Corrosion Behavior of AZ31 Magnesium Alloy in Dilute Sodium Chloride Solutions

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Corrosion behavior of AZ31 magnesium alloy in dilute NaCl solutions was studied by electrochemical techniques. Its surface film was chemically characterized by X-ray diffraction (XRD). A corrosion map in terms of electrode potential and chloride concentration [Cl\(^-\)] was obtained by using electrochemical measurements. With the map, passivation and corrosion zones were determined. The passivation zone was found to become narrow with the increasing of [Cl\(^-\)]. The values of \(E_{ocp}\), open-circuit potential, in nondeaerated NaCl solutions were in the passivation zone when \([\text{Cl}^-]<0.2\ \text{M}\) and in the corrosion zone when \([\text{Cl}^-]\geq0.2\ \text{M}\). The reduction reactions of dissolved oxygen and hydrogen evolution worked as cathodic reactions in nondeaerated solutions. By XRD analyses, Mg(OH)\(_2\), magnesium hydroxyl carbonate, and MgO were the dominant products in the corrosion zone, whereas magnesium hydroxyl carbonate and MgO were the main components in the passivated film.

**Key words:** AZ31 magnesium alloy, dilute chloride solution, corrosion map, XRD

1. Introduction

Magnesium (Mg) and its alloys are widely used as structural materials in many fields because of their considerable physical strength and mechanical properties such as low density and high strength-to-weight ratio. These alloys are extremely popular in the automotive industry as they reduce the total weight of a vehicle, leading to saving of fuel and a reduction in pollution\(^1\)-\(^3\). However, the number of applications in which these alloys are utilized is limited due to their relatively poor corrosion resistance, especially in saltwater environments\(^4\), \(^5\). Moreover, in alkaline or neutral environments, pitting corrosion occurs when the concentration of chloride ions exceeds a critical value \([\text{Cl}^-]\)_\(_c\)\(^6\), \(^7\). Lafront et al.\(^8\) studied the pitting corrosion of AZ91D (die cast and thixocast) and AJ62x (die cast) Mg alloys immersed in an alkaline chloride medium (0.1 M NaOH + 0.05 M NaCl + 2 ml H\(_2\)O\(_2\)) with a pH value of 12.3, and they derived results for the passivation zone, the pitting current, and the average corrosion rate using electrochemical noise (EN) techniques. The results of the EN analysis techniques showed that the relative duration of the active and passive periods depended on the casting conditions.

Generally, the corrosion resistance of Mg alloys depends on the formation of passive surface films and varies with the medium to which the specimen is exposed\(^9\). Hara et al.\(^9\) reported that the surface films that form in neutral NaCl and Na\(_2\)SO\(_4\) solutions on open-circuit exposure influence the corrosion and electrochemical behaviors of pure Mg and its alloys. The surface films, which are mainly composed of Mg(OH)\(_2\), have a protective ability to Mg in the solutions. Due to the existence of a barrier layer in the surface films during immersion, the growth of the surface film is hampered as there is a breakdown in passivity.

From the results of an atmospheric exposure test\(^10\), the test site did not have considerable effect on the corrosion behavior of an AZ31 Mg alloy. The results also implied that the corrosion behavior during rain, when the test coupons are immersed in dilute solutions, is important. Many studies have reported the corrosion behaviors of Mg alloys in concentrated aqueous solutions such as 3.5 wt% NaCl solution in literatures\(^11\)-\(^13\). However, the corrosion behavior of the AZ31 Mg alloy on immersion in rainwater containing Cl\(^-\) ions at a site in the seashore area is still unknown. In this study, the corrosion behavior of the AZ31 Mg alloy in dilute NaCl solutions was investigated by electrochemical measurements and X-ray diffraction (XRD).

2. Experimental procedure

A 10-mm-diameter bar of commercial AZ31 (3%Al-1% Zn) Mg alloy was used in this study. The specimen was prepared by cutting a cylinder with a length of 10 mm from the bar, connecting the cylinder to a lead wire, and then embedding them completely in epoxy resin with the exception of one of the round surfaces of the cylinder, which was left exposed. Prior to the performance of the electrochemical tests, the exposed surface was mechanically polished up to 800 grit SiC papers, following which it was polished with a silica reagent, and then finally rinsed with ethanol.

Electrochemical measurements were carried out in both nondeaerated and deaerated NaCl solutions with concentrations of 0.01~0.5 M at room temperature. The deaerated solutions were purged with pure N\(_2\) gas. A saturated calomel electrode (SCE) and a platinum foil were used as the reference electrode and the counter electrode, respectively. In order to measure the open-circuit potential, \(E_{ocp}\), the specimens were immersed in the test solutions and their electrode potentials were monitored for 72 ks. Polar-
ization curves were obtained by scanning the potential from $-1.70 \ V$ to $-1.30 \ V$ at a rate of $10 \ \text{mV/min}$. The potential when the current density, $i$, was $100 \ \mu\text{A/cm}^2$ defined as the pitting potential, $V'_{\text{corr}}$. Potentiostatic experiments were performed in order to observe the initiation of pitting corrosion and its growth in dilute NaCl solutions. In the experiment, the specimens were polarized at a given potential just after immersion and maintained at this potential for a given duration.

After the performance of the potentiostatic experiments, the surface morphologies (distribution, shape, and depth of pit) of the specimens were determined by using a digital camera and a laser microscope (LM : VK-8500, KEYENCE Inc., Japan). The crystal structure of the surface films were examined by X-ray diffraction (XRD : RINT-2500, Rigaku, Inc., Japan) analysis using Cu Kα radiation under 40 kV and 300 mA.

3. Results and discussion

3.1 Electrochemical measurements

Fig. 1 shows the time variations in $E_{\text{ocp}}$ for 0.01~$0.5 \ \text{M}$ nondeaerated NaCl solutions over a period of 72 ks. It can be observed that $E_{\text{ocp}}$ of the 0.01 M solution increased with time; this can be attributed to the stable growth of the surface film. On the other hand, in the case of the 0.03~$0.5 \ \text{M}$ solutions, the $E_{\text{ocp}}$ values increased during the first immersion time followed by a sharp drop, which indicates dissolution of the surface film. However, in case of the 0.03~$0.5 \ \text{M}$ solutions, the values reached a minimum and then started to increase again towards nobler potentials; this indicates that the surface film first corroded and then passivated with the increase in time in those NaCl solutions.

Fig. 2 shows the polarization curves of AZ31 in a 0.01 M NaCl solution under deaerated (■) and nondeaerated (○) conditions. The cathodic reaction in nondeaerated solution was much suppressed. The polarization curve of AZ31 was measured after 18 ks immersion in nondeaerated 0.01 M NaCl solution, and the result is also shown in Fig.2 (△). The anodic reaction after 18 ks immersion (△) was suppressed much more than that just after immersion (○), while the cathodic reaction was not affected by immersion time. This indicated that surface film formed in nondeaerated solution led to the inhibition of anodic process. For the cathodic reaction, it is considered that the cathodic polarization curve corresponded to the reduction of water, which can be given as follows:

$$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad (1)$$

Even in the nondeaerated solution, the cathodic polarization curve corresponding to the reduction of the dissolved oxygen:

$$\frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- \quad (2)$$

is not observed. However, it works as a cathodic reaction and the protective film as mentioned above was formed accompanied with the reaction (2). The current density for reaction (2) is small enough than that for reaction (1), so it is not observed in the polarization curve.

Fig. 3 shows the polarization curves of AZ31 immersed in nondeaerated NaCl solutions with various Cl$^-\text{M}$ concentrations. By using these results, the value of $V'_{\text{corr}}$ was determined. The value of $V'_{\text{corr}}$ did not show in the 0.5 M solution, whereas it located between $1.49 \ \text{V}$ and $1.36 \ \text{V}$ in 0.01~$0.3 \ \text{M}$ solutions. The sample in 0.01~$0.3 \ \text{M}$ solu-
tions was also observed to passivate spontaneously due to the presence of the protective surface film. The sample showed a steady passive current density, $i$, whose value was less than $100 \mu A/cm^2$. The passive zone became narrow with the increase in Cl$^-$, and this was accompanied by a shift in the pitting potentials towards a less noble direction. This shift might be attributed to the fact that metal-hydroxyl-chloride complex compounds were produced when Cl$^-$ ions were absorbed by the surface film, which results in an easier anodic dissolution of Mg accompanied by dissolution of the surface films in highly concentrated NaCl solutions\textsuperscript{14, 15}. After the polarization tests, the pits on the surface of the samples were studied. It is concluded that the breakdown of the protective surface films was responsible for the sharp increase in current density, as observed in the anodic polarization curves.

Fig. 4 shows the typical time variations in the current densities of AZ31 polarized in a 0.01 M nondeaerated NaCl solution at different potentials; $V_{\text{clo}}$ is $-1.36$ V in this solution as shown in Fig. 3. When polarization was performed at $-1.50$ V, $i$ increased slightly to $5 \mu A/cm^2$ and then decreased rapidly to the passivation state stage II\textsubscript{0} as shown in Fig. 4(a). Small pits started forming in stage I\textsubscript{0} but repassivated quickly in stage II\textsubscript{0}.

When the specimen was polarized at $-1.44$ V, as shown in Fig. 4(b), $i$ was found to increase rapidly up to $120 \mu A/cm^2$ before becoming stable after polarization for 10.8 ks in stage I\textsubscript{1}. It is possible that the surface film might undergo nucleation and the pits might start getting connected to each other in this period. After polarization for 10.8 ks, $i$ decreased sharply to $0-5 \mu A/cm^2$, and the specimen was covered with the passivated product.

When the specimen was polarized at $-1.40$ V, as shown in Fig. 4(c), $i$ increased to $250 \mu A/cm^2$ after polarization for 10.8 ks in stage I\textsubscript{1}, suggesting that a large number of pits were formed resulting in local corrosion during the initial 10.8 ks of polarization. After polarization for 10.8 ks, $i$ decreased to $100 \mu A/cm^2$ and then increased again with the immersion time. It was observed that after the test was preformed for 72 ks, the specimen was covered with corrosion products in stage III.

When the polarization potential was at $-1.35$ V, as shown in Fig. 4(d), $i$ increased to $400 \mu A/cm^2$ and stayed at almost the same value till stage III, which suggests a general corrosion of the specimen.

3.2 Pitting corrosion morphology

Fig. 5 shows the pits morphologies of AZ31 polarized in a 0.01 M nondeaerated NaCl solution. Two kinds of pits morphologies were observed: irregular and spherical. The irregular pit in Fig. 5(a) was a result of nucleated growth around the surface. On the other hand, the spherical pit in Fig. 5(b) was formed through the release of H\textsubscript{2} gas bubbles from the mouth of the pit during their initial growth stages. The different morphologies of the pits might be attributed to the diversity between the mass transport and the effective cathode area\textsuperscript{16}.

![Fig. 4 Time variations in the current densities of AZ31 polarized potentiostatically in a 0.01 M nondeaerated NaCl solution at the following potentials: (a) $-1.50$ V, (b) $-1.44$ V, (c) $-1.40$ V, and (d) $-1.35$ V.](image)

![Fig. 5 LM micrographs of AZ31 polarized potentiostatically in a 0.01 M nondeaerated NaCl solution at $-1.44$ V for 3.6 ks. Micrographs of (a) irregularly shaped pits and (b) spherical pits.](image)
Photographs of AZ31 polarized at various potentials in a 0.01 M nondeaerated NaCl solution captured by using a digital camera are illustrated in Fig. 6. Figs. 6(a)–(b) show the photographs of the corrosion in the specimens polarized at a potential of −1.44 V. It can be observed that the pits grew and connected to each other during the initial 10.8 ks of the polarization, as shown in Fig. 6(a). Finally, a small quantity of a white product, which was visible to the naked eyes, was formed at the center of the surface when the current density decreased to 0−5 μA/cm², as shown in Fig. 4(b). After the sample had been immersed for 72 ks, thick corrosion products appeared on the surface as shown in Fig. 6(b). Figs. 6(c)–(e) show the photographs of the specimens polarized at a potential of −1.40 V. The specimens had mild corrosion at the edges of the surface during the initial time of immersion and then the corrosion increased in severity as the immersion time increased to 72 ks. At the end of 72 ks, it was observed that the surfaces of the specimens were covered with corrosion products. Although the current density decreased to 100 μA/cm² after 10.8 ks, as shown in Fig. 4(c), as the immersion time increased, the current density also increased slowly, leading to the formation of pits. Fig. 6(f) shows the passivated specimen maintained at a potential of −1.50 V for 72 ks. A number of small and closed pits were observed on the surface. On the other hand, for a specimen maintained at a potential of −1.35 V for 72 ks, as shown in Fig. 6(g), a large number of pits were observed, which implies that the surface corroded almost entirely.

Fig. 7 shows the time variations in the pit depths at various potentials using the laser microscopy. It was observed that the depths of pits increased quickly during the initial immersion time for specimens polarized at electrode potentials of −1.44 V, −1.40 V, and −1.35 V. However, the pits almost stopped growing in the case of the specimen maintained at −1.44 V from 18 ks to 72 ks due to the formation of the passive film. Meanwhile, the depths of pits increased continuously up to 72 ks for specimens maintained at −1.40 V and −1.35 V. Metastable pits started forming just after immersion of the specimen at a potential of −1.50 V, that is, stage I, in Fig. 4(a) before repassivating.

On the basis of the observations of the pitting morphologies, it appears that the corrosion progressed preferentially in the horizontal direction during the initial immersion period. The dissolution in the pits then increased continuously till a large number of pits were formed. In order to maintain the active dissolution inside the pits, Run et al. suggested that the concentration of metal chloride in the anolyte on the inner surface of the pits should be above a critical concentration value. Isaacson reported that for stainless steel, the critical value is above 60% saturation. In our study, it is possible that the shallow pits were caused by the presence of dilute chloride within the mouth of the pits.

### 3.3 Corrosion map

A corrosion map was obtained in terms of the electrode potential and [Cl−] by using the results of the potentiodynamic polarization and potentiostatic polarization measurements, as shown in Fig. 8. Two zones—the passivation zone and the corrosion zone—were detected. The $E'_{ocp}$ values of the nondeaerated NaCl solutions at open-circuit potentials were measured after 72 ks. The $E'_{ocp}$ values in deaerated NaCl solutions, referred to as $E_{ocp}$, were also measured after 72 ks. $V_{c100}$ were obtained from Fig. 3 and the critical potentials $V_{c}$ for the propagation of the pits were also determined. The passivation zone became narrow with the increase in [Cl−]. Because of the induction time, the values of $V_{c}$ obtained from the potentiostatic polarization measurements were lower than those of $V_{c100}$ detected under potentiodynamic conditions. For the specimen immersed in a 0.1 M solution, the value of $E'_{ocp}$ was in
the passivation zone, and the specimen underwent corrosion, as shown in Fig. 1. This implies that the specimen was in the corrosion zone during the initial immersion time, before progressing into the passivation zone with the increase in immersion time; this could be attributed to the tendency of increase in the values shown in Fig. 1. For the specimen immersed in the 0.3 M solution, the potentiodynamic polarization curves indicated the presence of a passivation zone but the specimen did not show any evidence of passivity when observed using a laser microscope under potentiostatic conditions, and the specimen also showed severe corrosion. In the solutions of 0.3 M and 0.5 M, which had high concentrations of Cl\(^-\), localized corrosion occurred and increased quickly after a short time of immersion; moreover, the specimens did not go through a passivation zone and progressed directly into the corrosion zone with the increase in the immersion time.

It was observed that the values of \(E_{ocp}\) for nondeaerated NaCl solutions were in the passivation zone when \([\text{Cl}^-] < 0.2\) M, and they were in the corrosion zone when \([\text{Cl}^-] \geq 0.2\) M.

### 3.4 XRD analyses

After performed the potentiostatic polarization tests, the surface film in the two zones were analyzed by using XRD. Fig. 9 shows the XRD patterns for AZ31 with a polarization potential of \(-1.40\) V and \(-1.50\) V. In both cases the main peaks originated from the metallic Mg substrate. Despite of this, for specimen maintained at \(-1.40\) V, peaks could be referred to Mg(OH)\(_2\) and MgO crystal structures. Many small peaks were presented in the spectra which could not be attributed to a single compound. These are mostly likely associated with magnesium hydroxyl carbonate phase. The spectrum for specimen maintained at \(-1.50\) V shows magnesium hydroxyl carbonate and MgO phases. The atomic ratio O/Mg was 3.98 calculated from the XPS data, which was consistent with the product of Mg\(_5\)(CO\(_3\))\(_4\)(OH)\(_5\)\(\cdot\)8H\(_2\)O.

In this study, the AZ31 Mg alloy was immersed in diluted chloride solutions under potentiostatic conditions. Soluble ions formed a surface electrolyte layer on the surface during the immersion process. For a specimen with a polarization potential of \(-1.50\) V, the following reactions took place at the surface: anodic dissolution of Mg, which occurred on only a fraction of the surface.

\[
\text{Mg} (s) \rightarrow \text{Mg}^{2+} (aq) + 2e^- \tag{3}
\]

Cathodic reaction on the adjacent surface, which was believed to be due to hydrogen evolution and oxygen reduction, as shown in reactions (1) and (2). In order to balance excess electric charge, cations such as Na\(^+\) and Mg\(^{2+}\) migrated towards the cathodic areas, while anions such as OH\(^-\) and Cl\(^-\) moved towards the dissolution sites. As a result, in this process, Mg(OH)\(_2\) grew closer to the anodic sites\(^{[10]}\).

\[
\text{Mg}^{2+} (aq) + 2\text{OH}^- (aq) \rightarrow \text{Mg(OH)}_2(s) \tag{4}
\]

Due to the anodic dissolution, small pits were observed during the initial immersion; these pits then were filled up with Mg(OH)\(_2\) and repassivated quickly on the surface with the increase in immersion time. Considering carbon dioxide was present in the environment, the dissolution of CO\(_2\) in the surface electrolyte can be given as

\[
\text{CO}_2(g) \rightarrow \text{CO}_2(aq) \tag{5}
\]

\[
\text{CO}_2(aq) + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{HCO}_3^- \tag{6}
\]

The presence of carbonate caused Mg(OH)\(_2\) to form magnesium hydroxyl carbonate. The presence of magnesium hydroxyl carbonate was confirmed from the XRD spectra.

\[
5\text{Mg(OH)}_2(s) + 4\text{HCO}_3^- (aq) + 4\text{H}^+ \rightarrow \text{Mg}_5(\text{CO}_3)_4(\text{OH})_2\cdot 8\text{H}_2\text{O} (s) \tag{7}
\]

Some literatures reported that carbonate-containing cor-

![Image](image-url)
rosion products were nonconductive and would not be able to serve as substrates in cathodic reactions. They were expected to slow down the corrosion by blocking the anodic areas. This was in line with earlier suggestions by Whitty.

For a specimen maintained at the potential of −1.40 V, the surface films were destroyed due to the increase in the potential, which led to the formation of more chloride ions on the surface. XPS results (not shown) exhibited a higher Cl content in the corrosion zone as compared to the passivation zone, which enhances the dissolution process. The dissolution of the surface film resulted in the exposure of a fresh metal matrix, providing an active center for further electrochemical reaction.

4. Summary

(1) A corrosion map was obtained for the AZ31 Mg alloy on the basis of the values of the electrode potentials and chloride concentrations [Cl−] determined by using the potentiodynamic and potentiostatic polarizations. With the map, the passivation and corrosion zones were determined. It was observed that the passivation zone became narrow with the increase in [Cl−].

(2) The reduction reactions of dissolved oxygen and water were cathodic reactions for the AZ31 Mg alloy immersed in nondeaerated dilute chloride solutions. In nondeaerated dilute media, a protective film was formed by the reaction involving dissolved oxygen. The values of \( E_{\text{corr}} \) for nondeaerated NaCl solutions were in the passivation zone when \([\text{Cl}^-] < 0.2 \text{ M}\), and they were in the corrosion zone when \([\text{Cl}^-] \geq 0.2 \text{ M}\).

(3) In the passivation zone, small and closed pits started forming just after immersion but repassivation occurred after less than an hour. It was observed that the pits grew slowly initially, but the specimen surface was covered with passivated products after 72 ks. Further, it was also observed that stable pit growth occurred in the corrosion zone and the depths and diameters of pits increased with immersion time resulting in general corrosion through connection of pits.

(4) From the results of the XRD analysis, Mg(OH)\(_2\), magnesium hydroxyl carbonate, and MgO were the dominant products in the corrosion zone, whereas magnesium hydroxyl carbonate and MgO were the main components in the passivated film.

References

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