Corrosion Behaviors of AA5083 and AA6061 in Artificial Seawater: Effects of Cl⁻, HSO₃⁻ and Temperature

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The electrochemical character of intermetallic inclusions plays a crucial role in the corrosion behaviors of aluminum alloys. The Volta potential of the intermetallic inclusions in AA5083 and AA6061 was investigated. Furthermore, the effects of Cl⁻, HSO₃⁻ and temperature on the corrosion behaviors of AA5083 and AA6061 were studied. The microstructure and composition of the intermetallic inclusion were characterized by scanning electron microscope (SEM) and energy-dispersive spectroscopy (EDS). The Volta potential was analyzed by scanning Kelvin probe force microscopy (SKPFM). The alternate immersion test and potentiodynamic polarization curve test were used to evaluate the corrosion resistance. The results show that Al₆(Fe, Mn) has a higher potential than that of the AA5083 matrix, resulting in the dissolution of the surrounding matrix. The Mg₂Si phase has a lower potential compared to that of the matrix, leading to self-dissolution and dealloying. In addition, the AlFeSi phase has a higher potential and the Mg₂Si phase has a lower potential than that of the AA6061 matrix. Pitting corrosion occurs on the surface of both the AA5083 and AA6061 after the alternate immersion test. Increases in the concentration of Cl⁻ and HSO₃⁻ accelerates the corrosion of the aluminum alloys. The effect of temperature is affected by both the chemical reactivity and passivation ability. In the same conditions, the AA5083 has superior corrosion resistance to that of the AA6061, which is related to the potential difference between the matrix and intermetallic inclusions.

Keywords: aluminum alloys, intermetallic inclusion, Volta potential, corrosion behavior

1. INTRODUCTION

Aluminum alloys are widely used in the shipbuilding industry due to their high strength to weight ratio, superior conductivity and excellent corrosion resistance [1,2]. AA5083 and AA6061 are two
typical kinds of aluminum alloys for ship applications [3–6]. The presence of intermetallic inclusions enhances the mechanical properties of the aluminum alloy, but simultaneously reduces the corrosion resistance. The main types of intermetallic inclusions in the AA5083 are (Fe, Mn)-rich phases and Mg-rich phases [7,8], and the main types of intermetallic inclusions in the AA6061 are (Fe, Si)-rich phases and Mg-rich phases [9,10].

The microstructure of materials is closely related to corrosion behavior. Scanning Kelvin probe force microscopy (SKPFM), as an emerging microscopic approach, has been successfully used in the field of corrosion [11–13]. The measured Volta potential difference in air can be correlated with the OCP measured in liquid [14]. Therefore, SKPFM can be applied to investigate the electrochemical behavior of different metals [15–18]. In recent years, the intermetallic inclusions in the AA2024 and AA7075 have been studied by SKPFM [19–22]. However, the investigation of the intermetallic inclusions in the AA5083 and AA6061 by SKPFM is rarely reported.

Corrosion behavior of the aluminum alloy in seawater is affected by many factors [23–25]. Chloride ions have a strong corrosive effect on metals, which can destroy passive films, and can eventually cause localized corrosion [26]. $\text{HSO}_3^-$ is formed by SO$_2$ dissolved in seawater, which can accelerate the corrosion of aluminum alloys [27,28]. In addition, the temperature is also one of the crucial factors affecting the corrosion behavior of aluminum alloys. It is necessary to study the effects of different factors on the corrosion behaviors of AA5083 and AA6061.

In the present work, the microstructure of the AA5083 and AA6061 and the Volta potential of the intermetallic inclusions are investigated by SEM-BSE and SKPFM. In addition, the effects of Cl$^-$, $\text{HSO}_3^-$ and temperature on the corrosion behaviors of AA5083 and AA6061 are studied by an alternate immersion test and a potentiodynamic polarization curves test.

2. EXPERIMENTS

2.1 Experimental material

The experimental material was the 5083 and 6061 aluminum alloys. The chemical composition (wt.%) of the AA5083 was: Zn 0.01, Mg 4.76, Cr 0.1, Si 0.1, Fe 0.31, Cu 0.026, Mn 0.52, Ti 0.029, and Al balance. The chemical composition (wt.%) of the AA6061 was: Zn 0.012, Mg 1.18, Cr 0.12, Si 0.64, Fe 0.32, Cu 0.25, Mn 0.1, Ti 0.011, and Al balance.

2.2 Morphology and Volta potential analysis

For the microstructural characterization and Volta potential analysis with SEM and AFM, the samples with a size of $\varnothing$10 mm×3 mm were wet ground with SiC papers up to 4000-grit, and then mechanically polished using a 0.5 μm diamond paste. After mechanical polishing, the samples were vibrationally polished again by employing a 0.02 μm paste to remove polishing scratches, followed by sequential cleaning with acetone, deionized water, and anhydrous alcohol.

The surface morphologies of the samples were observed by scanning electron microscopy (FEI
Quanta 250). The local components of intermetallic particles were analyzed by energy-dispersive spectroscopy (EDS). Volta potential images were taken using an atomic force microscope (Burker Multimode 8). All mappings were performed in air at room temperature with relative humidity between 20 and 30% [29]. The AFM used a pyramidal single crystal silicon probe tip coated by conductive PtIr. For Volta potential mapping, the lift scan height was approximately 80 nm. Topography and Volta potentials were scanned with a square area of 20 μm×20 μm and a scan frequency rate of 0.1 Hz.

2.3 Alternate immersion test

The samples with a size of 30 mm×40 mm×3 mm were ground with SiC papers up to 1000 grit for alternate immersion tests. In accordance with ASTM G44 Practice, all the samples were immersed in a solution for a period of 10 min, after which it was exposed to air for 50 min. To study the effect of Cl− concentration, solutions with concentrations of 3.5 wt.%, 5 wt.% and 7 wt.% NaCl were used in the alternate immersion experiment, and the temperature was 25 °C. To study the effect of HSO3− concentration, the solutions were 3.5 wt.% NaCl with 0 M, 0.01 M and 0.02 M NaHSO3, and the temperature was 25 °C. To study the effect of temperature, the immersion experiment was conducted with 3.5 wt.% NaCl solution at 25 °C, 35 °C and 45 °C. The corrosion morphology was observed by stereoscopic microscope.

2.4 Polarization curve test

The samples were machined into a square sheet with dimensions of 10x10x3 mm, and then sequentially wet ground to 2000 grit SiC paper, degreased with alcohol, cleaned in water, and finally dried in cold air. An electrochemical workstation (Autolab, PGSTAT302N) was used to test the polarization curve with a standard three-electrode system, in which a saturated calomel electrode (SCE), a platinum electrode and a sample were used as a reference, counter, and working electrode, respectively. The temperature of the solution was controlled by water bath heating. Potentiodynamic polarization measurements were performed at a scan rate of 0.5 mV/s.

To study the influence of Cl− concentration, the electrochemical test solution was treated with NaCl solution at concentrations of 1 wt.%, 2 wt.%, 3.5 wt.%, 5 wt.%, and 7 wt.%, at a temperature of 25 °C. To study the effect of HSO3− concentration, electrochemical tests were performed in 3.5 wt.% NaCl with 0 M, 0.005 M, 0.01 M, 0.02 M, and 0.05 M NaHSO3 at a temperature of 25 °C. To study the effect of temperature, the tests were conducted in a 3.5% NaCl solution at temperatures of 25 °C, 35 °C, 45 °C, 50 °C, 55 °C, and 65 °C.

3. RESULTS AND DISCUSSION

3.1 Microstructure and Volta potential analysis

Fig. 1(a) shows the SEM-BSE image of 5083 aluminum alloy. AA5083 includes two types of
Intermetallic inclusions, the white phase (e.g., square A) and the grey phase (e.g., square B). The composition of the two types of intermetallic inclusions on squares A and B were analyzed by EDS (Fig. 1(b) and 1(c)). As shown in Fig. 1(b), the intermetallic inclusion in square A mainly contains Al, Fe and Mn and should be Al$_6$(Fe, Mn). As shown in Fig. 1(c), the intermetallic inclusion in square B mainly includes Mg and Si and should be Mg$_2$Si [8].

Figure 1. (a) SEM-BSE image of the AA5083 surface; (b) the EDS result of the intermetallic inclusion in square A; and (c) the EDS result of the intermetallic inclusion in square B.

Fig. 2(a) presents the SEM-BSE image of 6061 aluminum alloy. The main types of intermetallic inclusions are the white phase (e.g., square C) and the grey phase (e.g., square D). The composition of the two types of intermetallic inclusions in squares C and D were analyzed by EDS (Fig. 2(b) and 2(c)). As shown in Fig. 2(b), the intermetallic inclusion in square C mainly contains Al, Fe and Si and should be AlFeSi. As shown in Fig 2(c), the intermetallic inclusion in square D mainly includes Mg and Si and should be Mg$_2$Si [30].

Figure 2. (a) SEM-BSE images of the AA6061 surface; (b) the EDS result of the intermetallic inclusion in square C; and (c) the EDS result of the intermetallic inclusion in square D.
Positioning was performed using a microhardness tester to further investigate the Volta potential using the SKPFM technique. Fig. 3(a) shows the SKPFM image of Al$_6$(Fe, Mn) from square A shown in Fig. 1. The Al$_6$(Fe, Mn) phase is brighter, indicating that the Volta potential of the Al$_6$(Fe, Mn) is higher than the matrix. According to the result of line scanning (Fig. 3(b)), the Volta potential of Al$_6$(Fe, Mn) is approximately 500 mV higher compared to that of the Al matrix, which is similar to the KA’s results [8]. Fig. 3(c) shows the SKPFM image of Mg$_2$Si from square B shown in Fig. 1. According to the results of line-scanning (Fig. 3(d)), the Volta potential of Mg$_2$Si is approximately 100 mV lower than that of the Al matrix.

Figure 3. (a) SKPFM image of Al$_6$(Fe, Mn) from square A shown in Fig. 1; (b) Volta potential line scanning of (a); (c) SKPFM image of the Mg$_2$Si from square B shown in Fig. 1; and (d) Volta potential line scanning of (c).

Figure 4. (a) SKPFM image of AlFeSi from square C shown in Fig. 2; (b) Volta potential line scanning of (a); (c) SKPFM image of Mg$_2$Si from square D shown in Fig. 2; (d) Volta potential line scanning of (c).
Fig. 4(a) presents the SKPFM image of AlFeSi phase from square C in Fig. 2. The AlFeSi phase is brighter, indicating that the Volta potential of the AlFeSi is higher than that of the matrix. According to the result of line scanning (Fig. 4(b)), the Volta potential of AlFeSi is approximately 800 mV higher than that of the Al matrix. Fig. 4(c) shows the SKPFM image of Mg$_2$Si from square D shown in Fig. 2. According to the result of line scanning (Fig. 4(d)), the Volta potential of Mg$_2$Si is approximately 130 mV lower than that of the Al matrix. This result is consistent with the Andreatta’s conclusion [21].

The intermetallic inclusions with higher Volta potential compared to the matrix, such as Al$_6$(Fe, Mn) and AlFeSi, play a cathodic role, resulting in the dissolution of the surrounding matrix. In addition, the intermetallic inclusions with lower Volta potential compared to the matrix, such as Mg$_2$Si, act as an anode, leading to self-dissolution and dealloying. Therefore, the relative difference in the potential between the intermetallic inclusions and the matrix determines the corrosion resistance of the aluminum alloys.

### 3.2 Effect of Cl$^-$ concentration

Fig. 5 shows the effect of different Cl$^-$ concentrations on the corrosion morphology of AA5083 and AA6061 after the alternate immersion test for 30 days. It can be seen from Fig. 5 that the pitting density increases with the increase in Cl$^-$ concentration. When the concentration of NaCl increases to 7 wt.%, the pits gradually expand and partially connect into larger defects. At the same concentration of Cl$^-$, the corrosion area of AA6061 is larger than that of AA5083, indicating that AA5083 has better corrosion resistance than AA6061.

![Figure 5](image_url)

**Figure 5.** Corrosion morphology of aluminum alloys with different concentrations of NaCl after the alternate immersion test for 30 days: (a) AA5083, 3.5%; (b) AA5083, 5%; (c) AA5083, 7%; (d) AA6061, 3.5%; (e) AA6061, 5%; (f) AA6061, 7%.

Fig. 6 shows the potentiodynamic polarization curves of aluminum alloys at different concentrations of Cl$^-$. Aluminum alloy dissolves without the formation of a passive film during the
anodic reaction [31]. The corrosion current density ($I_{\text{corr}}$) and corrosion potential ($E_{\text{corr}}$) are calculated from the intercept of the Tafel slopes tabulated in Table 1. As the Cl$^-$ concentration increases, $E_{\text{corr}}$ decreases and $I_{\text{corr}}$ increases, indicating that the Cl$^-$ increase accelerates the corrosion of aluminum alloys. In addition, at the same Cl$^-$ concentration, the $I_{\text{corr}}$ of AA5083 is smaller than the $I_{\text{corr}}$ of AA 6061, indicating that the corrosion resistance of AA5083 is better than that of AA6061.

![Figure 6. Potentiodynamic polarization curves of aluminum alloys with different concentrations of NaCl: (a) AA5083 and (b) AA6061.](image)

**Table 1.** Electrochemical parameters obtained from the potentiodynamic polarization curves of aluminum alloys with different concentrations of Cl$^-$.  

<table>
<thead>
<tr>
<th>materials</th>
<th>concentration of NaCl/wt.%</th>
<th>$E_{\text{corr}}$/V</th>
<th>$I_{\text{corr}}$/μA·cm$^{-2}$</th>
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<td>-0.697</td>
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<td>0.183</td>
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<tr>
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<td>1.132</td>
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<tr>
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<td>-0.717</td>
<td>3.376</td>
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3.3 Effect of HSO$_3^-$ concentration

Fig. 7 shows the effect of different HSO$_3^-$ concentrations on the corrosion morphology of AA5083 and AA6061 after the alternate immersion test for 30 days. As shown in Fig. 7, pitting corrosion occurs on the surface of the aluminum alloy, and the addition of NaHSO$_3$ leads to an increase in the corrosion area. Meanwhile, the corrosion area increases with increasing NaHSO$_3$ content. Comparing
AA5083 and AA6061, the corrosion degree of AA6061 is more serious than that of AA5083 at the same concentration.

Figure 7. Corrosion morphology of aluminum alloys with different NaHSO$_3$ concentrations after the alternate immersion test for 30 days: (a) AA5083, 0 M; (b) AA5083, 0.01M; (c) AA5083, 0.02M; (d) AA6061, 0 M; (e) AA6061, 0.01M; (f) AA6061, 0.02M.

Fig. 8 shows the potentiodynamic polarization curves of aluminum alloys with different concentrations of NaHSO$_3$. The corrosion current density ($I_{corr}$) and corrosion potential ($E_{corr}$) are calculated from the intercept of the Tafel slopes tabulated in Table 2. As the HSO$_3^-$ concentration increases, $E_{corr}$ slightly changes and $I_{corr}$ increases, indicating that the HSO$_3^-$ increase accelerates the corrosion of the aluminum alloys [32]. Besides, at the same HSO$_3^-$ concentration, the $I_{corr}$ of AA5083 is similar to the $I_{corr}$ of the AA6061, indicating that the corrosion resistance of AA5083 is comparable to that of AA6061 in this environment. The HSO$_3^-$ dissolves in seawater to form an acidic environment, which is damaging to the protective passive film.

Figure 8. Potentiodynamic polarization curves of the aluminum alloys with different HSO$_3^-$ concentrations: (a) AA5083 and (b) AA6061.
Table 2. Electrochemical parameters obtained from the potentiodynamic polarization curves of aluminum alloys with different NaHSO$_3$ concentrations.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Concentration of NaCl/wt.%</th>
<th>Concentration of NaHSO$_3$/mol·L$^{-1}$</th>
<th>$E_{corr}$/V</th>
<th>$I_{corr}$/μA·cm$^{-2}$</th>
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<td>-0.680</td>
<td>46.008</td>
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3.4 Effect of temperature

Fig. 9 shows the effect of different temperatures on the corrosion morphology of AA5083 and AA6061 after the alternate immersion test for 30 days. When the solution temperature is 35$^\circ$C, the metal loses metallic luster. Simultaneously, the number of pits on AA5083 increases, and the pits on AA6061 become larger and connect into larger defects. When the solution temperature increases to 45 $^\circ$C, the surface of the two aluminum alloys is grey, and a small number of white corrosion products are distributed on the surface of AA5083 and AA6061. By comparing Fig.9(c) and Fig. 9(f), the corrosion products of AA6061 are more than those of AA5083.

**Figure 9.** Corrosion morphology of aluminum alloys with different temperatures after the alternate immersion test for 30 days: (a) AA5083, 25 $^\circ$C; (b) AA5083, 35 $^\circ$C; (c) AA5083, 45 $^\circ$C; (d) AA6061, 25 $^\circ$C; (e) AA6061, 35 $^\circ$C; (f) AA6061, 45 $^\circ$C.
Fig. 10 shows the potentiodynamic polarization curves of AA5083 and AA6061 at different temperatures. The electrochemical parameters obtained from the potentiodynamic polarization curves of aluminum alloys at different temperatures are shown in Table 3. As the temperature increases from 25 °C to 45 °C, the corrosion rate gradually increases. The $I_{\text{corr}}$ begins to decrease at 50 °C, and passivation occurs at 55 °C. The reason is that the increase in temperature results in an increase in chemical reactivity. However, the binding ability between the surface of the aluminum alloys and dissolved oxygen improves with increasing temperature, resulting in the improvement of passivation ability and a subsequent decrease in the corrosion rate [33]. Therefore, the corrosion rate is determined by the synergistic effect between the chemical reactivity and passivation ability. At the same temperature, the $I_{\text{corr}}$ of AA6061 is higher than that of AA5083, which indicates that the corrosion resistance of AA5083 is superior to that of AA6061.

![Figure 10. Potentiodynamic polarization curves of the aluminum alloys at different temperatures: (a) AA5083 and (b) AA6061.](image)

**Table 3.** Electrochemical parameters obtained from the potentiodynamic polarization curves of aluminum alloys at different temperatures

<table>
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<th>materials</th>
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4. CONCLUSIONS

The electrochemical character of different intermetallic inclusions in the AA5083 and AA 6061 were investigated by SKPFP. For AA5083, the Volta potential of Al$_6$(Fe, Mn) is approximately 500 mV higher than that of the aluminum matrix, and the Volta potential of Mg$_2$Si is approximately 100 mV lower than that of the matrix. For AA6061, the Volta potential of AlFeSi is approximately 800 mV higher than that of the aluminum matrix, and the Volta potential of Mg$_2$Si is approximately 130 mV lower than that of the matrix. The micro-battery that forms from the potential difference between the intermetallic inclusions and the matrix is an important factor affecting the corrosion resistance of the material.

Pitting corrosion occurred on the surface of both the AA5083 and AA6061 after the alternate immersion test. The increase in Cl$^-$ destroys the formation of a passive film. The addition of HSO$_3^-$ leads to an acidic solution. The increase in the concentration of Cl$^-$ and HSO$_3^-$ accelerates the corrosion of the aluminum alloy. The effect of temperature is affected by both the chemical reactivity and passivation ability. In the same conditions, the AA5083 has superior corrosion resistance to that of AA6061, which is consistent with the results of the SKPFP.

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