Corrosion Monitoring of Zn and Zn–Al Coated Steels under Wet-Dry Cyclic Conditions Using AC Impedance Method

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AC impedance method has been applied to evaluate the performance of Zn, Zn–5%Al and Zn–55%Al coated steels under wet-dry cycles. The wet-dry cycles were carried out by exposure to the alternate conditions of 1 h-immersion in a 0.5 or a 0.05 kmol/m³ NaCl solution and drying for various times at 298 K and 60%RH. The impedances at two frequency points, a high frequency (10 kHz) and a low frequency (10 mHz), were monitored during the cyclic wet-dry exposure. The reciprocals of the high frequency and low frequency impedances were taken as the solution conductance of water layer on the coating surface and the corrosion rate of the coated steels, respectively. The impedance monitoring results showed that the Zn–55%Al coating exhibited the most excellent corrosion resistance under the given conditions. This is attributed to the formation of aluminum oxide on the specimen surface. On the other hand, the corrosion resistances of Zn coated and Zn–5%Al coated steels were almost the same under relatively wet and highly chloride-concentrated conditions. An increase in the chloride concentration of the test solution employed during the wet-dry cyclic test decreased the average corrosion rate in all cases. The average corrosion rate of the Zn–55%Al coating under a wet-dry cyclic condition in 0.5 kmol/m³ NaCl solution was lower than that in 0.05 kmol/m³ NaCl by one order of magnitude. The combined wet-dry cyclic exposure test and AC impedance corrosion monitoring is very useful for the mechanistic study of the corrosion of coated steels, as well as the evaluation of their corrosion performance, in marine atmospheric environments.

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I. Introduction

Atmospheric corrosion is a complex process involving interactions between a dynamic atmosphere and a metallic substrate. There are many factors which determine the corrosion rate, for example, the "Time-of-wetness" of the metal surface, the atmospheric contaminants (SO₂, NOₓ, Cl⁻, etc.), and the condition of exposure (open air, sheltered exposures, etc.). Therefore, the variability of the environment makes the study of the atmospheric corrosion process especially difficult.

Galvanized steel and Zn–Al alloy-coated steels are some of the materials that are, currently, under extensive studies. They are widely studied because their coatings exhibit excellent protective characteristics against corrosion. The protection of the steel substrate is due to (1) the primary barrier action exhibited by the coating, (2) the secondary barrier action exhibited by the corrosion product layer, and (3) the sacrificial anodic protection exhibited by the coating on the steel substrate.

Besides the use of corrosion-resistant materials, there are also on-going researches being done on the testing of material performance, by employing natural exposure tests and accelerated tests, such as the salt spray test and the combined cyclic corrosion test.

Electrochemical impedance spectroscopy (EIS) is used widely to characterize the behavior of various coated metals under aggressive conditions. The availability of modern instrumentation in obtaining impedance data, as well as of computer programs to interpret the results, have made the technique popular. Nishikata et al. have applied the EIS to atmospheric corrosion studies. They found that the interface of a metal and a thin electrolyte layer can be expressed by a one-dimensional transmission line (TML) circuit, and the current distribution profile over a working electrode can be clarified using a TML model. They monitored the corrosion rates of steels and copper under wet-dry cyclic conditions and discussed the corrosion mechanisms based on the monitoring results.

In the present paper, AC impedance method has been applied to evaluate the performances of Zn and Zn–Al alloy coated steels under various cyclic wet-dry conditions. Furthermore, the corrosion behavior in an environment containing chloride ions is discussed.

II. Experimental Procedures

1. Sample preparation

Three different coated-steel sheets were selected for this study, Zn-coated (GI), Zn–5%Al alloy-coated (GF), and Zn–55%Al alloy-coated (GL). The thickness of the coatings was approximately 40 μm.
A two-electrode cell arrangement was used for the impedance measurement, as shown in Fig. 1. Two metal plates were placed in an epoxy-resin holder in such a way that 10 mm × 5 mm of each plate was exposed, 0.5 mm lower than the epoxy-resin surface. This was done by attaching a 0.5 mm-thick polyethylene sheet on both metal plates using a double adhesive tape during mounting in epoxy. Furthermore, the two metal plates were separated by 0.1 mm by using a mylar sheet. The edges of the exposed area and the edges separating the two metal pieces were sealed with thin layers of epoxy-resin to prevent crevice corrosion.

2. Corrosion monitoring under cyclic wet-dry conditions

The wet-dry cycle was conducted by exposure to alternate conditions of 1 h-immersion in a test solution and various hours of drying at 298 K and 60% RH. NaCl solutions of 0.5 kmol/m³ and 0.05 kmol/m³ concentrations were used as the test solutions. The drying times were 2, 4 and 7 h. The electrolyte layer at the onset of each dry cycle was constant (about 0.5 mm as shown in Fig. 1). The wet-dry cycle apparatus has been described elsewhere).

The corrosion monitoring was carried out by using an AC impedance corrosion monitor (RIKEN DENSISHI CT-3) with a multiplexer controlled by a computer. The impedances at 10 mHz (Z_e) and 10 kHz (Z_H) were measured simultaneously, and the polarization resistance R_p was determined by subtracting Z_e from Z_H. According to the Stern-Geary equation (eq. (1)), the corrosion current density i_corr can be calculated using the monitored value of R_p.

\[ i_{\text{corr}} = \frac{k}{R_p} \]  

(1)

where, k is a proportionality constant. After exposure to a cyclic wet-dry condition, the impedance characteristics of the specimens were also measured over the frequency range of 10 mHz to 10 kHz using a FRA (Frequency Response Analyzer, Schlumberger SI 1280). Furthermore, X-ray diffraction (XRD) was used to analyze the corrosion products.

3. Polarization measurement

After exposure to a cyclic wet-dry condition, polarization measurements were conducted on the specimens in a 0.05 kmol/m³ NaCl solution in open air. The potential was swept at 1 mV/s from the open circuit potential towards either the anodic or the cathodic direction.

III. Results and Discussion

1. Impedance characteristics

The impedance characteristics of GI, GF and GL exposed to 0.05 kmol/m³ NaCl solution for 140 h under a wet-dry condition are shown in Fig. 2. The drying time in each cycle was 7 h. The impedance measurements were carried out as the specimen was immersed in a 0.05 kmol/m³ NaCl solution. The surfaces of GI and GF after the 140 h-exposure was covered with thick, white corrosion products, while that of GL, with a relatively more compact layer. The impedances exhibited by the specimens in the high frequency and low frequency ranges were independent of the frequency. Thus, the impedance at high frequency could be considered as the solution resistance, and that at the low frequency, as the polarization resistance. On the other hand, the negative slope

![Fig. 1 Schematic diagram of a two-electrode cell used in the AC impedance corrosion monitoring of coated steels: (a) top view and (b) transverse cross-sectional view.](image1)

![Fig. 2 Impedance characteristics of Zn (GI), Zn-5%Al (GF) and Zn-55%Al (GL) coated steels after 140 h-exposure to alternate conditions of 1 h-immersion in a 0.05 kmol/m³ NaCl solution and 7 h-drying at 60%RH and 298 K. Measurement was done during immersion in a 0.05 kmol/m³ NaCl solution.](image2)
exhibited in the intermediate frequency range represents a capacitance. The interface of a metal covered with an oxide film and immersed in a solution can generally be represented by the equivalent circuit shown in Fig. 3, where \( R_c \) and \( C_{dl} \) are the charge transfer resistance and the double layer capacitance, respectively, \( R_f \) and \( C_f \) are the oxide film resistance and capacitance, respectively, and \( Z_n \) is the diffusion impedance.

It can be seen from the impedance behavior for GL in Fig. 2 that the time constants \( R_c C_{dl} \) and \( R_f C_f \) are relatively close to each other, and as a result they are not distinguishable on the Bode diagram. From the fact that the phase shift \( \theta \) approaches zero as the frequency is decreased, the diffusion process could be considered as a finite diffusion\(^{10}\). Thus, the \( Z_n \) can be written as

\[
Z_n = R_n \tanh \left( \frac{\delta_0}{j\omega D_0} \right) \left( \frac{1}{j\omega D_0} \right)^{1/2}
\]

where, \( R_n \) is the convective diffusion resistance\(^{10}\), \( j = (-1)^{1/2} \), \( \omega \) is the angular frequency \((= 2\pi f, f: \text{frequency})\), \( \delta_0 \) is the thickness of diffusion layer, and \( D_0 \) is the diffusion coefficient of the species involved in corrosion reaction. Since the polarization resistance \( R_p \) is defined as the impedance at the low frequency limit, it could be expressed as follows

\[
R_p = \frac{R_r + R_c}{(R_r + R_c + R_f)}
\]

On the other hand, in the case of GI and GF, the impedance cannot be described by the simple lumped-type equivalent circuit of Fig. 3. Both specimens showed the typical impedance characteristics of an electrode covered with a thick, porous oxide layer\(^{9}\), which is characterized by the shift of the frequency-dependent region of the impedance \(|Z|\) to the low frequency side, in other words, exhibiting apparently a large capacitance. In such cases, the impedance can be described by a TML equivalent circuit\(^{9}\), where the current distribution on the inside-wall of the pore of the porous oxide film is considered. From the impedance characteristics obtained, the reciprocals of the impedances at 10 mHz and 10 kHz were employed for monitoring the corrosion rate and the solution conductance of water layer on the coating surface, respectively.

2. Corrosion monitoring under a wet-dry cycle

The results of corrosion monitoring for GI, GF and GL exposed to 0.5 kmol/m\(^3\) NaCl solution under wet-dry cycles are shown in Fig. 4, respectively. The drying time was 7 h and the electrolyte was allowed to dry up completely in each cycle. The surfaces of the three coatings were covered with white rusts (zinc corrosion products), and red rusts (iron corrosion products) were not observed even after the 140 h-exposure. The corrosion rates of GI and GF were slightly accelerated by the wet-dry cycle, while that of GL remained relatively unchanged. The corrosion rate of GL was one order of magnitude lower than that of GI and GF. Thus GL seems to be the most corrosion resistant coating.

Next the results of XRD analysis for all samples, after exposure to wet-dry cycles, are shown in Fig. 5. XRD analysis for all samples showed the presence of ZnO, Zn\(_2\)(CO\(_3\))\(_2\)(OH)\(_6\) and 4Zn(OH)\(_2\):ZnCl\(_2\). It is generally known that Zn\(_2\)(CO\(_3\))\(_2\)(OH)\(_6\) and 4Zn(OH)\(_2\):ZnCl\(_2\) are protective, and ZnO is not protective against corrosion\(^{11}\). According to the results of field tests, it has been reported that the amount of ZnO increases with the progress of corrosion. Regarding the protective mechanism of GL against corrosion, Suzuki\(^{12}\) explains that protective Zn corrosion products are trapped within the interdendritic network along with aluminum oxide to provide optimum protection. Hence, the combined protection given by aluminum oxide and zinc corrosion products is most effective against corrosion.

3. "Time-of-wetness" (t\(_{row}\))

The average corrosion rate used to evaluate the corrosion resistance is generally calculated by taking the total
time of corrosion test into account. However, it is considered that corrosion proceeds at a negligibly small rate under the condition when the sample surface dries up completely. Therefore, it can be mentioned that the time period when the sample surface is covered with a water layer, so-called “Time-of-wetness” ($t_{ROW}$), is a very important factor which influences the atmospheric corrosion.

In this study, the solution conductance $1/R_s$ of the water layer on the sample surface was monitored under wet-dry cycles from high frequency impedance (10 kHz). The monitored $1/R_s$ value depends on the thickness of the water layer and the concentration of ions present in it. When the surface dries up completely, the $1/R_s$ value becomes zero. The monitoring results of the $1/R_s$ for GI under cyclic 1 h-immersion/different drying periods of 2, 4 h and 7 h are shown in Fig. 6. The $1/R_s$ value ranges $5 \times 10^{-2}$ to $7 \times 10^{-3}$ $\Omega^{-1}$ during the immersion. Just after the removal of the bulk solution, i.e., at the onset of the drying cycle, it drops to $2-3 \times 10^{-2}$ $\Omega^{-1}$ because of the extreme reduction of the electrolyte volume (about 300 $\mu$m in thickness at the starting point of the drying cycle). In the latter stage of the drying (see Fig. 6(c)), when the water layer becomes extremely thin (maybe invisible), it rapidly changes from $2 \times 10^{-3}$ $\Omega^{-1}$ to almost zero because the surface dries up. Therefore, in this study, $t_{ROW}$ is defined as the time period when the $1/R_s$ value is greater than $1 \times 10^{-2}$ $\Omega^{-1}$. The $t_{ROW}$ data obtained for GI from Fig. 6 are summarized in Table 1, together with those for GF and GL. It can be seen that the coating surface was always covered with water layer under the 2 h-drying condition, the surface just dried up at the end of the drying stage under 4 h-drying condition and dried up completely for about the last 3 h of the drying stage under the 7 h-drying condition. If the $t_{ROW}$ for the three coatings are compared, the highest corrosion resistant GL exhibits the shortest $t_{ROW}$, while GI and GF have a longer $t_{ROW}$, indicating that it takes a longer time for a coating surface covered with thick, porous corrosion products to dry up.

4. Corrosion performance of the three coatings

(1) Influence of drying period

Figure 7 shows the corrosion monitoring results for GI, which were obtained under the cyclic conditions of 1 h-immersion in 0.05 kmol/m$^3$ NaCl solution and 2 h-, 4 h- and 7 h-drying at 60% and 298 K. Since the polarization resistance $R_p$ is inversely proportional to the corrosion current $i_{corr}$, the integration of the $1/R_s$ vs time curves in Fig. 7 provides an average corrosion current $i_{avg}$ during 140 h exposure. The $I_{avg}$ can be written as.

![Fig. 5 Result of XRD analysis for Zn (GI), Zn-5%Al (GF) and Zn-55%Al (GL) coated steels after 140 h-exposure to alternate conditions of 1 h-immersion in a 0.05 kmol/m$^3$ NaCl solution and 7 h-drying at 60%RH and 298 K. 1: ZnO, 2: ZnCl$_2$, 3: Zn$_5$(CO$_3$)$_2$(OH)$_7$.](image1)

![Fig. 6 Solution conductance $R_s^{-1}$ of Zn coated steels (GI) exposed to alternate conditions of 1 h-immersion in a 0.05 kmol/m$^3$ NaCl solution and (a) 2 h-, (b) 4 h- and (c) 7 h-drying at 60%RH and 298 K.](image2)

<table>
<thead>
<tr>
<th>Drying period (h)</th>
<th>Time of wetness (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GI</td>
<td>GF</td>
</tr>
<tr>
<td>2</td>
<td>140</td>
</tr>
<tr>
<td>4</td>
<td>128</td>
</tr>
<tr>
<td>7</td>
<td>79</td>
</tr>
</tbody>
</table>
When the drying times in the cycle are 4 h and 7 h, the \( i_{\text{avg}} \) decreases with increasing aluminum content of the coating. It is considered that this is attributed to the formation of aluminum oxide on the surface. These results qualitatively coincide with the result of long term exposure tests in marine atmospheric environments\(^\text{(14)}\). However, in the 2 h-drying condition where the surface never dried up, the \( i_{\text{avg}} \) for GI and GF was almost the same, hence, the addition of 5%Al is not enough to improve the corrosion resistance under a wet environment containing chloride ions. The polarization curves for GI, GF and GL after 140 h-exposure to cyclic conditions of 1 h-immersion in 0.05 kmol/m\(^3\) NaCl solution and 7 h-drying at 298 K and 60%RH, are shown in Fig. 8. Polarization measurements were done as the specimen was immersed in 0.05 kmol/m\(^3\) NaCl solution at 298 K. Comparing the polarization behaviors of GI and GF, the anodic dissolution currents of both were close to each other, however, the cathodic current due to oxygen reduction for GF was somewhat lower than that for GI. The cathodic current for GL was further inhibited compared to that for GI and GF. Accordingly, improvement of corrosion resistance of Zn coating due to addition of Al could be attributed to the inhibition of the oxygen reduction.

The \( i_{\text{avg}} \) of GI was lowest for the exposure with longer wet condition, e.g. exposure with only 2 h-drying. This can be attributed to the formation Zn(OH)\(_2\) when the specimen surface is wet and its conversion to ZnO when drying takes place. It is known that Zn(OH)\(_2\) provides better protection compared to ZnO\(^{\text{(13)}}\). On the other hand, the \( i_{\text{avg}} \) of GL was the lowest for the exposure with 7 h-drying, followed by the exposure with 4 h-drying, in the wet-dry cycle. This is attributed to the formation of the more compact aluminum oxide with increasing the

\[
I_{\text{avg}} = k \int \frac{1}{R_p} \mathrm{d}t / t_{\text{total}}
\]

where, \( k \) is the proportionality constant in eq. (1), and \( t_{\text{total}} \) is the total exposure time (140 h). However, as mentioned before, atmospheric corrosion proceeds at a negligibly small rate when the specimen surface dries up. Accordingly, in order to investigate the influence of the length of the dry cycle, the average corrosion rate \( i_{\text{avg}} \) should take into account only the time when a water layer is present on the specimen surface. By using the "Time-of-wetness" \( t_{\text{ROW}} \) instead of the total exposure time \( t_{\text{total}} \), the \( i_{\text{avg}} \) is given as follows

\[
i_{\text{avg}} = k \int \frac{1}{R_p} \mathrm{d}t / t_{\text{ROW}}
\]

The \( i_{\text{avg}} \) values of GI, GF and GL under different drying times as calculated by eq. (5), assuming that the \( k \) is 20 mV\(^{\text{(13)}}\), are summarized in Table 2. The \( i_{\text{avg}} \) of GL is much smaller than that of the other two coatings in all cases.

<table>
<thead>
<tr>
<th>Drying period (h)</th>
<th>Average corrosion rate, ( i_{\text{avg}} ) ( \times 10^{-2} \text{A} \cdot \text{m}^{-2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GI</td>
</tr>
<tr>
<td>2</td>
<td>8.4</td>
</tr>
<tr>
<td>4</td>
<td>14.6</td>
</tr>
<tr>
<td>7</td>
<td>10.9</td>
</tr>
</tbody>
</table>

Fig. 8 Polarization curves of Zn (GI), Zn-5%Al (GF) and Zn-55%Al (GL) coated steels after 140 h-exposure to alternate conditions of 1 h-immersion in a 0.05 kmol/m\(^3\) NaCl solution and 7 h-drying at 60%RH and 298 K. Measurement was done during immersion in a 0.05 kmol/m\(^3\) NaCl solution.
drying time. As for GF, there was no significant influence of the drying time on the $i_{\text{avg}}$.

(2) Influence of chloride concentration

The results of the $i_{\text{avg}}$ adjusted according the $t_{\text{ROW}}$ under the alternate condition of 1 h-immersion in 0.5 kmol/m$^3$ NaCl or 0.05 kmol/m$^3$ NaCl solutions and 7 h-drying at 25°C and 60%RH are shown in Table 3. The $i_{\text{avg}}$ for GI and GF under 0.05 kmol/m$^3$ NaCl solution is slightly higher than that under 0.5 kmol/m$^3$ NaCl solution. This is attributed to the difference of oxygen solubility. It is well known that oxygen solubility in aqueous solutions increases with increasing chloride concentration\(^{(15)}\). On the other hand, GL indicates a higher $i_{\text{avg}}$ value under 0.05 kmol/m$^3$ NaCl solution than that under 0.5 kmol/m$^3$ NaCl solution by one order of magnitude. This great difference can not be explained only by the difference of oxygen solubility. The reason of this is not clear at the present time but seems related to the differences in the electrochemical property and the microstructure of the corrosion products formed under solutions of different NaCl concentrations.

The $i_{\text{avg}}$ for GF is almost the same as that for GI under the cyclic wet-dry exposure in 0.5 kmol/m$^3$ NaCl solution, but is somewhat lower than that for GI under the same exposure in a much more lower concentration, e.g. 0.05 kmol/m$^3$ NaCl solution (Table 3). The $i_{\text{avg}}$ for GF is also lower than that for GI under exposures with longer drying times, e.g. either 4 h- or 7 h-drying, but is almost equal to that for GI under a relatively wet condition, i.e. 2 h-drying. These results suggest that the addition of 5% Al in a Zn coating is not sufficient to give the coating greater corrosion resistance under either relatively wet conditions or conditions with relatively high chloride concentrations.

IV. Conclusions

From the corrosion monitoring of the three different coated steels under wet-dry cyclic environments containing chloride ions, the following conclusions are drawn.

(1) "Time of wetness" ($t_{\text{ROW}}$) can be determined from the monitoring impedance data at a high frequency (e.g. 10 kHz). Thus, the average corrosion rate $i_{\text{avg}}$ when the specimen surface is covered with a water layer can be calculated using both data from the $t_{\text{ROW}}$ and the polarization resistance $R_p$ obtained from impedance at a low frequency (e.g. 10 mHz).

(2) From the comparison between the 140 h laboratory test using AC impedance monitoring data and the long term field exposure test data, it was found that the AC impedance method is a very useful tool for evaluating the corrosion performance of coated steels in marine atmospheric environments.

(3) The average corrosion rate $i_{\text{avg}}$ of the Zn-55%Al coated steel (GL) was the lowest among the coated steels employed in the experiment under the given wet-dry conditions, but the $i_{\text{avg}}$ of GL was greatly affected by concentration of chloride ions present in the environments, e.g. the $i_{\text{avg}}$ under conditions employing a 0.5 kmol/m$^3$ NaCl solution was lower than those in 0.05 kmol/m$^3$ NaCl solution by one order of magnitude.

(4) The average corrosion rate of the Zn-5%Al coated steel (GF) was somewhat lower than that of the Zn-coated steel (GI) under the alternate conditions of 1 h-immersion in a 0.05 kmol/m$^3$ NaCl solution and 4 h- or 7 h-drying at 60%RH and 298 K. However, GF exhibited an almost the same corrosion rate as that of GI under relatively wet, chloride-concentrated conditions, e.g. under 1 h-immersion in a 0.05 kmol/m$^3$ NaCl solution and 2 h-drying (relatively wet condition), and under 1 h-immersion in a 0.5 kmol/m$^3$ NaCl solution and 7 h-drying (high chloride-concentration condition).

REFERENCES