



Contents lists available at ScienceDirect

Corrosion Science

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



Influence of surface pre-treatment on the deposition and corrosion properties of hydrophobic coatings on a magnesium alloy

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ARTICLE INFO

Article history:

Received 9 May 2016

Received in revised form 13 August 2016

Accepted 23 August 2016

Available online xxx

Keywords:

A. Magnesium

B. EIS

B. Polarization

B. SEM

B. XRD

ABSTRACT

Calcium stearate based hydrophobic coatings were deposited on pre-treated Mg alloy substrates. The influence of four different pre-treatments including plasma electrolytic oxidation (as prepared and etched), anodizing and hydrothermal treatment was studied. The results indicate that the pre-treatments have strong influences on the morphology, thickness, and wettability of the coatings, without affecting their phase composition. The coating system based on the etched plasma electrolytic oxidation pre-treatment shows the best corrosion resistance in a simulated body fluid. The superior protection effect is mainly related to the differences in the morphologies and thickness of the pre-treatment layers.

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1. Introduction

Magnesium based alloys offer many beneficial properties such as low density, high strength and good biocompatibility [1,2]. Additionally, they are considered as promising candidates for construction of biomedical devices [2–8] and have attracted increasing attention for load-bearing biocompatible implant applications [9–11]. However, the relatively poor corrosion resistance of magnesium alloys in aggressive environments limits their application range.

Applying a protective coating is an effective way to improve the corrosion resistance of magnesium alloys. Several coating approaches have been followed including chemical conversion processes, electro/electroless plating, anodic/micro-arc oxidation, sol-gel and physical vapor deposition [12–21]. However, when talking about biomedical applications some of those coatings are not suitable, because of toxicity or release of unwanted debris [14,22].

A recent trend to protect magnesium alloys is the development of hydrophobic coatings, which can provide self-cleaning, anti-contamination and anti-icing properties as well as corrosion

protection [23–27]. Normally, the hydrophobicity can be achieved by a combination of micro/nanostructuring the surface and low surface energy. High hydrophobicity ensures an important decrease of the contact area of the material surface with the corrosive medium and the fraction of solid at the solid/water interface is normally around 20% [28,29]. Thus, hydrophobic coatings can offer an additional delay of the corrosion processes especially in the initial stages of contact with electrolyte or in the case of exposure to wet-dry cycles. In addition, good hemocompatibility and low bacteria adhesion were reported for metallic substrates coated with hydrophobic coatings [30,31], suggesting a good potential for biomedical applications. The improvement of corrosion resistance of magnesium alloys via application of hydrophobic coatings has been reported in previous studies [30–34]. However, most of the studies on hydrophobic coatings have been carried out on copper, aluminum, titanium and other engineering metallic substrates [35–39]. Traditionally, a two-step process is applied including the development of a micro/nanostructure which is followed by the modification of the surface with a low surface energy material [23,29,40,41]. In the case of magnesium, a rough surface was obtained by hydrothermal treatment [30], micro-arc oxidation [32], in situ crystallization [33], or etching [31,34]. Subsequently, stearic acid [30–32,34] or the silane coupling agents [33] are applied in order to reduce the surface energy. Recently, electrodeposition processes, combining the

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Table 1
Chemical composition of the received material.

Element wt.%	Al 1.92000	Cu 0.01330	Mn 0.37700	Fe 0.01200	Ni 0.00108
Element wt.%	Zn 1.18000	Be 0.00004	Si 0.05190	Ag <0.00010	Ca 0.00444
Element wt.%	Sn <0.00050	Zr <0.00060	Ce 0.00535	La 0.01410	Mg 96.42000

two steps together, have been suggested to prepare hydrophobic coatings in an effective and time saving one-step approach. Such coatings have been produced on copper and zinc, based on zinc-laurylamine, Cu(II)-laurylamine, and zinc tetradecanoate [42–46]. These studies have focused on the self-cleaning effect and the corrosion protection performance of the hydrophobic coatings. Moreover, the effect of processing parameters on the formation of hydrophobic coatings was also investigated. However, the deposition of hydrophobic coatings on magnesium and its alloys with a one-step electrodeposition method is scarcely explored.

Many factors can affect the microstructure and the corrosion resistance of hydrophobic coatings on magnesium alloys [23,24,47]. Change in coating composition, deposition time, and other processing parameters can lead to different results. Recently, we have successfully demonstrated electrodeposition of calcium stearate coating on an anodized magnesium alloy. The obtained coatings ensure high hydrophobicity and the formation mechanism of such coatings has been discussed in detail in our previous work [48]. It was found that the deposition parameters have a significant effect on the corrosion properties of such a coating [48]. However, relatively little is known about the effect of pre-treatment on the deposition of the hydrophobic coating on the magnesium alloy. Moreover, the influence of pre-treatment on the effectiveness of the corrosion protection of the magnesium alloy in simulated body fluid is not studied yet. In this work, we focus on understanding the role of pre-treatment on the microstructure and electrochemical characteristic of the hydrophobic coating on the AZ21 magnesium alloy. The corrosion mechanisms of the pre-treated magnesium alloy with and without the hydrophobic coatings are also discussed in detail.

2. Experimental

2.1. Materials

Commercial magnesium alloy AZ21 sheet (0.6 mm thickness) was cut into rectangular specimen of 20 mm × 40 mm. The chemical composition of the material is shown in Table 1. Prior to the pre-treatment, the specimens were abraded with SiC emery paper up to 1500 grade, cleaned in deionized water and ethanol and dried in compressed air.

2.2. Pre-treatments

Four different pre-treatments were carried out on the magnesium alloy. The details of treatment bath composition and process parameters are shown in Table 2. The first pre-treatment was a plasma electrolytic oxidation (PEO) treatment only. The PEO process was carried out in an alkaline phosphate-based electrolyte (2 g/L Ca(OH)₂ and 12 g/L Na₃PO₄) using a pulsed DC power supply ($t_{on}: t_{off} = 0.5 \text{ ms}: 4.5 \text{ ms}$) under a constant voltage of 380 V for 5 min limiting the current density to a maximum of 0.05 A/cm². During the PEO process, the specimen and a stainless steel tube were used as anode and cathode, respectively. The electrolyte was continuously agitated combining mechanical stirring with continuous air bubbling to ensure the uniform distribution of the particles in the

Table 2
Details of the pre-treatments on AZ21 Mg alloy.

Pre-treatments	Electrolyte	Parameters
Plasma electrolytic oxidation (PEO)	Ca(OH) ₂ 2 g/L	380 V
	Na ₃ PO ₄ 12 g/L	0.8 A 20 °C 5 min $t_{on} = 0.5 \text{ ms}$ $t_{off} = 4.5 \text{ ms}$ Cathode: steel Room temperature 10 s
Etched plasma electrolytic oxidation (EPEO)	H ₃ PO ₄ 60 g/L	Direct current
Anodizing treatment (AT)	Na ₂ C ₂ O ₄ 2.5 g/L	4 V 40 °C 10 min Cathode: steel
	NaOH 240 g/L C ₂ H ₆ O ₂ 65 ml/L	90 °C Humidity 90% 24 h
Hydrothermal treatment (HT)		

electrolyte and to avoid their sedimentation. The temperature of the PEO electrolyte was kept at 20 °C by a water cooling system. In the second pre-treatment, the PEO coated magnesium alloy was additionally etched in a diluted phosphoric acid (60 g/L H₃PO₄) for 10 s at room temperature.

The third pre-treatment was a conventional anodizing treatment. The anodizing process was carried out with a DC power supply applying 4 V for 10 min. The specimen was used as the anode and a steel sheet was used as the cathode. The electrolyte contained 2.5 g/L sodium oxalate (Na₂C₂O₄), 240 g/L sodium hydroxide (NaOH), 65 ml/L ethanediol (C₂H₆O₂) and the solvent was deionized water. During the process, a magnetic stirrer was used and the electrolyte temperature was controlled at 40 °C.

The fourth pre-treatment was a hydrothermal treatment method exposing the specimens to 90 °C and 90% humidity in a climate chamber (Weiss WK111-340).

The corresponding pre-treatments are named PEO (plasma electrolytic oxidation), EPEO (etched plasma electrolytic oxidation), AT (anodizing treatment), and HT (hydrothermal treatment), respectively.

2.3. Deposition of the hydrophobic coatings

The coatings were deposited on the pre-treated magnesium alloy using a two-electrode cell, in which, the pre-treated substrates were used as the cathode and a graphite sheet was used as the anode. The electrolyte contained 0.05 mol/L calcium nitrate (Ca(NO₃)₂), 0.05 mol/L stearic acid and the solvent was ethanol (≥99.5%). The deposition process was performed at 50 V for 60 min using a DC power supply (Elektro-Automatik GmbH, EA-PS 8720-15) in voltage control mode at room temperature. The current density vs. time curve was recorded during the first 900 s of the deposition process. After deposition, the coated specimens were cleaned with ethanol and dried in air. The details of electrolyte composition and parameters of the fabrication process are summarized in Table 3. In order to simplify the nomenclature of the hydrophobic coatings formed on different pre-treated substrates, these coating systems are referred to as PEO-HC, EPEO-HC, AT-HC, and HT-HC, respectively. If not a specific coating is addressed the combination of pre-treatment and hydrophobic coating is referred to as full coating system. It should be noted that no hydrophobic

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