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Short Communication

Corrosion protection afforded by praseodymium conversion film on Mg alloy AZNd in simulated biological fluid studied by scanning electrochemical microscopy

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ABSTRACT

Surface passivation of AZNd Mg alloy with $Pr(NO_3)_3$ is studied using scanning electrochemical microscopy (SECM) in surface generation/tip collection (SG/TC) and AC modes. Corrosion protection afforded by the Pr treatment and the degradation mechanism in a simulated biological environment was examined on a local scale and compared with non-treated AZNd. SG/TC mode results revealed a drastic decrease in H_2 evolution due to the Pr treatment. Mapping the local insulating characteristics using AC–SECM showed higher conductivity of the surface where H_2 evolution was most favorable.

1. Introduction

The rapid corrosion of magnesium and its tendency for localized corrosion in biological environments [1] are serious drawbacks that significantly limit its biomedical applications [2]. One effective method to overcome these issues is chemical modification of the magnesium surface. Chemically formed conversion coatings that occur via reaction of an active species (e.g. a rare earth element (REE)) can be more inert with respect to corrosion. Conversion coatings based on lanthanum (La), cerium (Ce) and praseodymium (Pr) has been shown to provide levels of corrosion protection to the underlying metal substrate and their protective properties have been studied for number of Mg alloys such as WE43 [3] AZ31 [4], AZ91, AM50 [5], AZ63 [6] and WE43 [7]. Majority of these studies have shown effective corrosion protection afforded by the REE conversion coating in the short term (e.g. under 24 h) that tends to deteriorate as exposure time to corrosive environment increases. The corrosion inhibition mechanism of REE is often attributed to the deposition of an insoluble passive RE oxide/hydroxide film at cathodic domains [4,8], facilitated by the alkaline pH which arises from the reduction of water and/or oxygen [9]. The failure mechanism of these conversion coatings have been generally attributed to penetration of corrosive species (e.g. chloride) through the conversion coating towards the metal substrate. However, the role of coating inhomogeneities and localized defects in corrosion mechanism has not been fully understood due to the lack of studies with localized electrochemical methods.

The robust data collection modes of SECM present a unique localized electrochemical technique that combines capabilities of physically assessing insulating/conducting domains of a surface with highly sensitive chemical detection [10]. SECM in AC mode allows for localized detection of active/passive domains and defective areas of corrosion protective films on an active metal [11,12]. In generation/collection (G/C) mode of SECM, electrochemically oxidisable or reducible species produced at the substrate can be sensed via an electrochemical reaction at the SECM probe. Applying an oxidative potential at the SECM, flux of H_2 evolution can be sensed and implemented to evaluate corrosion behaviour on Mg surface with a localized approach [13–15]. In comparison to other well-trusted corrosion measurement methods such as

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weight loss measurement and hydrogen collection [16,17], SECM presents the unique capability of studying spontaneous corrosion phenomena while cumulative methods such as weight loss and hydrogen collection can only affords corrosion rate data after a certain period of immersion.

We investigate here a Pr surface treatment to impart corrosion protection to AZNd. In biomedical application, use of RE compounds should also be considered from the perspective of their potential cytotoxicity. Anti-carcinogenic properties of REs has been shown in number of studies [18–21], however some studies have also reported cytotoxic and hepatotoxic effects at high dose [22–25]. It has been shown that rare-earth alloying elements including Ce, Nd, Y, and Yb have no adverse effect on growth of living cells but they can induce inflammatory effects at high concentration [26]. *In vitro* studies of cytotoxicity of REs on primary human and mouse cells demonstrated highest relative cytotoxicity of La and Ce while good cell viability was achieved in presence of Eu, Nd and Pr [27]. A recently advanced [13,15] electrochemical approach using SECM was used to evaluate H_2 evolution as a measure of corrosion protection afforded by the surface treatment. Degradation of the Pr conversion layer on AZNd is also studied at a local scale using SECM in AC mode. The aim of this study is to help for better understanding of the degradation mechanism of a Pr conversion layer in a simulated biological environment.

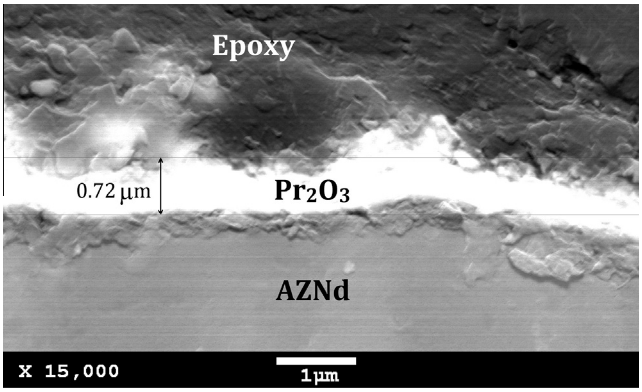

Fig. 1. SEM micrograph (in back scatter mode) from cross-section of AZNd treated in 0.2 M $Pr(NO_3)_3$ solution for 30 s to form a Pr_2O_3 conversion coating on the surface. The specimen was mounted in epoxy for the purpose of sample preparation.

2. Experimental

2.1. Material

AZNd was supplied by Boston Scientific with the approximate composition of Al 7.26%, Zn 0.59%, Mn 0.10%, Nd 0.66% (all in Wt%) and the balance Mg. XRF analysis measured the composition as Al 7.3%, Zn 0.32%, Mn 0.024%, Nd 0.63% and the balance Mg. The first composition detailed above is the actual quantities of elements used during the casting of the AZNd alloy. The XRF analysis was performed to investigate if contaminants entered the alloy composition during the casting process. The mismatch between the two compositions arises because the XRF results are collected at random locations on the surface of the alloy and do not match the average bulk composition. Further detail regarding the composition and corrosion properties of this alloy may be found in Ref. [28]. Simulated biological fluid (SBF) was prepared using analytical grade reagents consisting of 5.403 g/l NaCl, 0.504 g/l $NaHCO_3$, 0.426 g/l $NaCO_3$, 0.225 g/l KCl, 0.230 g/l $K_2HPO_4{\cdot}3H_2O$, 0.311 g/l $MgCl_2.6H_2O$, 0.8 g/l NaOH, 0.293 g/l $CaCl_2$, 0.072 g/l Na_2SO_4 and 17.892 g/l HEPES (4-(2-Hydroxyethyl)piperazine-1-ethanesulfonic acid – $C_8H_{18}N_2O_4S$) as buffer agent [29]. The pH was adjusted to 7.40 ± 0.05 using 1 M NaOH (Sigma) solution. $Pr(NO_3)_3{\cdot}6H_2O$ and NaOH were analytical grade and purchased from Sigma–Aldrich Australia.

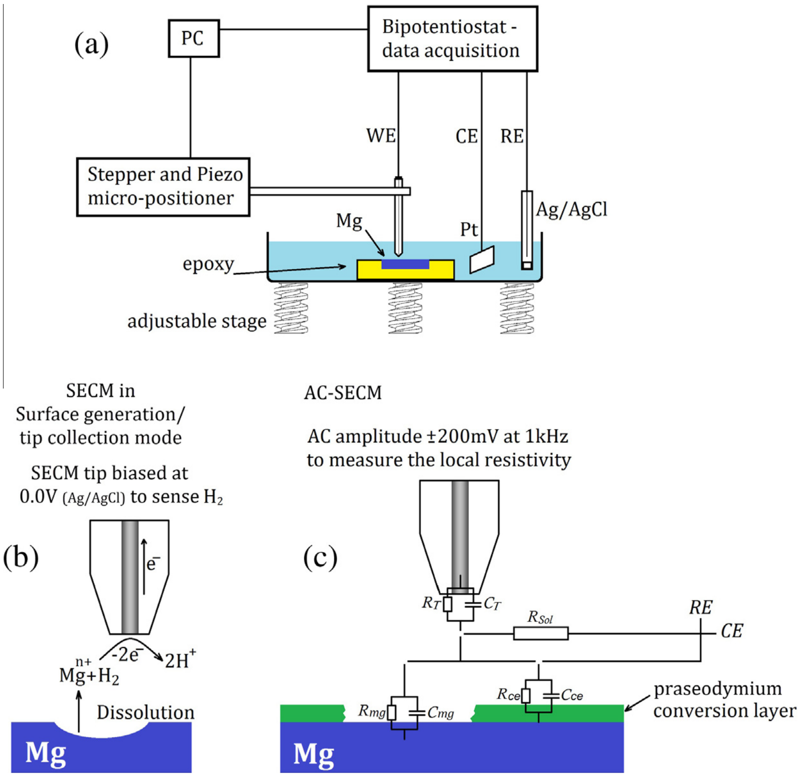

Fig. 2. Schematic representation of (a) SECM set-up, (b) H_2 detection in SG/TC mode of SECM and (c) the electrical model of AC mode data acquisition at conducting and insulating regions of a Mg surface.