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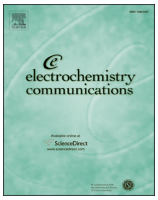

Self-healing characteristic of praseodymium conversion coating on AZNd Mg alloy studied by scanning electrochemical microscopy

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ABSTRACT

Application of rare earth conversion coatings as a surface treatment for magnesium has been the subject of several studies revealing the potential to act as an effective passivating layer. Herein a mechanistic study is presented on the formation of a rare earth conversion layer based on $Pr(NO_3)_3$ on AZ80X magnesium alloy in simulated biological (buffered) solution. Scanning electrochemical microscopy (SECM) was used to investigate the insulating properties and degradation behaviour of the Pr conversion layer. The self-healing properties of the conversion layer in the presence of Pr^{3+} were also studied using SECM. Results revealed the self-healing characteristic of the Pr conversion film in the presence of active, Pr^{3+}, species. The Pr conversion layer provided passivation in the short term by producing an electrochemically inert and insulating layer. SECM results in potentiometric mode elucidated the role of near surface pH in the formation of the conversion coating.

1. Introduction

Conversion coatings based on lanthanum (La), cerium (Ce) and praseodymium (Pr) have been shown to provide levels of corrosion protection to the underlying metal substrate and their protective properties for a number of Mg alloys such as WE43 [1] AZ31 [2], AZ91, AM50 [3], AZ63 [4] and WE43 [5] have been studied. The majority of these studies have shown effective corrosion protection afforded by the rare earth element (REE) conversion coating in the short term (e.g. under 24 h) that tends to deteriorate as exposure time to the corrosive environment increases. The corrosion inhibition mechanism of REE is often attributed to the deposition of an insoluble passive rare earth (RE) oxide/hydroxide film at cathodic domains [2,6], facilitated by the alkaline pH which arises from the reduction of water and/or oxygen [7]. In the present study, a recently advanced [8] electrochemical approach using SECM is used to evaluate H_2 evolution as a measure of corrosion protection afforded by the Pr surface treatment. Insulating characteristics of the Pr conversion layer on AZNd were also studied at a local scale using SECM in AC mode. The aim of this study is to provide a better understanding of the film formation and self-healing mechanism of a Pr conversion layer in a buffered solution.

2. Materials and methods

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 [9]. Simulated biological fluid (SBF) was prepared according to the recipe outlined in ref. [10]. Praseodymium conversion layers were formed by immersing the AZNd coupons in 0.2 M $Pr(NO_3)_3$ solution for 30 s. Specimens were then rinsed with DI water and dried with N_2.

SECM was conducted using a 25 μm Pt ultra-micro-electrode (UME) with RG > 10 as working electrode. A Pt mesh and an Ag/AgCl electrode served as counter and reference electrodes, respectively. In surface generation/tip collection (SG/TC) mode, the SECM tip potential was adjusted at 0.0 V(Ag/AgCl) for sensing H_2 evolution via H_2 electro-oxidation [8] with the tip-to-substrate distance adjusted to 5 μm. AC-SECM data was obtained in dilute solutions (i.e. low ionic activity) in order to drive the AC signal towards the substrate and maximize the contribution of substrate surface to the AC response. Further details on SECM experimental set up and formation/deposition of conversion coating can be found in ref. [11]. Localized pH sensing was conducted by SECM with an Ir/IrOx microelectrode with 7 μm diameter tip. Fabrication and calibration procedure have been outlined in ref. [8]. SECM images

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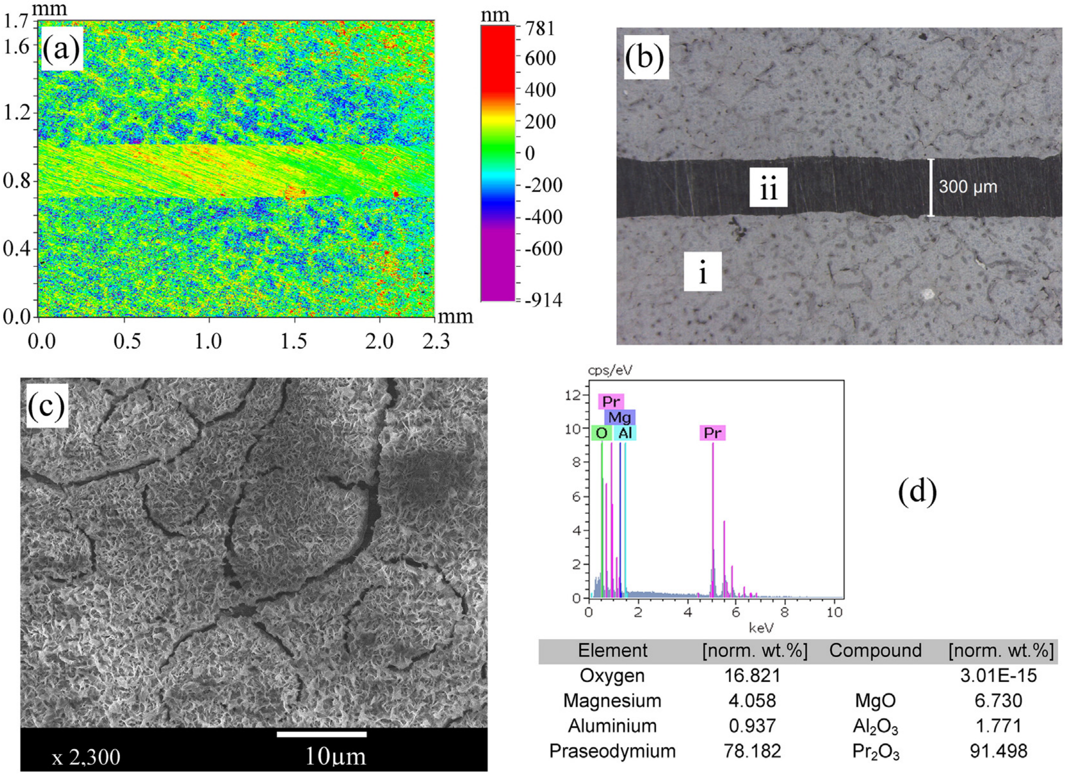

Element	[norm. wt.%]	Compound	[norm. wt.%]
Oxygen	16.821		3.01E-15
Magnesium	4.058	MgO	6.730
Aluminium	0.937	Al_2O_3	1.771
Praseodymium	78.182	Pr_2O_3	91.498

Fig. 1. Micrographs from (a) optical profilometry, (b) optical microscopy and (c) SEM of AZNd surface treated by Pr conversion coating. Domain (i) in the inset (b) represents the area that was treated with Pr_2O_3 conversion coating prior to experiment. Domain (ii) is untreated/clean AZNd surface. Results of EDX compositional analysis is presents in (d).

and approach curves were collected at several locations to ensure that the results are reproducible.

AZNd substrate was partially masked with tape before deposition of conversion coating in order to introduce an artificial defect. Surface profiles were examined using a Wyko NT9100 optical profilometer (Veeco instruments Inc.).

3. Results and discussion

The profilometry of the surface with artificial defect (partially conversion coated) is shown in Fig. 1a. Statistical parameters of the surface profile were $R_a = 138$ nm, $R_q = 170$ nm and $R_z = 1.69$ μm. The negatively profiled domains (blue areas) indicate the domains attacked by oxidizing agent (NO_3^-), during deposition of the PrOx conversion coating. Elemental (Fig. 1d) and structural analysis (Fig. 1c) confirmed formation of a nano-porous layer with chemical composition of Pr_2O_3 and the film thickness in the range of 500–700 nm. It is noteworthy that the vacuum condition of the EDX elemental analysis tends to cause dehydration of hydroxides and the Pr conversion layer in-situ is probably the hydrated oxide form. Fig. 1b shows the optical micrograph of specimen with 300 μm wide domain in the middle without Pr conversion coating. Neighbouring the Pr treated and non-treated surface also brings about the possibility of immediate comparison between surfaces in terms of electrochemical active/passive state.

Fig. 2 shows the SECM results in SG/TC mode for probing the H_2 generated at the surface of AZNd during corrosion. An earlier study indicated that the major domains of H_2 generation are in fact where the corrosion attack/dissolution takes place more significantly and the near-surface pH is highly alkaline [8]. As shown in Fig. 2, the non-treated part of Mg surface (light brown domains) exhibited significantly

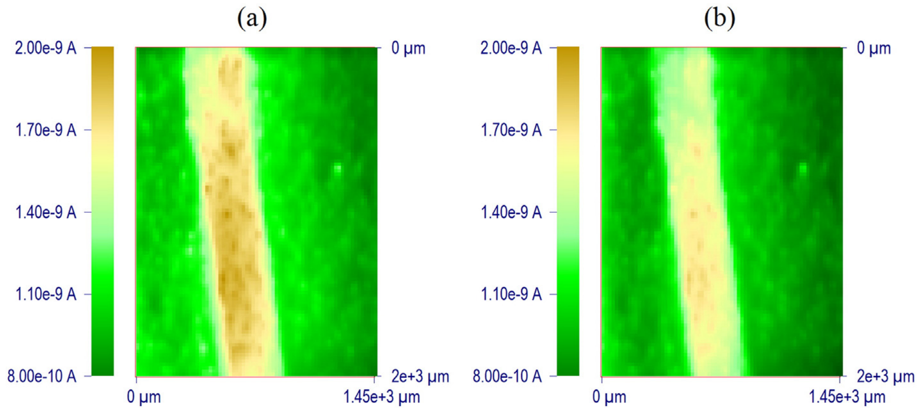

Fig. 2. SECM image of H_2 evolution in SG/TC mode on the surface of AZNd, partially treated with Pr conversion coating immersed in dilute SBF after (a) 10 min and (b) 3 h immersion. The SG/TC maps were obtained using a 25 μm Pt UME with bias tip potential of 0.0 V (Ag.AgCl) to detect H_2 evolution via electro-oxidation of H_2. Larger current, e.g. light brown domains, corresponds to higher flux of H_2. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)