Corrosion and characterisation of dual phase Mg–Li–Ca alloy in Hank’s solution: The influence of microstructural features

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A R T I C L E   I N F O
Article history:
Received 20 August 2013
Accepted 24 October 2013
Available online 6 November 2013

Keywords:
A. Magnesium
B. EPMA
B. XPS
C. Pitting corrosion
C. Oxidation

A B S T R A C T
The influence of the microstructure and the oxide film of the Mg–9.29Li–0.88Ca alloy on its corrosion behaviour was investigated using SEM, EPMA, XPS and corrosion measurements. The results demonstrated that the fine-grained microstructure improved the mechanical and corrosion resistance of the alloy and shifted pitting corrosion to overall corrosion. The oxide film contained a multi-layered structure, with the outer layer being enriched in lithium-bearing compounds; the interior layer predominantly consisting of oxides, hydroxides and carbonates of lithium and magnesium; and the bottom layer containing oxides. The Pilling–Bedworth ratio for chemical compounds was proposed, and the corrosion rates were characterised.

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1. Introduction
Mg–Li alloys such as LAE442 (Li 4%, Al 4% and RE 2%), Mg–8Li, Mg–8Li–3Al, Mg–8Li–1Y, and Mg–8Li–3Al–1Ce have potential applications in aerospace, automobile, 3C products, anodes and biomaterials due to their high specific strength, excellent formability, high Faradic capacity and good biocompatibility [1–6].

The introduction of elemental lithium, which has a body-centred cubic (bcc) structure, into the hexagonal closed packed (hcp) magnesium can change the structure of magnesium. Mg–Li alloys can be categorised into three types based on the lithium content: α, dual phase (α + β) and β alloys. When the lithium content is greater than 5 wt% and less than 11 wt%, the alloy is composed of α and β phases. The dual phase structure of Mg–Li alloys results in excellent superplasticity and ductility [7–9]. These unique properties are attributed to a decrease in the lattice constant ratio (c/a) as lithium content increases, activating non-basal slip planes and resulting in a significant increase in the volume fraction of the bcc phase [2,10]. The latter effect is the major reason for the enhanced ductility and superplasticity of the dual phase Mg–Li alloys. The elastic modulus of Mg–Li alloys decreases with increasing lithium concentration [11] and is close to that of bones. Lithium has no influence on cell viability or the inflammatory response [12].

Ca is one of the major elements in bones, and has the potential to further reduce the density of Mg–Li alloys, refine the microstructure and improve the strength by forming the intermetallic compound Mg2Ca, and limit oxidation [13]. CaO oxides in MgO film were suggested to provide an effective barrier inhibiting oxygen diffusion into Mg alloys [14].

Unfortunately, scientists have little knowledge about the role of Ca in the corrosion of Mg alloys. Song [15] claimed that alkaline metal elements (e.g., Ca) have no significant influence on the corrosion of magnesium. However, Kim et al. [16] demonstrated that the addition of Ca into pure Mg gave rise to the formation of Mg2Ca particles, thus accelerating the corrosion rate of pure Mg due to the presence of micro-galvanic corrosion between the Mg2Ca phase and the α-Mg phase. Hanawalt and Hassel [17,18] reported that an increase in Ca content reduced the corrosion of magnesium alloys in NaCl solutions. However, Ca can improve the corrosion resistance of Mg–Li alloys [13,19].

Recently, scientists have focused on the preparation and surface modification of magnesium alloys for biomedical applications because existing commercial magnesium alloys cannot achieve the required mechanical properties, particularly the ductility and corrosion properties.

The alloying elements for Mg–Li alloys include Al, Zn, Ca, Ag, Mn, Sr and RE (Nd, Ce, Y and Sc) [1,19,20]. Solid solution Mg–Li alloys with low amounts of precipitation exhibit significantly increased ductility. β-(Mg, Li) is well known to exhibit good formability but relatively low strength and work hardening capacity [21].
Grain refinement is an important approach to improving the strength of metals. Severe plastic deformation such as extrusion has been extensively used to refine grains and enhance the corrosion resistance of magnesium alloys [22].

In vivo degradation revealed that the LAE442 alloy has a longer durability in vivo than AZ91D [23], which is the reverse of the in vitro corrosion rates [23]. Thus, evaluation of the in vitro degradation rates of magnesium alloys is a critical issue [23]. Particular attention has been devoted to the development of Mg–Li alloys as degradable biomaterials [24–28]. Nevertheless, the corrosion mechanism of Mg–Li alloys remains poorly understood [29].

Generally, the corrosion behaviour of Mg–Li alloys is affected by factors including alloying elements, microstructure, the microstructural features of the natural oxide film and corrosion product film, and the environmental medium [30]. Song [9,29] found that in ambient atmosphere, the oxide film of etched Mg–8Li alloys possesses multiple layers, including Mg(OH)2, Li2O, MgO, LiOH, Mg and Li. Lithium oxide was enriched at the outer oxide layer, leading to a decrease in the corrosion resistance of Mg–8Li alloys compared to pure magnesium [9]. Pitting corrosion occurred in the initial immersion stage, followed by filiform corrosion [9].

Moreover, the weight losses in synthetic seawater of hcp Mg–9Li alloys with minor additions of lithium decreased with increasing lithium content, whereas the Mg–Li alloys with bcc structures corroded much faster and built thick layers that immediately fell off, thus exhibiting the largest weight loss. The dual phase (a(Mg) + b(Li)) Mg–8Li alloy exhibited the smallest weight loss [13,19,30]. Meyer-Lindenberg [31] confirmed that lithium can improve the corrosion resistance of an MgAl2RE alloy through a mechanism in which corroding lithium increased the pH value of the solution to greater than 11.5, which stabilised the Mg(OH)2 film on the alloy surface. As mentioned above, the effects of the oxide film and the corrosion product films on the corrosion resistance of Mg–Li alloys is ambiguous, and contradictory results have been reported.

Additionally, solution media have a significant impact on the corrosion of Mg–Li alloys. Increasing the pH value and decreasing the concentration of Cl– ions resulted in an increase in the corrosion resistance of Mg–Li alloys [32]. Thus, the influences of lithium on the characteristics of natural oxide film and corrosion product film remain unclear.

Unfortunately, little information is available in the literature regarding the corrosion of the ternary Mg–Li–Ca alloys. Song [14,21] found that the addition of Ca improves the oxidation resistance of the Mg–12Li–0.5Ca alloy in air at 350 °C and that oxidation preferentially occurred on the primary / phase of Mg–12Li–5Ca. Our previous study [5] demonstrated that Mg–Li–Ca alloys had lower pH values and better corrosion resistance in Hank’s solutions compared with Mg–Ca alloys. The corrosion mechanism of the dual phase Mg–Li–Ca alloy is absolutely different from that of the Mg–Li alloy [9], and needs to be clarified.

This paper aims to investigate the influence of the microstructure, the natural oxide film and the corrosion product films on the corrosion behaviour of Mg–Li–Ca alloys and to gain further insight into the corrosion mechanism of dual phase Mg–Li–Ca alloys.

2. Experimental

2.1. Materials

The cast Mg–9.29 wt% Li–0.88 wt% Ca ingots were extruded into sheets on an extrusion machine (Yuan hang, 800 t) at the Magnesium Industry in Chongqing Science and Technology Company, Ltd., at an extrusion ratio of 20.4:1 and an extrusion rate of 1 m/min. The mould and extrusion temperatures were 350 °C and 300 °C, respectively.

2.2. Corrosion characterisation

Magnesium is prone to attack in Hank’s solution. The following reactions occur.

\[ \text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg}^{2+} + 2\text{OH}^- + \text{H}_2 \uparrow \]  
\[ \text{Mg}^{2+} + 2\text{OH}^- \rightarrow \text{Mg(OH)}_2 \downarrow \]  

The attack results in three changes: (1) the weight loss of the samples, (2) the increase in solution pH and (3) hydrogen evolution. Thus, the above approaches can be used to characterise the corrosion rate of magnesium alloys in aggressive solutions. In particular, the hydrogen evolution rate (HER) is a significant parameter in the assessment of the biodegradability of magnesium alloys because 1 mol of H2 evolved corresponds to 1 mol of Mg dissolved, with the result that HER is equivalent to the biodegradation rate of a magnesium alloy [29]. HER can spontaneously and reliably reflect the local degradation rate of magnesium alloys. Therefore, hydrogen evolution was monitored to evaluate the biodegradability of magnesium alloys.

2.2.1. Corrosive medium

Hank’s solution was used as the medium, consisting of 8.0 g/L NaCl, 0.4 g/L KCl, 0.14 g/L CaCl2, 0.35 g/L NaHCO3, 1.0 g/L glucose (C6H12O6), 0.1 g/L MgCl2·6H2O, 0.06 g/L MgSO4·7H2O, 0.06 g/L Na2HPO4 and 0.06 g/L KH2PO4 in distilled water. The pH 7.2 solution was prepared by weighing A.R. grade chemicals.

2.2.2. Weight loss

The immersion test of the samples was carried out at room temperature according to GB10124-88. Before the immersion test, the samples (45 mm × 26 mm × 4 mm) were ground on progressively finer grades of emery papers up to 1200# grit and then weighed. The ground and pre-weighed samples were exposed to 436 ml of Hank’s solution for different intervals of time. The tests were carried out without agitation or circulation and without disturbing the corrosion system. At the end of the experiment, final cleaning of the sample was carried out by dipping it in 200 g CrO3, 10 g AgNO3, 20 g Ba(NO3)2 and 1000 ml distilled water for 5 min followed by washing with acetone. The weight loss was measured after each experiment. The immersion tests were repeated three times to obtain reproducible results. The corrosion rate, \( \text{m}_w \), was calculated according to the weight loss

\[ \text{m}_w = \frac{m_0 - m_f}{S \cdot t} \ (\text{mg cm}^{-2} \cdot \text{day}^{-1}) \]  

where \( m_f \) represents the mass prior to immersion, \( m_0 \) is the mass after immersion, \( S \) is the surface area of the samples, and \( t \) is the immersion time.

2.2.3. Hydrogen evolution measurement

Hydrogen evolution can be used to evaluate both instantaneous and average corrosion rates. As mentioned above, the cathodic reaction mainly results in hydrogen evolution upon the corrosion of magnesium in Hank’s solution. The measurement of evolved hydrogen is an easy way to measure the corrosion rate of magnesium alloys exposed to aqueous solutions. In this study, the HER from the samples was measured for 430 min in Hank’s solution. The data were recorded at 10 min intervals for the first 100 min.
and then at 20 min intervals. The corresponding corrosion rate, \( v_H \), is then obtained from the following equation:

\[
v_H = \frac{V_a - V_0}{St} \quad (\text{ml cm}^{-2} \text{ day}^{-1})
\]

2.2.4. pH measurement

The pH values of the solution were measured by a pH meter (PHS-25 type). The volume of solution depended on the surface area of the sample according to a solution volume to sample area ratio of 35 ml/cm². The data were recorded at an interval of 10 min in the first 4 h, and at an interval of 20 min thereafter.

2.2.5. Potentiodynamic polarisation measurement

The electrochemical corrosion behaviour of the samples was studied using a potentiostat/galvanostat corrosion measurement system (EG&G model 273). Prior to the experiment, the samples were ground up to 1200 grit emery paper, and then washed with distilled water and acetone. Polarisation measurements were carried out in a corrosion cell containing 400 ml of Hank’s solution using a standard three-electrode system. A saturated calomel electrode (SCE) was used as a reference with a platinum counter electrode, and the sample was the working electrode. The exposed area was 2.84 cm². Potentiodynamic polarisation curves were measured after 5 min immersion of the samples in the solution. The scanning potentials ranged between ±300 mV at a scan rate of 1 mV/s. All the potentials in this study are with respect to the SCE. The tests were repeated three times for each alloy.

2.3. Tensile test

The tensile tests were performed on a CMT5105 type tensile machine at a strain rate of 3 mm/min. The gauge length and width were 25 mm and 6 mm, respectively.

2.4. Surface analysis

Producing a thick oxide film on Mg alloy requires a longer exposure time in ambient atmosphere. Thus, the samples of Mg–Li–Ca alloys were stored in the laboratory in an ambient atmosphere for more than 3 years. A dense and thick natural oxide film was obtained, with a grey colour dotted with white filiform tracks. The procedure used to map the whole structure of the natural oxide film consisted of four steps: First, the samples were probed using X-ray photoelectron spectroscopy (XPS) to obtain the elemental information of the topmost layer of the oxide film; Second, the samples were examined using X-ray diffraction (XRD) to determine the constituents under the topmost layer of the oxide film; Third, the samples were ground and exposed to air in ambient atmosphere for more than 3 years, and the ground sample exposed to air in ambient atmosphere for approximately 16 h.

3. Results

3.1. Change in microstructure

The microstructure of the cast Mg–8Li–1Ca alloy was characterised by the \( \alpha \)-Mg phase, \( \beta \)-(Li) phase and the intermetallic compound \( \text{Mg}_2\text{Ca} \) at grain boundaries (GBs) (Fig. 1a), whereas refined and elongated grains developed in the extruded Mg–9.29Li–0.88Ca alloy (Fig. 1b).

![Fig. 1. Optical micrographs: (a) the cast and (b) extruded Mg–9.29Li–0.88Ca alloys. The phase with the white colour represents the \( \alpha \) phase, while the grey phase is the \( \beta \) phase. \( \text{Mg}_2\text{Ca} \) particles are located in GBs and in the phase interiors.](image-url)
The phase Mg$_2$Ca, segregated at GBs, was identified by EDS, as shown in Fig. 2a. Fig. 2b shows that broken-up and dispersive Mg$_2$Ca particles were embedded at the interface of the α and β phases in the extruded alloy along the extrusion direction. Hot extrusion caused a reduction in average grain size from approximately 279 μm to 59 μm. This result is different from the average grain size of the α phase alloy Mg–2Li–0.3Ca and the β phase alloy Mg–15Li–1.5Ca fabricated by electrochemical codeposition, which are 100 μm and 70 μm, respectively [33]. The coarse grained microstructure in the cast Mg–9.29Li–0.88Ca alloy is ascribed to a post homogenisation process. The volume fractions of the α phase and β phase are 26% and 74%, respectively, based on computations by the lever rule. The volume fractions of Mg$_2$Ca (Fig. 2) in the cast and extruded alloys are 5.54% and 6.29%, respectively. Mg$_2$Ca particles are clearly more dispersed in the extruded alloy than in the cast alloy.

Obviously, the microstructure of the cast Mg–9.29Li–0.88Ca alloy is different from that of the Mg–12Li–5Ca alloy, which has an interdendritic lamellar structure with primary dendrites and interdendritic eutectic regions due to its higher calcium content [21]. As demonstrated by the EDS spectrum inserted in Fig. 2, the compound is Mg$_2$Ca rather than Li$_2$Ca, as Ca has a larger negative enthalpy of formation with magnesium (Mg$_2$Ca) than with lithium (Li$_2$Ca) [21]. However, Mg$_2$Ca is one of the eutectic constituents of the Mg–12Li–5Ca alloy. The addition of Ca into an Mg–12Li alloy resulted in an as-cast microstructure with primary dendrites of the β phase, a solid solution of hcp magnesium in bcc lithium, and a lamellar interdendritic eutectic of the β-phase and Mg$_2$Ca. Cold-rolling led to the re-distribution of the micro-constituents Mg$_2$Ca in the alloys [21].

3.2. Changes in mechanical properties

The fine-grained magnesium alloy is stronger than the coarse-grained alloy, as the former has a greater total GB area to impede the slip of dislocations [22]. In comparison with the cast alloys, the average ultimate tensile strength (UTS) and yield strength (YS) of the extruded Mg–9.29Li–0.88Ca alloys (Fig. 3a) increase 15.8% from 97.9 MPa to 113.4 MPa and 46.5% from 73.6 MPa to 107.8 MPa, respectively. The YS/UTS values of the cast and extrusion are 75% and 95%, respectively. The elongation to failures (EL) of the cast alloy and the extruded alloy are 4.2% and 52.8%, respectively. Accordingly, the EL of the extruded alloys is 12.7 times that of the cast alloys. The significant improvement in the strength and ductility after extrusion is ascribed to the decrease in grain size and the increase in the volume fraction of Mg$_2$Ca from 5.54% to 6.29%.

For magnesium alloys, the yield strength $\sigma_y$ varies with grain size according to the Hall–Petch equation

$$\sigma_y = \sigma_0 + k d^{-1/2}$$

where $d$ is the average grain diameter, and $\sigma_0$ and $k$ are constants related to the material of interest.

In comparison to the extruded Mg–8Li and Mg–8.5Li alloys in Fig. 3b, the higher yield strength of the extruded Mg–9.29Li–0.88Ca alloy is ascribed to the dispersion strengthening resulting from the intermetallic compound Mg$_2$Ca particles [1,28]. This finding suggests that calcium improves the yield strength of Mg–Li alloys. The excellent ductility of the alloy indicates potential clinical applications in stents.

![Fig. 2. SEM images of (a) the cast Mg–9.29Li–0.88Ca alloy, with the EDS spectrum indicating that the intermetallic compound Mg$_2$Ca was predominately distributed at the GBs and, to a small degree, within the grains. (b) The broken-up and dispersed Mg$_2$Ca particles were embedded at the interface between the α phase and β phase in the extruded alloy along the extrusion direction.](image1)

![Fig. 3. Ultimate tensile strength (UTS), yielding strength (YS) and elongation to failure (EL) of (a) the cast and extruded Mg–9.29Li–0.88Ca alloys and (b) as-extruded Mg–9.29Li–0.88Ca, Mg–8Li and Mg–8.5Li alloys [1,28].](image2)
3.3. Change in corrosion rate

3.3.1. Change in rate of weight loss

The immersion test shows that the average rates of weight loss of the cast and extruded alloys are 1.268 mg/cm$^2$/day and 0.248 mg/cm$^2$/day, respectively, after 430 min immersion in Hank’s solution. The corrosion resistance of the extruded alloy is 4-fold lower than that of the cast alloy due to the fine grained microstructure of the extruded alloy. Previous investigations have demonstrated that smaller grains in the microstructures of magnesium alloys improve the corrosion resistance of the alloys [34].

3.3.2. Change in current density

The free corrosion potentials of the extruded Mg–9.29Li–0.88Ca alloy and the cast alloy are $-1.58$ V vs. SCE and $-1.65$ V vs. SCE, respectively. The corrosion current densities of the extruded and cast alloys are $6.74 \times 10^{-5}$ A/cm$^2$ and $8.36 \times 10^{-5}$ A/cm$^2$, respectively, as shown in Fig. 4. The extruded alloy has a slightly higher corrosion resistance than the cast alloy, consistent with the rate of weight loss. However, the slight distinction between current densities implies that the polarisation technique has a limited ability to evaluate the in vitro corrosion rate of magnesium alloys because the anodic branch of magnesium cannot fit the Tafel law and there is a negative difference effect (NDE) [35].

3.3.3. Change in HER

The HER vs. time curves consist of two distinct stages for each alloy (Fig. 5). For the cast alloy, in the initial 130 min of immersion, a continuous decrease in HER indicates the formation of a dense layer of corrosion products and a period of incubation of corrosion pits. In the subsequent immersion period, continuous acceleration in the HER elucidates the breakdown of the oxide film and the exposure of more fresh surface to the solution (Figs. 5 and 6a). The HERs of the cast and extruded alloys are 1.22 ml/cm$^2$/day and 0.702 ml/cm$^2$/day, respectively, after 430 min of immersion.

In contrast, for the extruded alloy, the increase in the HER over 168 min of immersion time indicates the dissolution of magnesium and the subsequent reduction in HER implies the formation of a compact layer of corrosion products (Figs. 5 and 6b). Additionally, the area constructed by curves 1 and 2 in Fig. 5 can be divided into the three zones A, B and C by the two immersion times 0.5 h and 4.6 h. The HER difference $A_H$ between curve 2 and curve 1 is assumed to be

$$A_H = V_{H2} - V_{H1}$$

In zone A and zone C, $A_H$ is less than zero. This scenario is consistent with the weight loss and polarisation curves. However, in the middle period of immersion, $A_H$ is greater than zero. This result is unexpected. This shows that the corrosion rate derived from the weight loss and polarisation curves cannot reflect the instantaneous corrosion rate of the dual phase Mg–Li–Ca alloys.

3.3.4. Change in the pH value of the solution

For the samples soaked in Hank’s solution, the pH value of the solution increased with immersion time (Fig. 5). The formation of magnesium hydroxide and lithium hydroxide produced a compact layer of corrosion products. Therefore, no obvious change in pH values between the extruded and cast alloys was observed in the first hour. The difference in pH between the two alloys progressively increased in the following period, indicating that passivity could develop more quickly on the surface of the extruded alloy than on the cast alloy.
4. Discussion

4.1. Influence of the microstructure on corrosion

It is well-known that microstructural features such as grain size and the amount and distribution of intermetallic compounds of magnesium alloys have important influences on corrosion resistance [22,25].

4.1.1. Influence of grain size

Usually, alloys with fine-grained microstructures exhibit better corrosion resistance than those with coarsened grains [22,34]. Kim et al. [22] reported that the corrosion rate of the ultrafine-grained magnesium alloy AZ61 obtained from current density and weight loss is proportional to the reciprocal square root of grain size.

4.1.2. Influence of intermetallic compounds

Generally, the size and distribution of the intermetallic compounds play predominant roles in corrosion behaviour of metals. Fig. 6 shows the corrosion morphologies of the two alloys after immersion in Hank’s solution for 430 min. The presence of corrosion pits (Fig. 6a) on the surface of the cast alloy reveals that micro-galvanic corrosion occurred between the intermetallic compounds Mg2Ca and its neighbouring β phase. The Mg2Ca phase had a relatively higher potential of -1.54 V vs. SCE [16] and thus became the cathode, whereas the β phase had a much lower potential of -3.41 V vs. SHE (= -3.17 V vs. SCE) and was the anode. Similarly, the difference in corrosion potentials between Mg2Ca and the α-Mg matrix accelerated the corrosion of the Mg–Ca alloys [16]. Moreover, the break-up of the secondary phase Mg2Ca during extrusion led to a greater dispersion of the particles in the microstructure. As a consequence, the corrosion pits caused by the micro-galvanic corrosion between the Mg2Ca and α-Mg matrix became relatively smaller and shallower (Fig. 7b). Thus, the refinement of second phase may have played an equally important or more important role than the refinement of the grains.

In contrast, the formation of a dense layer of corrosion products prevented any localised attack on the extruded alloy (Fig. 6b). This can be attributed to the formation of a hydroxide, carbonate and phosphate film and will be discussed in subsequent sections. Therefore, the refined microstructure of dual phase Mg–Li–Ca alloys changed the corrosion type from pitting corrosion to overall corrosion.

Further investigation by SEM observation reveals that for the cast alloy, pitting corrosion or intergranular corrosion occurred at grain boundaries, where the β phase surrounding the Mg2Ca particles were initially attacked (Fig. 7a). More concisely, the attack initiated at the interface of the α and β phases due to Mg2Ca particles were embedded in the α phase (Fig. 7b). The EDS results in the inset of Fig. 7 designated the formation of the corrosion product Mg(OH)2 adjacent to Mg2Ca particles.

Our findings are different from the filiform corrosion observed for Mg–8Li alloy in 0.1 M NaCl solution [9]. Song [9] found that localised attack occurred at the boundary of the α and β phases at the early stage of immersion for Mg–8Li alloys, and filiform corrosion occurred after a longer immersion time. Thus, the addition of Ca into dual phase Mg–Li alloys caused the change in corrosion from filiform corrosion to pitting corrosion due to the formation of cathodic Mg2Ca phases.

4.2. Influence of the natural oxide film and corrosion products on corrosion

Natural oxide films and corrosion product films of magnesium alloys have crucial impacts on the corrosion rates. To better understand the corrosion mechanism of Mg–Li–Ca alloys, it is necessary to probe the characteristics of natural oxide films and corrosion product films.

4.2.1. The natural oxide film after long-term exposure to air

In ambient temperature, the oxide film naturally formed on the surface of Mg alloys is very thin [29,36]. A thick oxide film could develop upon the exposure of samples to ambient atmosphere for a longer period of time. Studying the thick oxide film is helpful to elucidate the diffusion process of alloying elements and species such as oxygen, carbon dioxide, and moist water in humid air in the oxide film.

Alkaline and alkaline earth metals such as Li, Mg and Ca have a high negative energy of oxide formation. Therefore, they readily react with oxygen when exposed to air. The moist water molecules in the ambient atmosphere can bond with Li2O, MgO and CaO to form LiOH, Mg(OH)2 and Ca(OH)2. Similarly, carbon dioxide reacts with the oxides to form Li2CO3, MgCO3 and CaCO3. Table 1 shows the standard enthalpy of formation of the oxides, hydroxides and carbonates of Li, Mg and Ca. Lower enthalpy values indicate greater chemical stability. It is evident in Table 1 that the carbonates are

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Enthalpy (kJ/mol)</th>
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<tbody>
<tr>
<td>Li2CO3</td>
<td>-1216.04</td>
</tr>
<tr>
<td>LiOH</td>
<td>-484.93</td>
</tr>
<tr>
<td>Li2O</td>
<td>-597.9</td>
</tr>
<tr>
<td>Li2O2</td>
<td>-632.62</td>
</tr>
<tr>
<td>MgCO3</td>
<td>-1096</td>
</tr>
<tr>
<td>Mg(OH)2</td>
<td>-924.66</td>
</tr>
<tr>
<td>MgO</td>
<td>-601.7</td>
</tr>
<tr>
<td>Li</td>
<td>-90.6</td>
</tr>
<tr>
<td>CaO</td>
<td>-635.1</td>
</tr>
<tr>
<td>Ca(OH)2</td>
<td>-986.1</td>
</tr>
<tr>
<td>Li2O2</td>
<td>-83.68</td>
</tr>
</tbody>
</table>
more stable than the hydroxides and oxides. Mg(OH)$_2$ and Ca(OH)$_2$ are more stable than MgO and CaO, but LiOH is less stable than Li$_2$O [29]. LiO cannot exist in the oxide film, but LiH is most likely present (see Table 1).

For the extruded Mg–9.29Li–0.88Ca sample, the XPS analysis in Fig. 8 demonstrates that the oxide film that formed naturally in laboratory air over more than 3 years only contained Mg, Ca, and Li. Fig. 8a demonstrates that the content of Li, O, and C at depths in the oxide film ranging from 971 μm to 2697 μm changed slightly from 33.07: 30.38: 36.55 to 30.8: 37.15, respectively. Lithium content decreased from the outer layer to the interior, while the contents of O and C increased. This result indicates that the outer layer of the oxide film is too thick to be probed. The XPS survey scanning spectrum at a depth of 500 μm in the oxide film revealed that the chemical composition of the oxide film was O, C and Li (Fig. 8b). The XPS analysis generally indicates a high content of carbon in the film because of the adventitious hydrocarbons from the environment (Fig. 8c). Another source of carbon is the reaction of the alloy with the CO$_2$ in air. The binding energies of O 1s peaks at 531.5 eV, 531.3 eV and 531.0 eV (Fig. 8d) and Li 1s peaks at 55.2 eV, 55.6 eV and 54.9 eV (Fig. 8e) correspond to the compounds Li$_2$CO$_3$, Li$_2$O and LiOH, respectively. The peak at 54.9 eV is the signal of the 1s electron of lithium. Li exhibited greater mobility and activity in the oxide film, and easily reacted with O$_2$ to form Li$_2$O in the outer layer of the sample.

$4\text{Li} + \text{O}_2 \rightarrow 2\text{Li}_2\text{O}$ (s) \hspace{1cm} (7)

$2\text{Li} + \text{H}_2\text{O} (g) \rightarrow \text{Li}_2\text{O} (s) + \text{H}_2 \uparrow$ \hspace{1cm} (8)

Fig. 8. XPS analysis of naturally formed oxide film on the extruded Mg–9.29Li–0.88Ca alloy: (a) depth profiles of Li, O and C; (b) survey scanning spectrum; (c) high-resolution C1s spectrum; (d) high-resolution O1s spectrum; (e) high-resolution Li1s spectrum; and (f) high-resolution Mg 1s spectrum.
The Pilling–Bedworth ratio (PBR) of Li$_2$O is 0.58, less than one [37], indicating the formation of a porous oxide film on the surface of the alloy. The defect oxide film provided open routes for the entrance of H$_2$O and CO$_2$ into the interior of the film. Thus, LiOH and Li$_2$CO$_3$ were formed in the film. LiOH is clearly the predominant compound in the film. Thus, the outer layer of the natural oxide film is composed of Li$_2$O, LiOH and Li$_2$CO$_3$.

\[
\text{Li}_2\text{O} (s) + \text{H}_2\text{O} (g) \rightarrow 2\text{LiOH} (s) \\
\text{Li}_2\text{O} (s) + \text{CO}_2 (g) \rightarrow \text{Li}_2\text{CO}_3 (s)
\]

The Mg 1s peak indicating the presence of MgO was not detected, as indicated in Fig. 8f. For the ground sample of the Mg–8Li alloy, the Mg 1s peak was detected after 30 s of sputtering [29]. Interestingly, the Li 1s and Mg 2p peaks were detected on the outer layer of the oxide film of the Mg–8Li alloy, indicating the existence of Li$_2$O and Mg(OH)$_2$ [29]. Additionally, the Ca 2s and 2p peaks were not detected spontaneously, implying that no Ca, CaO or CaCO$_3$ existed in the outer layer of the oxide film.

Further investigation by XRD examination (Fig. 9) demonstrated that the natural oxide film on the alloy, exposed to air in ambient atmosphere for more than 3 years, consisted of LiOH, Li$_2$O$_2$, Li$_2$CO$_3$ and LiH. This result is in agreement with the results of XPS analysis, except that LiH was not identified by XPS.

The natural oxide film on the freshly ground surface of the alloy exposed to air in ambient atmosphere for approximately 16 h consisted of LiOH, Li$_2$O, Li$_2$CO$_3$, MgCO$_3$ and LiH. This finding is completely different from the result for EPMA due to differences in the environments during the exposure time. That is, water molecules and carbon dioxide gas were absorbed on the oxide film to form LiOH, Li$_2$CO$_3$, MgCO$_3$ and LiH. Thus, this layer can be considered as the second layer of the natural oxide film, which consists of LiOH, Li$_2$O$_2$, Li$_2$CO$_3$, MgCO$_3$ and LiH.

The natural oxide film on the freshly ground surface of Mg–8Li alloy [29] exposed to ambient atmosphere contained four layers: the top layer is a mixture of Mg(OH)$_2$ and Li$_2$O; the second layer is a mixture of Mg(OH)$_2$, Li$_2$O and MgO; the third layer is a mixture of Mg(OH)$_2$, MgO, LiOH, Li$_2$O and Mg; the bottom layer contains MgO, Li$_2$O, Li and Mg. No carbonates such as Li$_2$CO$_3$ or MgCO$_3$ were found on Mg–8Li alloy. This distinction between the natural oxide films of Mg–9.9Li–0.88Ca and Mg–8Li alloys is ascribed to the variation in exposure time, as carbonate formation may take a longer time.

4.2.2. The natural oxide film formed on the fresh surface of the $\alpha$ and $\beta$ phases

Fig. 10 presents the EPMA image and the composition distribution of Mg, O and Ca by area scan on the etched surface of the extruded Mg–9.29Li–0.88Ca alloy exposed to dry air for approximately 16 h. The phase with the light white colour represents the $\alpha$-Mg phase, and the phase indicated with grey designates the $\beta$ phase. The pits, as indicated by the arrows, imply the...

![Fig. 9. XRD pattern of the natural oxide film on the extruded alloys exposed to air in ambient atmosphere.](image-url)

![Fig. 10. (a) EPMA image of the etched surface of the extruded Mg–9.29Li–0.88Ca alloy after exposure to dry air for approximately 16 h. The voids resulting from the peeled off Mg,Ca particles are indicated by arrows. Spectra 1–3 show the results of spot scanning, the data of which are shown in Table 2. (b–d) The elemental distributions of oxygen, magnesium and calcium, respectively.](image-url)
formation of Mg₂Ca particles, which were embedded in the α phase at the interface of the α and β phases, most of which peeled off during sample preparation (Fig. 10a). Fig. 10c and d can further demonstrate the presence of Mg₂Ca phases. Moreover, a trace amount of CaO may exist (Fig. 10d).

To compare the difference in oxygen concentration between the α and β phases, spot scans were performed as indicated by spectra 1–3 in Fig. 10a. Table 1 shows the standard enthalpies of formation of various chemical compounds [38]. It is clear that the β phase has a higher oxygen content than the α phase. This result is in agreement with the occurrence of selective oxidation on the β phase of dual phase Mg–12Li–5Ca alloy [21]. In addition, our earlier XPS probe [39] demonstrated that the oxide film of Mg–Ca alloys was composed of MgO and a trace amount of CaO. Therefore, the natural oxide film formed on the etched surface exposed to dry air can be regarded as the third layer consisting only of oxides: Li₂O, MgO and CaO.

2Mg + O₂ → 2MgO  \hspace{1cm} (11)
2Ca + O₂ → 2CaO  \hspace{1cm} (12)

Fig. 11 schematically illustrates the mechanism of formation of the natural oxide film on dual phase Mg–Li–Ca alloys.

oxide towards the outer surface of the oxide because lithium has a small atomic diameter and higher mobility, and a high reactivity with oxygen.

Atomic diffusion coefficients are well known to depend on temperature, the type of solid solution, crystal structure, crystal defects, chemical composition and stress. Thus, the high mobility of Li is attributed to two factors: the diffusion coefficient of Li in bcc Li is greater than that of Li in hcp Mg, as the atomic packing factor of bcc Li, 0.68, is lower than that of hcp Mg, 0.74. The higher dislocation density led to a higher diffusion rate of Li in the extruded alloy than in the cast alloy. The lithium-ion migration causes a large amount of vacancies in the alloy, with crystalline vacancies accumulating at the interface between the alloy and the oxide. The coalescence of vacancies led to the formation of voids, and when these voids reached a critical size, the oxide film experienced localized collapse. As a consequence, considerable micro-crack formation was observed in the oxide film (Fig. 11b).

The perfection or compactness of oxide films on metals can be characterised by the Pilling-Bedworth ratio (PBR). This is the ratio of volume of oxide to volume of metal, and can be mathematically expressed as:

$$\text{PBR} = \frac{V_{\text{ox}}}{V_{\text{st}}} = \frac{M_{\text{ox}} \cdot \rho_{\text{M}}}{n \cdot \rho_{\text{A}} \cdot n_{\text{ox}}}$$

where $M_{\text{ox}}$ and $A$ are the molar weight and atomic weight, respectively, of the oxide and the metal; $\rho_{\text{ox}}$ and $\rho_{\text{M}}$ are the oxide and metal densities, respectively; and $n$ is the number of metal atoms in the oxide molecules.

### 4.2.3. Influence of the corrosion product film

PBR is representative of the stress state of the oxide film. It is generally accepted that when PBR is less than one, insufficient oxide is present to cover and protect the metal. As a result, a tensile stress develops in the oxide scale, while a compressive stress develops in scales with PBR values greater than one. The greater the difference of PBR from one, the greater the growth stress, which causes scale cracking and spallation.

If the oxide in Eq. (13) is replaced by chemical compounds or reaction products produced during the corrosion of magnesium alloys, then the compactness of the layer of the corrosion products can be used to elucidate the corrosion mechanism, regardless of the discrepancy between the oxides and the compounds. The PBR of the chemical compounds can be calculated through

$$\text{PBR}_{\text{com}} = \frac{M_{\text{com}} \cdot \rho_{\text{M}}}{n \cdot \rho_{\text{A}} \cdot n_{\text{com}}}$$

where $M_{\text{com}}$ and $\rho_{\text{com}}$ are the molecular weight and density of the chemical compounds, respectively. The PBR values of the chemical compounds are shown in Table 3. Note that the PBR values of all the chemical compounds of Li and Ca are between one and two, indicating that the layer of their corrosion products on the Mg–Li–Ca alloy is dense and protective.

The PBR of Li$_2$O and MgO is less than one [37], leading to the production of a discontinuous, cellular and porous film with low protective properties on the surface of the alloy under tensile stress. Li$_2$O has a cubic antifluorite (CaF$_2$) structure (space group Fm3m) with a lattice parameter of 0.46 nm [40]. Li has a bcc structure with a lattice distance of 0.35 nm. Thus, the 31.4% mismatch between the Li$_2$O crystal and Li substrate led to a high susceptibility of cracking of the Li$_2$O layer and the interface between Li$_2$O and Li. Tensile stresses parallel and compression stresses perpendicular to the substrate surface are produced in oxide films due to the reduction in volume [36]. Above a critical oxide thickness, however, oxides including Li$_2$O, CaO and MgO were formed, and the resulting stresses lead to the cracking of the film. These stresses increase as the film thickens. The carbon dioxide in air can then combine with moisture to form a carbonate that further reacts with Mg(OH)$_2$ to produce Mg carbonate. Therefore, the micro-cracks provided paths for the entrance of molecules of oxygen, water and carbon dioxide in air into the oxide film and the GBs of the matrix, resulting in the formation of LiOH, Li$_2$CO$_3$ and oxides along the chemical compounds of Li and Ca.

Furthermore, Kim et al. [22] claimed that the formation of a great number of isolated MgO nanocrystals in the refined Mg substrate below the MgO layer is attributable to the diffusion of oxygen atoms from the surface into the GBs of the matrix. The intermediate layer of the mixture of MgO and Mg phases between the MgO layer and the Mg substrate is favourable for reducing the tensile stress in the MgO layer by acting as a buffer layer that decreases the sharpness of the stress gradient across the boundary between MgO and the Mg substrate. Thus, it is postulated that with increasing time, the diffusion of lithium towards the outer layer of the oxide film and oxygen into the substrate through the porous oxide film and along the GBs are responsible for the thickening of the oxide films of dual phase Mg–Li–Ca alloys.

As the samples were soaked in Hank’s solution, they would be susceptible to attack as schematically indicated in Fig. 12. Note from Fig. 5 that pH value of the solutions continuously increased, indicating the alkalinisation of corrosion pits. Our previous investigation [5] on the Mg–1.33Li–0.6Ca alloy showed that the corrosion products comprised of LiH, Mg(OH)$_2$, CaCO$_3$, MgCO$_3$, CaMgCO$_3$ and CaMgPO$_4$.

Table 3: PBR of the oxide and the chemical compounds.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>PBR</th>
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<th>Compounds</th>
<th>PBR</th>
<th>Compounds</th>
<th>PBR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$O</td>
<td>0.57[37]</td>
<td>LiOH</td>
<td>1.26</td>
<td>Li$_2$CO$_3$</td>
<td>1.35</td>
<td>Li$_3$PO$_4$</td>
<td>1.20</td>
</tr>
<tr>
<td>CaO</td>
<td>0.64[37]</td>
<td>Ca(OH)$_2$</td>
<td>1.30</td>
<td>CaCO$_3$</td>
<td>1.43</td>
<td>Ca$_3$(PO$_4$)$_2$</td>
<td>1.27</td>
</tr>
<tr>
<td>MgO</td>
<td>0.80[37]</td>
<td>Mg(OH)$_2$</td>
<td>1.80</td>
<td>MgCO$_3$</td>
<td>2.04</td>
<td>Mg$_5$(PO$_4$)$_2$</td>
<td>2.29</td>
</tr>
</tbody>
</table>

Asodic reactions:

$$\text{Li} \rightarrow \text{Li}^+ + e^-$$

$$\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^-$$

Cathodic reactions:

$$2\text{H}_2\text{O} + e^- \rightarrow 2\text{OH}^- + \text{H}_2 \uparrow$$

$$\text{Li}_2\text{O} + \text{H}_2\text{O} (s) \rightarrow 2\text{LiOH}$$

$$\text{MgO} + \text{H}_2\text{O} (s) \rightarrow \text{Mg(OH)}_2$$

$$\text{CaO} + \text{H}_2\text{O} (s) \rightarrow \text{Ca(OH)}_2$$
film can be greater than that of the dissolution of the alloy, and Ca layers were found on both alloy. At higher pH, the layers on AZ31. After a longer immersion time, the formation of occluded cells for the cast alloy, a passive film was established instantaneously in the oxide film on the coarse-grained cast alloy was subjected to much higher tensile stress than that of the fine-grained extruded alloy. After the surface film broke down and corrosion pits initiated in a specific area, it was relatively difficult for the surface film to repair itself. Consequently, more fresh surfaces were exposed to the aggressive solution, accelerating the corrosion rate of the cast alloy. After some time, the tubular paths in the oxide film were jammed and sealed by compounds such as LiOH, Mg(OH)2, CaCO3 and MgCO3.

4.3. Influence of Li content on corrosion resistance

The introduction of lithium into Mg–Ca alloys lead to an enhancement in corrosion resistance in comparison to the Mg–0.54Ca alloy [5], and the corrosion resistance increases with increasing lithium content, as shown in Fig. 13. The HER of the Mg–0.54Ca alloy was the lowest in the initial 1 h of immersion, as shown in the inset of Fig. 13. Later, the HER of Mg–Li–Ca alloys slowed down due to the formation of a compact corrosion product layer stabilised by the increase in the pH value of lithium and carbonate [30]. A previous report [42] demonstrated that uniform and continuous Mg(OH)2 layers were found on both Mg–Li–Zn (LAZ1231 and LAZ1291) alloys in comparison with the irregular and loose Mg(OH)2 layers on AZ31. At higher pH, the precipitated Mg(OH)2 can provide better protection for the extruded alloy, inhibiting the corrosion to some degree. The HER decreased with decreasing lithium content in the sequence Mg–9.29Li–0.88Ca, Mg–1.33Li–0.6Ca and Mg–0.54Ca. This
finding is in good agreement with the result from Bialobrzeski [30].

4.4. Characterisation of corrosion rates

The weight loss rate, $V_w$ (mg/cm$^2$/day) can be expressed as the average corrosion rate, $P_w$ (mm/year) through [43]

$$P_w = 3.65 \frac{V_w}{\rho} \text{ (mm/year)}$$  \hspace{1cm} (30)

where $\rho$ is the density of metals (g/cm$^3$).

To calculate the volume fractions of the $x$ and $\beta$ phases, their densities are needed.

For dual phase Mg–xLi (5 wt% $< x <$ 11 wt%) alloys, the mass fractions $W_x$ and $W_\beta$ corresponding to the $x$ and $\beta$ phases are determined by the lever rule

$$w_x = \frac{C_x - C_0}{C_\beta - C_x} = \frac{11 - x}{6}$$ \hspace{1cm} (31)

and

$$w_\beta = 1 - w_x$$ \hspace{1cm} (32)

To compute volume fractions, it is necessary to determine the densities of the $x$ and $\beta$ phases. Thus,

$$\rho_x = \frac{100}{C_{Mg(x)} + \frac{C_{Li(x)}}{\rho_{Li}}} \text{ (g/cm$^3$)}$$ \hspace{1cm} (33)

where $C_{Mg(x)}$ and $C_{Li(x)}$ denote the Mg and Li concentrations, respectively, in weight per cent in the $x$ phase. At room temperature, these values are 95 wt% and 5 wt%. Incorpoation of these values along with the densities of pure Mg and Li lead to

$$\rho_x = 1.56 \text{ (g/cm$^3$)}$$ \hspace{1cm} (34)

Similarly, for the $\beta$ phase

$$\rho_\beta = \frac{100}{C_{Mg(\beta)} + \frac{C_{Li(\beta)}}{\rho_{Li}}} = 1.39 \text{ (g/cm$^3$)}$$ \hspace{1cm} (35)

Thus, while the density of the $x$ phase, 1.56 g/cm$^3$, is the same as that in the literature [44], the 1.39 g/cm$^3$ density of the $\beta$ phase is not in agreement with that (1.47 g/cm$^3$) in the literature [44].

The volume fraction of the $x$ phase, $V_x$, is defined as

$$V_x = \frac{V_w}{V_x + V_\beta}$$ \hspace{1cm} (36)

$$V_x = \frac{W_x}{\frac{\rho_x}{\rho_{Mg}} + \frac{W_\beta}{\rho_{Li}}} = 26.2\%$$ \hspace{1cm} (37)

and

$$V_\beta = 1 - V_x = 73.8\%$$ \hspace{1cm} (38)

Thus, the density of the dual phase Mg–xLi alloys is determined by

$$\rho = V_x \rho_x + V_\beta \rho_\beta = 1.39 + \frac{0.24}{1 - 0.24} \text{ (g/cm$^3$)}$$ \hspace{1cm} (39)

Thus, the Mg–9.29Li–0.88Ca alloy has a density of 1.44 g/cm$^3$. For the Mg–9.29Li–0.88Ca alloy,

$$P_w = 2.54 i_{corr} \text{ (mm/year)}$$ \hspace{1cm} (40)

For pure Mg [43,46],

$$P_{w,Mg} = 2.10 V_w \text{ (mm/year)}$$ \hspace{1cm} (41)

For pure Li,

$$P_{w, Li} = 6.84 V_w \text{ (mm/year)}$$ \hspace{1cm} (42)

If general corrosion occurs on the surface of the alloy, the lithium and magnesium components are simultaneously corroded. Therefore, the weight loss of the alloy, $P_w$, should be the sum of the weight losses of the $x$ and $\beta$ phases based on the volume fractions of Mg and Li in the $\beta$ phase of 26.2% and 73.8%, respectively, thus

$$P_w = V_x \times P_{w,Mg} + V_\beta \times P_{w, Li} = 5.60 V_w \text{ (mm/year)}$$ \hspace{1cm} (43)

In comparing Eq. (43) with Eq. (40), there is a 220% difference between $P_w$ and $P_{w,Mg}$, Eq. (43) provides a more reasonable result.

If uniform corrosion occurs, then the relationship of the weight loss rate, $V_w$ (mg/cm$^2$/day) and corrosion current density, $i_{corr}$ (mA/cm$^2$) is established according to Faraday’s law,

$$V_w = 24 \times \frac{A}{F} i_{corr}$$ \hspace{1cm} (44)

where $A$ is the atomic mass (g/mol), $F$ is the Faraday constant (26.8 A h/mol), and $n$ is valence.

For pure Mg,

$$V_{w,Mg} = 10.89 i_{corr}$$ \hspace{1cm} (45)

For pure Li,

$$V_{w, Li} = 6.22 i_{corr}$$ \hspace{1cm} (46)

Thus,

$$V_{w} = V_x \times V_{w,Mg} + V_\beta \times V_{w, Li} = 7.44 i_{corr}$$ \hspace{1cm} (47)

Substituting Eq. (47) into Eq. (43), the corrosion current density is related to the corrosion rate, $P_l$ (mm/year) using

$$P_l = 41.664 i_{corr}$$ \hspace{1cm} (48)

Eqs. (18) and (19), i.e., the corrosion reaction of lithium and magnesium, indicate that one molecule of hydrogen is evolved for each atom of corroded magnesium. Two moles (i.e., 13.88 g) of Li metal or one mole (i.e., 24.31 g) of Mg metal corrodes for each mol (i.e., 22.4 L) of hydrogen gas produced. Therefore, the HER, $V_H$, [ml/cm$^2$/day], is related to the metallic weight loss rate, $V_w$ [mg/cm$^2$/day], using [43,46,47]

$$V_{w,Mg} = 1.085 V_H$$ \hspace{1cm} (49)

$$V_{w, Li} = 0.620 V_H$$ \hspace{1cm} (50)

The total weight loss rate of the dual phase Mg–Li–Ca alloy,

$$V_{w,H} = 0.742 V_H$$ \hspace{1cm} (51)

The corresponding penetration rate, $P_h$, is evaluated by substituting Eq. (51) into Eq. (44) to obtain

$$P_h = 4.154 V_H \text{ (mm/year)}$$ \hspace{1cm} (52)

The corrosion rates of the alloys normalised by the above methods are summarised in Table 4. The HER results are in agreement with those of current density, implying that the calculations of HER are reliable. Note that the deviation in corrosion rate determined by weight loss is much greater than that determined by the hydrogen evolution and polarisation method. This deviation may be attributed to the effects of the corrosion product layers and the negative difference effect (NDE) [45], a special electrochemical phenomenon. Moreover, the weight loss method is not appropriate for evaluating pitting corrosion. With sufficient immersion time, HER could instantaneously and much more briefly respond to the attack by the media. Thus, the hydrogen evolution method should be used to evaluate the corrosion rate of magnesium alloys [16,46,47]. However, the ambient temperature has a significant impact on the volume of hydrogen evolution.
5. Conclusions

The impact of the microstructure, the oxide film and the corrosion product film of the dual phase Mg–9.29Li–0.88Ca alloy on its corrosion behaviour in Hank’s solution has been investigated using SEM, EPMA, XPS and corrosion measurements. The main findings are summarised as follows:

(1) The microstructure of the Mg–9.29Li–0.88Ca alloy is characterised by α-Mg, β(-Li) phases and intermetallic compound Mg$_2$Ca particles, most of which are distributed at the grain boundaries of the cast alloy with coarse grains. In contrast, these particles were embedded in the α phase at the interface of the α and β phases in the extruded alloy and exhibited relatively refined and elongated grains.

(2) The comprehensive mechanical properties of the Mg–9.29Li–0.88Ca alloy, including UTS, YS and EL, and the corrosion resistance were promoted by the extrusion process. The form of corrosion shifted from pitting corrosion for the cast alloy to general corrosion or uniform corrosion for the extruded alloy.

(3) The oxide film that naturally formed on the alloy is composed of four layers: the outer layer is composed of litharge (MgO), MgO and Mg$_2$CO$_3$; the second layer contains LiOH, Li$_2$O$_2$, Li$_2$CO$_3$, MgCO$_3$ and LiF; the third layer consists of oxides (Li$_2$O, Li$_2$O, MgO and CaO); and the bottom layer includes the oxides at GBs and in the α-Mg, β(-Li) phases.

(4) Pitting corrosion occurred on the cast alloy with a long incubation period, whereas overall corrosion occurred on the extruded alloy, with corrosion products being jammed into the micro-cracks of the natural oxide film. A novel concept involving the Pilling–Bedworth Ratios of chemical compounds is proposed to elucidate the mechanism of corrosion for dual phase Mg–Li–Ca alloys.

(5) The corrosion mechanism of dual phase Mg–Li–Ca alloys is completely different from that of other types of magnesium alloys. The two phases (α-Mg and β-Li) of the Mg–Li–Ca alloys are simultaneously subjected to corrosion, and the contribution of the β phase to corrosion cannot be ignored. For the other alloys such as Mg–Al alloys, only the α-Mg matrix is attacked. Therefore, a particular method of corrosion characterisation was proposed for dual phase Mg–Li–Ca alloys based on the volume fraction of each phase.

Acknowledgements

This work was supported by National Natural Science Foundation of China (51241001) and Natural Science Foundation of Shandong Province (ZR2011EM0004), the Open Foundation of State Key Laboratory for Corrosion and Protection (SKLCP2012KF03), Taishan Scholarship Project of Shandong Province (TS20110828), Scientific Research Foundation of Shandong for Outstanding Young Scientist (NO. B52013CL009) as well as Doctoral Program Foundation of State Education Ministry (NO. 20133718120003).

Table 4

Comparison of corrosion rates obtained from different methods.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Weight loss rate $P_w$ = 5.60V$_{cor}$, mm/year</th>
<th>HER $P_h = 4.154$ V$_{cor}$, mm/year</th>
<th>Current density $I_{corr}$ = 41.664 I$<em>{H</em>{corr}}$, mm/year</th>
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</thead>
<tbody>
<tr>
<td>As-cast</td>
<td>7.06 ± 0.76</td>
<td>5.07 ± 0.98</td>
<td>3.48 ± 0.35</td>
</tr>
<tr>
<td>As-extruded</td>
<td>1.38 ± 0.16</td>
<td>2.92 ± 0.63</td>
<td>2.81 ± 0.22</td>
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</table>

References


