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Plasma anodized ZE41 magnesium alloy sealed with hybrid epoxy-silane coating

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ABSTRACT

Anodic coatings on magnesium ZE41 alloy were formed by DC plasma electrolytic oxidation (PEO) in spark regime in solution composed of NaOH, Na_2SiO_3 and KF. The positive effect of poly(ethylene oxide) addition into the anodizing electrolyte on PEO process, anodic film porosity and its protective performance was described. Anodic films were sealed with hybrid epoxy-silane formulation. The corrosion behavior of the coated ZE41 was studied through electrochemical impedance spectroscopy (EIS) in 0.6 M NaCl solution. Resulting duplex PEO/epoxy-silane coating provides good protective performance without significant signs of corrosion during 1 month of immersion test.

1. Introduction

Magnesium alloys are the lightest of all alloys used as structural materials for industrial applications. Due to unique combination of low density (2/3 of that of aluminum and 1/4 of that of steel) with unique physical and mechanical properties, such as high specific strength, good electrical and thermal conductivity and high vibration absorption, Mg alloys are ideal materials in the fields where weight reduction is critical [1]. Nowadays magnesium alloys are used in the aerospace and automotive industry, in the production of military and civil equipment parts and medical orthopedic equipment. However, in many cases the application of Mg alloys is limited due to high electrochemical reactivity of Mg and its susceptibility to corrosion attack [2]. Therefore, effective surface treatment strategies are needed to protect Mg alloys from corrosion.

Along with a variety of surface treatment techniques such as electrochemical and electroless deposition, chemical surface conversion, deposition from gas-phase, laser surface alloying and organic polymer coating [3–5], plasma electrolytic oxidation (PEO) has been intensively studied [6–13]. At present several commercial processes of PEO are available [14–16]. Anodized layers formed under PEO treatment are usually described as well adherent, hard, ceramic-like coatings comprised of a dense inner and outer porous layer. Depending on electrolyte composition PEO coatings are usually composed of MgO, $Mg(OH)_2$, Mg_2SiO_4, $MgAl_2O_4$, etc. [6]. Incorporating more stable oxides and compounds such as Nb_2O_5, ZrO_2, CeO_2, MgF_2, ZrF_4 into PEO films by modifying the constituents of the electrolytes was found to be favorable for improving their corrosion resistance [7–9]. Irregular pores and cracks that appear in the oxide layer form the pathways for corrosive species thus impairing the total protective effect of anodization. Adjustment of appropriate electrical parameters (pulsed DC, AC, current frequency) for a PEO process might significantly decrease the porosity of the coating and increase the inner dense layer thickness [10–13]. However, specialized power supplies are required to enable an appropriate electrical regime.

Another way to improve corrosion performance of PEO coatings is the addition of additives into the anodizing electrolyte [17–19]. Shi et al. [17] demonstrated that addition of EDTA in the anodizing electrolyte improved the general corrosion resistance of the coating and the doping of the electrolyte with $Na_2B_4O_7$ remarkably enhanced the pitting corrosion resistance. Guo and An [18] reported that addition of dodecyl sodium sulfate, diphenylamine-4-sulfonic acid sodium or dodecyl phenyl sodium sulfonate into the electrolyte had negligible effect on electrical behaviors of coatings during the PEO process and did not change the nature of the defects of the coating, but considerably decreased the porosity. Zhu et al. [19] has

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reported a positive effect of ethylene glycol and some of its oligomers on the structure and composition of PEO coatings, reducing the surface roughness due to decreasing pore sizes and the cracks in the anodic films. Although supplementing anodizing electrolyte with the additives improves coatings corrosion resistance, it is not usually sufficient and sealing is recommended for these coatings [6]. Sealing with sol–gel and polymer coatings, phosphates and treatment with silicates, electroless metal deposition, E-coating, etc. are commonly used to improve protective stability of anodic films created using PEO [20–26].

In this paper we focus on the effect of the addition of poly(ethylene oxide) into the anodizing electrolyte based on NaOH, Na_2SiO_3 and KF with the aim to reduce porosity and increase protective stability of PEO formed coatings on ZE41 magnesium alloy. We report on preparation of highly corrosion resistant, duplex coating based on an improved plasma anodized layer sealed with a hybrid epoxy-silane coating.

2. Experimental

2.1. Materials and reagents

The plates of extruded commercial ZE41 magnesium alloy (mass fraction: 3.5% Zn, 0.6% Zr, 0.8% Ce, 0.3% La, and Mg balance) were used as metallic substrates. The samples were cut to the size of 40 mm × 25 mm × 2 mm and ground with SiC paper 600, 800 and 1200 grits using absolute ethanol as an antifriction media at completion stage. The samples were then washed in ethanol in an ultrasonic bath and dried in a compressed air flow at room temperature. All the reagents used in this work were high purity grade products from Sigma–Aldrich. The aqueous solutions were prepared using MilliPore purified water ($\rho > 18\ \text{M}\Omega\ \text{cm}$).

2.2. Anodizing

The cleaned ZE41 samples were treated before anodizing in 8.5 M HF aqueous solution for 15–20 min at room temperature. After HF treatment the substrates were washed with distilled water and dried in a compressed air flow. An Agilent® N5751A DC power supply (300 V, 2.5 A, 750 W) was used as the DC source in all anodization experiments with the sample as the anode and a stainless steel cup (200 ml) as cathode. Anodization was performed in two electrolytes: 0.15 M NaOH + 0.13 M Na_2SiO_3 + 0.17 M KF (electrolyte ***1***) and the same solutions with the addition of 7.5 g/l poly(ethylene oxide), M.W. ~600.000 (electrolyte ***2***). ZE41 sheets were anodized under a constant current density 3 mA cm^{-2} for 9 min in stirred electrolyte at a temperature 20 ± 2 °C. After anodizing the samples were rigorously washed with distilled water and dried in a compressed air stream at room temperature.

2.3. Hybrid coating preparation and application

The hybrid formulations used as sealing agents for anodized magnesium were produced as described in [27]. Briefly, the coating solution consisted of three main ingredients: a silane, (aminopropyltriethoxysilane (APTES), Ref. 741442), an epoxy component (poly (bisphenol A-co-epichlorohydrin)glycidyl end-capped, Ref. 387703) and an amine (diethylenetriamine (DETA) Ref. 93856), all were acquired from Sigma–Aldrich. Ethanol and acetone were used as solvents. The final concentration of the main components was 3 wt.% silane (0.14 M), 34.9 wt.% epoxy (0.98 M) and 3.8 wt.% amine (0.37 M). The coating was deposited on the ZE41 magnesium alloy by dipping the substrate into solution, keeping the substrate there for 5 s and withdrawing the sample at a speed of 36 cm/min. The dipping procedure was repeated four times using programmable dip coater RDC15 from Bungard Elektronik. After three dippings, the samples were cured in an oven at 150 °C for 1.5 h.

Prior to the coating application, ZE41 samples were either anodized as described in Section 2.2 or mechanically ground in water with silicon/carbon paper with mesh sizes 220 and 500 followed by mechanical grounding in ethanol with silicon–carbon paper with a mesh size of 1200.

2.4. Electrochemical techniques

Polarization measurements were carried out in 0.5 M NaCl solution using a three-electrode cell (10 ml) with the sample a platinum counter-electrode and saturated calomel electrode (SCE) as reference. EIS on anodized samples was performed in 0.005 M NaCl solution at 20 °C using Gamry FAS2 Femtostat coupled with a PCI4 controller at open circuit potential applying 10 mV sinusoidal perturbations (peak to zero) in the 100 kHz to 10 mHz frequency range. Seven experimental points per frequency decade were collected during the measurements. The exposed surface area was 3.3 cm^2. At least three samples were measured for each anodic coating to check reproducibility of the results.

In the case of sealed coating systems the EIS measurements were intermittently taken in course of the immersion in a pH neutral 0.6 M NaCl solution during 1 month. EIS measurements in this case were carried out using an Autolab PGSTAT302 at open circuit potential applying 10 mV of sinusoidal perturbations (peak to zero) in the frequency range of 100 kHz to 10 mHz. All of the measurements were preformed in a Faraday cage in order to avoid any electro-magnetic interference.

2.5. Microscopic and structural characterization

Investigation of the structure of the obtained anodic films and their composition was performed using a Semi-in-lens Hitachi SU-70 UHR Schottky Analytical FE-SEM coupled with a Bruker EDS detector. The samples for cross-section analysis were prepared by embedding the treated coupons of ZE41 into epoxy resin. After solidification of the epoxy resin, the specimens were ground sequentially with 320, 1000, 2400 grit SiC paper in water and finally with 4000 grit SiC paper in ethanol. X-ray diffraction (XRD) studies of anodic coatings were performed using a Philips X'Pert MPD diffractometer (Bragg–Brentano geometry, Cu Kα radiation).

3. Results and discussion

3.1. Preparation of anodized samples

The voltage–time transients for PEO ZE41 galvanostatic anodization in electrolytes without (black line) and with poly(ethylene oxide) additive (red line) are presented in Fig. 1. The voltage curve is an important characteristic of PEO process. An anodizing process can generally be divided into several stages [28–31] corresponding to voltage–time transient and phenomena that occurred in the bath. During PEO processing four different stages could be clearly identified. Stage 1 represents the period when the bath voltage increases linearly with time and there is no sparking at this stage. Initial Mg dissolution and thin passive film formation occurs at stage 1. Voltage–time curves are practically identical for both electrolytes during the first 30 s of anodization. Stage 2 represents the period when electric breakdown of the passive film occurs, resulting in tiny, rapidly flashing sparks on the electrode surface. No significant voltage oscillations are observed. The increase occurs slower with time at this stage when compared to the first one. It is noteworthy that the applied potential in the electrolyte with