Applied Surface Science 433 (2018) 653–667

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

Influence of sealing post-treatments on the corrosion resistance of PEO coated AZ91 magnesium alloy

B. Mingo[a,b,*], R. Arrabal[b], M. Mohedano[b], Y. Llamazares[b], E. Matykina[b], A. Yerokhin[a], A. Pardo[b]

[a] *School of Materials, University of Manchester, Oxford Road, Manchester, M13 9PL, UK*
[b] *Departamento de Ciencia de Materiales, Facultad de Ciencias Químicas, Universidad Complutense, 28040, Madrid, Spain*

ARTICLE INFO

Article history:
Received 25 July 2017
Received in revised form 10 October 2017
Accepted 11 October 2017
Available online 13 October 2017

Keywords:
PEO
Magnesium
Corrosion
Coatings
Sealing
Contact angle

ABSTRACT

The effect of three different post-treatments carried out on Plasma Electrolytic Oxidation (PEO) coated magnesium alloys are evaluated in terms of characterisation and corrosion resistance. Special interest is given to the role of a common additive (NaF) to the coating properties. The post–treatments are based on immersion sealing processes in aqueous solutions of inorganic salts (cerium and stannate based salts) and alcoholic solution of an organic acid (octodecylphosphate acid, ODP). Sealing mechanisms for each post-treatment are proposed. Cerium and stannate sealings are based on filling of the pores with the products of dissolution/precipitation reactions, while the ODP acid sealing is based on the formation of a thin layer of ODP over the coating through specific interactions between the polar part of the organic acid and the coating surface. All coatings are evaluated by salt fog test and analysed by electrochemical impedance spectroscopy. All sealings show a slight increase in the corrosion resistance of the coatings formed in the NaF-free electrolyte, but their positive influence is boosted in case of the coatings obtained in the NaF-containing electrolyte. This is related to the chemical and morphological changes at the coating surface induced by the presence of NaF in the electrolyte.

1. Introduction

The growing use of magnesium in weight-sensitive applications has triggered the development of surface modification treatments capable of increasing its performance, especially its corrosion resistance. Amongst them, Plasma Electrolytic Oxidation (PEO) stands out as an eco-friendly plasma-assisted electrolytic technique capable of obtaining highly stable ceramic coatings with improved hardness, adhesion, corrosion and wear resistance compared to the coatings obtained by other electrolytic methods, such as anodising [1].

PEO operates at direct, alternating, unipolar or bipolar current modes in the voltage range of 400–1000 V [2] using, generally, alkaline aqueous solutions, although acidic electrolytes can also be used [3]. During the treatment, plasma micro-discharges are generated at the substrate-electrolyte interface due to the dielectric breakdown of the surface oxide film formed at the early stages of the process. At the micro-discharge sites, plasma-assisted thermochemical reactions take place whose products solidify within the discharge channels at extremely high cooling rates (10^8 K s^{-1}) [4], leading to the formation of high-temperature phases and metastable compounds containing elements from both the substrate and the electrolyte.

PEO coatings usually possess a layered structure comprising a nanometre scale (100–600 nm) dense inner barrier layer and a thick (5–100 μm) outer layer with variable porosity [1,5]. Although the morphology of the barrier layer is difficult to modify, the thickness, porosity and composition of the outer layer can be tailored as required for specific applications. Such versatility is one of the major advantages of this technique since it allows it to be used in a wide variety of applications. For instance, porous coatings are usually preferred in biomaterials, since they promote cell adhesion, while dense, compact and impermeable coatings are desired to prevent corrosion.

To achieve required coating properties, the following three approaches are usually pursued: (i) optimisation of the electrical parameters, (ii) selection of the electrolyte composition and (iii) application of post-treatments.

Regarding the first approach, the applied current mode, voltage, current density, pulse frequency and duty cycle have been

---

[*] Corresponding author at: School of Materials, University of Manchester, Oxford Road, Manchester, M13 9PL, UK.

E-mail address: beatriz.mingo@manchester.ac.uk (B. Mingo).

https://doi.org/10.1016/j.apsusc.2017.10.083

previously reported to influence the nature and characteristics of micro-discharges (e.g. ignition voltage and plasma temperature) [6], which affected drastically the coating morphology [1]. Generally, AC and bipolar current modes result in denser and more homogeneous coatings compared to those produced by DC and unipolar modes, as the former allow the discharge lifetime to be controlled. High voltages and current densities increase the oxidation rate of magnesium due to the higher energy input, which leads to higher growth rates and, therefore, coatings thickness [7]. Increasing the duty cycle causes a greater energy intensity and lower density of micro-discharges [8,9] which results in higher coating porosity and lower thickness [1]. However, in case of PEO coatings formed on magnesium alloys, contradictory results have been observed. Gao et al. [10] evaluated the influence of the current mode (pulsed unipolar and pulsed biopolar) formed on cp-Mg and observed that the passivation of the metal surface depends on the applied negative pulse. They observed that passivation was hindered under more energetic negative pulses, which results in lower growth rates. The coatings formed under bipolar conditions presented more defects compared to the ones formed under unipolar conditions, which lead to coatings with lower corrosion resistance. Gnedenkov et al. [11] also studied the effect of current mode on the properties of PEO coatings formed on a Mg-Mn alloy and observed the opposite behaviour, coatings formed under biopolar mode had a higher growth rate and improved mechanical and corrosion properties compared to the coatings formed under unipolar conditions.

This suggests that there are other factors that influence the coatings growth mechanism and therefore the coatings morphology. The selection of the electrolyte is one of these fundamental factors that affect both the composition and morphology of the coatings [4].

NaF is a common additive to PEO electrolytes and it is able to modify greatly the coating morphology. It has been demonstrated that F^- ions promote Mg passivation [12] which leads to lower breakdown potentials and results in materials with increased hardness, wear [13] and corrosion resistance [14]. The composition of the coating can also be tailored modifying the composition of the electrolyte, since cataphoretic effects occur during the treatments which allows the incorporation of insoluble particles added to the electrolyte. Previous works by the authors demonstrated successful incorporation of various nanoparticles, e.g. ZrO_2 [15] and CeO_2 [16] to enhance the corrosion resistance, Al_2O_3 [17] and SiC [18] to improve the tribological properties and Ca- and P-rich [19] compounds to promote the biocompatibility of PEO coatings.

However, these strategies do not always confer sufficient protection against corrosion in aggressive environments since the inherent porosity of PEO coatings allows the penetration of aggressive species, which would eventually reach the metal substrate. Therefore, the application of post-treatments adapted from the sealing processes used in anodising is currently becoming a wide spread strategy to improve the long-term corrosion resistance of PEO coatings.

The simplest post-treatment consists in immersion of PEO-coated specimens in boiling water. Following this procedure, Chu et al. [20] observed an improvement in the corrosion resistance of PEO coatings on a magnesium alloy due to partial blocking of the coating porosity by hydroxides and oxides formed in the pores. Based on the same principle, different types of immersion post-treatments have been carried out using different solutions. For instance, immersion in aqueous solutions of various salts provides a simple and economic treatment based on the formation of compounds with low solubility, which would precipitate into pores and cracks of the coating, thus obstructing the paths for corrosive agents [21]. Different types of solutions have been successfully used, including phosphates [22], silicates [23], hydroxyapatite [24] or rare earth based compounds (Ce [22], La [25]). However, these processes are often reversible so the deposited salts can be re-dissolved with time, losing the sealing capacity.

An alternative approach to the immersion in salt solutions is the application of organic top-coats. Organic compounds penetrate easily into the pores and cracks of PEO coatings, sealing them completely and resulting in a smooth surface layer very effective against corrosion. Organic top-coats are based on either organic acids or polymeric compounds synthesised mainly by sol–gel processes. Octadecylphosphonicacid (ODP), on the other hand, is an organic type of sealant which has the ability to interact metal oxide surfaces during simple immersion, forming a hydrophobic monolayer (or a few monolayers) film that improves the corrosion resistance. There are a few examples in the literature where the sealing properties of ODP acid are evaluated on aluminium alloys, i.e. in organic coatings and on a PEO coating [26,27]. However, the results are rather limited and further studies are needed. On the contrary, there are numerous works where the improvement in the corrosion resistance of PEO coatings was promoted by the application of polymeric top-coats [23,28–30], but their main limitation is their low mechanical properties. Scratches or external impacts can easily damage the organic film and the corrosion attack can spread relatively easily under the undamaged areas [31], therefore it is important to have an effective corrosion inhibiting sealant under the polymer top-coats.

In this work, three different types of post-treatments performed on PEO coated AZ91 magnesium alloy are studied and compared from a characterisation and corrosion protection points of view. The applied post-treatments are based on immersion sealings in different media (aqueous solutions of cerium salts and sodium stannate as well as an alcoholic solution of phosphonic acid). Although the use of post-treatments is a common practice in Mg based coatings, there is little information available related to these three types of sealing post-treatments. The main objective of this work is to elucidate the mechanisms of different sealing post-treatments on PEO coatings formed on AZ91 magnesium alloy and their effect on the corrosion resistance. Special interest is given to the role of NaF, a common additive of PEO electrolytes, on the resulting coating morphology and composition.

2. Materials and methods

2.1. Material

A commercial alloy AZ91D with nominal composition of (*wt.%*) 8.80 Al, 0.68 Zn, 0.30 Mn, 0.01 Si, < 0.008 Ni, 0.004 Fe, < 0.001 Cu, Mg – balance supplied by *Magnesium Elektron Ltd*. was used to carry out the investigation. The metallic substrates ($34 \times 24 \times 2\,mm^3$) were ground using successive grades of SiC paper (up to P1200), rinsed in water, cleaned with isopropyl alcohol and dried in warm air. Then the working area was delimited to $\sim 4\,cm^2$ using a commercial resin (Lacquer 45, MacDermid plc.).

2.2. PEO coatings

PEO coatings were obtained using an AC voltage-controlled power supply (EAC-S2000 ET Systems electronic) and an electrochemical cell equipped with a thermostatic jacket $(20 \pm 1)^\circ C$ under continuous electrolyte agitation. An AISI 316 steel plate of $7.5 \times 15\,cm^2$ size was used as a counter electrode. A square waveform voltage signal was applied with a positive-to-negative pulse ratio of 420 V/60 V, using a 60 s initial ramp to reach the voltage amplitude, at 500 Hz frequency. The voltage peak-to-peak value was kept constant and the root mean square (rms) current density was limited to $200\,mA\,cm^{-2}$. To evaluate the influence of NaF on the composition and morphological features of PEO coatings, two dif-