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Influence of surface chemistry on the formation of crystalline hydroxide coatings on Mg alloys in liquid water and steam systems

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ABSTRACT

An environmentally-friendly 'steam-coating' treatment was employed to prepare protective coatings on magnesium (Mg) and its alloys against corrosion. This involved a hydrothermal surface treatment performed in water vapour using a closed stainless steel autoclave at 150 °C for 3 h. The correlation between coating functionality and alloy chemistry, including the concentration of alloying elements of aluminium, zinc and rare earth, was studied. It was determined that Al played a significant role in the formation of a protective $Mg(OH)_2$ coating, whilst Zn and RE elements were not a key contributor to protective development.

1. Introduction

Magnesium hydroxide ($Mg(OH)_2$) and magnesium oxide (MgO), have been extensively studied as bactericides [1], pollutant absorbers [2], and reinforcing particles in polymers imparting flame retardation [3,4]. The important role and mechanisms by which $Mg(OH)_2$ and MgO nano-particles lead to flame suppression of polymer based composites are well studied [5–7]. Furthermore, $Mg(OH)_2$ and MgO surface layers play a role in dictating the corrosion of Mg and its alloys. $Mg(OH)_2$ or MgO are the primary constituents of the native surface film on Mg and its alloys in atmospheric conditions. However, such films are not highly protective in their native state, as they are either defective or incomplete in surface coverage; moreover, when in direct contact with water such films can be soluble and offer little protective function.

Controlled surface film development for $Mg(OH)_2$ produced by either hydrothermal treatment on Mg alloys [8] or by chemical additives, *i.e.* BTA [9], have been shown to substantially improve the corrosion resistance of Mg substrates. It was proposed that the high protectiveness of such coatings was due to the highly crystallinity and dense structure of the $Mg(OH)_2$ produced. Recently, hydrotalcite based coatings – where hydrotalcite refers to a layered double hydroxide (LDH) of $Mg_6Al_2CO_3(OH)_{16}·4(H_2O)$ – reveal a new pathway to address the corrosion issue associated with Mg alloys. Such hydroxides, noting the requirement of the presence of Al, exhibit a characteristic layered structure [10,11], in which species such as Cl^- ions can be trapped through ion exchange, and consequently the intactness of the hydrotalcite film remains for sufficient corrosion protection [12–14]. Two techniques were developed to prepare hydrotalcite coatings on Mg alloys, including co-precipitation followed by post-treatment and *in situ* synthesis. The former one normally requires multiple steps [15,16] and/or excessively long processing time, up to 84 h [17,18], which is not feasible for upscale production. The latter one-step chemical conversion method yields functional Mg-Al hydrotalcite layers on a number of Mg alloys by means of immersing the samples in to a certain chemical bath, for instance, $CO_3{}^{2-}/HCO_3{}^-$ [12,19] or $NO_3{}^-$ [20] aqueous solutions with various pH values for a time duration up to 72 h.

To simplify the synthesis process of hydrotalcite coatings and minimise the impact of hazardous chemicals on the environment, a chemical-free coating technique was developed to produce Mg-Al hydrotalcite film on Mg alloy AZ31 [21] where AZ31 specimens were put into water steam and the released Mg and Al ions from substrate were used as feedstock to generate Mg-Al hydrotalcite films. The synthesised film was identified to contain $Mg(OH)_2$ as a main component. XRD spectra indicated the film could also contain Mg-Al hydrotalcite ingredients [21,22]. Such a film was supposed to supply satisfactory protection to Mg substrate. It was postulated that structural nature (*e.g.* morphology, crystallinity, size distribution, thickness, *etc.*) and protective performance of the Mg-Al based LDH coatings were significantly dependent of the volume/mass

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fraction of Al in the Mg substrate [15,18] and processing parameters. However, to the best of our knowledge, research in the open literature only focuses on the Mg alloys containing a low quantity of Al, for instance AZ31 (3 wt.% Al and 1 wt.% Zn), and has not been extended yet to a broad range of alloy compositions (*e.g.* AZ61and AZ91).

Protective coatings have been extensively explored for a number of Mg alloys for different applications [23–30], whilst conversely, limited coating techniques [31,32] applicable to Mg alloys containing rare earth (RE) elements have been reported to date. Therefore, there remains a challenge in the regards to the corrosion protection of Mg-RE alloys [33], albeit that RE elements are crucial for Mg alloys given their role in improving mechanical properties and creep resistance [34,35]. A number of RE alloying elements commonly used in Mg alloys, which include cerium (Ce) and lanthanum (La), can contribute to corrosion products on the surface of Mg alloy substrates in contact with aqueous environments, which may act as a physical barrier to corrosion [33]. However, scarce studies on the role of RE elements in the formation of oxide/hydroxide film on Mg-RE alloys have been reported so far. Moreover, the formation of $MgO/Mg(OH)_2$ film on Mg surface is inevitable in a variety of aqueous coating procedures, such as chemical conversion coatings, electro- and electroless platings. As such, a mechanistic understanding of the growth of $MgO/Mg(OH)_2$ film will provide critical knowledge in controlling the structure and quality of the surface films which serve as corrosion protective coatings.

The present work aims to address the following challenges related to the formation of $MgO/Mg(OH)_2$ films on Al and/or RE containing Mg alloys: a) Is the formation of LDH film on Mg-Al alloys influenced by the content of Al (*e.g.* AZ91D and AE44)? b) Can RE elements be involved to the formation of protective Mg-RE LDH coatings on Mg-RE alloys (*e.g.* Mg-6.6Ce-4.5La in wt.%)? and c) How is the (liquid/gas) state of water as a reactant affecting the interfacial chemistry during the formation of Mg hydroxide coatings? All alloys used herein have a similar sum concentration of alloying elements (ranging from 8 to 11 wt.%), which allows an evaluation on the correlation between the alloying elements and coating properties.

To accomplish these particular aims, a 'steam coating' process (which represents a hydrothermal surface treatment performed in water vapour using a closed stainless steel autoclave at 150 °C for 3 h) was utilised to produce coatings on the above-listed Mg alloys. Such an environment was employed to probe the formation of $MgO/Mg(OH)_2$ on Mg alloys through omitting the intervention from additional variables (such as solute, ionic concentration, pH, ratio of cations and anions). SEM, XRD, XPS, EDX FTIR and TEM techniques were applied to examine the structure of the resulting coatings. Protective efficacy of the yielded coatings was monitored by means of electrochemical analysis and mass loss measurement in 0.1 M NaCl solution. The selection of preparation methods, *i.e.* either direct immersion in liquid water, or exposure to vapour water, determines coating structure, morphology and corrosion protectiveness. The findings are relevant to the development of protective coating systems on various Mg alloys, where the controlled formation and tuning of the surface $Mg(OH)_2$ – including its composition and structure – are required.

2. Material and methods

2.1. Materials preparation

High purity Mg (99.9%, Fe 40 < ppm) was purchased from Amac alloys (Croydon South VIC, Australia). High-pressure-die-cast Mg alloys in the form of AZ91D and AE44 plates (600 × 700 × 2 mm) were supplied by Magontec Pty. Ltd. (Sydney, NSW, Australia). AZ91 contains 9.1 wt.% Al, 0.66 wt.% Zn and 0.24 wt.% Mn; whilst AE44 contains 4.3 wt.% Al and 4.05 wt.% RE, where RE represents rare earth elements, principally Ce (2.62 wt.%) and La (1.43 wt.%). Mg alloy Mg-6.6Ce-4.5La (wt.%) was produced in-house using 99.9% Mg and Mg-16.5Ce-10.8La (wt.%) master alloy. In-house production was carried out in a graphite-coated steel crucible. The crucible was heated and held at 200 °C for 5 min to remove any moisture residual. The furnace chamber was evacuated to approximately 1 kPa and backfilled with argon to avoid ignition of molten Mg. The mixture of all material was heated to ~720 °C at approximately 3–5 $°C\,s^{-1}$ and then held for 30 min, during which the molten alloy was stirred several times. The molten alloy was cast into a mould pre-heated to 200 °C. The chemical composition of all Mg materials used for this study were analysed using ICP-OES (Spectrometer Services Pty. Ltd., Coburg, VIC, Australia) and listed in Table 1.

All tested metals were cut into 15 × 15 × 2 mm specimens and ground progressively down to a 2000 grit finish using silicon carbide papers to remove contamination and oxides. Ultrasonic cleaning was conducted in acetone and ethanol for 5 min each, followed by drying with nitrogen gas prior to any subsequent treatments.

2.2. Coating preparation through hydrothermal treatments

In terms of 'steam coating' treatment, cleaned specimens were placed in a stainless steel Teflon-lined autoclave with 80 ml capacity and a smaller Teflon container with 15 ml capacity was filled with distilled water and placed in the middle of the autoclave. The autoclave was heated up to 150 °C and held for 3 h, followed by water-cooling down to room temperature within a few min.

'Direct immersion' treatment, which represents hydrothermal by the immersion of specimens into distilled water at 150 °C for 3 h in autoclaves, was also applied to all specimens for comparison. All specimens were ultrasonically cleaned in acetone and ethanol for 5 min each, and dried with nitrogen gas prior to any test.

2.3. Corrosion evaluation

Electrochemical analyses were performed at room temperature on a BioLogic® VMP-3Z potentiostat using EC-lab 11.01 software. A quartz flat-cell (PAR, K0235), which contains 300 ml of 0.1 M sodium chloride (NaCl) electrolyte, was used with an exposed working electrode area of 1 cm^2, with a saturated calomel electrode (SCE) reference electrode and a Pt-mesh counter electrode. Potentiodynamic polarisation curves were recorded at a sweep rate of 1 $mV\,s^{-1}$, after 10 min open circuit potential (OCP) stabilisation. Corrosion current density, i_{corr}, and corrosion potential, E_{corr}, were determined from the polarisation curves via Tafel-type fitting using EC-Lab software. Fits were conducted by selecting a portion of the curve that commenced >50 mV from corrosion potential, E_{corr}, and i_{corr} was subsequently estimated from the value where the fit intercepted the potential value of the true E_{corr}. At least 5 replicate tests were performed for each sample to ensure the reproducibility. Electrochemical impedance spectroscopy (EIS) tests were also conducted over the frequency range of 100 kHz to 10 mHz using 10 points per decade and a +/−10 mV polarising signal. In all cases, 10 min OCP stabilisation was employed, and at least 3 replicate tests were conducted for each test condition.

In order to examine the long-term corrosion performance of the specimens, mass loss testing was performed in 0.1 M NaCl at room temperature for 5 days. After the exposure period, specimens were cleaned in a solution containing 200 $g\,l^{-1}$ chromium trioxide (CrO_3), 20 $g\,l^{-1}$ silver nitrate ($AgNO_3$) and 10 $g\,l^{-1}$ barium nitrate ($Ba(NO_3)_2$) for 1 min at room temperature, in order to remove the corrosion products as per ASTM G01-03. The mass change after immersion testing was divided by the original surface area of the

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