Corrosion Science 111 (2016) 175–185

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Composite fluoropolymer coatings on the MA8 magnesium alloy surface

S.V. Gnedenkov[a], S.L. Sinebryukhov[a], D.V. Mashtalyar[a,b,*], K.V. Nadaraia[a,b], A.S. Gnedenkov[a], V.M. Bouznik[a]

[a] Institute of Chemistry of FEB RAS, 159 Pr. 100-letiya Vladivostoka, Vladivostok, 690022, Russia
[b] Far Eastern Federal University, 8 Sukhanova St., Vladivostok, 690950, Russia

ARTICLE INFO

Article history:
Received 18 February 2016
Received in revised form 27 April 2016
Accepted 27 April 2016
Available online 6 May 2016

Keywords:
A. Magnesium
A. Polymer
B. EIS
B. Electrochemical calculation
B. Modeling studies
C. Oxide coatings

ABSTRACT

The methods to form protective coatings by the plasma electrolytic oxidation method (PEO) using the superdispersed polytetrafluoroethylene (SPTFE) suspension have been developed. Electrochemical, salt spray corrosion testing, hydrogen evolution, and tribological studies of the composite polymer-containing coatings have been carried out. Models of the coatings structure have been suggested. The obtained results corroborated the increase of the corrosion protection and wear-resistance parameters by more than 4 orders of magnitude for the composite coating in comparison with the base PEO-coating. The fabricated composite coatings are characterised with high antifriction properties due to the presence of polytetrafluoroethylene in the surface layer pores.

1. Introduction

At present, magnesium alloys are widely used in various fields of industry (automobile and aircraft manufacture and aerospace industry). In general, magnesium alloys are used in the fields of industry, in which a small weight of the construction with high durability is required. Taking into account their combination of low specific density and acceptable in practice durability characteristics, it can be stated that magnesium alloys will be one of the base materials for manufacture of machine parts in different areas of the national economy in the near future. Nevertheless, magnesium alloys have certain disadvantages limiting the area of their possible applications. Such disadvantages include low resistance to the corrosion and wear processes.

Recently, different methods of the magnesium alloys protection against destruction factors have been developed. One of the most often used methods consists in formation of the coatings [1–3] imparting the surface with special functional properties [4–7]. Plasma electrolytic oxidation (PEO) is one of the most promising ways of the alloys and metals surface treatment [8–14]. The plasma electrolytic oxidation method is widely used for production of oxide coatings on the surface of metals and alloys [2,15–21]. During the PEO-process, the oxidation of the treated article is performed using high values of the applied electrode potential difference, in comparison with conventional anodisation. Plasma discharges occur on the electrode surface at the critical values of the electric field strength (up to 1–10 MV cm^{-1}). The temperature and pressure inside the discharge channel achieve the values of up to 10000 °C and 100 MPa, respectively. During the PEO-process, an intensive ion and electric transfer is realised. This process promotes the electrochemical and plasma-chemical synthesis of the coating material with the electrolyte components [11,21]. After the discharge attenuation, a sharp cooling of the breakdown zone down to the electrolyte temperature is realised. This effect affects the physicochemical properties of the formed surface layers [22,23]. This method enables one to form wear and corrosion resistant, dielectric, ceramic-like, and decorative coatings on the surface of different metals and alloys [24–33]. However, in some cases, the protective properties of PEO-layers are not sufficient to protect metals and alloys against negative factors, since all PEO-coatings have pores and microdefects. Through such pores aggressive environment agents could penetrate until the substrate material and destroy it. On the other hand, the convoluted and rough surface of PEO-coatings can serve as an appropriate base for the formation of composite layers [2,34] containing chemically stable materials,

---

* Corresponding author at: Institute of Chemistry of FEB RAS, 159 Pr. 100-letiya Vladivostoka, Vladivostok, 690022, Russia.
E-mail address: madiva@inbox.ru (D.V. Mashtalyar).

http://dx.doi.org/10.1016/j.corsci.2016.04.052
0010-938X/

such as polytetrafluoroethylene [35–38]. In this case, the fluoropolymer material covers the surface of the PEO-layer, penetrates into the pores, and seals them. Such composite polymer-containing coatings have higher protective characteristics in comparison with the base PEO-coatings [39–42] and can be used in applications, where maximum protective properties of coatings are required.

Superdispersed polytetrafluoroethylene (SPTFE) by the trademark Forum® [43] has a number of characteristics, which are of great importance for protective coatings formation: high chemical inertness, durability to high temperature drop, and low conductivity. The SPTFE particles have a diameter from 0.1 up to 1 μm (average value about 550 nm).

There are several possible ways to form composite coatings based on the PEO-layer using SPTFE. One of the examples consists in the formation of composite coatings immediately during the PEO process [44,45]. However, there is high probability of thermal destruction of the fluorine-organic material during PEO, since the temperature in the channel of plasma microdischarges could reach up to 10000 °C [8,46]. At the same time, the maximal temperature, at which polytetrafluoroethylene preserves its properties, is limited up to 415 °C [43,47]. Another way to obtain composite layers is two-stage coating formation [36,40,41]. In this case, the heterooxide PEO-layer is formed on the surface of the material during the first stage. Thereafter, the formed layer is treated with SPTFE.

The present work is a continuation of the previous studies [36,40,42] devoted to development of optimal ways, which can be used in practice, to form composite coatings on the surface of the magnesium alloy. The present work describes the developed new method of the composite coating formation on articles made of magnesium alloy.

2. Experimental

2.1. Samples

Plates made of the magnesium alloy of the MA8 grade (Mg–Mn–Ce system, 1.30 wt.% Mn; 0.15 wt.% Ce; balance – Mg) purchased from JSC All-Russia Institute of Light Alloys were used as samples. Samples having the following sizes were prepared: $30 \times 15 \times 1$ mm^3 for electrochemical measurements and wear estimation; $100 \times 20 \times 1$ mm^3 for galvanic corrosion measurements; $100 \times 50 \times 1$ mm^3 for salt spray testing; $10 \times 10 \times 1.5$ mm^3 for hydrogen evolution tests. Plates made of the aluminium alloy of the D16 grade (Al–Cu–Mg system, 4.18 wt.% Cu; 1.80 wt.% Mg; 0.50 wt.% Si; 0.30 wt.% Mn; 0.27 wt.% Fe; balance – Al) purchased from Kamensk Uralsky Metallurgical Works were used for the galvanic corrosion measurements as a counter electrode. The size of the aluminium samples was $100 \times 20 \times 1$ mm^3. All specimens were mechanically ground successively to P1200 grit with silicon carbide (SiC) papers and further polished with aluminium oxide papers with the grain size down to 3 μm for surface standardization. After the polishing, the samples were washed with deionized water and ethanol using ultrasonic bath and then air dried.

In accordance with earlier developed principles of the direct plasma electrochemical synthesis of the coatings on the surface of metals and alloys [41,48] and the literature data analysis [49–52], the silicate-fluoride electrolyte containing 15 g l^{-1} sodium orthosilicate (Na_4SiO_4) and 5 g l^{-1} sodium fluoride (NaF) was used for the base PEO-layer formation. This electrolyte was chosen for formation of protective layers, which have convoluted and rough surface. Such a surface is necessary to form composite coatings. The process of the coating formation was realised on the plasma electrolytic oxidation unit with an automatic operation and control system connected to PC with relevant software. A conventional reversible thyristor rectifier was used as a power supply [6,48]. All the samples were processed in two stages in the bipolar mode of PEO, in which the anodic pulses periodically alternate with cathodic ones. At the first stage, the anodic component voltage was increased from 30 to 240 V at a sweep rate of 1.05 V s^{-1}; the cathodic component was fixed in the potentiostatic mode at a value of −40 V. At the second stage, the voltage was changed in the anodic component from 240 down to 200 V at a sweep rate of 0.07 V s^{-1}, in the cathodic one from −40 up to −10 V at a sweep rate of 0.05 V s^{-1}. The duration of the first stage of the PEO process was equal to 200 s, while for the second one it was equal to 600 s. The duration ratio of the anodic and cathodic pulses was equal to 1, i.e. the duty cycle was 50%. The polarization frequency was 300 Hz. The root-mean square values of the applied potential amplitude were used in the formation process. During the oxidation process, the temperature of the electrolyte (25 °C) was controlled by means of a ChillerSmart H150-3000 device (LabTech Group, UK).

Superdispersed polytetrafluoroethylene by the trademark Forum® was used as a fluorine-organic material to form the composite layers. SPTFE was obtained by thermogradient synthesis at heat destruction of the fluoroplastic waste in the Institute of Chemistry of the Far Eastern Branch of Russian Academy of Sciences [43]. 15 wt.% suspension of SPTFE powder in isopropanol was used to obtain the composite coatings. Polymer has been applied to the base PEO-layer using the dip-coating technique. It was earlier established that the most homogeneous layer could be obtained at slow dipping of the sample, exposure to the suspension for up to 10–15 s, and rapid removal of the specimen. Then the sample was dried under ambient conditions for 20 min. Based on positive experimental results of earlier studies of the composite coating formation using superdispersed polytetrafluoroethylene [36] and the data of our earlier research experiments, the optimal mode of thermal treatment of the samples with composite coatings after the polymer spreading by the dip-coating method was suggested: temperature was about 315 °C for 5 min. In case of multiple treatment, the samples with polymer coating were cooled after heat treatment at the ambient condition down to 25 °C, after which the operations of dip-coating and heat treatment were repeated. In this work, the results of studies of the effect of the polymer layers on the PEO-coating surface on the properties of the formed composite coatings were presented for the samples with single (CC-1x) and fourfold (CC-4x) polymer treatment. Abbreviations CC-1x and CC-4x mean that the samples were subject to one and four repeated cycles of the treatment, respectively.

2.2. Electrochemical measurements

Electrochemical properties of the formed surface layers on the magnesium alloy were studied using a ModuLab electrochemical system (Solartron Analytical, UK). The studies were carried out in the three-electrode cell at room temperature in the 3 wt.% NaCl solution. A platinum mesh was used as a counter electrode. The saturated calomel electrode (SCE) was used as a reference electrode. In all our experiments, the samples area exposed to electrolyte was equal to 1 cm^2. The samples were kept in the solution for 15 min at the open circuit potential (OCP) to achieve the steady state conditions prior to electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurements. The last OCP value was used for EIS measurements. During EIS measurements, the open circuit potential was stabilized potentiostatically. The sinusoidal signal with 10 mV (rms) amplitude was used for impedance measurements. The spectra were recorded at the stabilized OCP in the frequency range 0.01 Hz – 0.1 MHz at the logarithmic sweep 10 points per decade. Potentiodynamic measurements were carried out at a scan rate of 1 mV s^{-1}. The Levenberg-Marquardt (LEV) method [53,54] was used to fit the measured polarization curve