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Role of particle type and concentration on characteristics of PEO coatings on AM50 magnesium alloy

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ABSTRACT

Composite ceramic coatings were formed on a magnesium alloy by AC plasma electrolytic oxidation using a phosphate-based electrolyte with α-Al_2O_3, monoclinic ZrO_2 or CeO_2 particles in suspension. Effects of particles concentration (2, 5 and 10 g/L) on the electrical response, composition/morphology and corrosion behaviour of the coatings were investigated. Findings revealed successful incorporation of particles, which were preferentially located in the outer coating layer. Due to high temperatures at the locations of microdischarges, zirconia particles underwent transformation from monoclinic to tetragonal structure. The majority of alumina and ceria particles remained unaffected, although some of the alumina particles possibly formed $MgAl_2O_4$ by reaction with the substrate. Porosity and thickness of the coatings tended to decrease with increasing particles concentration in the electrolyte. Coatings formed in the electrolytes containing CeO_2 particles revealed the best long-term corrosion performance in 0.5 wt% NaCl solution.

1. Introduction

There are numerous studies on anodizing of magnesium alloys [1–3]. The main driving force behind such interest is to improve the corrosion resistance and, therefore, to exploit the excellent physical and mechanical properties of magnesium alloys, such as their high strength-to-mass ratio and damping capacity. In particular, plasma electrolytic oxidation (PEO) is receiving great attention as one of the most effective ways to coat Mg materials using an environmentally friendly process that confers the required improvement of corrosion and wear properties in one step [4,5]. The formation of PEO coatings involves polarization of the material to relatively high voltages with contributions from plasma-chemical, thermal and anodic oxidation processes [6]. Coating properties are mainly influenced by processing parameters (treatment time, electrical regime, electrical wave design) and the electrolyte composition [7,8].

Despite their excellent short-term corrosion resistance, PEO coatings on magnesium alloys are relatively porous and the inner barrier layer eventually fails after long-term corrosion testing [9]. Hence, most strategies acknowledged the need for optimization of PEO processes and electrolyte conditions and/or for application of post-treatments [10,11]. A novel approach to overcoming this problem consists in use of colloidal suspensions of ceramic particles so that they are incorporated into the coating at the locations of plasma microdischarges, reducing the coating porosity [12]. The mechanism of incorporation of particles into PEO coatings is still not clear, although it is generally agreed that particles migrate towards the anode due to electrophoretic and/or mechanical forces and then undergo reactive or inert incorporation depending on the nature of the particles and applied conditions [13].

Various kinds of particles (Al_2O_3, SiO_2, TiO_2, SiC, CeO_2, etc.) have been added into PEO coatings on magnesium alloys [12,14]. For instance, Al_2O_3 particles have shown to increase the short-term corrosion resistance, wear resistance and scratch hardness due to formation of more compact coatings [15,16]. It also appears that these particles participate in chemical reactions during the PEO process resulting in formation of $MgAl_2O_4$ [15–17], although unaltered particles have also been observed [18].

Under DC and AC conditions, ZrO_2 particles are incorporated at the surface and followed by subsequent transport along short-circuit paths into the inner coating regions. Additionally, due to locally high temperatures, transition from monoclinic to tetragonal zirconia and formation of $Mg_2Zr_5O_{12}$ have also been observed, suggesting temperatures in the range of 1240 to 2100 °C at the locations of microdischarges [19–22]. From a corrosion point of view, Lee [20], Gnedenkov [23] and Tang [22] reported improved corrosion resistance in PEO-coated magnesium alloys with incorporated ZrO_2 particles due to reduced coating porosity, whereas Mandelli [24] did not get satisfactory results, possibly due to negligible incorporation of particles into the coating.

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The incorporation of CeO_2 particles into PEO coatings under DC regime has been explored by Lim [25] and Xiong [26]. Lim et al. observed an increased incorporation of CeO_2 particles at pores and cracks with the increasing CeO_2 concentration in the electrolyte from 10 to 30 g/L. They also found that 30 g/L CeO_2 in the electrolyte yielded the highest corrosion potential and lowest corrosion current density, possibly due to the reduced coating porosity and high chemical stability of CeO_2. This is similar to the results by Xiong et al. who also observed inert incorporation of CeO_2 particles during the PEO process. A partial reactive incorporation of CeO_2 particles under AC electrical conditions was reported in author's previous work [27], which points out that not only the electrolyte composition but also the electrical parameters play an important role in the final morphology and composition of the coating. That work revealed that low concentration of CeO_2 in the electrolyte (3 g/L) partially blocked the pores in the coating leading to improved corrosion properties. Higher concentration of CeO_2 in the electrolyte (10 g/L) changed the characteristics of local microdischarges generating coatings with more heterogeneous microstructure and a higher number of unsealed pores and cracks.

Most of the previous studies of PEO containing particles do not take into consideration the effect of particles concentration on the electrical response and/or long-term corrosion performance of the coatings. In addition, it is not common to compare different particles for an individual electrolyte, and in particular, for electrolytes with fluoride species, as most of the work has been done in fluoride-free electrolytes [12,13,22,27]. Therefore, in the present study, the effects of α-Al_2O_3, ZrO_2 and CeO_2 particles (2, 5 and 10 g/L) in fluoride-containing phosphate electrolyte on the electrical response, morphology, composition and corrosion behaviour of PEO coatings on AM50 magnesium alloy have been investigated.

2. Material and methods

2.1. Materials

AM50 magnesium alloy (4.5% Al, < 0.26% Mn, < 0.2% Zn, < 0.004% Fe and balance Mg in weight percent), of size 30 mm × 25 mm × 3 mm supplied by Magnesium Elektron Ltd., was used as substrate for PEO. Specimens were ground to P1200 grit silicon carbide and a working area of ~2 cm^2 was defined by application of Lacquer 45 resin (MacDermid plc).

2.2. PEO treatment

PEO treatment was carried out for 900 s using an EAC-S2000 power supply (ET Systems electronic) with a square electrical signal (50 Hz, + 420 V/− 60 V, 50% duty cycle), an initial ramp of 60 s and a root mean square (rms) current density limit of 250 mA/cm^2. The electrolyte, comprising 10 g/L $Na_3PO_4{\cdot}12H_2O$, 1 g/L KOH and 8 g/L NaF, prepared from deionised water and high-purity chemicals, was continuously stirred during the treatment. Additions of 2, 5 and 10 g/L of α-Al_2O_3 (~300 nm, Buehler), ZrO_2 (300–700 nm, Inframat Advanced Materials) or CeO_2 (~560 nm, Inframat Advanced Materials) were made as required. The coatings were formed in a 2 L double-walled glass cell through which cooled water was pumped in order to maintain the electrolyte temperature close to 20 °C. A sheet of type 316 stainless steel, with the dimensions of 7.5 × 15 cm, was used as the counter-electrode. After PEO treatment, the specimens were rinsed in deionised water and dried in warm air.

2.3. Characterization

Surface and cross-sectional morphologies of PEO coatings were examined by scanning electron microscopy using a JEOL JSM-6400 instrument equipped with Oxford Link energy-dispersive X-ray (EDS) microanalysis hardware. Phase composition was investigated by X-ray diffraction (XRD) using a Philips X'Pert-MPD (PW 3040) instrument with a Bragg-Brentano geometry and a step size of 0.005° in the 2θ range from 10° to 80°. Provided XRD patterns of PEO coatings with incorporated particles correspond to those formed in the electrolytes with 5 g/L of particles.

The thicknesses of the coatings were measured at 20 randomly selected places using an eddy-current meter (Isoscope FMP10, Fischer). Surface roughness was measured over a distance of 15 mm in five different locations using a Surtronic 25 tester (Taylor Hobson Precision) and TalyProfile software applying a Gaussian filter of 2.5 mm.

2.4. Electrochemical tests

A Gill AC computer-controlled potentiostat (ACM Instruments) equipped with a frequency response analyzer and connected to a three-electrode cell was used for the electrochemical measurements. The working electrode was the test material with an immersed area of 1 cm^2. Graphite and silver/silver chloride (Ag/AgCl, 3 M KCl) electrodes were used as the counter and reference electrodes, respectively. The test solution consisted of naturally-aerated 0.5 wt% NaCl solution at room temperature (22 °C). EIS measurements were conducted at various times up to 7 days of immersion. The frequency range was from 30 kHz to 10 mHz and the amplitude of the sinusoidal potential signal was 10 mV with respect to the open circuit potential (OCP). Measurements were performed at least twice to ensure reproducibility of the results.

3. Results and discussion

3.1. Coating characterization

Fig. 1 depicts the typical rms current-time transients during the different PEO treatments.

Without particles in the electrolyte, PEO coating reveals a current drop after 450 s of processing (Fig. 1a), which is a common feature under voltage-controlled mode. This drop is related to an increase of the coating impedance and consequently the higher resistance of the oxide material to mass transfer [28].

The addition of ZrO_2 particles into the bath shifts the current drop to earlier times, e.g. for 2 g/L the drop occurs after 330 s and is further reduced to 190 s for 10 g/L (Fig. 1b). A more significant effect is observed in the case of Al_2O_3 particles, with current drop times of 280 s and 120 s for concentrations of 2 g/L and 10 g/L respectively. The incorporation of 2 g/L CeO_2 reveals only a slight difference in the current drop compared to the electrolyte without particles, but this difference increases for higher concentrations of CeO_2 with a current drop time of 280 s for PEO-10 g/L CeO_2.

It ought to be mentioned that most of the studies reported in the literature do not disclose the influence of particles on the electrical response of the PEO process, focusing instead on the mechanisms of incorporation and/or the final coating properties such as corrosion, wear and photovoltaic behaviour [12]. When electrical parameters (current/voltage) and the coating growth rate are disclosed, the results are usually controversial [17,25,29–31]. This is associated with the wide range of different processing parameters (voltage, current, pulse form, frequency and duty cycle) that can be used which directly influence the individual and collective characteristics of the micro discharges, affecting the resultant coating [32]. The systematic study performed in the present work reveals that, under AC voltage control, there is an early current drop for all PEO treatments with suspended particles and furthermore it is influenced by both the nature and concentration of the particles.

Scanning electron micrographs of the coating formed in the particle-free electrolyte are shown in Fig. 2 with the corresponding EDS point analysis along the thickness of the coating gathered in Table 1. The plan view (Fig. 2a) reveals the typical PEO features, i.e. volcano-like pores