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Full Length Article

Formation of a cerium conversion coating on magnesium alloy using ascorbic acid as additive. Characterisation and anticorrosive properties of the formed films

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Abstract

Cerium-based conversion coatings were formed on AZ91D magnesium alloy by immersion of the substrate in solutions containing $Ce(NO_3)_3$, H_2O_2 and ascorbic acid (HAsc). The characterisation of the films was performed by electrochemical and surface analysis techniques such as SEM, EDS, X-ray diffraction and X-ray photoelectron spectroscopy (XPS). The degree of corrosion protection achieved was evaluated in simulated physiological solution by the open circuit potential monitoring, polarisation techniques and electrochemical impedance spectroscopy (EIS).

The presence of HAsc in the conversion solution causes changes in the morphology, adherence and anticorrosive performance of the films. The improvement in the corrosion resistance is closely associated with the corrosion inhibition properties of HAsc.

Keywords: Cerium coatings; AZ91D alloy; Ascorbic acid; Anticorrosive properties

1. Introduction

Biodegradable metallic materials have been extensively studied in recent years due to their use in substitution and generation of tissues. Among others, magnesium appears as a very promising biomaterial [1]. Magnesium and magnesium alloys possess many excellent properties such as biocompatibility, low density and biodegradability, making them ideal candidates for implant biomaterials. Temporary implants of biodegradable materials are destined to corrode and dissolve postoperatively, hence they provide the advantage to avoiding a second surgery for implant removal [2].

However, magnesium and its alloys present a poor corrosion resistance in physiological solution and their degradation produces a layer of corrosion products mainly composed of magnesium hydroxide. Simultaneously, the hydrogen release reaction is produced. This corrosion process makes magnesium alloys subject to lose their mechanical properties in the physiological environment, a problem that needs to be settled to use the material in the biomedical field [3,4].

To improve the corrosion resistance different electrochemical treatments were investigated [5]. Among these, conversion processes are known for their low cost and simplicity of operation [6,7]. In the latest years lanthanide conversion coatings on magnesium alloys have been intensively studied because they are an environmental friendly technology. There is a lot of research about the use of cerium on conversion coatings in order to improve the corrosion resistance of magnesium biodegradable implants in physiological solution. Several studies showed that the presence of additives in a cerium conversion solution or a pre-treatment process improves the corrosion resistance of Mg alloy [8–11]. Moreover, there is no evidence that cerium compounds pose a health hazard to humans. Cui et al. reported that a cerium conversion coating acts as a protective film against corrosion of magnesium degradable implants in Hanks solution during 24 hours [9]. The coating contains trivalent and tetravalent cerium oxides. The effect of different cerium salts on the conversion treatment on AZ31 alloys was reported by Montemor et al. [10]. All coatings significantly reduce the corrosion rate of AZ31 alloys in chloride media.

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Some researchers showed that better corrosion protection may be obtained by using electrochemical treatment methods. Wang and Sun reported that a uniform and protective cerium based coating can be prepared by a cathodic electrochemical technique on AZ91D magnesium alloy [11].

The formation of a conversion coating by simple immersion involves several steps, including the corrosion of the substrate, the mass transport in the liquid–substrate interface and the coating formation. The die-cast AZ91D alloy generally consists of primary α phase and eutectic α/β phase, in which β phase (intermetallic $Mg_{17}Al_{12}$) is a second phase [12]. Generally, the β phase is chemically nobler than the α phase [13]. The reduction potentials of the α and β phases are different (−1.71 V vs SHE and −1.0 V vs SHE, respectively), which leads to galvanic corrosion between the α and β phases [14,15]. The AZ91D alloy immersed in a conversion solution displays a selective dissolution which is attributed to the inherent properties of the constituent phases. In this way, the mechanism of formation of the conversion coating depends strongly on the composition and microstructure of the Mg alloy. Moreover, the dissolution behavior of the AZ91D alloy may strongly depend on the pH of the solution [16].

The main objective of the present study was to obtain cerium based conversion coatings on AZ91D magnesium alloy by a potentiostatic technique. Optimal experimental conditions were determined to obtain films with improved corrosion protection properties in simulated physiological solution. The influence of the composition of the conversion solution was analysed on both, coating formation and anticorrosive performance in simulated physiological solution.

2. Experimental procedures

The working electrodes were prepared from rods of AZ91D magnesium alloy (composition: 8.978% Al, 0.6172% Zn, 0.2373% Mn, 0.2987% Si, 0.1189% Cu, 0.00256% Ni, 0.0176% Fe, 0.00164% Ca, 0.01154% Zr, balance Mg). The rods were embedded in a Teflon holder with an exposed area of 0.070 cm^2. Before each experiment, the exposed surfaces were polished to a 1000 grit finish using SiC, then degreased with acetone and washed with triply distilled water. Following this pretreatment, the electrode was immediately transferred to the electrochemical cell. All the potentials were measured against a saturated Ag/AgCl and a platinum sheet was used as a counter electrode. The cell was a 20 cm^3 Metrohm measuring cell.

The electrodes were treated in an electrolyte solution containing cerium nitrate hexahydrate $Ce(NO_3)_3.6H2O$ (5–50 mM) in a purified nitrogen gas saturated atmosphere. The temperature employed was 50 °C. Hydrogen peroxide (H_2O_2) and ascorbic acid (HAsc) concentrations were varied between 1–20 mM and 1–10 mM, respectively. All chemicals were reagent grade and solutions were made in twice distilled water.

Electrochemical measurements were done using a potentiostat–galvanostat PAR Model 273A and VoltaLab40 Potentiostat PGZ301. The frequency used for the impedance measurements was changed from 100 kHz to 10 mHz, and the signal amplitude was 10 mV. A dual stage ISI DS 130 SEM and an EDAX 9600 quantitative energy dispersive X-ray analyser were used to examine the electrode surface. X-ray diffraction analysis was carried out using a Rigaku X-ray diffractometer (model Dmax III-C) with Cu Kα radiation and a graphite monochromator. X-ray photoelectron spectroscopy (XPS) has been measured in a Specs setup operatingsystem. The XPS analysis chamber is equipped with a dual anode (Al/Mg) X-ray source and a 150 mm hemispherical electron energy analyser (PHOIBOS). The analyser operated in fixed analyser transmission (FAT) mode with pass energy of 30 eV. The energies of all spectra were referenced to the C 1s peak at 285.0 eV. All the XPS spectra were deconvoluted using the CASA XPS software with a Gaussian–Lorentzian mix function.

Electrical conductivity was measured by the two-probe method using a homemade device and film adhesion was tested measuring the force necessary to peel-off the film using a Scotch® MagicTM double coated Tape 810 (3M) and a Mecmesin basic force gauge (BFG 50N).

The corrosion performance was investigated in Ringer solution at 37 °C by a potentiodynamic method, the variation of the open circuit potential (OCP) as a function of time and electrochemical impedance spectroscopy (EIS). The electrodes were allowed to equilibrate at a fixed voltage before the ac measurements. The composition of Ringer solution is (per 1 L) 8.60 g NaCl, 0.30 g KCl and 0.32 g $CaCl_2.2H_2O$.

Tafel tests were carried out by polarising from cathodic to anodic potentials with respect to the open circuit potential at 0.001 Vs^{-1} in Ringer solution. Estimation of corrosion parameters was realised by the Tafel extrapolation method. The extrapolation of anodic and/or cathodic lines for charge transfer controlled reactions gives the corrosion current density (i_{corr}) at the corrosion potential (E_{corr}). All experiments were conducted after the steady-state E_{corr} was attained, which normally took 1 h after immersion in the solution.

Each set of experiments was repeated two to four times to ensure reproducibility.

3. Results and discussion

3.1. Coating formation

In order to obtain an effectively protective cerium coating, it is essential to determine the optimal conversion parameters including the applied potential, pH of the solution and immersion time. The performance of the samples treated in different cerium-based baths was evaluated by potentiodynamic polarisation measurements in Ringer solution at 37 °C, as will be shown later. Thus, the best formation conditions were established.

A discontinuous and not adherent white coating was obtained on AZ91D alloy after immersion in a 50 mM $Ce(NO_3)_3$ solution pH 4.7 at 50 °C during 30 min under open circuit potential conditions. In order to check the effects of polarisation, different potentials were applied to the working electrode employing the same electrolyte solution. The polarisation curves in Ringer solution for the alloy covered with cerium coatings synthesised at different potentials are presented in Fig. 1. The curve for the bare alloy is also presented

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