Corrosion Behavior of AZ31 Magnesium Alloy in Highly Alkaline Environment

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Abstract Industrial components made with a magnesium–aluminum alloy AZ31 are often used in diverse engineering applications where component weight, strength, and durability are critical. Similarly as other Mg alloys, however, the AZ31 is susceptible to corrosion in alkaline environments. In this work, corrosion of commercial grade AZ31 alloy plate was examined in potassium hydroxide (KOH) using immersion and potentiodynamic studies. The results suggest that the concentration of Al and Mn in the alloy may govern the kinetics of micro-galvanic corrosion and the initiation of corrosion pits. Further, trace amounts of Ni in the AZ31 alloy were seen to enable formation of Ni(OH)₂ surface layer, which may have further accelerated alloy corrosion due to its cracking and void coalescence. The effect of pH on the corrosion behavior of AZ31 was studied with reference to Pourbaix diagrams.

KEY WORDS: Magnesium alloy; AZ31; KOH

1 Introduction

Magnesium (Mg) alloys are often used in automotive and aircraft applications due to their high strength-to-weight ratios. Specifically, the magnesium–aluminum (Mg–Al) alloy systems show excellent mechanical performance, ease of processing and optimal cost [1]. AZ31 magnesium alloy (3 wt% Al, 1 wt% Zn, bal. Mg) is a popular wrought alloy with good room-temperature properties [4, 5]. Due to Mg's highly negative electrode potential (−1.5 V with respect to saturated calomel electrode [2]), the alloy has been considered for novel applications as anodes in fuel

cells [3]. However, the use of AZ31 and many other Mg alloys has been hindered by the poor corrosion resistance of the Mg solid solution matrix, or the degradation of intermetallic compounds present in the alloy [4, 6].

To mitigate corrosion of AZ31 alloy, special surface coatings were developed and applied via plasma arc oxidation techniques. Ceramic oxides such as MgSiO₃, CeO₂, Al₂O₃, and TiO₂ were seen to enhance corrosion protection of AZ31, but with a significant increase in the manufacturing cost [8–12]. In addition to surface treatments, corrosion of Mg alloys has been also manipulated via strict control of impurities and alloying elements [13], leading to reduced rates of micro-galvanic, pitting, and crevice corrosion [14, 15].

Once initiated, corrosion of Mg alloys in basic aqueous electrolytes often results in the formation of a Mg(OH)₂ layer [16, 17] or MgO layer [19]. However, due to the Pilling–Bedworth (PB) ratio for Mg/Mg(OH)₂ equal to 1.73 [18], this layer readily nucleates voids and subsequently cracks, thus promoting localized and accelerated corrosion of Mg alloys if the electrolyte is able to penetrate the hydroxide layer. As a result, the MgO/Mg(OH)₂ layer is

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only partially protective [19, 20]. In contrast, surface treatment with fluoride solution enables formation of a fully protective coherent MgF_2 surface layer, which inhibits further corrosion [18].

Corrosion of magnesium alloys has been extensively studied over the past decades. Literature on corrosion performance in diverse alloys and electrolytes is available. Although Al and Mn are added to Mg alloys to improve strength and cast ability, these elements readily form secondary intermetallic compounds, which are noble with respect to the magnesium solid solution matrix (α -Mg), thereby enabling formation of micro-galvanic cells [21]. For example, Sudholz *et al.* [22] reported that aluminum-containing precipitates were more noble than others such as Mg_2Ca or MgZn_2 . In contrast, the $\text{Mg}_{17}\text{Al}_{12}$ phase present in Mg–Al alloys has been shown to form a cathodic couple with the α -Mg matrix [5, 23]. Pitting corrosion was reported to relate to the formation and degradation of the $\text{Mg}_{17}\text{Al}_{12}$, Al_xMn_y , and Al–Mn–Fe intermetallics [24]. Lunder *et al.* [25] observed in situ production of hydrogen gas at the Al–Mn–Fe precipitates when AZ91 alloy was exposed to 5 wt% NaCl electrolyte. Pardo *et al.* [21] studied the corrosion of AZ91, AZ31, and AZ80 alloys in 3.5 wt% NaCl electrolyte and determined that aluminum in the solid solution directly governed the corrosion resistance of the alloy. Specifically, they observed that α -Mg was preferentially attacked due to presence of intermetallic particles like $\text{Mg}_{17}\text{Al}_{12}$ or Al–Mn-rich compounds by forming micro-galvanic cells with them [21]. Impurities such as nickel (Ni), iron (Fe), and copper (Cu) may further accelerate corrosion process due to their low solid solubility in magnesium and active cathodic nature [16, 26]. Matsubara *et al.* [27] studied the effect of Fe on the corrosion behavior of AM50 and AM60 Mg alloy, and found that regions with localized elevated concentrations of Fe were associated with the onset of corrosion in the alloys [27]. As a result, the concentration of impurities must be maintained at or below tolerance limits for industrial magnesium alloys.

Published literature on the corrosion behavior of Mg alloys usually focuses on casting alloys, rather than wrought alloys [28] because of the ease of producing a shape part via metal casting. Further, the electrolytes generally involved salts encountered in automotive applications. The critical chloride ion concentration required for corrosion of AZ31 in NaCl solution with 0.1 mol/l NaOH was studied by Alsagabi *et al.* [7]. As a result, there is a paucity of literature on corrosion of AZ31 alloys in highly alkaline environment.

To date, the corrosion behavior of AZ31 in highly alkaline aqueous solutions (pH 15) has not been reported. As a result, this work focuses on examining the corrosion behavior of AZ31 alloy in 45 wt% KOH electrolyte using electrochemical and microstructural approach.

2 Experimental

A commercially available 10-mm-thick AZ31 plate (composition provided in Table 1) was cut into rectangular samples ($\sim 15 \text{ mm} \times 10 \text{ mm}$) using a vertical band saw and was polished following standard metallographic techniques [29] with SiC papers (from 120 grit to 600 grit), followed by diamond compounds (9–1 μm). After each polishing step, the samples were ultrasonically washed in alcohol. The final polish was achieved with 0.05 μm colloidal alumina. After polishing, the samples were washed in an ultrasonic bath (containing alcohol) and stored in a vacuum desiccator. All polishing steps were performed in non-aqueous media.

The composition [as measured with scanning electron microscopy–X-Max energy-dispersive spectroscopy (SEM–XEDS)] of the AZ31 plate and the precipitates in this research is listed in Table 1.

After polishing, the edges of the samples were sealed with Teflon and immersed in 100 ml of static KOH electrolyte at 21 °C and 1 atm pressure and pH of 15, with a molarity 8.02 mol/l. In order to study, the evolution of any surface films and corrosion products, immersion tests were performed for 3, 6, 9, 12, 15, and 18 days. Also, a Parstat 4000 potentiostat connected to a P.A.R. flat cell (model K0235) was used for all electrochemical studies. The area of exposure of the AZ31 sample in the flat cell was 1 cm^2 . Potentiodynamic polarization was performed using a standard three-electrode configuration with Ag/AgCl/KCl (with a potential of 0.197 V with respect to standard hydrogen electrode) as the reference electrode, while a platinum wire mesh was used as the counter electrode. The KCl solution in the reference electrode was replenished after every measurement to prevent the formation or accumulation of Ag precipitates in the electrode. The applied potential was varied from -0.3 to 1.2 mV with respect to the open circuit potential (approx. -1.4 V), at a scan rate of 0.2 mV/s . Electrochemical impedance spectroscopy (EIS) was also carried out with the three-electrode configuration, and signal frequency ranged from 10,000 to 0.01 Hz at a fixed amplitude of 10 mV. The data obtained conformed to KK transforms with a $\chi^2 = 7.11 \times 10^{-2}$.

After immersion testing, the corroded samples were cold mounted in a resin and sectioned to reveal the cross section of the samples. SEM was performed with a Tescan Mira³ XMU field emission gun scanning electron microscope (FEG-SEM). An Oxford Aztec XEDS system was used to study the chemical composition of the corrosion products. Low-angle X-ray diffraction (XRD) was performed using a Bruker D8 Advance X-ray diffractometer with $\text{CuK}\alpha$ radiation. Scans were performed from 15° to 85° with a step size 0.04° and a time per step of 145 s.

Table 1 Composition of AZ31 plate (wt%)

	Mg	Al	Zn	Mn	Fe	Ni	Cu
Matrix	95.49	2.99	1.2	0.2	0.08	0.01	0.03
Al–Mn precipitates	11.02	39.98	0.36	48.49	0.09	0.02	0.04

3 Results and Discussion

The microstructure of the AZ31 alloy (Fig. 1) consisted of an Mg–Al solid solution and precipitation of cuboidal Al–Mn precipitates. The size of these precipitates ranged from a few microns up to $\sim 25\ \mu\text{m}$, as seen in Fig. 1b.

The surface of the samples after immersion for 3 and 6 days did not exhibit a noticeable change. However, after 9 days of immersion, as shown in Fig. 2, the surface began to exhibit localized pitting with corrosion active on two length scales. Figure 2a shows that micro-pits/voids ($<10\ \mu\text{m}$ in size) were observed across the surface of the sample. Also, pit regions ($\sim 75\ \mu\text{m}$ in size) with corrosion products attached to the AZ31 substrate were observed, with extensive cracking in the vicinity of the pits. The morphology of the pits often had similar geometry as that of the large Al–Mn precipitates (or agglomerates of fine Al–Mn precipitates) found in the virgin AZ31 alloy (Fig. 1). It was also observed that the fine ($<10\ \mu\text{m}$) Al–Mn precipitates were absent from the surface after 9 days of immersion.

With continued immersion, the size of the pits increased. Figure 3 shows the surface of the AZ31 alloy after 18 days of immersion in the electrolyte. The surface contained large voids denuded of corrosion products. These voids were scattered across the entire surface. Further, several

regions on the AZ31 substrate were observed where a surface film fractured and exposed new pits (Fig. 3b). These new pits were similar in appearance and scale as those observed after 9 days of immersion (Fig. 2a), suggesting a cyclic corrosion process.

SEM-BSE images revealed a Z-contrast sensitivity on the surface of the material in the immediate vicinity of the pits (light-gray region marked with arrows in Fig. 3a). The composition of these regions and the matrix is provided in Table 2. The results suggest an increase in the concentration of manganese and potassium around the pits relative to the matrix. Interestingly, the concentration of aluminum significantly decreased in these regions.

Detailed elemental mapping (Fig. 4) of a representative pit revealed that Mn was retained in the pit interior, while K crystals (possibly from trapped electrolyte) were clearly visible in and around the pit region. The shape and size of the pit suggest that it nucleated at the Al–Mn precipitate. Danaie et al. reported a similar corrosive attack on Al–Mn-rich precipitates in AM50 alloy in 1.6 wt% NaCl solution [30]. The elemental XEDS maps show that the Al did not have a similar profile as Mn, indicating dissolution of Al. Referring to the Pourbaix diagram for aluminum in highly alkaline (15 pH) solutions, formation of AlO_2^- ions is expected [31]. Therefore, the results suggest that dissolution of the Al–Mn precipitate possibly enabled formation

Fig. 1 SEM-BSE images of AZ31 alloy: **a** at low magnification, **b** at higher magnification showing the Al–Mn precipitates

Fig. 2 SEM-BSE images of surface of AZ31 alloy after 9 days of exposure to 45 wt% KOH: **a** revealing pits on the surface, **b** with corrosion products still attached to the pits

Fig. 3 SEM-BSE images of the surface of AZ31 alloy after 18 days of exposure to KOH electrolyte: **a** revealing pits on the surface, **b** with corrosion product still attached to the pit

Table 2 Composition of corroded surface (wt%)

	O	Mg	Al	K	Mn	Fe	Ni	Cu	Zn
Matrix	33.29	63.1	1.21	0.84	0.53	0.22	0	0.01	0.79
Gray area near the pit	30.02	41.32	0.89	14.36	12.02	0.79	0	0.18	0.41

of AlO_2^- , leaving Mn on the surface, in the form of $\text{Mn}(\text{OH})_2$ according to the Pourbaix diagram for manganese [31]. Dissolution of Al from the magnesium matrix solid solution was reported in literature for AZ31 alloy sheet immersed in 0.01 mol/l NaCl electrolyte [32], while Asmussen *et al.* [20] specifically observed dissolution of aluminum from degrading Al–Mn-rich magnesium alloys.

Figure 4 also shows that iron and copper were present in the central region of the pit. Fe has a deleterious effect on corrosion of Mg alloys when present at concentrations exceeding 0.07 wt% for AZ91 alloy [33], while Cu should be maintained at less than 0.03 wt% for most of Mg–Al–Zn alloys [18]. Since both elements are cathodic with respect to Mg, their presence would enable micro-galvanic

Fig. 4 SEM-XEDS map in the vicinity of a pit observed in AZ31 exposed to KOH after 18 days of exposure

corrosion of the AZ31 alloy provided an electrolyte channel connecting the two phases [18].

The cross section of the immersed samples was analyzed to examine the evolution of the corrosion products. As seen in Fig. 5, after 3 days of immersion, a uniform and continuous surface layer $\sim 3 \mu\text{m}$ thick was observed and its thickness increased by $\sim 1 \mu\text{m}/\text{day}$ until 9 days of immersion. Thereafter, an accelerated growth was observed ($\sim 2 \mu\text{m}/\text{day}$), with an evolution of cracks, voids and pores in the layer. These results correlate well with the observed stability and degradation of the Al–Mn

precipitates seen in Fig. 2. At 9 days, the fine ($<10 \mu\text{m}$) Al–Mn precipitates were seen to dissolve (or fall out), contributing to the fragmentation of any protective surface film and resulting in its increased porosity and cracking. The resulting cracks enabled penetration of the KOH electrolyte to the AZ31 substrate and its accelerated localized corrosion with undercutting of the surface layer thereafter, as seen in Fig. 5 (12 days). Subsequently, continued immersion enabled rapid growth of the surface layer, reaching to over $\sim 25 \mu\text{m}$ after 18 days.

Fig. 5 SEM-BSE cross-sectional images of corroded surface after immersion for 3 **a**, 6 **b**, 9 **c**, 12 **d**, 15 **e**, 18 **f** days

Fig. 6 SEM line scan across a corroded surface after 18 days of immersion in 45 wt% KOH electrolyte

Fig. 7 Elemental mapping by SEM-XEDS of the cross section of the corroded surface after 18 days of immersion in 45 wt% KOH

A line scan (Fig. 6) and elemental mapping (Fig. 7) of the cross section at 18 days revealed that the growth of the surface layer was diffusion driven. A copper-zinc rich layer ($\sim 7 \mu\text{m}$ thick) was present in the immediate vicinity of the AZ31 substrate, with a composition of 66 at.% Mg, 11 at.% Zn, and 23 at.% Cu, corresponding to the $\text{Mg}(\text{Cu}_2\text{Zn}_x)$ eutectic [34]. Copper-rich intermetallics are generally known to be cathodic with respect to aluminum and magnesium matrix [16, 35, 36]. This layer may have protected the AZ31 alloy during the initial 9 days of

immersion by not allowing the KOH electrolyte to be in direct contact with the α -Mg matrix. However, with the thickness of this layer on the same order as the fine Al–Mn precipitates, their degradation after 9 days would result in fragmentation of this Cu-rich layer. Following such fragmentation, a $\sim 20\text{-}\mu\text{m}$ -thick Ni layer evolved, and constituted the bulk of the resulting surface layer. XRD analysis confirmed the presence of $\text{Ni}(\text{OH})_2$, as seen in Fig. 8. With Ni being highly cathodic with respect to the α -Mg matrix [16], a micro-galvanic cell likely formed between the

Fig. 8 XRD results for surface of AZ31 immersed for 18 days in 45 wt% KOH electrolyte

porous surface film (allowing the electrolyte to enter) and the α -Mg solid solution, resulting in enhanced localized corrosion of the substrate. The mechanisms of the Cu and Ni to combine with other intermetallics in the AZ31 alloy, as well as their contribution to de-alloying or re-precipitation are not clearly understood, and thus further work is necessary [24].

As seen in Fig. 6, the concentration of Mg at the surface has gradually decreased toward the interface exposed to the electrolyte, suggesting a diffusion driven dissolution of Mg into the electrolyte. Cano et al. [39] also observed dissolution of magnesium in AZ31 under the film of corrosion products when AZ31 was immersed in 0.01 mol/l NaCl solution. At pH of 15, the Pourbaix diagram predicts the formation of a $\text{Mg}(\text{OH})_2$ surface layer [31], which has been reported to be highly porous and brittle [16]. At a pH 13, Alsagabi et al. observed an external layer of $\text{Mg}(\text{OH})_2$ and inner layer of Al_2O_3 on AZ31 surface exposed to 0.1 mol/l NaOH with NaCl additions (pH 13) [7]. Dissolution of Mg may also lead to the formation of voids, and their subsequent coalescence leading to the formation of micro fissures and cracks, as was also reported by Chao et al. [37, 38].

Applying the Schottky pair reaction model [37], negatively charged vacancies may form on the surface exposed to the electrolyte due to desorption of Mg^{2+} ions. In order to maintain a charge equilibrium, cations may be absorbed from the electrolyte [37]. This was noticed in the present work by detecting K in the X-ray maps in the corrosion product seen in Fig. 7. If the rate of formation of vacancies exceeds the rate of absorption of ions, cracks may form on the corroded surface, as seen in Fig. 9. Further, the formation of pores in the inner layer of the corrosion products observed on the exposed AZ31 samples is in agreement with model of Chao et al. [37] on the nucleation and

Fig. 9 Cross-sectional view of the corroded AZ31 sample after 18 days of immersion in 45 wt% KOH electrolyte

coalescence of point defects as a result of diffusion of negatively charged vacancies toward the substrate/corrosion product interface [40]. This process was driven by Mg^{2+} dissolution into the electrolyte and concomitant migration of voids. Clustering of voids into larger porosity regions was observed in Fig. 9 as well.

Figure 9 also reveals the formation of “double” cracks, which likely enabled the electrolyte to reach the AZ31 substrate underneath the surface layer and thus initiate a new corrosion site (marked with a yellow arrow). Due to the high P/B ratio of the Mg-based corrosion products, such newly formed region was seen to crack and locally detach from the AZ31 substrate, leading to a subsequent delamination. Song et al. [19] observed cracking of $\text{Mg}(\text{OH})_2$ during sample drying and also due to the application of vacuum during SEM observation. In the present study, however, the cracks in the corrosion products were not detected before 9 days of immersion (Fig. 5). Thus, crack evolution in this work was driven by electrolyte attack, high P/B ratio and spallation of the Al–Mn-rich precipitates.

Figure 10 shows the change in the concentration of different elements in the surface layer with respect to the immersion time. The solid-state diffusivity of Ni in Mg is low ($\log D = -16 \text{ m}^2/\text{s}$ at 740 K) [41]. Therefore, the formation of the Ni-rich layer was likely the result of a preferential dissolution of the AZ31 matrix, leaving behind a surface layer enriched in Ni. The Ni layer was observed to be highly porous, suggesting that its formation was not exclusively driven by a transport of Ni from the substrate interior.

The corrosion rate of the AZ31 alloy in KOH was also examined using Tafel curve analysis and is calculated using Eq. (1) [42]:

$$\text{CR} = \frac{K E W I_{\text{corr}}}{D A} \quad (1)$$

Fig. 10 Change of concentration of during immersion test as a function of exposure time evaluated by SEM-XEDS

where CR was the corrosion rate in mm/y, K was the constant for unit conversion (0.13), EW was the equivalent weight of the corroding species (12.19 g), I_{corr} was the corrosion current, D was the density (1.63 g/cm^3) and A was the area exposed to the electrolyte (1 cm^2). Figure 11 shows a representative Tafel plot, which yielded a corrosion current of $\sim 7.7 \mu\text{A/cm}^2$, resulting in a corrosion rate of 0.188 mm/y. At a potential of -1.25 V , there was a steep increase in corrosion current, possibly due to onset of pitting on the surface of the alloy [16], which was associated with accelerated dissolution of magnesium due to the spallation of the fine Al–Mn precipitates.

Figure 12 shows the Nyquist plot and the equivalent circuit obtained from EIS analysis. Performing curve fitting revealed that the test conditions corresponded to the modified Randle's circuit [43], where R_s was the solution resistance, R_t was the charge transfer resistance, Q was the

Fig. 11 Potentiodynamic polarization curve of AZ31 in 45 wt% KOH electrolyte

Fig. 12 Nyquist and the equivalent circuit obtained from EIS analysis for AZ31 sample immersed in 45 wt% KOH

constant phase element and Z_w was the Warburg's impedance.

A single semicircle was observed in Fig. 12, suggesting the presence of a unique time constant value (since only a single semicircle was observed) [44]. The capacitance in the circuit may have been present due to the electrical double layer and the charge transfer resistance [43, 45]. The charge transfer resistance may have been associated with the presence of the Cu-rich layer and dissolution of Mg into the electrolyte as soon as the material was immersed [43, 46]. The deflection of the curve at lower frequencies from the semicircle profile might be attributed to increased Warburg impedance, possibly due to diffusion of aluminum and magnesium in the solution [47, 48], which is consistent with the observed disintegration of the Al–Mn precipitates.

4 Conclusions

The corrosion behavior of the AZ31 magnesium alloy was studied in highly alkaline electrolyte. The results revealed that dissolution of the fine Al–Mn precipitates likely initiated the loss of integrity of a protective $\text{Mg}(\text{OH})_2$ surface film that may have formed immediately upon immersion of the AZ31 into KOH. Further exposure resulted in the formation of surface layers with cracks and voids. EIS and SEM-XEDS analyses confirmed that formation of the surface layer was diffusion driven.

Aluminum and magnesium may diffuse from the Al–Mn intermetallics or bulk α -Mg solid solution, respectively. Formation of AlO_2^- and Mg^{2+} ions, coupled with absorption of K ions leads to effective formation of an active galvanic cell.

Trace levels of Ni, Cu, and Fe in industrial-grade AZ31 alloy may significantly contribute in accelerating micro-galvanic corrosion. Formation of Ni(OH)₂- and Cu-rich layers has been observed to significantly accelerate once large cracks and voids formed in the surface layer (after 9 days of immersion).

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References

- [1] A. Pardo, M.C. Merino, A.E. Coy, F. Viejo, R. Arrabal, Feliú. *Electrochim. Acta* **53**(27), 7890 (2008)
- [2] G.G. Perrault, J. Electroanalyt. Chem. Interf. Electrochem. **51**, 107 (1974)
- [3] J. Larminie, A. Dicks, *Fuel Cell Systems Explained* (Wiley, Chichester, 2003)
- [4] M.F. Montemor, A.M. Simoes, M.J. Carmezim, *Appl. Surf. Sci.* **253**, 6922 (2007)
- [5] G. Ben Hamu, D. Eliezer, L. Wagner, *J. Alloys Compd.* **468**, 222 (2009)
- [6] G.L. Song, Z. Xu, *Electrochim. Acta* **55**, 4148 (2010)
- [7] J. Ninlchart, K.S. Raja, I. Charit, *J. Mater. Eng. Perform.* **25**, 2364 (2016)
- [8] J.E. Gray, B. Luan, *J. Alloys Compd.* **336**, 88 (2002)
- [9] N. Mahallawy, A. Bakkar, M. Shoeib, H. Palkowski, V. Neubert, *Surf. Coat. Technol.* **202**, 5151 (2008)
- [10] H. Zhao, Z. Huang, J. Cui, *Surf. Coat. Technol.* **202**, 133 (2007)
- [11] T.S. Lim, H.S. Ryu, S.H. Hong, *Corros. Sci.* **62**, 104 (2012)
- [12] F. Chen, H. Zhou, B. Yao, Z. Qin, Q. Zhang, *Surf. Coat. Technol.* **201**, 4905 (2007)
- [13] Y.L. Cheng, T.-W. Qin, H.M. Wang, Z. Zhang, *Trans. Nonferrous Metals Soc. China* **19**, 517 (2009)
- [14] A. Atrens, *Corrosion of Magnesium Alloys* (Woodhead Publishing Limited, Cambridge, 2009)
- [15] E. Ghali, W. Dietzel, K.U. Kainer, *J. Mater. Eng. Perform.* **22**, 7 (2004)
- [16] G.L. Song, A. Atrens, *Adv. Eng. Mater.* **5**, 837 (2003)
- [17] G.L. Song, A. Atrens, D. StJohn, J. Nairn, Y. Li, *Corros. Sci.* **39**, 855 (1997)
- [18] G.L. Song, A. Atrens, *Adv. Eng. Mater.* **1**, 11 (1999)
- [19] G.L. Song, K.A. Unocic, *Corros. Sci.* **98**, 758 (2015)
- [20] R.M. Asmussen, W.J. Binns, R. Partovi-Nia, P. Jakupi, D.W. Shoesmith, *Materials, Corrosion* **67**, 39 (2016)
- [21] A. Pardo, M.C. Merino, A.E. Coy, R. Arrabal, F. Viejo, E. Matykina, *Corros. Sci.* **50**, 823 (2008)
- [22] A.D. Südholz, N.T. Kirkland, R.G. Buchheit, N. Birbilis, *Electrochim. Solid-State Lett.* **14**, C5 (2011)
- [23] G. Williams, H. ap Llwyd Dafydd, R. Grace, *Electrochim. Acta* **109**, 489 (2013)
- [24] R.C. Zeng, J. Zhang, W.J. Huang, W. Dietzel, K.U. Kainer, C. Blawert, K.E. Wei, *Trans. Non-Ferrous Metals Soc. China* **16**, 763 (2006)
- [25] O. Lunder, T.K.R. Aune, K. Nisancioglu, *Corrosion* **43**, 291 (1987)
- [26] S. D. Cramer, Jr. B. S. Covino, *ASM Handbook, Electrochemical Series, Corrosion: Materials*, vol. 13B (ASM International), pp. 665–671
- [27] M. Hiroshi, Y. Ichige, K. Fujita, H. Nishiyama, K. Hodouchi, *Corros. Sci.* **66**, 203 (2013)
- [28] T. Zhang, Y. Li, F. Wang, *Corros. Sci.* **48**, 1249 (2006)
- [29] G.F. Vander Voort, *Metallographic Practices Generally Applicable to All Metals*. ASM International (1984)
- [30] M. Danaie, R.M. Asmussen, P. Jakupi, D.W. Shoesmith, G.A. Botton, *Corros. Sci.* **83**, 299 (2014)
- [31] M. Pourbaix, *Atlas of electrochemical equilibria in aqueous solutions* (National Association of Corrosion Engineers, 1974)
- [32] G. Oktay, M. Urgan, *Corros. Eng.* **50**, 380 (2015)
- [33] K. Reichek, K. Clark, J. Hillis, SAE Technical Paper (1985)
- [34] P. Liang, H.J. Seifert, H.L. Lukas, G. Ghosh, G. Effenberg, F. Aldinger, *Calphad* **22**, 527 (1998)
- [35] S.S. Wang, I.W. Huang, L. Yang, J.T. Jiang, J.F. Chen, S.L. Dai, D.N. Seidman, G.S. Frankel, L. Zhen, *J. Electrochem. Soc.* **162**, C150 (2015)
- [36] G.L. Makar, J. Kruger, *Int. Mater. Rev.* **38**, 138 (1993)
- [37] C.Y. Chao, L.F. Lin, D.D. Macdonald, *J. Electrochem. Soc.* **128**, 1194 (1981)
- [38] D.D. Macdonald, *J. Electrochem. Soc.* **139**, 3434 (1992)
- [39] Z.P. Cano, J.R. Kish, J.R. McDermid, *Minerals Metals Mater.* **1**, 335 (2014)
- [40] M. Urquidi, D.D. Macdonald, *J. Electrochem. Soc.* **132**, 555 (1985)
- [41] Z.L. Bryan, P. Alieninov, I.S. Berglund, M.V. Manuel, *Calphad* **48**, 123 (2015)
- [42] Gamry Instruments, *Getting Started with Electrochemical Corrosion Measurement*. July 30, 2016. <http://www.gamry.com/application-notes/corrosion-coatings/basics-of-electrochemical-corrosion-measurements/>
- [43] Y.F. Yuan, J.P. Tu, H.M. Wu, C.Q. Zhang, S.F. Wang, X.B. Zhao, *J. Power Sour.* **165**, 905 (2007)
- [44] G.L. Song, M. Liu, *Corros. Sci.* **62**, 61 (2012)
- [45] Y.L. Cheng, W.U. Hai-Ian, Z.H. Chen, H.M. Wang, Z. Zhang, Y.W. Wu, *Trans. Nonferrous Metals Soc. China* **17**, 502 (2007)
- [46] J. Liao, M. Hotta, *Corros. Sci.* **112**, 276 (2016)
- [47] J. Backholm, P. Georen, G.A. Niklasson, *J. Appl. Phys.* **103**, 023702 (2008)
- [48] P.L. Bonora, M. Andrei, A. Eliezer, E.M. Gutman, *Corros. Sci.* **44**, 729 (2002)