Passivation and Potential Fluctuation of Mg Alloy AZ31B in Alkaline Environments

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Abstract

The passivation and corrosion behaviors of Mg alloy AZ31B were investigated in chloride-free NaOH solutions with pH range from 10 to 14. The results indicate that various phases behave differently at different pH levels. Al-Mn intermetallics serve as strong cathode at $\text{pH} \leq 11$, but dissolve at $\text{pH} \geq 13$. Ambient oxygen is responsible for the potential rise at $\text{pH} \geq 13$ and subsequent significant potential oscillation ($> 1\text{V}$) is attributed to the passive film breakdown at the intergranular boundaries in the oxide film. Optimal passivation is achieved at pH 12 with thin uniform passive film formed across the surface.

Keywords: A: Magnesium; B: Polarization; C: Alkaline corrosion; C: Oxygen reduction; C: Pitting corrosion; C: Passive films

1. Introduction

Magnesium alloys are promising candidate materials in automotive and aerospace applications because of their low density, high strength-weight and stiffness-weight ratios, as compared to steel and aluminum alloys [1]. They are also gaining popularity in many other areas such as portable electronics, medical implants, and sports and recreation equipment. However, their widespread application is limited by poor corrosion resistance, owing to high chemical reactivity of Mg and poor protection provided by the surface oxide film in near-neutral and atmospheric conditions [2,3]. Therefore, a comprehensive understanding of the corrosion of Mg alloys is of vital importance.

In Al-containing Mg alloys such as AZ31B (nominally 3 wt.% Al, 1 wt.% Zn), there is the deliberate presence of Mn (typically at ~0.4 wt.%) on the basis of grain refinement and sequestering any impurity iron. As such, common secondary phases in Al-containing Mg alloys include β -phase (Mg_xAl_y , commonly $\text{Mg}_{17}\text{Al}_{12}$) and Al_xMn_y intermetallics. It has also been reported that substitutional Zn is present in β -phase ($\text{Mg}_{17}(\text{Al,Zn})_{12}$) when unique processing conditions are used [4]. The Al_xMn_y phase in Al-containing Mg alloys has been reported to have various compositions, such as Al_8Mn_5 , Al_2Mn , Al_3Mn , Al_4Mn , $\text{Al}_{10}\text{Mn}_3$, $\text{Al}_{11}\text{Mn}_4$, and $\text{Al}_{19}\text{Mn}_4$, according to characterization using transmission electron microscopy (TEM) [5]. In addition, coring during solidification causes considerable variation in the distribution of aluminum (as well as zinc) in the microstructure of Mg-Al alloys [6]. It has been found that the aluminum concentration at α region near to β -phase is generally high and it is identified as eutectic α -phase. This eutectic α phase has been shown by proper etching [6–8] and regarded in the literature as an independent metallurgical entity [9]. High resolution FE-SEM examination suggests that the

eutectic α phase is possibly a mixture of α -Mg solid solution and ultrathin β -Mg₁₇(Al,Zn)₁₂ precipitates [10].

It is well known that the presence of secondary phases and intermetallics accelerate the corrosion of the Mg matrix in near-neutral aqueous environments due to micro-galvanic coupling effect [11]. In Mg-Al alloys, β -phase and Al_xMn_y intermetallics are more noble than the α -Mg matrix in NaCl solutions [8,10,12,13]. Jönsson et al. reported the potentials of α -Mg, β -phase (Mg₁₇Al₁₂) and Al-Mn intermetallics (Al₈Mn₅) of AZ91 in a range of NaCl concentrations by SKP and SKPFM techniques [14]. They found that the potential of β -phase is 400 mV higher than α -Mg and the potential of Al₈Mn₅ intermetallics is 1000 mV higher than α -Mg. Birbilis et al. studied the electrochemical behavior of common secondary phase analogs in 0.1 M NaCl and found that these phases were all more noble than Mg (for Mg in isolation), with the exception of Mg₂Ca [15]. The corrosion potentials for Mg-Al phases were found to be -1.35 V_{SCE} and -1.01 V_{SCE} for Mg₁₇Al₁₂ and Mg₂Al₃, respectively, as compared to -1.65 V_{SCE} for pure Mg [15]. In addition to more noble unique corrosion potentials, secondary phases also support reduction reactions at greater rates than Mg [15] and thus have much larger cathodic current density than the α -matrix [16]. It has been reported that the galvanic corrosion current density between α - and β -phases can even be as high as 5 mA/cm² [12,13]. Besides Mg_xAl_y phase, the Al_xMn_y intermetallics are another phase that affects the corrosion of Mg-Al alloys. The addition of Mn to the Mg alloys can limit the distribution of the detrimental elements Fe and Cu and therefore improve overall corrosion performance [17,18]. However, the formation of Al_xMn_y intermetallics might cause micro-galvanic corrosion of the α -Mg matrix by acting as strong cathodes, especially when they are contaminated with Fe [19]. Cathodic reaction (i.e., hydrogen evolution reaction) occurring on these particles can significantly increase the local pH and alter

the particle morphology at the interface [18,20]. The corrosion behavior of eutectic α is somewhat controversial for Mg-Al alloys [21]. It has been reported that eutectic α is more resistant than the Al-depleted bulk matrix and the bulk matrix is anodically more active than the β -phase and eutectic α in NaCl solution [7,8]. However, by using microcapillary technique, Krawiec et al. found that eutectic α was more active compared to primary α - and β -phases in sodium perchlorate solution [10]. Immersion experiments also showed that eutectic α suffered extensive localized corrosion under the influence of cathodic action of the adjoining β -phase [9]. It is speculated that the width of the eutectic zone relative to size of β -phase is the cause of different behaviors [7,9].

Although Mg and its alloys corrode in neutral and acid solutions, they passivate in strong alkaline environments according to the electrochemical equilibrium diagram for the Mg-H₂O system [22] and as previously demonstrated [23–26]. The passivation of Mg in alkaline solutions results in a surface film that is more protective than that form in solutions with lower pH [24,27,28]. The applications of Mg passivation in alkaline solutions include the preparation of protective oxide films (e.g., anodization) [25,29–32] and surface pre-treatment for coating applications [33,34]. It was believed that the surface films on Mg in both neutral [35–38] and alkaline [39] solutions are composed of mainly Mg(OH)₂. However, in neutral solutions, Mg(OH)₂ forms by a dissolution-precipitation reaction; while in alkaline solutions, it forms by a solid state (direct) anodic reaction [39]. Thus difference in corrosion resistance is possible for Mg(OH)₂ surface films that form under different conditions. Besides Mg(OH)₂, crystalline MgO also forms in the inner layers of the surface films on Mg exposed to alkaline solutions [39]. For Mg-Al alloys, it is generally agreed that the presence of aluminum is beneficial in improving the corrosion behavior and an optimum level of Al for effective protection is required [7]. Makar et

al. has identified the oxide film on Mg-Al alloys as a layer structure composed of MgO/Mg-Al-oxide/substrate, with the oxide (Mg-rich) thinner with increasing Al content [40]. Others have reported that the presence of Al-enriched superficial layer at the interface enhances the corrosion resistance of some phases, such as eutectic α [13,20].

An interesting phenomenon associated with the passivation of Mg in alkaline solutions has been reported recently, which showed that the oxide films formed on pure Mg and its alloys experienced intermittent ruptures in open circuit conditions when exposed to alkaline solutions. The corrosion potential fluctuates between the active state ($-1.5 - -1.6 \text{ V}_{\text{SCE}}$) and the passive state ($-0.5 - -0.6 \text{ V}_{\text{SCE}}$) [39,41]. The volume increase caused by the transformation of MgO to $\text{Mg}(\text{OH})_2$ was believed to be the cause of the ruptures. However, the effect of secondary phases and intermetallics on the oxide film formation and rupture in alkaline solutions has not been reported to date.

The present study aims to investigate the passivation/corrosion behavior of a die cast AZ31B Mg alloy in chloride-free alkaline solutions (i.e., NaOH) with different concentrations ($\text{pH} = 10 - 14$). The pH effect on the electrochemical behavior of AZ31B was explored using OCP measurements, potentiodynamic and potentiostatic polarizations. Morphology of different phases and intermetallics (primary α , eutectic α , β , and Al-Mn intermetallic) was examined by SEM/EDS/FIB and correlated to the electrochemical behavior. *In-situ* techniques such as SVET and stereomicroscope were used to study the cathodic reaction activity. The effect of oxygen on the passivation of AZ31B in strongly alkaline solutions was also investigated.

2. Experimental

2.1 Sample preparation

The material used was a die cast AZ31B Mg alloy with chemical compositions shown in Table 1. The samples with a dimension of 25 mm × 25 mm × 3 mm were cut from a die cast block using a high-precision Struers Accutom-5 cutting machine. The samples were then ground with 600-grit SiC paper and polished successively with 9 μm, 3 μm, and 1 μm oil-based diamond slurries (Buehler). Ethanol was used as a lubricant during grinding and polishing and was used to rinse the samples between each polishing step. After polishing, the samples were ultrasonically cleaned in ethanol for 5 min, followed by rinsing using ethanol and blow-drying using high purity argon gas (99.998%).

The microstructure of AZ31B Mg alloy was revealed by etching the polished surfaces using Acetic-Picral composed of 5 g picric acid, 5 ml acetic acid, 10 ml H₂O, and 100 ml ethanol [42–44]. An etching time of 5 – 20 s was sufficient to reveal grain boundaries of AZ31B Mg alloy and CP Mg while 2 – 5 min was required to over-etch AZ31B to reveal β-phase and its eutectic α-phase.

2.2 Electrochemical measurements

A Gamry Reference 600 potentiostat (Gamry Instruments Inc., USA) was used for open circuit potential (OCP) and polarization tests in a glass flat cell with a three-electrode configuration. The input impedance of this potentiostat is larger than 10¹⁴ Ω. A saturated calomel electrode (SCE)¹ and a platinum mesh were used as the reference and counter electrode, respectively. The exposed area of the working electrode was approximately 1 cm². The cell was purged with pure argon (99.998%) to achieve deaerated condition. The test solutions with pH in the range of 10 – 14 were made using deionized water (18.2 MΩ cm) and analytical grade NaOH pellets. Solution pH was measured with a calibrated pH meter before and after testing. Minimal

¹ The reference electrode (Fisher Scientific accumetTM) has a working pH range of 0 – 14.

pH change (± 0.1) was found for all tests except the case of pH 10, where pH rose to around 10.5 after testing [8,22].

The OCP tests were performed in various conditions with durations of either 24 h or 120 h. The potentiodynamic polarization experiments were conducted using a scan rate of 1 mV/s (unless specified otherwise). The single-scan anodic polarization experiments were conducted from OCP to 1.0 V_{SCE} , while the cathodic polarization were from OCP to -2.8 V_{SCE} . The cyclic potentiodynamic polarizations (CPP) were scanned from OCP to -0.5 V_{SCE} and then reversed back to OCP. The potentiostatic polarization experiments were conducted at -1.0 V_{SCE} for one hour in selected NaOH solutions. All electrochemical tests were conducted multiple times (≥ 3) to assure repeatability.

A VersaSCAN scanning vibrating electrode technique (SVET) system from Princeton Applied Research (PAR), USA was employed to obtain localized corrosion information on the AZ31B Mg alloy in various NaOH solutions. The SVET probe was an insulated Pt wire with a tip diameter of approximately 20 μm . The probe was positioned approximately 100 μm above the sample surface and vibrated at an amplitude of 30 μm . AZ31B was flush-mounted in epoxy resin to fit into the L-cell (from PAR) for SVET measurements. A chromium wire with a diameter of 3 mm was also mounted together with but ~ 2 mm away from the AZ31B sample in the epoxy resin for calibration purpose. For calibration, a selected range of cathodic current values was applied to the chromium wire and the corresponding voltage outputs were recorded. The calibration results were used to convert the measured potential values to current density values.

2.3 Sample characterization

A TESCAN LYRA3 field emission scanning electron microscope (FE-SEM) coupled with energy dispersive spectroscopy (EDS) was used for surface observation and elemental analysis of the AZ31B samples. To facilitate the observation of the passivation/corrosion morphology, regions of interests were also cut cross-sectionally using a gallium focused ion beam (FIB) integrated in the TESCAN FE-SEM. Optical microscopic images of tested samples were taken using a Nikon Eclipse MA100 inverted metallurgical microscope. Hydrogen evolution on AZ31B samples immersed in NaOH solutions with different pH were observed using a Nikon SMZ 745T stereomicroscope.

3. Results

3.1 Microstructure of die cast AZ31B

Fig. 1 shows typical secondary phases: β -phase and Al-Mn intermetallics in the die cast AZ31B Mg alloy. The chemical compositions of these secondary phases are shown in Table 2. The Al-Mn intermetallics have high Mn and Al contents, low Mg and residual Fe contents (1a in Table 2), while the β -phase has high Mg content, relatively high Al and Zn contents (1b in Table 2). The composition varies from particle to particle as demonstrated later in the results section. Microstructure of the AZ31B Mg alloy was revealed by polarized light optical microscope to contain large well crystallized grains (Fig. 2a). Extensive etching using Acetic-Picral separated the Al-Mn intermetallics, β -phase, and more importantly, eutectic α -phase from the primary α -matrix (Fig. 2b). The Al-Mn intermetallics were found to be embedded in the α -matrix and isolated from the β -phase and its surrounding eutectic α -phase.

3.2 Passivation of AZ31B Mg alloy in 1 M NaOH ($pH = 14$)

Fig. 3 (curve $\blacksquare$) shows an example of the OCP behavior of AZ31B in 1 M NaOH solution in the ambient (non-deaerated) environment during 120-h immersion. The OCP rose to high

value region (-0.6 to -0.4 V_{SCE} range) within approximately 4 – 6 h. Then, the OCP dropped significantly to low value region (-1.5 V_{SCE}) within a very short time. This potential drop was over 1 V, as reported before [39,41]. The oscillation of OCP between high value region and low value region occurred frequently (~19 times) during the 120-h immersion. This potential oscillation appears similar to those reported for localized corrosion [45]. Repeat tests indicated that the OCP drop did not occur at a constant frequency and also varied from sample to sample. Although not shown, tests in a glass-free setup using a polycarbonate cell and a Pt-wire pseudo reference showed similar potential oscillations (> 1 V), which eliminated the possible interference from dissolved silicate or leaked chloride ions.

After 120-h immersion in 1 M NaOH, surface morphology of the AZ31B sample was examined using SEM/EDS/FIB. It is interesting to find corrosion product nodules (Fig. 4a) formed at the interface of primary α -matrix (darker regions) and eutectic α -phase (lighter regions). An SEM image of an oxide nodule tilted at 55° shows that it has higher profile than the surrounding areas (Fig. 4b). Cross-sectional view of the nodule in Fig. 4b indicates deep oxidation into the primary α -matrix substrate and crack was found at the nodule/ α -matrix interface (Fig. 4c and d). EDS measurement showed these nodules are likely magnesium oxide/hydroxide (Table 3). Much thicker oxide film (1400 nm) was observed on the primary α -matrix side of the nodule and the thickness decreases away from the nodule. Cross-sectional view of the primary α -matrix away from the nodule (Fig. 4f) show an oxide film thickness of 720 nm (Fig. 4h). In contrast, oxide film thickness of 76 nm was found on the eutectic α -phase (Fig. 4e), which is approximately 1/10 of that on the primary α -matrix. Also included in Fig. 4h (solid arrow) is an example of the cross-sectional views of small cracks found in the oxide film on the primary α -matrix (dashed arrows in Fig. 4g). These relatively small cracks that formed away

from the primary α -matrix/eutectic α interface did not induce deep and non-uniform oxidation into the Mg matrix. The Pilling-Bedworth ratio of 0.81 between MgO and Mg has been used to explain the formation of these cracks and fissures [41,46]. Another possible explanation is dehydration of the oxide film after being removed from the solutions.

After 120-h immersion (Fig. 3), small Al-Mn intermetallics ($< 1 \mu\text{m}$) disappeared and large Al-Mn intermetallics partially dissolved in this strongly alkaline solution. Fig. 5a shows an example and the boundary between this partially dissolved Al-Mn intermetallics and primary α -matrix can be clearly seen. A cross-sectional view by FIB indicates that recession occurred on this intermetallics relative to the α -matrix and a corrosion product layer formed on top of the particle (dashed arrow in Fig. 5b). This corrosion product layer is approximately 630 nm thick (Fig. 5c) and it consists mainly of magnesium and manganese oxide with possible aluminum oxide and residual iron oxide (Table 3). In comparison, the percentage of Al, Mn and Fe is higher in the remaining particle under the corrosion product layer (Table 3). It is believed that the formation of this corrosion product layer with the presence of ambient oxygen prevented further dissolution of the intermetallics. Fig. 5c also clearly shows the trench/crevice formed between the corrosion product layer and the α -matrix. As compared to the Al-Mn intermetallics, the β -phase and eutectic α -phase dissolved less significantly after 120-h immersion in 1 M NaOH (Fig. 5d and e). A cross-sectional view (Fig. 5f) of the β -phase indicates that the oxide film is approximately 112 nm thick. Similarly, a thin oxide/hydroxide film of 30 nm thickness formed on the eutectic α -phase surrounding the β -phase.

Based on the corrosion morphology examination, it is hypothesized that oxygen reduction reaction (ORR) as a cathodic half-cell reaction is responsible for raising the OCP to high value region ($-0.4 V_{\text{SCE}}$). To study the effect of oxygen on the potential oscillation and oxide film

formation, the OCP evolution of AZ31B was recorded in deaerated (Ar-sparging) 1 M NaOH over 120-h period. Fig. 3 (curve $-\bullet-$) shows that the maximum OCP ($-1.3 \text{ V}_{\text{SCE}}$) is significantly lower without the presence of ambient oxygen. This results demonstrates the effect of ORR in raising the corrosion potential of AZ31B in strongly alkaline environment. However, potential fluctuations ($\sim 0.3 \text{ V}$) were still observed from -1.3 to $-1.6 \text{ V}_{\text{SCE}}$.

Under the deaerated condition, most of the Al-Mn intermetallics disappeared entirely, except for the relatively large ones ($\geq 5 \text{ }\mu\text{m}$) which partially dissolved. Fig. 6a shows an SEM image of a severely corroded Al-Mn intermetallics, which appears different from that in ambient solution (Fig. 5a). A cross-sectional view (Fig. 6b) show that more than 2/3 of the particle was corroded and the corrosion products were mainly magnesium and manganese oxide (2 in Table 4). High percentage of Mn was found in this remaining intermetallics, but only a small percentage of Al. This indicates that Al has been completely leached out of the intermetallics in the absence of ambient oxygen. Oxide nodules also formed at the primary α -matrix/eutectic α -phase interface under deaerated condition, similar to Fig. 4a. However, the number (density) as well as the size of the oxide nodule is much smaller without the presence of ambient oxygen. A cross-sectional view of a nodule in Fig. 6d indicates that the oxide film on the α -matrix is much thicker (dashed arrow) than that on the eutectic α -phase (solid arrow). The oxide film formed on the α -matrix adjacent to the oxide nodule is $\sim 800 \text{ nm}$ (Fig. 6e), which is about 1/2 of that under the ambient condition (Fig. 4c). EDS measurements suggest that these nodules and oxide film are mainly magnesium oxide with trace amounts of Al, Mn, and Fe (Table 4). The oxide nodule in Fig. 6e also features a crack on the α -matrix side. Through film cracks were found in the oxide film on the α -matrix away from the interface (Fig. 6f).

3.3 Effect of pH/NaOH concentration

It is of interest to understand if the potential rise ($-0.4 V_{SCE}$) and significant drop ($> 1 V$) occurs to AZ31B in NaOH solutions at different pH levels. Therefore, the effect of NaOH concentration was first studied at pH 10 – 14 for 24-h immersion. The results (Fig. 7) showed that the OCP reached high value region in NaOH solutions with pH of 13 and 14, but not in solutions with pH of 10, 11, and 12. The time for the OCP to reach high value region is much shorter for pH 14 (2 h) than pH 13 (8 h). In solutions with pH of 10 and 11, the OCP reached a steady state of $-1.5 V_{SCE}$ and the OCP trends overlapped with each other. The AZ31B sample tested in the pH 12 solution reached a steady state OCP value of $-1.4 V_{SCE}$, which is about 0.1 V higher than pH 10 and 11 cases.

Different corrosion morphologies were observed using an optical microscope after 24-h immersion in different pH NaOH solutions (Fig. 8). At pH 10 and 11, large coverage of light brown corrosion products formed on the surfaces (Fig. 8a and b). Several dark regions (marked by arrows) were also observed on these two samples, especially at pH 10 (Fig. 8a). These regions feature the buildup of thick corrosion products. Al-Mn intermetallics were found in these regions, which are believed to be the cathodic sites during corrosion (see following discussion). The sample tested at pH 12 showed substantially less corrosion (Fig. 8c) in comparison. It should be pointed out that there was no buildup of corrosion products on the Al-Mn intermetallics since the intermetallics resemble those in the unexposed AZ31B sample (Fig. 8d). Significant oxidation occurred on AZ31B samples immersed in pH 13 and 14 NaOH solutions (Fig. 8e and f). Corrosion was found to occur on the Al-Mn intermetallics in these two cases, as an example shown in the inserted image in Fig. 8f.

Based on the short-term (24 h) immersion results, NaOH solutions with pH of 11 and 12 were selected for long-term OCP tests (i.e., 120 h) in order to compare the electrochemical

behavior of various phases with that in pH 14 solution. Fig. 9 shows that OCP reached a steady state of $-1.2 V_{SCE}$ in pH 12 solution and $-1.4 V_{SCE}$ in pH 11 solution at the end of long-term immersion. Potential oscillation did not occur at $pH \leq 12$.

After 120-h immersion in pH 11 solution, “dome” structures were found to form on AZ31B in scattered locations (Fig. 10a). FIB/SEM cross-sectional observation of a dome revealed an Al-Mn intermetallics (Table 5) underneath with a corrosion product layer on top (Fig. 10b and c). A high-resolution cross-sectional SEM image shows the smooth surface of this Al-Mn intermetallics (Fig. 10c), which possibly indicates that minimal corrosion has occurred on this intermetallics. Besides, the fact that the profile of this intermetallics is higher than the surrounding primary α -Mg matrix (difference in hardness) also implies the absence of corrosion on this particle. The corrosion product layer on top of the intermetallics is likely $Mg(OH)_2$ (Table 5). The formation of similar corrosion product domes has been observed on Mg-Al alloys exposed to NaCl solutions, and was related to local cathodic activities [18,47]. Fig. 10f shows the oxide film thickness decreases with increasing distance from the Al-Mn intermetallics. In addition, the primary α -Mg matrix adjacent to the Al-Mn intermetallics has a relatively rough surface, indicating slight corrosion occurred. The corrosion behavior of the Al-Mn intermetallic at pH 11 was found to be significantly different than the pH 14 case (Fig. 4c, Table 4).

The primary α -Mg matrix, eutectic α -phase, and the β -phase had different surface morphology after 120-h immersion in the pH 11 NaOH solution (Fig. 10d). A cross-sectional view of these phases (Fig. 10e) indicates that severe corrosion occurred on the primary α -Mg matrix (Fig. 10g, Table 5) and a trench/crack as deep as $1.7 \mu m$ can be seen. Magnesium oxide/hydroxide is determined to be the corrosion product inside the trench (Table 5). In contrast, only insignificant corrosion happened on the β -phase and the surrounding eutectic α -phase (Fig.

10h, Table 5). The interfacial region between the eutectic α -phase and the primary α -matrix also shows corrosion (Fig. 10i) but less significant than that on the primary α -Mg matrix, which suggests minimal micro-galvanic coupling between these two phases at pH 11.

The surface morphology of AZ31B appears significantly different after 120-h immersion in pH 12 NaOH solution (Fig. 11). The polishing marks can be clearly seen and the features of Al-Mn intermetallics and β -phase (Table 6) were well preserved (Fig. 11a and d). The cross-sectional views indicate that minimal corrosion/oxidation occurred on AZ31B as compared to the samples from other NaOH solutions (e.g., pH 11 or 14). Extremely thin (i.e., 40 – 100 nm) oxide film formed on Al-Mn intermetallics (Fig. 11b and c), β -phase (Fig. 11e and f) as well as primary α -matrix and eutectic α -phase after 120-h immersion. It should be pointed out that the boundary between primary α -matrix and eutectic α -phase cannot be distinguished in this condition, similar to a freshly abraded surface without etching (Fig. 1). Therefore, it appears that the best uniform passive film forms across the AZ31B surface in pH 12 NaOH solution.

3.4 In-situ detection of cathodic activities on/around intermetallics

The cathodic activities (i.e., H_2 generation) on AZ31B immersed in NaOH solutions with different pH were studied *in-situ* using a stereomicroscope (Fig. 12). A large amount of bubbles formed on the sample immersed in the pH 11 solution (Fig. 12a) and their size increased with immersion time (Fig. 12b). These bubbles are believed to be H_2 bubbles that were generated by hydrogen evolution reaction (HER) as the cathodic reaction. The continuing increase of the bubble size indicates strong corrosion activity. On the sample immersed in the pH 12 solution, very few bubbles (Fig. 12c) formed and most of them quickly disappeared (Fig. 12d). Therefore, AZ31B exhibited very low corrosion activity and the absence of persistent cathodes at this pH. In the solutions with pH of 13 and 14, some H_2 bubbles formed on the AZ31B surfaces upon their

immersion, which indicates HER as the cathodic reaction in the initial stage of immersion (refer to first 2 h in Fig. 7). However, most bubbles quickly disappeared in the pH 13 solution, especially the large bubbles that formed around the Al-Mn intermetallics (marked by arrows in Fig. 12e and f). In the pH 14 solution, some bubbles around the Al-Mn intermetallics (marked by arrows in Fig. 12g and h) disappeared within 30 min, however, other bubbles persisted and their size increased slightly after 30 min. After extended immersion to 3 h (Fig. 12i), some bubbles remained almost constant in their size while others disappeared.

The cathodic behavior of Al-Mn intermetallics in NaOH solutions with pH 10, 11 and 12 was also investigated using SVET. Fig. 13a shows a typical SVET map of a cathodic site (500 μm diameter) on AZ31B in pH 10 NaOH solution. EDS elemental information from this site confirms the presence of Al-Mn intermetallics (Table 7), indicating that strong cathodic activities primarily occurred on the Al-Mn intermetallics. Similar results were obtained for pH 11 case. In contrast, no localized corrosion current was detected on AZ31B immersed in pH 12 solution (Fig. 13d). SEM images of this sample showed a very thin layer of oxide film and no apparent persistent cathodic sites (Fig. 13e and f) even with the presence of Al-Mn intermetallics.

3.5 Potentiodynamic and potentiostatic polarization

The electrochemical behavior of AZ31B in NaOH solutions with different concentrations/pH levels was also investigated using CPP technique, and the results are shown in Fig. 14a. Active to passive transition is more noticeable in pH 13 and 14, compared to pH 12 and below. Potentiostatic hold at $-1.0 V_{\text{SCE}}$ was also performed in three pH levels (11, 12, and 14) for 1 h (Fig. 14b). Fig. 14c summarizes the anodic current densities at three applied potentials (-1.2 , -1.0 , and $-0.8 V_{\text{SCE}}$) from the CPP curves (forward scan). Also included in Fig. 14c are the steady state current densities from the potentiostatic hold experiments. The results indicate that the

lowest anodic current density occurred at pH 12. Therefore, AZ31B surface had the slowest electrochemical reactivity (both passivation and corrosion) in pH 12 NaOH solution. This result agrees well with the optical microscopic observation (Fig. 8c), SEM examination (Fig. 11) and *in-situ* stereomicroscope (Fig. 12d) and SVET (Fig. 13d) results. In comparison, anodic currents of at least one order of magnitude higher were found for pH 14 and the optical microscope image (Fig. 14d) shows significant oxidation in the primary α -matrix.

To help understand the OCP oscillation phenomenon between high value region (-0.6 to -0.4 V_{SCE}) and low value region (-1.5 V_{SCE}) in high pH environment, single scan anodic polarization and cathodic polarization experiments were performed on both “aged” and freshly-polished AZ31B samples in 1 M NaOH solution. A typical anodic polarization curve of freshly polished AZ31B in 1 M NaOH (—■— in Fig. 15) shows an active-passive characteristic (-1.7 V_{SCE} to -0.7 V_{SCE}) as previous reported [25]. However, after the AZ31B surface was aged for 6 h in 1 M NaOH (OCP reached maximum of $\sim$ -0.6 V_{SCE}), the anodic polarization curve (—●— in Fig. 15) showed a much smaller passivation current density than the fresh-polished surface. This result indicates that a protective oxide film formed on the AZ31B surface, which may contribute to the OCP rise to high value region. The protectiveness of the passive film resembles that of various coatings on Mg alloys such as hydroxide coating [48] and MgO coating [49]. These coated Mg samples all showed higher OCP values and lower anodic current density values as compared to the uncoated samples, similar to the findings shown in Fig. 15.

Fig. 16 shows the comparison of cathodic polarization behavior between aged and fresh AZ31B samples. The OCP of the freshly polished AZ31B was approximately -1.7 V_{SCE} . HER seems to be the dominant cathodic reaction and the effect of ambient oxygen is negligible. In comparison, the cathodic reaction appears to be dominated by ORR on the aged AZ31B and a

diffusion controlled region can be clearly seen. Therefore, the cathodic polarization confirms that the dominant cathodic reaction is ORR at $-0.4 V_{SCE}$ and HER at $-1.5 V_{SCE}$ in 1 M NaOH solution. The corrosion current density is at least one order of magnitude higher for the fresh surface as compared to the aged surface. The possible exposure of fresh surface may cause the potential to drop from $-0.4 V_{SCE}$ to $-1.5 V_{SCE}$ when the limiting current density of ORR is insufficient to support rapid oxidation of Mg as discussed later.

4. Discussion

In this research, the electrochemical behavior of a die cast AZ31B Mg alloy was investigated in chloride-free NaOH solutions in the pH range from 10 to 14. Based on the results obtained, three different pH regimes can be identified: (i) $pH \leq 11$; (ii) $pH = 12$; and (iii) $pH \geq 13$. Different corrosion behavior of the primary α -Mg matrix, eutectic α -phase, β -phase, and Al-Mn intermetallics was observed in each pH regime, discussed as follows.

4.1 $pH \leq 11$ regime

Two pH levels were studied here: pH 10 and 11. Severe corrosion/discoloration was observed on AZ31B surface after 24-h immersion (Fig. 8). OCP quickly reached a steady state of approximately $-1.5 V_{SCE}$ and no difference in OCP was found between pH 10 and 11 (Fig. 7). This was further confirmed by prolonged immersion up to 120 h and OCP increase was insignificant (Fig. 9). Cathodic polarizations (Fig. 16) suggest the HER is the dominant cathodic reaction and ambient dissolved oxygen has no effect on the cathodic kinetics. This is consistent with the findings of Mg corrosion in sodium sulfate solution [50]. SEM examination revealed that primary α -Mg matrix was severely corroded (Fig. 10d) and a trench/crack as deep as $1.7 \mu m$ was identified (Fig. 10g). Corrosion product, possibly $MgO/Mg(OH)_2$ formed on the primary α -

Mg matrix by dissolution-precipitation mechanism. A “dome” structure was found to form on top of Al-Mn intermetallics (Fig. 10a) and minimal corrosion occurred to the particle underneath (Fig. 10c). The composition of the dome was determined to be Mg(OH)₂ by EDS (Table 5). It is postulated that a micro-galvanic couple forms between cathodic Al-Mn intermetallics and anodic primary α-Mg matrix. HER reaction occurs on the Al-Mn intermetallics as:

Mg dissolution occurs on the primary α-Mg matrix surrounding the Al-Mn intermetallics:

The cathodic nature of the Al-Mn intermetallics was verified by two *in-situ* techniques. SVET detected the cathodic current on Al-Mn intermetallics and *in-situ* stereomicroscopic observation shows the formation and growth of bubbles, presumably H₂, especially on the Al-Mn intermetallics. Therefore, it is reasonable to conclude that the Al-Mn intermetallics served as the cathodic sites in the pH 11 NaOH solution, similar as previous research results in other aqueous environments [5,13,14,51].

Through the micro-galvanic coupling, HER reaction (Eq. 1) generated OH⁻ anions on Al-Mn intermetallics, which attracted Mg²⁺ cations from the actively corroding α-Mg matrix. The combination of OH⁻ and Mg²⁺ resulted in the precipitation of Mg(OH)₂ on top of the Al-Mn intermetallics (Eq. 3).

The oxide film thickness profile (Fig. 10f) on the primary α-Mg matrix adjacent to the Al-Mn intermetallics exhibits a classic galvanic behavior under the assumption that oxide thickness is proportional to anodic current density through Faraday’s law. After extended immersion, corrosion product covered the entire intermetallics, and thus reduced the cathodic activities

around the Al-Mn intermetallics, which in turn slowed down corrosion of the Mg matrix near the Al-Mn intermetallics. Previous research found that when Mg^{2+} was added in the test solution, the deposition of a thicker $\text{Mg}(\text{OH})_2$ layer caused further suppression of H_2O reduction as compared to NaCl solution [18].

In comparison, minimal corrosion/oxidation occurred on the β -phase and the surrounding eutectic α -phase. It has been reported [20] that a thin Al-rich layer at the alloy/oxide interface in the eutectic α -phase (surrounding β -phase) prevents further corrosion of AM50 alloy in NaCl solution. In contrast, the absence of Al-rich layer in the primary α -Mg matrix leads to the formation of a thick corrosion product layer. Our results seem to agree with these findings. Table 5 indicates that there is ~5% Al in the eutectic α -phase adjacent to the β -phase, but none in the primary α - matrix. It should be pointed out that β -phase being weakly cathodic to the α -matrix has been well documented in previous research conducted in other aqueous systems [10,21,52,53]. Micro-galvanic couple may form between primary α -matrix and the eutectic $\alpha + \beta$ zone. However, the eutectic $\alpha + \beta$ zone is considered a weak cathode based on the surface morphology examination and the absence of accelerated corrosion at the interface (Fig. 10i). In contrast, the strong micro-galvanic coupling between Al-Mn intermetallics and primary α matrix is evident from the dome formation (Fig. 10c) and oxide film profile at the interface (Fig. 10f).

4.2 $\text{pH} \geq 13$ regime

Different passivation/corrosion morphologies were observed after AZ31B samples were immersed in pH 13 and 14 NaOH solutions. An interesting phenomenon was found that Al-Mn intermetallics dissolved at $\text{pH} \geq 13$ (Fig. 5b and c). EDS results show significant reduction of Al and Mn content in the corrosion product layer relative to Mg content (Table 3). Based on EDS analysis, the corrosion product layer possibly consists of MgO , Al_2O_3 and Mn_3O_4 [51]. The

dissolution of Al-Mn intermetallics was more severe in deaerated condition (Fig. 6b). Table 4 suggests that Al was completely dissolved from the Al-Mn intermetallics and there is significant reduction of Mn and Fe content. The dissolution of Al-Mn intermetallics may be explained by selective leaching of various element(s) from the particles [18,51]. According to the equilibrium E-pH diagrams [22], Al exhibits the strongest amphoteric characteristics among all the major alloying elements (Zn, Mn and Fe) and higher Al content possibly leads to more severe dealloying (Table 2). For example, dealloying of MnAl in 1 M NaOH solution to obtain octahedral Mn_3O_4 nanostructure has been performed successfully at room temperature [54]. Due to the significant anodic dissolution of Al-Mn intermetallics in strongly alkaline solutions (e.g., pH 14), cathodic activities (HER in the early stage) are expected to occur on the intermetallics or the region surrounding it (primary α -Mg matrix). This can explain the observation of the H_2 gas bubbles in/around the Al-Mn intermetallics (Fig. 12). The severe dissolution of particles or the formation of oxide film reduces the anodic activities and therefore the cathodic activities as evidenced by the reduction of H_2 bubbles under the stereomicroscope (Fig. 12).

In comparison, passive film formed on the other phases: primary α -matrix (Fig. 4h), eutectic α -phase (Fig. 5e) and β -phases (Fig. 5f) with minimal corrosion. The oxide film formed on the α -matrix ranges from 700 nm to 1400 nm (Fig. 4d and h) while it has a thickness in the range of 30 – 100 nm on the eutectic α -phase and β -phase (Fig. 5f). This is consistent with the findings that β -phase corrodes little in the pH range 4 to 14 [8]. Anodization of Mg-Al alloy in 3 M KOH solution also indicates better passivity on the $\text{Mg}_{17}\text{Al}_{12}$ phase, which shows lower passive current than pure Mg and Mg-Al alloys [55]. Similarly, previous work has shown that the β -phase in AZ91 only partially dissolved in 5 M NaOH even after extended immersion or at elevated temperature (e.g., 60 °C) [33]. This phenomenon was explained by a high aluminum content in

the oxide film on the $\text{Mg}_{17}\text{Al}_{12}$ phase [55]. It should be pointed out that selective leaching of Al does not seem to occur on β -phase (40 at.% Al) in these extremely alkaline environment, as compared to Al-Mn intermetallics. The exact reason is unknown.

Significant higher OCP ($-0.4 \text{ V}_{\text{SCE}}$) was achieved in $\text{pH} \geq 13$ NaOH solutions. Cathodic polarization results show that ORR (Eq. 4) is the dominant cathodic reaction at high OCP (Fig. 16). It is speculated that the formation of polarizable passive film rendered the rise of OCP and ORR primarily occurs on the passivated β -phase and surrounding eutectic α -phase.

The cathodic nature of the β -phase and the surrounding eutectic α -phase is corroborated by its extremely less oxidation as compared to the α -matrix. The gradual decrease in oxide thickness away from the interface also indicates the anodic nature of α -matrix (Fig. 4d).

Another interesting phenomenon observed at $\text{pH} \geq 13$ is the oscillation of OCP between high value region ($-0.4 \text{ V}_{\text{SCE}}$) and low value region ($-1.5 \text{ V}_{\text{SCE}}$) with the presence of ambient oxygen (Fig. 3). This potential profile resembles the typical localized corrosion phenomenon under OCP condition, such as pitting corrosion of copper in high pH potable water [45]. Therefore, this oscillation can be explained by the passive film breakdown and repassivation model proposed by Marcus et al. [56,57]. Their model emphasizes the role of inter-granular boundaries in the barrier oxide layer. It is speculated that in the passive state, metal ion release rate is faster at the inter-granular boundaries because these defective sites are less restrictive to ion transfer. This in turn leads to an inward vacancy flux and creates voids at the metal/oxide interface. These voids not only act as channels for transport of Mg ions, but also form the local stress risers which contributes to film cracking [48]. As a consequence, the metal surface depassivates locally in the less resistive boundaries by local thinning (dissolution) or rupture of the barrier layer, even in the

absence of aggressive species, such as halides. In the present study, first, etching has revealed the interface between primary α -matrix and eutectic α -phase as two independent metallurgical entities (Fig. 2b). Therefore, inherent defective sites are likely to exist at the intergranular boundaries in the base metal. Second, SEM/FIB results indicate significant difference in oxide film thickness between primary α -matrix (~ 700 nm) and eutectic α -phase (~ 70 nm) in ambient pH 14 NaOH solution (Fig. 4). The mismatch of the oxide film will impose great stress at the oxide interface. This difference in passive film thickness was also observed in deaerated condition (Fig. 6d), which signifies the pH effect on the passivation kinetics between primary α -matrix and eutectic α -phase. Lastly, a micro-galvanic coupling effect forms between these two phases. When ORR becomes the dominant cathodic reaction occurring on the eutectic α -phase and β -phase, anodic reaction occurs on the primary α -matrix. Significant high anodic current is expected at the interface based on the galvanic current distribution [58]. As a result of all these factors, passive film breaks down frequently at the interface between primary α -matrix and eutectic α -phase.

When passive film breakdown occurs, Mg dissolves rapidly at the breakdown sites, which may be considered as “pitting” current. This local high current demand exceeds the limit of ORR current ($\sim 1 \mu\text{A}/\text{cm}^2$) and HER replaces ORR as the dominant cathodic reaction, as evidenced in Fig. 16. The exposure of fresh surface and change of cathodic reaction cause OCP to drop significantly from $-0.4 V_{\text{SCE}}$ to $-1.5 V_{\text{SCE}}$ region. HER may occur on the passive film nearby or the freshly exposed surface. Frankel et al. found that the exchange current density of HER may be significantly higher in an actively corroding environment for Mg [59]. It should also be pointed out that Nisancioglu et al. studied the pH of the pit anolyte for Mg alloys by galvanostatic polarization tests with separate anode and cathode compartments [8]. Their results

indicated that the pH of the pit anolyte was around 10 – 10.5 and was not acidic. Therefore, it appears that a critical acidic environment is not required for the pitting corrosion of Mg.

The local surge of Mg^{2+} will be quickly annihilated by the diffusion of OH^- from the bulk solution via Eq. 3. The precipitation of $\text{Mg}(\text{OH})_2/\text{MgO}$ will slow down further active dissolution of Mg, i.e., pits start to repassivate and OCP starts to rise gradually until it reaches the maximum region. As a result of this breakdown and repassivation process, oxide nodules form along the interface between primary α -matrix and eutectic α -phase (Fig. 4b and c). These oxide nodules reside in the α -matrix as expected. Different nodule sizes were observed (Fig. 4a) which may be correlated to the different repassivation time during OCP oscillation (Fig. 3). Cracks were found on top of the nodules as well as underneath the nodule on the α -matrix side (Fig. 4b). Similar nodular oxide growth has been observed on Mg alloys oxidized in air at high temperature and was attributed to the phase inhomogeneity [46]. As suggested by Marcus et al. [56,57], selective pit nucleation occurs at the less restrictive sites of the large population of inter-granular boundaries of the oxide film and statistical fluctuations are expected depending on the atomic structure of the inter-granular boundaries and on their evolution with time. Fig. 4a shows an example of the distribution of oxide nodules which may have initiated from “less restrictive sites” in the oxide film.

Higher anodic current was observed in pH 14 NaOH solution under polarized condition, either potentiodynamic or potentiostatic (Fig. 14 a-c). Non-uniform passive film can be clearly seen under the optical microscope, especially within primary α -matrix (Fig. 14d). It is speculated that the accelerated oxidation of Mg initiates at the interface between primary α -matrix and eutectic α -phase and spreads into the α -matrix. The oxidation occurs at a much faster speed and relatively uniformly along the inter-granular boundaries under polarized condition and therefore

no random individual oxide nodules were found. This can actually be considered as intergranular corrosion and the shape of potentiodynamic polarizations in Fig. 14a and Fig. 15 resemble the typical electrochemical potentiokinetic repassivation (EPR) results [60].

In addition to the oxide nodules, cracks were also found in the passive film on the primary α -matrix (Fig. 4g and Fig. 6f). This has been attributed to the potential oscillation by several researchers [39,41]. However, it is also likely that these cracks occurred during the dehydration process, since no further corrosion occurred at the bottom of these cracks. Small cracks/crevice were found at the interface between primary α -matrix and Al-Mn intermetallics (Fig. 5c), which may contribute to the potential fluctuation. However, given the frequency of the OCP oscillation, passive film breakdown and subsequent formation of oxide nodules (repassivation) seems to be the most probable cause. It should be pointed out that the potential oscillation studied here is different than those reported for austenitic stainless steel in concentrated sulfuric acid at elevated temperature [61,62]. In those cases, passivation is a consequence of the production of some intermediate corrosion product at the active site. Subsequent dissolution of this product causes re-activation.

4.3 pH = 12 regime

It appears that the optimal passivation for AZ31B Mg alloy was achieved at this pH. Minimal corrosion was observed under the optical microscope (Fig. 8c) and high-resolution SEM images (Fig. 11) show that the features were well preserved for all phases with thin film (< 100 nm) formed on top. It is believed that the oxide film forms via direct solid state reaction at this pH. Uniform passive film forms across the entire surface and no mismatch is found at the interface between primary α -matrix and eutectic α -phase. In addition, microgalvanic coupling between primary α -matrix and eutectic α -phase seems to be nonexistent. Therefore, no local passive film

breakdown occurs at this pH and oxide nodules do not form. Both potentiodynamic and potentiostatic polarizations indicate the lowest anodic current density at this pH (Fig. 14). This pH coincides with the isoelectric point, or pH of zero charge (pH_{pzc}) of $\text{MgO}/\text{Mg}(\text{OH})_2$. It was reported that $\text{pH}_{\text{pzc}} \approx 12$ for MgO and $\text{Mg}(\text{OH})_2$ and the passive film is expected to be electrically neutral at this pH [63,64]. Similarly, a previous work has shown that Mg alloy ZE41 had the slowest corrosion rate in pH 12 Na_2SO_4 solution as compared to solutions with pH of 2, 5, 7, and 9 [65].

Finally, it is worthwhile mentioning that the present study not only provides a fundamental understanding of the reactivity of different phases commonly identified in Mg-Al binary alloys in alkaline solutions, but also sheds light on the alkaline pretreatment (i.e., conditioning) of Mg-Al alloys for coating purposes.

5. Conclusions

The passivation and corrosion behavior of AZ31B Mg alloy was investigated in chloride-free NaOH solutions in the pH range of 10 – 14 and the following conclusions can be drawn:

- 1) In highly alkaline NaOH solutions ($\text{pH} \geq 13$), thick oxide film formed on primary α -matrix and thin oxide film formed on eutectic α -phase and β -phase. Al-Mn intermetallics dissolved at high pH by dealloying. The presence of ambient oxygen significantly increased the OCP to around $-0.4 \text{ V}_{\text{SCE}}$ in $\text{pH} \geq 13$ NaOH solutions. Frequent potential oscillation ($>1 \text{ V}$) was observed and attributed to the passive film breakdown at the oxide interface between primary α -matrix and eutectic α -phase. Oxide nodules formed as a result of the repassivation process.

- 2) In pH 12 NaOH solution, a uniform thin passive film (< 100 nm) formed across the surface on all phases: primary α -Mg matrix, eutectic α -phase, β -phase, and Al-Mn intermetallics. No preferential corrosion was observed. The potentiodynamic and potentiostatic polarization results showed the smallest anodic current density at this pH.
- 3) In slightly alkaline solutions ($\text{pH} \leq 11$), severe corrosion occurred on the primary α -matrix. Minimal corrosion occurred on β -phase and its surrounding eutectic α -phase. The Al-Mn intermetallics served as strong cathodic sites with H_2 bubbles generated on top. The cathodic nature of the Al-Mn intermetallics was verified by *in-situ* stereomicroscope and SVET techniques.

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Figure captions:

Fig. 1. The primary secondary phases in the die cast AZ31B Mg alloy: (a) Al-Mn intermetallics and (b) β -phase.

Fig. 2. Microstructure of the die cast AZ31B Mg alloy: (a) polarized light optical microscope image of an etched surface; (b) SEM image of an over-etched surface showing the contrast between primary α -matrix, eutectic α -phase, β -phase, and Al-Mn intermetallics.

Fig. 3. The 120-h OCP profiles of AZ31B in ambient (—■—) and deaerated (—●—) 1 M NaOH (pH 14) solutions.

Fig. 4. (a) An SEM image showing the formation of several oxide nodules on AZ31B after 120-h immersion in ambient 1 M NaOH (pH 14); (b) an SEM image (tilted at 55°) of one oxide nodule; (c and d) cross-sectional views of the oxide nodule formed at the primary α -matrix/eutectic α -phase interface; (e) a cross-sectional view of the oxide film on the eutectic α -phase; (f, g and h) an SEM image and its cross-sectional views of the oxide film on the primary α -matrix. Notice that the contrast of the primary α -matrix and eutectic α -phase in Fig. 4b is opposite to that in Fig. 4a.

Fig. 5. (a, b, and c) SEM images of an Al-Mn intermetallics in AZ31B after 120-h immersion in ambient 1 M NaOH (pH 14) and its cross-sectional views; (d, e, and f) SEM images of the β -phase and its surrounding eutectic α -phase and their cross-sectional views from the same sample.

Fig. 6. (a and c) SEM images (tilted at 55°) of the AZ31B surface after 120-h immersion in deaerated 1 M NaOH (pH 14); (b) a cross-sectional view of an Al-Mn intermetallics; (d, e, and f) cross-sectional views of an oxide nodule and oxide film.

Fig. 7. OCP profiles of AZ31B for 24-h immersion in ambient NaOH solutions with different concentrations/pH values (pH = 10 – 14).

Fig. 8. Optical images of AZ31B surfaces after the 24-h OCP tests (Fig. 7) in NaOH solutions with different concentrations/pH levels (pH = 10 – 14). The arrows indicate the locations of Al-Mn intermetallics. The 100 μ m scale bar applies to all images.

Fig. 9. Comparison of the 120-h OCP profiles of AZ31B in ambient NaOH solutions with pH levels of 11, 12, and 14.

Fig. 10. (a and d) SEM images (tilted at 55°) of AZ31B surface after 120-h immersion in ambient pH 11 NaOH solution; (b, c, and f) cross-sectional views of oxide dome grown on an Al-Mn intermetallics; (e, g, h, and i) cross-sectional views of the primary α -matrix, eutectic α -phase, and β -phase.

Fig. 11. (a and d) SEM images (tilted at 55°) of AZ31B surface after 120-h immersion in ambient pH 12 NaOH solution; (b and c) cross-sectional views of an Al-Mn intermetallics; (e and f) cross-sectional views of β -phase.

Fig. 12. Stereomicroscopic images of AZ31B surfaces in NaOH solutions with different pH levels (pH = 11 – 14). The 2-mm scale bar applies to all images.

Fig. 13. SVET maps obtained from AZ31B immersed in NaOH solutions with pH of (a) 10 and (d) 12 for 3 h; (b and c) SEM images of the AZ31B surface (after 6-h immersion) from which the SVET map in (a) was obtained; (e and f) SEM images of the AZ31B surface (after 6-h immersion) from which the SVET map in (d) was obtained.

Fig. 14. (a) Cyclic anodic polarization curves of AZ31B in deaerated NaOH solutions with different concentrations/pH values (pH = 10 – 14); (b) potentiostatic hold at -1.0 V_{SCE} for one hour at selected pH levels; (c) comparison of the anodic current densities at selected potentials from the CPP (forward scan) and potentiostatic hold experiments at different pH levels; (d) an optical image of AZ31B surface after 1-h potentiostatic hold at -1.0 V_{SCE} in pH 14 NaOH solution.

Fig. 15. Anodic polarization curves obtained from a freshly polished AZ31B sample (—■—) and a AZ31B sample after the OCP first reached its maximum value (—●—), both in ambient 1 M NaOH solutions.

832 Fig. 16. A cathodic polarization curve obtained from AZ31B surfaces after the OCP reached its
833 maximum value (—■—) as compared to those from the fresh-polished AZ31B surfaces in ambient
834 (—●—) and deaerated (—▲—) conditions, all in 1 M NaOH solutions.

835

Tables:

Table 1. The chemical compositions (wt.%) of AZ31B Mg alloy.

Material	Al	Zn	Mn	Fe	Mg
AZ31B	3.28	0.86	0.38	0.01	Balance

Table 2. Elemental compositions (at.%) of the secondary phases in AZ31B Mg alloy (a and b) as shown in Fig. 1.

Particles	Mg	Al	Zn	Mn	Fe
Figure 1a	3.30	39.84	-	55.19	1.66
Figure 1b	69.06	23.67	7.26	-	-

Table 3. Elemental compositions (at.%) of an oxide nodule (Fig. 4c), oxide film AZ31B (Fig. 4h) and an Al-Mn intermetallics (Fig. 5c) on AZ31B after 120-h immersion in ambient 1 M NaOH (pH 14) solution.

Locations	O	Mg	Al	Mn	Fe
1 in Fig. 4c	36.42	63.58	-	-	-
2 in Fig. 4h	32.80	67.20	-	-	-
1 in Fig. 5c	51.87	21.02	6.79	19.65	0.66
2 in Fig. 5c	2.92	22.85	24.90	45.51	3.82

Table 4. Elemental compositions (at.%) of an Al-Mn intermetallics (Fig. 6b), an oxide nodule and oxide film (Fig. 6e) on AZ31B after 120-h immersion in deaerated 1 M NaOH (pH 14) solution.

Locations	O	Mg	Al	Mn	Fe
1 in Fig. 6b	0.10	33.61	1.77	60.15	4.37
2 in Fig. 6b	42.96	31.61	-	23.31	2.13
3 in Fig. 6e	42.97	56.82	0.03	0.14	0.03
4 in Fig. 6e	31.10	67.84	0.89	0.11	0.05

851 Table 5. Elemental compositions (at.%) of the sites of interest on an AZ31B sample after 120-h
852 immersion in ambient pH 11 NaOH solution (locations marked in Fig. 10).

Locations	O	Mg	Al	Mn	Fe	Zn
1 in Fig. 10	-	30.71	6.47	59.56	3.25	-
2 in Fig. 10	60.48	39.52	-	-	-	-
3 in Fig. 10	-	100	-	-	-	-
4 in Fig. 10	14.64	85.36	-	-	-	-
5 in Fig. 10	-	94.76	5.24	-	-	-
6 in Fig. 10	-	80.79	10.34	-	-	8.87

853
854 Table 6. Elemental compositions (at.%) of an Al-Mn intermetallics (Fig. 11b) and β -phase (Fig.
855 11e) on an AZ31B sample after 120-h immersion in ambient pH 12 NaOH solution.

Locations	Mg	Al	Mn	Zn
1 in Fig. 11	12.36	9.15	78.49	-
2 in Fig. 11	79.15	7.47	-	13.38

856
857 Table 7. Elemental compositions (at.%) of an Al-Mn intermetallics and corrosion products (Fig.
858 13c) on an AZ31B sample surface after 6-h immersion in pH 10 NaOH for SVET measurements.

Locations	O	Mg	Al	Mn
1 in Fig. 13c	35.89	6.57	39.62	17.92
2 in Fig. 13c	48.85	51.15	-	-

859

Figure1

Figure2a

(a)

Figure2b

Figure3

Figure4

Figure5

Figure6

Figure7

Figure8

Figure9

Figure10

Figure11

Figure12

Figure13

Figure14a

Figure14b

Figure14c

Figure14d

Figure15

Figure16