Effect of Environmental Conditions on the Corrosion near Shear Cut Edge of 55 mass% Al–Zn Alloy Coated Steel Sheets

Masamitsu MATSUMOTO,1) Nobuhiro OKADA,1) Katsuhiro NISHIHARA,1) Masanari KIMOTO,1) Takeo KUDO,1,2) and Shinji FUJIMOTO3)

1) Corporate Research and Development Laboratories, Sumitomo Metal Industries, Ltd., 1-8 Fuso-cho, Amagasaki, Hyogo 660-0891 Japan. 2) Graduate School of Engineering, University of Hyogo, 2167 Shosha, Himeji, Hyogo 671-2280 Japan. 3) Department of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871 Japan.

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The purpose of this study is to clarify the effect of dry and wet processes on the mechanisms of edge corrosion of hot dip 55 mass% Al–Zn alloy coated steel sheet. The corrosion tests employed were continuous salt-spray tests and cyclic corrosion tests using NaCl solution or artificial seawater. It was confirmed that the edge corrosion is suppressed during the salt-spray test using artificial seawater. Furthermore, the suppression was not prevented by dry and wet processes. In order to reveal the corrosion mechanisms, the galvanic current and the cathodic polarization curves at exposed steel were measured and the corrosion products were characterized. It is suggested that the artificial seawater forms anti-corrosive corrosion products and that suppress the cathodic reaction on the steel which is exposed on the shear cut edge. The corrosion products are not changed by dry and wet processes. The numerical analysis also revealed the influence of the dry and wet process on edge corrosion.

KEY WORDS: 55 mass% Al–Zn alloy coated steel sheet; edge corrosion; artificial seawater; salt-spray test; dry and wet processes; numerical analysis; X-ray diffractometry (XRD); Fourier transform infrared spectroscopy (FTIR)

I. Introduction

Hot dip 55 mass% Al–Zn coated steel sheets are widely used for roofs and walls of buildings, and for parts of home appliances because of their superior corrosion resistance. The building materials are processed by roll-forming, pressing or punching. Therefore, the edges of sheets are exposed to the atmosphere. Long term outdoor exposure tests, however, indicate that the anti-corrosion durability of the coating near the shear cut edge is sufficient, and is the same as that of the flat portion far from the edge.1–3) In recent years, the Al–Zn coated steel sheets have been more widely applied due to their tough durability. In accordance with their expanding application area, the performance under severe test conditions far from the actual environment has been requested. One such severe test is the salt-spray test standardized in ISO 9227. In the salt-spray test, the corrosion rate of the coating near the shear cut edge is remarkably large, and iron rust appears near the shear cut edge. This result is, however, quite different from that in an outdoor exposure test.4) Therefore, many kinds of corrosion testing methods have been proposed for automotive materials.5,6) Furthermore, the detailed corrosion mechanisms have been discussed.7) These studies revealed the corrosion depth of steel in hemming and lapped portions and the mechanisms to form blisters from defects of polymer coating. However, the mechanisms of edge corrosion of 55% Al–Zn coating have not been clarified.

The materials for buildings and the parts of home appliances have been assessed by outdoor exposure tests as mentioned above. The corrosion products of 55% Al–Zn coating after outdoor exposure tests have been characterized9) but the effects of corrosion products on the corrosion process have not been sufficiently understood. Furthermore, for 55% Al–Zn coating, the swift testing method is required to evaluate durability in real conditions. A testing method including dry and wet processes in addition to salt-spraying process has been proposed by Sakamoto et al.10) Furthermore, Nishikata et al. discussed the corrosion mechanisms of 55% Al–Zn coating in dry and wet test using NaCl solution by means of a monitoring method.11) The atmospheric corrosion test environment contains exposure to solution of not only NaCl but also various salts. Therefore, various testing methods using artificial seawater have been proposed in order to simulate atmospheric corrosion.12) One of the corrosion testing methods using artificial
seawater was standardized in ISO 16151. In order to consider the corrosion under a thin water film, Shinohara et al. discussed the relationship between thickness and chemical contents of the water film which is formed by moisture adsorption. There are, however, only a few reports to describe the effects of artificial seawater on edge corrosion.

Prior to the present work, we studied the edge corrosion of 55% Al–Zn coating in NaCl salt-spray test. We revealed that the corrosion rate of the coating near the shear cut edge is significantly large, and that the corrosion is accelerated by the galvanic action; the cathode is iron exposed at the edge and the anode is Al–Zn coating near the exposed iron. We also revealed that the corrosion of the coating near the cut edge is mainly controlled by oxygen reduction on iron exposed at the edge. In order to reveal the difference in corrosion mechanisms between what happens in NaCl solution and what happens in artificial seawater, the salt-spray test using artificial seawater was also carried out. We confirmed that Mg$^{2+}$, which modifies the corrosion products on iron, suppresses the cathodic reaction.

The aim of this study is to reveal the effects of dry and wet processes and artificial seawater on the corrosion behavior of 55 mass% Al–Zn coating near the shear cut edge. The role of corrosion products is clarified by the electrochemical measurements, then verified with numerical analysis and characterization of corrosion products, with consideration of the cathodic reaction at iron exposed at the edge.

2. Material and Methods

2.1. Specimens

A cold rolled carbon steel sheet was galvanized with 55 mass% Al–Zn alloy by commercial continuous-galvanizing line, CGL, with the coating weight of 150 g m$^{-2}$ on both sides. Surface finish such as chromate coating, chrome-free coating or phosphate coating was not applied for any specimen. After cutting into 70×150 mm sheet by shearing, (a) flat panel specimens and (b) galvanic specimens were prepared as shown in Fig. 1. The four edges and the back of the specimens were covered with polyester adhesive tape. In order to prepare specimens for simulating galvanic corrosion near the shear cut edge, the coating is removed mechanically to expose substrate steel along the center axis of longitudinal direction, with the cut width of $x=10$ mm as shown in Fig. 1(b), which corresponds to the thickness of steel sheet at the cut edge. The width of $x=10$ mm which is larger than actual thickness of steel sheet, contributes to reducing the test period as described in the previous paper and is within the range of galvanic action during a salt-spray test using 5% NaCl solution.

A galvanic couple electrode composed of Fe and Al–Zn alloy (AZ) was also prepared as shown in Fig. 2. The AZ electrode was made of 55% Al–Zn alloy block, and the Fe electrode was made of the cold rolled steel sheet which is used for the substrate of the AZ coated steel sheet. The two electrodes were connected with lead wires, and were placed with a clearance of 50 μm so as to be electrically isolated from each other, then mounted in epoxy resin. Finally, the galvanic couple electrode was wet polished with #2000 emery paper. The electrode width of $x=5$ mm for Fe is consistent as half size of the galvanic specimen and also with the numerical model described later.

2.2. Corrosion Tests

Salt-spray tests (SST) and cyclic-corrosion tests (CCT) were carried out using 5% NaCl aqueous solution ([Na$^+$]=0.85 M, [Cl$^-$]=0.85 M) or artificial seawater (ASW). The SST is in accordance with ISO 9227; the temperature of the solution for the spray is 35°C. The CCT is carried out in accordance with ISO 14993; the cyclic corrosion test consists of the salt-spraying process for 2 h, the dry process at 60°C for 4 h and the wet process at 50°C with relative humidity of 95% for 2 h. The ASW is prepared in accordance with ISO 11130; [Na$^+$]=0.48 M, [Mg$^{2+}$]=0.055 M, [K$^+$]=0.010 M, [Ca$^{2+}$]=0.010 M, [Cl$^-$]=0.56 M, [SO$^{4-}_4$]=0.029 M, [HCO$_3^-$]=0.0024 M and the other ions with pH adjusted at 8.2.

The specimens and the galvanic couple electrodes were placed at 15 degrees to the vertical in the testing chamber.

2.3. Evaluation Methods

2.3.1. Time to Formation of Iron Rust

The evaluation of the corrosion rate for the galvanic specimens was described in detail in the previous report. The time when the iron rust started to propagate over the
coating from the edge of the sheet was evaluated. The iron rust on the exposed steel is not discussed in this study.

2.3.2. Galvanic Current

The galvanic current between AZ and Fe electrode was continuously measured by zero-shunt ammeter (HM-102, Hokuto Denko Co.). The test period of measurement was 24 h and 120 h. A polarization curve was also measured immediately after measurement of the galvanic current.

2.3.3. Polarization Curve

Before measurement of the polarization curves of Fe and AZ, the galvanic couple electrodes were exposed to the corrosion environment (CCT or SST). During exposure, the lead wires of the galvanic couple electrodes were connected to each other. After exposure, the electrodes were immediately immersed in the electrochemical cell filled with the same solution used for the exposure test, disconnecting the lead wires between Fe and AZ. The cathodic polarization curve of Fe, then anodic polarization curve of AZ electrode were measured. The test solution was kept at 35°C and was stirred continuously with air bubbling to make the thickness of oxygen diffusion layer constant during measurement. The constancy of the thickness of diffusion layer was confirmed by measuring the diffusion limited current density of the oxygen reduction on pure copper in the same testing solution. The diffusion current density for the oxygen reduction during stirring is larger than when not stirring. Although the diffusion limited current density for the oxygen reduction is often measured using Pt, we have confirmed that the diffusion limiting current density for the oxygen reduction using pure copper is the same as that using Pt and we have adopted the pure copper. A carbon electrode and a saturated calomel electrode (SCE) were used as a counter electrode and as a reference electrode, respectively. The saturated calomel electrode (SCE) were used as a counter electrode and as a reference electrode, respectively. The measuring conditions are as follows: immersion for 600 s, then potentiodynamic polarization with the scanning rate of 1.0 mV s⁻¹ from the open circuit potential.

2.3.4. Numerical Analysis

Numerical analysis was performed to simulate the galvanic current during the corrosion tests. The governing equation of galvanic corrosion is as follows:

\[
\nabla \cdot \mathbf{J} = \nabla \cdot (-\sigma \nabla \phi) = 0 \quad \text{(1)}
\]

where \( \mathbf{J} \) is the current density vector, \( \phi \) is the potential and \( \sigma \) is the electric conductivity. The following assumptions and simplifications are made in this model.

1. Cathodic current density depends on oxygen flux and does not depend on potential.
2. Oxygen is saturated at the surface of the electrolyte and becomes zero on the metal surface because it is consumed by cathodic reaction.
3. Anodic current density is represented by a Tafel equation.

As described above, the potential and the current density distributions in the electrolyte are computed by solving Eq. (1), subjected to the following boundary conditions:

\[
\mathbf{J} = \mathbf{J}_a - \mathbf{J}_c \quad \text{at the metal surface} \quad \text{(2)}
\]

\[ \mathbf{J} = 0 \quad \text{at the electrolyte surface and the symmetry boundary} \quad \text{(3)} \]

where \( \mathbf{J}_a \) is the anodic current density and \( \mathbf{J}_c \) is the cathodic current density. In this model, the polarization curve is given by a simple model. The anodic current density is represented by Eq. (4) and the cathodic current density is decided by oxygen flux. Here, \( R \) is the gas constant and \( T \) is the absolute temperature, and \( J_{a0}, \alpha, \phi_f, \alpha_F \) and \( \alpha_F \) are constants that depend on the electrolyte and metals. We used \( \alpha_F=1.2, \alpha_F=0.38, \alpha_F=0.25 \text{ (A m}^{-2} \text{)} \) and \( J_{a0}=0.18 \text{ (A m}^{-2} \text{)} \), these values being fitted from the experimentally obtained polarization curves in 5% NaCl solution. It was assumed that the corrosion potential \( \phi_f \) depends on the activity of NaCl. Therefore, we used Eqs. (4)–(7) where \( \gamma \) is the activity coefficient, \( m \) is the mole per kilogram and \( \Lambda \) is the constant value of 0.130 for NaCl.

\[
\mathbf{J}_a = J_{a0} \exp \left( \left( \phi - \phi_f \right) \frac{\gamma m F}{RT} \right) \quad \text{(4)}
\]

\[
\phi_f = 0.059 \log(\gamma m) - 0.5105 \quad \text{(5)}
\]

\[
\phi_f = -0.059 \log(\gamma m) - 1.0242 \quad \text{(6)}
\]

\[
\log \gamma = -0.5115 \sqrt{m} / (1 + \sqrt{m}) + \Lambda m \quad \text{(7)}
\]

2.3.5. Analysis for Corrosion Products

The corrosion products formed on the Fe surface of the galvanic specimens were scraped off with a micro spatula made of stainless steel, then ground into powder specimens with a pestle and mortar made of agate. The powdered corrosion products were analyzed by Fourier transform infrared (FTIR) spectroscopy and X-ray diffractometry (XRD).

With Fourier transform infrared spectroscopy it is possible to identify non-crystalline substances as well as crystalline substances. In order to identify non-crystalline substances, reference specimens that are ZnO, ZnCl₂, 4Zn(OH)₂, 22ZnCO₃, 3Zn(OH)₂, Zn₆Al₆(OH)₁₆CO₃·4H₂O, Mg(OH)₂ and CaCO₃ were adopted. These components were purchased or synthesized in our laboratory, and were verified to be pure substances by X-ray probe micro-analysis (EPMA) and XRD.

3. Results

3.1. Corrosion Tests

The salt-spray test (SST) and the cyclic-corrosion test (CCT) using NaCl solution or artificial seawater (ASW) were carried out. Figure 3 shows appearances of specimens after 480 h of corrosion tests. Iron rust did not appear on the flat panel specimens during any corrosion tests. For the galvanic specimens, iron rust started to propagate over the coating from the edge of the Fe exposed during the corrosion tests using NaCl. During the corrosion tests using ASW on the other hand, iron rust did not start from the edge.

In order to evaluate the corrosion of the galvanic specimen, the starting time of iron rust propagation was measured. As shown in Fig. 4, the time to iron rust appearance...
The time to iron rust appearance in the corrosion tests using ASW was more than 1300 h. The time to iron rust appearance in the corrosion tests using NaCl was 200 h, and that in the SST using NaCl was 400 h, and that in the CCT using ASW was more than 800 h. The larger time to iron rust appearance was also observed for the CCT using ASW than that using NaCl. It is noticeable that the test time, \( t \), of the CCT includes the salt-spraying, the dry and the wet processes.

### 3.2. Galvanic Current

The galvanic current between AZ and Fe of the galvanic couple electrode was measured during the SST and the CCT using NaCl or ASW. As shown in Fig. 5(a), the galvanic currents during the SST using ASW and NaCl are 50–100 µA and 150–250 µA, respectively. Therefore, it is clarified that the galvanic current during corrosion test using ASW is smaller than that using NaCl. During the ‘drying’ period which is for 20 min from the onset of the dry process, the thickness of water film may decrease. The mechanism of the increase in the galvanic current will be discussed later. After 60 min from the onset of the dry process, the galvanic current became negligible. After the onset of the wet process which succeeded the dry process, the galvanic current increased for about 20 min (e.g. \( t = 1560–1580 \) min), then decreased rapidly for about 40 min (\( t = 1580–1620 \) min). During the ‘drying’ period which is for 20 min from the onset of the dry process, the thickness of water film may decrease. The mechanism of the increase in the galvanic current will be discussed later. After 60 min from the onset of the dry process, the galvanic current became negligible. After the onset of the wet process which succeeded the dry process, the galvanic current increased for about 20 min (\( t = 1800–1820 \) min). During the ‘wetting’ period which is for 20 min from the onset of the wet process, the thickness of water film may increase by moisture adsorption to salts. Then, the galvanic current decreased gradually.

During the dry process in the CCT using ASW, the galvanic current increased once, then decreased gradually to the point where it became negligible. Then, the galvanic current increased for about 20 min (e.g. \( t = 1560–1580 \) min), then decreased rapidly for about 40 min (\( t = 1580–1620 \) min). The mechanism of the increase in the galvanic current will be discussed later. After 60 min from the onset of the dry process, the galvanic current became negligible. After the onset of the wet process which succeeded the dry process, the galvanic current increased for about 20 min (\( t = 1800–1820 \) min). During the ‘wetting’ period which is for 20 min from the onset of the wet process, the thickness of water film may increase by moisture adsorption to salts. Then, the galvanic current decreased gradually.

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current increased for 20 min from the onset of the wet process. Once again, the galvanic current decreased to the point where it became same as the current during the salt-spraying process. Such behavior of the galvanic current is similar to that during the CCT using NaCl. In addition, the galvanic current during the CCT using ASW was smaller than NaCl throughout the process. The mechanism of the increase and decrease in the galvanic current during the ‘drying’ and ‘wetting’ period will be discussed later.

The monitoring of current was continued until \( t = 7200 \text{ min} \). It was revealed that the behavior of the galvanic current did not change during the monitoring period.

4. Discussion

4.1. Suppression of Cathodic Reaction in the Tests Using ASW

It is observed that corrosion rate of 55 mass% Al–Zn coating near the shear cut edge in the SST using ASW is smaller than that using NaCl solution. As shown in Fig. 4, the smaller corrosion rate in the corrosion tests using ASW was confirmed not only in the SST but also in the CCT. Additionally, as shown in Fig. 5, the galvanic current during the corrosion tests using ASW is smaller than that using NaCl. In order to discuss the reduced corrosion rate during the corrosion tests using ASW, we measured polarization curves. The appearances of the galvanic couple electrodes after corrosion tests are shown in Fig. 6. The appearances are similar to that of the galvanic specimens after corrosion tests. The polarization curves obtained for the SST were already published in a previous report.17 In the present paper, these results were described again for comparison with those obtained for CCT.

Figures 7(a) and 7(b) show the polarization curves before and after the SST using NaCl and ASW, respectively. As shown in Fig. 7(a), the cathodic polarization curve of Fe in NaCl solution indicates the diffusion limited current density for the oxygen reduction within the potential range of \(-0.7 \text{ to } -1.0 \text{ V}_{\text{SCE}}\). This current density corresponds to that for the oxygen reduction on pure copper in NaCl solution. The cathodic polarization curves of Fe employed for the galvanic couple electrode revealed that the current density after 24 h or 120 h of the SST increased with decreasing potential in the range of \(-0.7 \text{ to } -1.0 \text{ V}_{\text{SCE}}\). This suggests that the reduction of iron rust formed on the Fe electrode increase cathodic current.18 The change in the rest potential of the Fe electrode before and after the SST was small. The rest potential of the AZ electrodes shifted in less noble direction after the SST. However, the reason for the shift in less noble direction is not clear.

As shown in Fig 7(b), the cathodic polarization curves of Fe in ASW before and after 24 h and 120 h of the SST also indicate the diffusion limited current densities within the potential range of \(-0.7 \text{ to } -1.0 \text{ V}_{\text{SCE}}\). The diffusion limited current density for the oxygen reduction on Fe is less than that on pure copper in ASW. The smaller diffusion limited current densities observed after SST was more obvious for the results obtained after 24 h and 120 h. This suggests that corrosion products which work as the barrier against oxygen diffusion are formed on the Fe electrode. In addition, the barrier does not significantly change the rest potential of the Fe electrode before and after SST. The change in the rest potential of AZ electrodes before and after SST is also small.

The corrosion current density which is estimated as the intersection of the anodic polarization curve of AZ and the cathodic polarization curve of Fe in SST using ASW is smaller than that using NaCl solution. The corrosion current density in SST using ASW and that using NaCl qualitatively corresponds to the galvanic current in SST using ASW and that using NaCl described in Fig. 5(a), respectively. We have reported that Mg(OH)\(_2\) formed on Fe during the SST using MgCl\(_2\) solution and that Mg(OH)\(_2\) works as the barrier for oxygen diffusion. Similarly, we suggested that the corrosion products formed on Fe during SST contained cations that were included in ASW used for the SST. The corrosion products worked as the barrier for oxygen diffusion.14 Namely, such corrosion products suppress the cathodic reaction. Consequently, the corrosion of the 55% Al–Zn coating near the shear cut edge is suppressed.

Similar results were also obtained for CCT. Figures 8(a) and 8(b) show the polarization curves before and after the CCT using NaCl and ASW, the CCT consists of the dry and wet processes and the salt-spraying process. As shown in Fig. 8(a), the cathodic current on the Fe employed for the galvanic couple electrode within the potential range of \(-0.7 \text{ to } -1.0 \text{ V}_{\text{SCE}}\) measured after 24 h or 120 h of the CCT using NaCl were larger than the diffusion limited current density for the oxygen reduction on pure copper in NaCl solution. On the other hand, the cathodic current in the polarization curve of Fe employed for the galvanic couple electrode within the potential range of \(-0.7 \text{ to } -1.0 \text{ V}_{\text{SCE}}\) measured after 24 h or 120 h of the CCT using
ASW was smaller than the oxygen reduction on pure copper in ASW. Similar results are also obtained for SST. It is suggested that corrosion products which work as the barrier against oxygen diffusion are formed on the Fe electrode during the corrosion test using ASW. Furthermore, the barrier is maintained after the dry and wet processes. In addition, the barrier does not significantly change the rest potential before and after the CCT.

As mentioned above, the cathodic current density on Fe electrode is suppressed after the corrosion tests using ASW because of the formation of corrosion products. It is worthwhile to characterize the chemical content and the physical structure of the corrosion products on Fe electrode. Table 1 shows the chemical content of corrosion products analyzed by energy dispersive X-ray spectroscopy, EDS. The corrosion products on Fe after SST and CCT using NaCl contain Fe, Zn, Al, Si, Na and Cl. The corrosion products on Fe after SST and CCT using ASW, on the other hand, contain Zn, Mg and Ca. Figure 9 shows the result of identification of crystalline structure of corrosion products by XRD. Alpha-FeOOH, γ-FeOOH and Fe₃O₄ were identified in the iron rust after the SST using NaCl. After the CCT using NaCl, on the other hand, Zn₆Al₂(OH)₁₆CO₃·4H₂O and NaZn₆(SO₄)(OH)₁₀Cl·6H₂O.

Results of characterization of corrosion products described above are summarized in Table 2. The corrosion products formed on Fe during the corrosion tests using ASW were CaCO₃, Zn₆Al₂(OH)₁₆CO₃·4H₂O and NaZn₆(SO₄)(OH)₁₀Cl·6H₂O. Leygraf et al. reported that NaZn₆(SO₄)(OH)₁₀Cl·6H₂O appears as the most stable corrosion product on Zn exposed in a marine environment. Furthermore, it is widely known that the ‘electro-coating’, a film which consists of CaCO₃ and Mg(OH)₂, is formed on steels that are subjected to a cathodic current in seawater or river-water, because of the increasing pH in the electrolyte adjacent to the steel surface. CaCO₃ and Mg(OH)₂ on Fe exposed at the shear cut confirmed in our study is formed by a similar process. It is found for the first time that such film is formed by galvanic corrosion at the edge of coated steel sheets without external cathodic current. Such films were formed on Fe as a result of pH increase by oxygen reduction which arises as the cathodic reaction of galvanic corrosion. The film controls diffusion of oxygen, resulting in suppression of the cathodic reaction on Fe substrate. Consequently, the corrosion of the coating near the shear cut edge is suppressed significantly.

It is suggested that NaCl and ASW used in corrosion tests, significantly affect the structure of corrosion products. However, the influence of the dry and wet processes is small.

### 4.2. Effect of Drying and Wetting Period

The measurement of the galvanic current revealed that the galvanic current increased, and then decreased after the

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**Table 1.** Elemental components of the corrosion products on Fe coupled with AZ after various corrosion tests (120h).

<table>
<thead>
<tr>
<th></th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>Cl</th>
<th>K</th>
<th>Ca</th>
<th>Fe</th>
<th>Zn</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl SST</td>
<td>1.2</td>
<td>2.4</td>
<td>0.4</td>
<td>2.4</td>
<td>90.0</td>
<td>3.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCT</td>
<td>4.3</td>
<td>8.0</td>
<td>1.7</td>
<td>1.7</td>
<td>75.5</td>
<td>10.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASW SST</td>
<td>11.0</td>
<td>4.1</td>
<td>1.5</td>
<td>1.2</td>
<td>1.5</td>
<td>46.3</td>
<td>7.7</td>
<td>24.4</td>
<td>2.2</td>
<td>9.5</td>
</tr>
<tr>
<td>CCT</td>
<td>0.9</td>
<td>33.1</td>
<td>7.0</td>
<td>0.3</td>
<td>1.8</td>
<td>3.0</td>
<td>9.5</td>
<td>28.3</td>
<td>16.2</td>
<td></td>
</tr>
</tbody>
</table>

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**Fig. 8.** Polarization curves of Fe coupled with AZ after NaCl CCT (a), ASW CCT (b).

**Table 2.** Corrosion products on Fe coupled with AZ after various corrosion tests (120h).

<table>
<thead>
<tr>
<th></th>
<th>NaCl</th>
<th>SST</th>
<th>CCT</th>
<th>ASW</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-FeOOH</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>γ-FeOOH</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Zn₆Al₂(OH)₁₆CO₃·4H₂O</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>NaZn₆(SO₄)(OH)₁₀Cl·6H₂O</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Mg(OH)₂</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

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onset of the dry and wet processes. This behavior is caused by the changes in the thickness and concentration of the water film. Therefore, we tried to calculate the change of the galvanic current.

In our calculation model, it is assumed that the Zn electrode (the width is 10 mm) and the Fe electrode (the width is 5 mm) are connected and water film containing 5 mass% NaCl ([Cl\textsuperscript{-}] = 0.85 M) covers them. The thickness of the water film during the SST is assumed to be \( d = 100 \mu m \) based on the measurement of the weight. In the ‘drying’ period, \( \text{H}_2\text{O} \), which is a solvent of NaCl solution, is assumed to vaporize at a constant rate. Therefore, the concentration of NaCl increases monotonously (\( (C_{\text{NaCl}}) = 1/d \)). The electric conductivity of water film, \( \sigma \), is given by Eq. (8) as a function of \( C_{\text{NaCl}} \) and the concentration of oxygen, \( C_{\text{O}_2} \), is provided by Eq. (9), which describes the salting-out effect.

\[
\sigma = F^2 \sum_{i=1}^{n} z_i^2 u_i c_i \quad \text{(8)}
\]

where \( F \) is Faraday constant, \( z_i, u_i \), and \( c_i \) are the valence number, the mobility, and the concentration of ion \( i \), respectively. Concentration of dissolved oxygen \( C_{\text{O}_2} \) is given by the following equation, as a function of absolute temperature, \( T \), and concentration of NaCl, \( C_{\text{NaCl}} \):

\[
C_{\text{O}_2}(T, C_{\text{NaCl}}) = 8.18 \times 10^{-2} \exp(1.92 \times 10^{-2} T) \cdot 10^{-k_{\text{sal}} C_{\text{NaCl}}} \quad \text{(9)}
\]

where \( k_{\text{sal}} \) is the coefficient of salting-out, \( k_{\text{sal}} = 0.139 \) for NaCl.\(^{21}\) In addition, the cathodic current density is induced by the reaction of oxygen reduction as shown in Eq. (10), the rate of which is proportional to the oxygen flux, \( N_{\text{O}_2} \), as shown in Eq. (11), and is independent of potential.

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \quad \text{(10)}
\]

\[
J_e = 4F N_{\text{O}_2} \quad \text{(11)}
\]

The current density distributions in the water films of various thicknesses were calculated with the conditions described above. Here, the changes in the properties of corrosion products and the composition of electrolyte are not considered but they are assumed to be stable. The metal surfaces are assumed to be active and the change of the distributions of current densities is not considered.

**Figure 10** shows the calculated distribution of current as a function of lateral position. The cathodic current density was independent of position based on the presumed condition and the minimum of 1.177 A m\(^{-2}\) is obtained for the water film of 100 \( \mu m \) in thickness. As the thickness of water film decreased, the cathodic current density increased, reached a maximum, and then decreased. The increase in the current density is due to decrease in the diffusion path of oxygen. On the other hand, as shown in Eq. (9), concentration of oxygen decreases with increasing salt concentration. Therefore, decreasing the thickness of water film gives the more concentration of NaCl which decreases oxygen concentration, resulting in a decrease in the cathodic current. In other words, a maximum of cathodic current appears due to a balance of increasing oxygen flux by decreasing diffusion path and decreasing oxygen content. The maximum current density was 1.979 A m\(^{-2}\) at 25 \( \mu m \) thickness of the water film. As the water film thickness becomes thinner, the cathodic current density decreases because of the decrease in oxygen concentration, and it reaches saturation at NaCl at 17.8 \( \mu m \) in thickness. This indicates that the cathodic current density increases 1.68 (= 1.979/1.177) times in the drying period.

On the other hand, the anodic current density revealed the maximum on Zn at the interface of Fe/Zn for all thicknesses of water film considered. The anodic current densities were 4.050 A m\(^{-2}\) at 100 \( \mu m \) thickness of water film and 8.906 A m\(^{-2}\) at 25 \( \mu m \), indicating that the anodic current density is accelerated by a factor of 2.20 (= 8.906/4.050) during the drying period. As the thickness of water film decreases, the anodic current density decreases.

The galvanic current calculated by the integral of the current density is shown in Fig. 10. **Figure 11** shows the estimated galvanic current for the galvanic couple electrode as a function of thickness of water film. The galvanic current increases 1.68 times with the decrease in the thickness of water film from 100 to 25 \( \mu m \); the further decrease in the thickness results in the decrease in the galvanic current. This change in the galvanic current estimated by the calculation corresponds quantitatively to that of the galvanic current measured in the drying period shown in Fig. 5(b). This quantitative correspondence indicates that the properties of corrosion products and electrolyte containing NaCl used for the corrosion tests do not affect suppression of the corrosion of the coating near the shear cut edge.

The water film is saturated with NaCl when the thickness decreases into less than 17.8 \( \mu m \). Nishikata et al. discussed...
the fact that the rate of oxygen reduction is limited by dissolution rate of oxygen at the interface of gas and liquid when the thickness of water film is less than 10 μm. The dissolution rate of oxygen into the saturated NaCl solution (5.4 M, \( v_{\text{O}_2} \)) is \( 6.8 \times 10^{-8} \text{mol m}^{-2} \text{s}^{-1} \), which corresponds to the cathodic current density of 2.632 A m\(^{-2}\). As the thickness of the water film containing 5 mass% NaCl is assumed to 100 μm, it is hardly conceivable that the cathodic current density becomes more than 2.632 A m\(^{-2}\) after drying and saturating. The maximum of cathodic current density at the thickness of water film of 100 μm is 2.236 (=2.632/1.177) times larger than that predicted for a water film of 100 μm in thickness.

As described above, anodic and cathodic current densities during the drying periods were estimated by numerical analysis and the galvanic current that is also estimated numerically corresponded to the measurement. The relationship between current densities and the thickness of water film during the wetting period is assumed to be similar to that during the drying period.

Corrosion loss of the Zn coating during the SST and the CCT corresponds to the integral of cathodic current densities. In the CCT, the periods of salt-spraying, drying, dry, wetting and wet are \( r=0–2 \text{ h}, 2–3 \text{ h}, 3–5 \text{ h}, 6–7 \text{ h} \) and \( 7–8 \text{ h} \), respectively. The ratio of the amount of corrosion of coating during the CCT to the SST, \( Q_{\text{CCT}}/Q_{\text{SST}} \), is given to be 0.77 (<1) by Eq. (12).

\[
0.77 = \frac{\int_{t=0}^{2h} j_{c, \text{salt-spraying}} \, dt + \int_{t=2h}^{3h} j_{c, \text{drying}} \, dt + \int_{t=3h}^{5h} j_{c, \text{dry}} \, dt + \int_{t=6h}^{7h} j_{c, \text{wetting}} \, dt + \int_{t=7h}^{8h} j_{c, \text{wetting}} \, dt}{\int_{t=0}^{8h} j_{c, \text{SST}} \, dt}
\] ....(12)

This suggests that the influence of the dry and wet process on the corrosion of coating is small although the cathodic current density during the drying period is around twice as large as that during the salt-spraying period.

The numerical analysis in the present work, is achieved with the following condition; coating material is Zn instead of AZ, electrolyte is NaCl solution, and effects of corrosion products are not considered. The results of numerical analysis using Zn well correspond to the measurement shown in Fig. 5(b), and also support the conclusion of our previous report\(^4\). The corrosion of 55% Al–Zn coating near the shear cut edge is supported by the numerical analysis, the measurement for galvanic current and the measurement of corrosion products. On the other hand, ASW used for the CCT and the SST suppresses the galvanic current because the corrosion products act as a barrier against oxygen diffusion to depress the cathodic reaction. Furthermore, the effect is not hindered during the dry and wet process.

Our numerical analysis has not demonstrated the corrosion current during the corrosion tests using ASW, which are necessary for consideration of the role of ions in ASW and for clarifying the chemical and the physical properties of the corrosion products, that will be future work.

5. Conclusions

In order to clarify the corrosion mechanisms near the shear cut edge of hot dip 55 mass% Al–Zn coated steel sheet, the effect of testing conditions which includes the dry and wet processes and salts used for test solutions were investigated based on exposure tests and numerical modeling. The following conclusions were derived.

(1) The corrosion of the coating near the shear cut edge is significantly suppressed in the corrosion tests using artificial seawater compared with tests using NaCl. It is confirmed that the galvanic current of AZ/Fe galvanic couple electrodes is suppressed during the corrosion tests, when artificial seawater was used for test solution. The suppression of the galvanic current in artificial seawater is not hindered during the dry and wet process.

(2) The suppression of galvanic current during the corrosion tests by using artificial seawater is due to the formation of corrosion products on Fe exposed at the cut edge, because the corrosion products act as barrier to oxygen diffusion. The barrier action of corrosion products to oxygen diffusion in the corrosion tests is retained for the dry and wet process.

(3) The corrosion products on Fe formed during the corrosion tests using artificial seawater are Na\(_2\)Zn\(_6\)(SO\(_4\))\(_6\)(OH)\(_6\).Cl\(_{3}\).6H\(_2\)O, 2ZnCO\(_3\)·3Zn(OH)\(_2\), Zn\(_6\)Al\(_2\)(OH)\(_{16}\)CO\(_3\)·4H\(_2\)O, CaCO\(_3\) and Mg(OH)\(_2\). On the other hand, the corrosion products obtained after identical tests using NaCl are \( \alpha \)-FeOOH, \( \gamma \)-FeOOH, Fe\(_2\)O\(_3\) and Zn\(_6\)Al\(_2\)(OH)\(_{16}\)CO\(_3\)·4H\(_2\)O. Corrosion products with similar structure are obtained in the corrosion test including the dry and wet process.

(4) The distribution of the anodic and cathodic current density during the drying and wetting period is estimated by numerical analysis and the corrosion during the SST and the CCT are also estimated. The influence of the dry and wet process on the corrosion for coating is small although the cathodic current density during the drying period is around twice as large as that during the salt-spraying period.

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