [1]. In Refs. [7,39] the scanning probe electrochemical methods were used to analyze the trends in the development of the corrosion processes in the area of an artificially-created defect in the PEO-coating. As a result, it was established that, in a corrosion-active chloride-containing medium, the corrosion process of a magnesium alloy developed, due to its high corrosion activity, predominantly at the coating/substrate interface, i.e. under the protective layer, which results in magnesium substrate corrosion with a

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subsequent disruption of the surface layer. In view of this, the development of the methods of deposition of coatings which, not only, are corrosion-stable, but also, have antifriction and anti-wear properties, is of extreme importance, since this would significantly reduce the probability of mechanical damage of the article in the process of exploitation. PEO-coatings having a good adhesion to the substrate and a developed surface can serve as the basis for the creation of composite layers [1]. Moreover, one of the methods of surface modification is the incorporation of polymer and inorganic nanoparticles in the electrolyte for the plasma electrolytic oxidation or in PEO pretreated surface layer [40,41]. It allows improvement of the practically-important physical and chemical properties of the PEO-coatings such as corrosion- and wear-resistance and hardness. The main problem in the preparation of such suspensions for PEO is to achieve their sufficient sedimentation and aggregation stability.

2. Experimental

2.1. Samples

In the present work, an original method of the formation of a composite polymer-containing layer, taking into consideration the multilayer polymer deposition and the conditions of subsequent thermal treatment, is suggested on the basis of generalization of the results of earlier works [5–7,14,42]. The creation of the composite layer possessing antifriction/inhibitive properties was based on the coating obtained by the PEO method using the bipolar (anode–cathode) polarization mode in the base silicate-fluoride electrolyte [4–6,14,43–48] on samples of size of 5 mm × 30 mm × 1 mm made of the wrought magnesium alloy MA8 (1.5–2.5 wt. % Mn; 0.15–0.35 wt. % Ce; balance – Mg). According to the earlier developed principles of the controlled plasma electrolytic synthesis on the surfaces of metals and alloys [6], PEO treatment in the present work was conducted in a silicate–fluoride electrolyte containing 15 g/l $Na_2SiO_3 \cdot 5H_2O$ and 5 g/l NaF. All samples were processed for 10 min in the bipolar mode of PEO, in which the anodic pulses periodically alternate with cathodic ones. During the anodic component of the process, the voltage values increased from 30 to 300 V at a rate of 0.45 V/s; the cathodic component was in potentiostatic mode fixed at a value of 30 V. The duration ratio of the anodic and cathodic pulses was equal to 1, so that the duty cycles were 50%, and the polarization frequency was 300 Hz. The root-mean-square values of the voltage were used in the formation process in this work. The electrical parameters were controlled using an automated control system connected to a PC with appropriate software. A conventional reversible thyristor rectifier was used as a power supply [6]. The thickness of the obtained coating was about 20 μm and its porosity was 5%.

An additional treatment of the PEO-coating surface using the trade marked Forum® superdispersed polytetrafluoroethylene was suggested to increase its hydrophobicity and to decrease the coating roughness which assists in further reduction of the corrosion intensity [7,18]. SPTFE was obtained from the products of fluoroplastic (F-4) by the gas-dynamic thermal destruction method. The SPTFE powder was put onto the PEO-coated surface by the tribo-electric method. Since the size of the superdispersed polytetrafluoroethylene particles (0.35 μm) is commensurable with the pore size, this method allows the polymer to be embedded into the porous layer. The subsequent heat treatment enables the polymer to penetrate inside the pores due to SPTFE softening. To fill the pores in the PEO-coatings, the SPTFE powder application followed by heat treatment of the composite structure at 265 °C for 1 h was used. Such a temperature results in embedding of a more stable protective plug into the pore. As shown by the experimental results of earlier studies [8], when pores are filled with the SPTFE powder, the thermal treatment is necessary to use the polymer to build smooth hydrophobic surface layers.

Processing with SPTFE powder ensures filling coating pores with the polymer and, therefore, forming an additional barrier layer that will hinder the release of metal ions into the solution and increase the sample stability in a corrosion-active media.

To reveal the effect of the number of cycles of treatment of PEO-layers on magnesium with SPTFE, the physical–chemical properties of composite coatings obtained as a result of single and five-fold polymer treatments were investigated.

Other materials we chose for this research are zirconia (ZrO_2) and silica (SiO_2) nanopowders with particle size of 100 nm. These powders were obtained in the A.A. Baikov Institute of Metallurgy and Materials Science of the Russian Academy of Sciences by A.V. Samokhin under the supervision of Academician Y.V. Tsvetkov [49]. These materials are promising for the surface modification in order to improve the properties and operating ability of the processed metal and alloy.

Nanoparticles were added into the electrolyte used for PEO and dispersed using a Bandelin HD 3200 ultrasonic disperser. The size and ξ-potential of the particles in a suspension was measured using a Zetasizer Nano ZS universal analyzer (Malvern Instruments) by a dynamic light scattering method.

A preliminary analysis of the stability of nanopowder suspensions was carried out in an aqueous medium with the concentration of nanoparticles and surfactants 0.1 g/l and 0.01 g/l, respectively. To obtain the electrolyte, a 100 ml suspension of ZrO_2 (or SiO_2) with concentration of 40 g/l was injected into 900 ml of solution of Na_2SiO_3 and NaF [1,50]. This electrolyte was used for plasma electrolytic oxidation of MA8 magnesium alloy samples in bipolar mode polarization as described elsewhere [5–7,14,42].

2.2. Electrochemical measurements

Electrochemical measurements were performed at room temperature using a VMC-4 electrochemical station (Princeton Applied Research, USA). Measurements were carried out in 3% NaCl solution (pH = 7) in a three-electrode cell. Platinum coated niobium mesh was used as a counter-electrode. A silver/silver chloride electrode filled with saturated KCl solution served as a reference electrode. In all our experiments, the exposed apparent area of the samples to electrolyte solution was 1 cm^2. All the electrochemical parameters were calculated per this visible exposed area. Prior to the electrochemical measurements, the samples were kept in the solution for 30 min in order to stabilize the free corrosion potential. The potentiodynamic polarization curves were registered at a sweep rate of 1 mV/s. Electrochemical impedance spectroscopy (EIS) measurements were conducted at an open circuit potential in the frequency range from 1.0 MHz to 0.01 Hz (logarithmic sweep, 7 points per decade), with a 10 mV (rms) sine-wave perturbation signal. The experiments were controlled and analyzed with the aid of VersaStudio (Princeton Applied Research, USA), ZView and CorrView software (Scribner Associates, USA).

2.3. Friction and tribological tests

The measurements for determination of the friction coefficient were carried out on a Revetest (RST) scratch tester (CSM Instruments, Switzerland) using a 100Cr6 steel ball of diameter of 6 mm as a counterbody at constant rate and load (14 mm/min and 7 N, respectively) over the whole route length (7 mm).

The additional tribological tests were carried out on a TRB-S-DE tribometer (CSM Instruments, Switzerland). The speed of rotation was $\nu = 10$ mm/s and the diameter of the corundum ball (counterface)