Corrosion behaviour of superplastic Zn–Al alloys in simulated acid rain

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A B S T R A C T
The influence of aluminium content on the corrosion behaviour of superplastic Zinc–Aluminium alloys immersed in simulated acid rain was investigated. ZA4, ZA8, ZA12, and ZA16 alloys were used for the test. The Al-rich phase was prone to preferential attack when the superplastic Zn–Al alloy was immersed for 5 d. However, with increasing ratios of the Al phase, the corrosion rates of the four samples decreased in the order ZA4 > ZA8 > ZA12 > ZA16. The corrosion rate of the alloy decreased with increasing Al content, which may be related to the distribution of the Al-rich phase. Corrosion kinetic parameters were also calculated.

1. Introduction
The properties of zinc (Zn) alloys could provide potential materials for use in a wide range of applications by various industries; however, such alloys are susceptible to corrosion [1–4]. Zinc–Aluminium (Al) alloys have long been reported to exhibit superplasticity [5]. For efficiency and economy, many applications use superplastic Zn–Al alloys instead of brass. The corrosion mechanism of Zn and its alloys have been studied in field exposures under controlled environments. The corrosion of Zn occurs in almost every atmospheric environment. However, industrial and marine environments are where corrosion most aggressively occurs due to the highly corrosive nature of airborne pollutants [6–10]. Previous studies have indicated that ZnO and Zn(OH)2 are formed during the initial stages of corrosion with aqueous droplets on Zn and that, through time, the development of pH and ion concentration gradients could lead to the formation of other corrosion products. Finally, oxide growth occurs as the droplets evaporate [11–14]. Most investigations have focused on Zn coatings [15–18], and limited studies concerning the corrosion behaviour of superplastic Zn–Al alloys in acid rain media have been conducted. As Zn–Al alloys are increasingly used outdoors, atmospheric influences on the corrosion processes of Zn–Al alloy components should not be ignored, especially in areas heavily polluted by acid rain. Magaino et al. [19] investigated the corrosion behaviour of Zn in simulated acid rain and concluded that the rate of Zn corrosion in simulated rain increases drastically at pH values of about 3. Acid rain corrosion of outdoor structures made with Zn–Al alloys instead of brass components has recently become a problem.

Al contents and the manufacturing processes of Zn–Al alloy components have considerable influences on the phase structure of the alloys, leads to differences in their corrosion behaviour [20]. The corrosion behaviour of Zn–Al alloys has been reported to be influenced by the Zn/Al weight ratio. Published literature has indicated that the corrosion of Zn–Al alloys with different Zn/Al weight ratios demonstrates an interesting phenomenon. On the one hand, Al is more active than Zn; on the other hand, when the Al content is increased, the corrosion rate of the alloy is decreased [21]. The mechanism of this abnormal phenomenon requires further study.

In the current work, the influence of Al content on the corrosion behaviour of extruded superplastic Zn–Al alloys in simulated acid rain was studied. The corrosion behaviour of these alloys were determined, with particular emphasis on the corrosion rate, corrosion product composition, and influence of acid rain, and a model for explaining the abnormal phenomenon was suggested. The results of our investigation may find wider applications for developing advanced materials.

2. Experimental
2.1. Materials
ZA4 (Zn–4 weight% Al), ZA8 (Zn–8 weight% Al), ZA12 (Zn–12 weight% Al), and ZA16 (Zn–16 weight% Al) alloys were used for the immersion study in a simulated acid rain solution. The Zn–Al alloy specimens were extruded at 280 °C by a 315 t vertical extruder with a deformation ratio of 1:18.8. The cross-sectional (vertical extrusion direction) microstructures of the specimens were observed under an S-4800 UHR FE-SEM (Hitachi, Japan).
2.2. Immersion test

The specimens for the immersion test were \( \Phi 14 \times 2 \) mm in size. Prior to the test, the specimen surfaces were ground to 2000 grit SiC paper and cleaned with acetone and de-ionised water. Every specimen was weighed (original weight, \( w_0 \)), and the surface area \( S \) was measured before the test. Immediately following the preparation procedure, the specimens were immersed several times in a simulated acid rain solution in open air at a room temperature of about 20 °C. The simulated acid rain solution was prepared using distilled water and analytical grade reagents. The composition of the simulated acid rain is shown in Table 1. The samples were immersed in the solution for \( (24, 48, 120, 240, \text{ and } 480) \) h. After each immersion test, the corroded specimens were rinsed with distilled water in an ultrasonic bath for 15 min to remove the corrosion products. Then, the specimens were washed quickly with distilled water, dried, and then weighed again to obtain the final weight \( (w_1) \). The difference between \( w_0 \) and \( w_1 \) was designated as the corrosion weight loss \( (\Delta w) \).

2.3. Polarisation measurement

Potentiodynamic polarisation curves were measured at room temperature in the corrosion solutions by a PGSTAT302 electrochemical workstation. A three-electrode cell was employed, with the sample acting as the working electrode, the saturated calomel electrode as the reference electrode, and a platinum sheet as the counter electrode. The working electrodes were embedded in an epoxy resin to provide insulation, leaving a surface of 1.0 cm² in contact with the electrolyte. The scanning rate was 1 mV/s.

2.4. Analysis and characterisation methods

The surface morphologies of the immersed samples were observed under the S-4800 UHR FE-SEM and a TM-1000 SEM (Hitachi, Japan), and the corrosion products were analysed by EDS, XRD (D8 Advance X-ray diffractometer), and XPS (AXIS Ultra DLD X-ray photoelectron spectroscope).

3. Results

3.1. Microstructures of the specimens

Fig. 1 shows the microstructures of the cross-sections of ZA4, ZA8, ZA12, and ZA16 Zn alloys. According to the binary phase diagram of the Zn–Al alloys [21] (Fig. 2), Zn–Al alloys are composed of the primary Zn phase (\( g \) phase) and eutectic phase (\( \alpha \)-Al rich phase). As the Al weight ratio increased, the alloys contained more eutectic phase (lamella).

3.2. Weight loss and corrosion rate

The corrosion rate and weight loss of the specimens are calculated as follows:

### Table 1

<table>
<thead>
<tr>
<th>Ion</th>
<th>F⁻</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
<th>NH₄⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration/mg L⁻¹</td>
<td>0.12</td>
<td>1.0</td>
<td>7.1</td>
<td>11.1</td>
<td>2.3</td>
<td>0.42</td>
<td>0.11</td>
<td>0.049</td>
<td>0.045</td>
</tr>
</tbody>
</table>

Fig. 1. Cross-sectional microstructures of superplastic Zn–Al alloys: (a) ZA4; (b) ZA8; (c) ZA12; (d) ZA16.
where \( C \) is the weight loss of metal due to corrosion (g cm\(^{-2}\)), \( \nu \) is the corrosion rate (g cm\(^{-2}\) d\(^{-1}\)), \( w_0 \) is the original weight (g), \( w_1 \) is the final weight without corrosion products (g), \( S \) is the surface area (cm\(^2\)), and \( t \) is the immersion time (d).

The weight losses of the specimens are shown in Fig. 3. Each type included three samples, so that the corrosion rates \( C \) of all exposed specimens had three sets of data each: the minimum, the median, and the maximum. The symbols shown in Fig. 3 represent average values. With prolonged immersion time, weight loss increased. Overall, the weight losses of the specimens were inversely proportional to the Al content; that is, the higher the Al content, the lower the weight loss. With extended immersion time, the weight losses of the ZA4 and ZA8 alloys became greater than those of the ZA12 and ZA16 alloys. When the specimens were immersed for 10 d, the weight loss of the ZA8 alloy became slightly greater than that of the ZA4 alloy. After 20 d of immersion, the weight losses of the ZA4 and ZA8 alloys were significantly greater than those of the ZA12 and ZA16 alloys.

Fig. 4 shows the relationship between the corrosion rate and the immersion time. The corrosion rates of the four samples decreased with immersion time, with an overall corrosion rate trend of ZA4 > ZA8 > ZA12 > ZA16. The dependence of the corrosion rate on the immersion time varied amongst the four alloys. The ZA4 alloy corrosion rate decreased first, and then increased when the immersion time exceeded 2 d until 5 d. When the immersion time exceeded 5 d, the corrosion rate decreased yet again. The ZA8 alloy demonstrated a similar trend, but its corrosion rate increased when the alloy was immersed for (5 to 10) d; the corrosion rates of the ZA12 and ZA16 alloys continued to decline.
3.3. Polarisation curves

Fig. 5 shows the steady-state polarisation curves of the specimens in the simulated acid rain solution. The corrosion potentials of the ZA4 and ZA8 alloys were markedly lower than those of the ZA12 and ZA16 alloys. The corrosion potentials of the ZA4 and ZA8 alloys were almost $-1.2 \, V_{SCC}$, whereas the corrosion potentials of both the ZA12 and ZA16 alloys were approximately $-1.06 \, V_{SCC}$. According to the polarisation curves, the corrosion currents $I_{corr}$ of the four specimens in the simulated acid rain solution can be obtained by the Tafel extrapolation method. The corrosion currents $I_{corr}$ of the ZA4, ZA8, ZA12, and ZA16 alloys were $(3.97 \times 10^{-6}, 3.02 \times 10^{-6}, 2.34 \times 10^{-6},$ and $2.06 \times 10^{-6}) \, A/cm^2$, respectively, and the corrosion current density was in the order of ZA4 > ZA8 > ZA12 > ZA16.

3.4. Corrosion product analysis

XRD experiments were performed to identify the corrosion products on the surfaces of the four specimens after 10 d of immersion. As shown in Fig. 6, ZnO and $Zn_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ were the main corrosion products in the ZA8, ZA12, and ZA16 alloys. The third strongest peak of $Zn_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ was disappeared because the product was little in amount. $Zn_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ was not detected on the surface of the ZA4 alloy, which may be caused by the minimal amount of Al in the alloy.

Fig. 6 shows the XPS patterns of the corrosion products of the four superplastic Zn–Al alloy specimens in the simulated acid rain solution after 10 d of immersion. All specimen corrosion products contained Zn, O, and C. Al was detected in all corrosion products except in the ZA4 alloy, which is consistent with the XRD results. Fig. 7.

3.5. Corrosion morphologies

3.5.1. Corrosion product morphologies

When the ZA4, ZA8, ZA12, and ZA16 alloys were immersed in the simulated acid rain solution for various times, surface alterations became obvious and visible even to the naked eye. As the corrosion time increased, the corrosion products on the sample surfaces gradually increased. As the Al content increased, the corrosion products on the sample surface decreased. The surface corrosion morphologies of the samples immersed in the simulated acid rain solution for 5 d are shown in Fig. 8. More corrosion products with looser adherence were observed on the surface of the ZA4 alloy. In several locations, an accumulation of corrosion products appeared. As the Al content increased, the amount of surface corrosion products decreased.

3.5.2. Surface morphologies without corrosion products

Fig. 9 shows the morphologies of the specimen surfaces where corrosion products had been removed. Pitting was evident on the surface of the ZA4 and ZA8 specimens immersed for 5 d (as shown in the top right corners of Fig. 9a and b) but the pits observed on the surfaces of the ZA12 and ZA16 specimens were much smaller in size. The Al-rich phase was corroded more rapidly than the primary Zn phase.

3.5.3. Cross-sectional observation of the product film

The cross-sectional morphologies of the ZA4, ZA8, ZA12, and ZA16 specimens were observed by SEM (Fig. 10). The ZA4 sample corroded more extensively than did the other samples. The depth of the film product on the ZA4 sample surface was about 2 μm (Fig. 10a). An obvious corrosion film product was observed on the ZA8 sample surface, although the film was slightly thinner than the ZA4 alloy surface, which was about 1.5 μm (Fig. 10b). No significant corrosion film product was found on the surfaces of the ZA12 and ZA16 alloys, indicating that corrosion on these two specimen surfaces was relatively light.

4. Discussion

4.1. The effect of Al content on the corrosion kinetics of superplastic Zn–Al alloys in simulated acid rain

According to Natesan [22], the corrosion kinetics equation of the superplastic Zn–Al alloys in a simulated acid rain solution can be expressed as:

$$C = Kt^n$$  \hspace{1cm} (3)

where $C$ is the weight loss of metal due to corrosion (gm $^{-2}$), $t$ is the immersion time (d), and $K$ and $n$ are constants.

Hence, the relationship of $C$ and $t$ fits a straight-line log–log plot of $C$ versus time $t$ in the logarithmic form:

$$\log C = \log K + n \log t$$  \hspace{1cm} (4)

According to the linear bilogarithmic law (Eq. (4)), the corrosion behaviour of a certain material at a certain location can be defined by the two parameters $K$ and $n$. The linear fit curves of the specimens
with the mean values of $C$ are shown in Fig. 11. A list of $K$ and $n$ values for specimens immersed for 20 d is presented in Table 2, together with their correlation coefficients $R$, showing the “fit” of this model to the actual measured corrosion rates.

According to the same bilogarithmic law (Eq. (4)), when $n = 0.5$, the increase in corrosion penetration is parabolic with diffusion through the corrosion product layers as the rate controlling step. At $n$ values that are appreciably <0.5, the corrosion products show protective, passivating characteristics. Higher $n$ values (>0.5), are indicative of non-protective corrosion products [23,24]. In the present study, the $n$ values of all the specimens were higher than 0.5, the $n$ value of the ZA8 alloy being the highest. The $K$ value for the specimens showed the opposite trend. These results indicate that loosely adhered layers formed on the surfaces of the specimens, with the layer on the ZA4 specimen being the loosest. The initial corrosion rate is described by $K$. Hence, based on these analyses, the ZA4 alloy had a higher initial corrosion rate than the other alloys.

The $K$ value of the ZA8 alloy was less than that of the ZA4 alloy, whereas their $n$ values showed the opposite trend. This result may be caused by the higher Al content of the ZA8 alloy in comparison with the ZA4 alloy, which induces relatively delayed pitting times, so that after about 10 d of immersion, the weight loss of the ZA8 alloy was higher than that of the ZA4 alloy, resulting in a higher $n$ value. During corrosion, the Al-rich phases of the ZA12 and ZA16 specimens act as barriers, resulting in decreased corrosion rates. Overall, as the Al content increased, the alloy corrosion rate decreased.

4.2. The effect of Al content on the corrosion mechanism of superplastic Zn–Al alloys in simulated acid rain

According to the adsorption model, ligands (e.g., OH$^-$) are adsorbed onto the active Zn surface as follows [25]:

$$\text{Zn} + 2\text{OH}^- \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2e^- \quad (5)$$

The anodic sweep exhibits an active/passive transition prior to the initiation of pitting corrosion. Active dissolution involves a net anodic contribution, which can be associated with the formation of a ZnO film under the prevailing pH conditions as a result of OH- ion adsorption onto the metal surface according to the overall reaction (5) [26].

The active Al-rich phase was prone to preferential attack when the superplastic Zn–Al alloy was immersed in the simulated acid rain solution. The Zn-rich phase was also corroded, but the corrosion rate was slower than that in the Al-rich phase. With prolonged immersion time, the Al concentration in the solution increased due to the dissolution of the Al-rich phase. In the current work, when the Al content was up to 8% (ZA8), the Al concentration in the solution increased and reached a threshold value for the precipitation of $\text{Zn}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3\cdot\text{H}_2\text{O}$, reaction (6) then began. When the Al concentration was less than 8%, the formation rate of $\text{Zn}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3\cdot\text{H}_2\text{O}$ by the right reaction was equal to the dissolution rate given by the left reaction; that is, $\text{Zn}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3\cdot\text{H}_2\text{O}$ was unsaturated in the solution. When the Al concentration was increased to 8%, the Al$^{3+}$ concentration increased. The concentration of $\text{Zn}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3\cdot\text{H}_2\text{O}$ in the solution gradually became supersaturated.
Fig. 8. SEM images of the specimens immersed in the simulated acid rain solution for 5 d: (a) ZA4; (b) ZA8; (c) ZA12; (d) ZA16.

Fig. 9. SEM images of the specimens immersed in the simulated acid rain solution for 5 d without products: (a) ZA4; (b) ZA8; (c) ZA12; (d) ZA16.
and began to precipitate. This precipitation reaction could explain why Zn$_6$Al$_2$(OH)$_{16}$CO$_3$.4H$_2$O was not found on the surface of the ZA4 alloy.

$$6\text{Zn}^{2+} + 2\text{Al}^{3+} + \text{CO}_3^{2-} + 16\text{OH}^- + 4\text{H}_2\text{O} = \text{Zn}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$$

4.3. Corrosion model for superplastic Zn–Al alloys in simulated acid rain

The Al-rich phase was prone to preferential attack when the superplastic Zn–Al alloy was immersed in the simulated acid rain solution but the alloy corrosion rate decreased when the Al content increased. This may be related to the distribution of the Al-rich phase. There was a critical value of the content of Al. When the Al content exceeded 8%, the corrosion resistance of the Zn–Al alloy in simulated acid rain would be improved greatly. Fig. 12a and b show schematic images of the corrosion process of the superplastic Zn–Al alloy (when the Al content is less than 8%) in the simulated acid rain solution. The schematic image is based on the results of the present work: (a) During the initial steps of corrosion, the Al-rich phases are attacked (Fig. 12a) due to the galvanic effects of the primary Zn-rich and Al-rich phases. At this stage, the corrosion products mainly cover the Al-rich phase. (b) After a longer immersion time, the whole

![Fig. 10](image)

**Fig. 10.** SEM images of the cross-sections of specimens immersed in the simulated acid rain solution for 5 d: (a) ZA4; (b) ZA8; (c) ZA12; (d) ZA16.

![Log corrosion losses of the Zn-Al alloys as a function of log time](image)

**Fig. 11.** Log corrosion losses of the Zn-Al alloys as a function of log time.

**Table 2**

<table>
<thead>
<tr>
<th>Samples</th>
<th>$K$</th>
<th>$n$</th>
<th>$R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZA4</td>
<td>1.868</td>
<td>0.783</td>
<td>0.992</td>
</tr>
<tr>
<td>ZA8</td>
<td>1.476</td>
<td>0.861</td>
<td>0.995</td>
</tr>
<tr>
<td>ZA12</td>
<td>1.263</td>
<td>0.687</td>
<td>0.993</td>
</tr>
<tr>
<td>ZA16</td>
<td>1.059</td>
<td>0.675</td>
<td>0.996</td>
</tr>
</tbody>
</table>

![Log corrosion losses of the Zn-Al alloys as a function of log time](image)
When the Al content was up to 12%, the distribution of the Al-rich phase presented a net, as shown in Fig. 12 c, that acts as a barrier and inhibits pitting when the specimen is corroded (Fig. 12 d), resulting in a decreased corrosion rate.

5. Conclusions

1. With increasing Al content, the corrosion rates of the four samples decreased. The overall corrosion rate trend was ZA4 > ZA8 > ZA12 > ZA16. ZnO and Zn₆Al₂(OH)₁₆CO₃·4H₂O were the main corrosion products.

2. Pitting was evident on the surface of the ZA4 and ZA8 specimens, which were immersed for 5 d, but the pits observed in the ZA12 and ZA16 specimens were much smaller in size.

3. The Al-rich phase was prone to preferential attack when the superplastic Zn–Al alloy was immersed in the simulated acid rain solution but the corrosion rate of the alloy decreased with increasing Al content. This result may be related to the distribution of the Al-rich phase.

Acknowledgements

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References


[24] Li.-jing Yang, Yan.-fang Li, Ying.-hui Wei, Li.-feng Hou, Yong.-gang Li, Yun Tian, Atmospheric corrosion of field-exposed AZ91D Mg alloys in a polluted environment, Corros. Sci. 52 (2010) 2188–2196.