Effect of Environmental Cation Species on Corrosion near Shear Cut Edge of 55%Al–Zn Alloy Coated Steel Sheet

Masamitsu MATSUMOTO, Nobuhiro OKADA, Katsuhiro NISHIHARA, Masanari KIMOTO and Takeo KUDO

1) Corporate Research & Development Labs., Sumitomo Metal Industries, Ltd., 1-8 Fuso-cho Amagasaki 660-0891 Japan.
2) Graduate School of Engineering, University of Hyogo, 2167 Shosha, Himeji 671-2280 Japan.

(Received on December 19, 2008; accepted on February 3, 2009; originally published in Tetsu-to-Hagané, Vol. 94, 2008, No. 11, pp. 545–552)

Hot-dip 55%Al–Zn alloy coated steel sheet has superior corrosion resistance both on flat panel and near shear cut edge in various atmospheric environments. However, the corrosion often occurs near the shear cut edge in continuous wet conditions, for example, NaCl solution spray test (SST, JIS Z2371), and has been explained by galvanic model. In this paper, it is clarified that the corrosion near shear cut edge is suppressed by artificial sea water and its second ingredient, MgCl₂.

To make clear the corrosion mechanisms on MgCl₂ suppression of the corrosion near shear cut edge, the measurement of cathodic polarization curve on the Fe electrode after the corrosion test using a AZ/Fe/AZ galvanic electrode, the estimation of corrosion products by numerical analysis in consideration of the substances migration and the precipitation reactions, and the analysis of corrosion products by FT-IR spectroscopy were conducted. As a result, in the galvanic condition, it is clarified that Mg(OH)₂ precipitates on the Fe exposed cut edge. Moreover, the corrosion near shear cut edge is suppressed by the effect of the cathodic reaction suppression of Mg(OH)₂.

KEY WORDS: 55%Al–Zn alloy coating; corrosion resistance near shear cut edge; galvanic corrosion; environmental cation; numerical analysis; FT-IR spectroscopy.

Introduction

It is widely known that hot dip 55mass%Al–Zn alloy coated steel sheet has superior corrosion resistance in actual environment. Therefore, Al–Zn coated steel sheet is widely used in long term usage. The corrosion loss of the coating near shear cut edge, in which the steel is exposed, is reported to be negligible after long term outdoor exposure tests.

In recent years, the use of Al–Zn coated steel sheet has been propagated due to the durability needs for materials. In accordance with the propagation, the performance in a severe test condition is required far from the actual environment. One of the severe tests is 5mass% NaCl salt spray test (SST). It was reported that the corrosion rate of the coating increases near shear cut edge when exposed in the SST. This phenomenon is explained by the galvanic model: the coating is anode and the steel exposed at the end of the edge is cathode. It is pointed out that the salts of multi-component system containing sea salt or other salts, or both, influence the thickness and the composition of the water film in actual environments, and they have the possibility of affecting the corrosion phenomenon. In addition, although the test methods using sea salt are proposed, the influence of the component ions on the corrosion mechanisms is not clarified.

The purpose of this paper is to clarify the influences of environmental cations on the corrosion mechanisms of the coating near shear cut edge of 55mass%Al–Zn coated steel sheets. The corrosion products and electrochemical properties are analyzed by physical and numerical analysis to solve the corrosion mechanisms, focusing on the influence of artificial sea salt and MgCl₂, which is the second component to NaCl.

Experimental

2.1. Specimens

The cold rolled carbon steel is galvanized with 55mass%Al–Zn alloy that the coating weight is 150 g m⁻² on both sides by actual continuous galvanizing line, CGL. After the 55%Al–Zn coated steel sheet is cut to 70x150 mm by shearing, the flat panel specimens and the galvanic specimens are prepared, as shown in Fig. 1. The four sides and backside of the flat panel specimens are protected with polyester tape to measure corrosion rate without cut edge. For comparative specimens, the cold rolled steel sheet of substrate and zinc plate are also prepared.

On the other hand, for the galvanic specimens simulating shear cut edge, the coating of the center is removed mechanically to steel substrate at exposed width, x=10 mm. Here, the exposed width corresponds to the thickness of steel sheet at the cut edge. The width x=10 mm is within the range of galvanic action during SST and contributes to
reduce the test period suggested in the previous paper. The edges and backside are also protected by polyester tape. Surface finish treatment such as chromate coating, chromate-free coating, phosphate coating is not carried out on every specimen. Next, to evaluate the corrosion mechanisms near shear cut edge, galvanic electrode is prepared, as shown in Fig. 2.

The galvanic electrode is composed of three electrodes that are AZ/Fe/AZ. Here, the AZ electrode is made of 55%Al–Zn alloy ingot, and the Fe electrode is made of cold rolled steel sheet for substrate. The electrodes are connected to lead wire, and they are closed to each other as keeping insulation, and buried in epoxy resin. After that, it is wetly polished with #2000 emery paper. One size for AZ electrode is prepared as \( x = 10.0 \) mm, and three sizes for Fe electrode are prepared as \( x = 0.8, 3.2, 10.0 \) mm. Here, the exposed width corresponds to the thickness of steel sheet at the cut edge.

2.2. Corrosion Test

A salt spray test is carried out in accordance with JIS Z2371, the same as ASTM B117. The temperature of the salt solutions is 35°C, and the solutions are 0.085 M NaCl, 0.85 M NaCl, 0.425 M MgCl₂, and artificial sea water. The artificial sea water is in accordance with ISO 11130. The chloride ion concentration of 0.85 M NaCl and 0.425 M MgCl₂ are equal to 0.85 M. The artificial sea water is a salt solution of a multi-component system containing NaCl, MgCl₂, and other salts, and it is prepared in accordance with ISO 11130. The concentrations of ions are \([\text{Na}^+] = 0.48 \text{ M}, [\text{Mg}^{2+}] = 0.055 \text{ M}, [\text{Cl}^-] = 0.56 \text{ M}\).

During the corrosion test, three lead wires of the galvanic electrode are shorted. In addition, the long side of the galvanic electrode and specimens is tilted at 15 degrees from a perpendicular position, the solution mist to be precipitated.

2.3. Evaluation Method

2.3.1. Corrosion Rate

The corrosion rate measures the mass changes before and after the corrosion test, where test period is 24 h. The mass, after the test, is measured after the corrosion products are removed. The corrosion products are removed by dissolving in the solutions as follows: For 55%Al–Zn, 2.0 mass% chromium oxide solution at 80°C, for Zn, 12.5 mass% ammonium and 2.0 mass% dichromate ammonium solution at room temperature, for C-steel, 10 mass% HCl and 0.1 mass% inhibitor (IBIT 700BK, Asahi Chemical Co.) at room temperature.

2.3.2. Iron Rust Occurrence Near Cut Edge

The evaluation of the corrosion rate for the galvanic specimens is described in detail in the previous paper. The time is evaluated when the iron rust starts to propagate over the coating from the edge of the exposed steel substrate. Here, the iron rust on the exposed steel substrate is outside of this paper.

2.3.3. Galvanic Current

The galvanic current between AZ and Fe electrodes is measured by zero-shunt ammeter (HM-102, Hokuto Denko Co.). Here, two lead wires from AZ electrode are shorted, and the current of between AZ and Fe electrodes is measured continuously.

2.3.4. Cathodic Polarization Curve on Fe Electrode

The cathodic polarization curve is measured on the Fe electrode of the galvanic electrode. During the corrosion test, the lead wires for the galvanic electrode are shorted. In measuring, every lead wires is opened, and the cathodic polarization curve on the Fe electrode stand-alone. For the measuring solution, the test solution is used. The temperature of the solution is 35°C, and the solution is constantly stirred by air bubbling during measuring. The thickness of the oxygen diffusion layer is constant. The constant of the thickness is confirmed by measuring the reduction reaction of oxygen on the pure Cu.

For measuring the polarization curve, a potentiostat (SI-1287, Solartron), carbon electrodes as counter electrode and a saturated calomel electrode (SCE) as a reference electrode are used. The measuring condition is as follows: the time to scan is 180 s, and the scanning rate is 1.0 mVs⁻¹ cathodically from rest potential.

2.3.5. Numerical Analysis for Corrosion and Precipitation Reaction

Ions transportation and their reactions are considered in numerical analysis model for galvanic corrosion of metals. The details are as follow:

The current density vector \( \mathbf{i} \) is defined by Ohm’s law, as shown in Eq. (1), where \( \phi \) is the potential in the electrolyte solution, \( \sigma \) is the electric conductivity of the solution.

\[
i = -\sigma \nabla \phi. \tag{1}\]
The electric conductivity \( \sigma \) is calculated by Eq. (2) using ion concentration and ion mobility. Where \( z_i, u_i, \) and \( c_i \) are the valence number, the mobility, and the concentration of ion \( i \), respectively, and \( k \) is the number of ion species, and \( F \) is the Faraday constant.

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

The divergence of Eq. (1) is equal to zero because of current conservation, which is Laplace’s equation shown in Eq. (3).

\[
\nabla \cdot \mathbf{i} = \nabla \cdot (-\sigma \nabla \phi) = 0 \quad \text{(3)}
\]

Equation (3) is solved by finite difference method subject to the boundary conditions of polarization properties for metals, as the results, the distribution of potential and that of the current density in the solution are obtained. The model of polarization properties is as follows: Anodic polarization properties are defined by Tafel equation, and cathodic polarization property is defined by oxygen flux.\(^{9}\) In the model, anodic and cathodic current density \( i_a \) and \( i_c \) are defined by Eq. (4) and Eq. (5), respectively.

\[
i_a = i_{a0} \exp \left\{ \frac{(\phi - \phi_0)}{RT} \right\} \quad \text{(4)}
\]

\[
i_c = 4FNC_{O_2} \quad \text{(5)}
\]

Where, \( i_{a0} \) is the corrosion current density, \( \phi_0 \) is the corrosion potential, \( R \) is the gas constant, \( T \) is temperature, \( \alpha \) is the Tafel parameter and \( \alpha \) is the valence number in anodic dissolution shown in Eq. (4). For these parameters, the values in the previous paper\(^ {9} \) are used, and \( i_{a0}, \phi_0 \), and \( \alpha \) are measured by experiment. In addition, \( N_{O_2} \) is the mole flux of oxygen to the metal surface in Eq. (5), which is calculated from the distribution of oxygen concentration in the solution.\(^ {10}\)

In solving Eq. (3), for the boundary condition on the metals, the current density is \( i_a = i_c \). from Eq. (4) and Eq. (5), for the other boundary conditions, the current density is equal to zero.

In a thin layer solution, convection flow is negligible; therefore, ion transportation is controlled by Eq. (6).

\[
\frac{\partial c_i}{\partial t} = - \nabla \cdot \mathbf{N}_i + R_i = - \nabla \left( \frac{t_i}{z_i F} \mathbf{i} \right) + \nabla \cdot (D_i \nabla c_i) + R_i \quad \text{(6)}
\]

Where, \( \mathbf{N}_i \) is the mole flux\(^ {11}\) of \( i \), \( D_i \) is the diffusion coefficient of \( i \), \( t_i \) is the transport number of \( i \) and \( R_i \) is the rate of generation and consumption of \( i \). Ions transportation is calculated by Eq. (6) using the distribution of current density and satisfying the principle of conservation of charge. In solving Eq. (6), for the boundary condition on the metals, the dissolution of metal ion corresponds to the anodic current density, and the generation of hydroxide ion corresponds to the cathodic current density. For the other boundary, ion flux is equal to zero. In addition, the transportation of oxygen by diffusion is only calculated in accordance with the second term in the right-hand side of the Eq. (6). Here, that by current density on the first term and that by \( R \) on the third term are equal to zero. In calculating the diffusion of oxygen, for the boundary condition on the solution surface, the oxygen concentration is saturated in air, for that on the metal surface, it is equal to zero. The saturated concentration of oxygen depends on the concentration of salt solution and the temperature; therefore, it is calculated by the empirical formula.\(^ {9}\) Values of ion mobility and diffusion coefficients are shown in Table 1, which are used for numerical analysis.\(^ {10}\)

It is assumed that the reaction in the solution is determined by transportation, and the reaction rate is finite. Therefore, in the calculation, the reaction reaches equilibrium in a cell of calculation grid immediately after transportation. The reactions are considered as follows: The precipitation reactions for \( \text{ZnO}, \text{Zn(OH)}_2 \), and \( \text{ZnCl}_2 \cdot 4\text{Zn(OH)}_2 \) are considered, which are corrosion products on the coating. Here, the solubility products of \( \text{ZnO} \) and \( \text{Zn(OH)}_2 \) are almost equal, therefore, \( \text{Zn(OH)}_2 \) is considered. The corrosion products of Al in Al–Zn coating are not considered because anodic reaction is the dissolution of zinc in an initial stage. In addition, the mechanisms of iron rust formation is complicated, therefore, \( \text{Fe(OH)}_3 \) is only considered. The solubility product of \( \text{Fe(OH)}_3 \) has various values in some papers, therefore it is calculated by Eq. (7) using the standard free energy for formation. Here, \( \Delta G \) is the change of Gibbs free energy in precipitation reaction.

\[
K_{sp} = \exp \left( -\frac{\Delta G}{RT} \right) \quad \text{(7)}
\]

Table 2 shows the equilibrium reaction and precipitation reactions considered in this numerical analysis.

Next, the geometry for numerical model simulating the SST is shown in Fig. 3. It is a two-dimensional model that the width of Fe and Zn are 10 mm respectively, and the thickness of solution film is 0.1 mm. Every cell of the calculation grid is 100 \( \mu \)m in long direction and 10 \( \mu \)m in the depth direction. The equations are solved by finite differ-

\[
\begin{array}{|c|c|c|}
\hline
\text{Ion} & \text{Mobility} u \text{ m}^2\text{V}^{-1}\text{s}^{-1} & \text{Diffusion Coefficient} D \text{ m}^2\text{s}^{-1} \\
\hline
\text{H}^+ & 3.76 \times 10^{-12} & 9.31 \times 10^{-5} \\
\text{OH}^- & 2.12 \times 10^{-12} & 5.26 \times 10^{-5} \\
\text{Cl}^- & 8.20 \times 10^{-13} & 2.03 \times 10^{-5} \\
\text{Zn}^{2+} & 2.85 \times 10^{-13} & 7.10 \times 10^{-5} \\
\text{Fe}^{2+} & 2.90 \times 10^{-13} & 7.20 \times 10^{-5} \\
\text{Na}^+ & 5.38 \times 10^{-13} & 1.33 \times 10^{-5} \\
\text{Mg}^{2+} & 5.70 \times 10^{-13} & 7.06 \times 10^{-5} \\
\text{O}_2 & - & 1.90 \times 10^{-5} \\
\hline
\end{array}
\]
ence method of successive over-relaxation (SOR).

2.3.6. Analysis of Corrosion Products

The corrosion products precipitated on the Fe surface of the galvanic specimens are scraped by micro spatula of stainless steel. Then, they are grounded into powder specimens by a mortar made of agate.

For analysis of the corrosion products, Fourier transform infrared (FTIR) spectroscopy is adopted because it is possible to identify the non-crystalline component as well as the crystalline component. To identify the non-crystalline component, the reference specimens are used, which are Mg(OH)\textsubscript{2}, Zn(OH)\textsubscript{2}, α-FeOOH, and γ-FeOOH. These are purchased as reagents or synthesized in our laboratory, and they are verified by XRD to be pure substances.

Infrared spectra are measured by Attenuated Total Reflectance (ATR) method using the FTIR spectrometer (Nicolet-8700 and SmartOrbit, Thermo Fisher Scientific Inc.). The ATR crystal is made of diamond. Each infrared spectrum is corrected by advanced ATR correction and base line correction, and the data of each spectrum are collected and analyzed using attached software “OMNIC”.

3. Experimental Results

3.1. Corrosion Rate of Flat Panel

Figure 4 shows the corrosion rates after 24 h in the SST using 0.85 M NaCl solution or 0.425 M MgCl\textsubscript{2} solution. The corrosion rate of 55mass%Al–Zn coating is small and under the measuring limit (<0.1 g m\textsuperscript{−2}(24 h)) in each test. C-steel is about 50 g m\textsuperscript{−2}(24 h) and is equal in each test. Those of zinc plate are about 20 g m\textsuperscript{−2}(24 h) in the NaCl SST and are suppressed to about 5 g m\textsuperscript{−2}(24 h) in the MgCl\textsubscript{2} SST.

3.2. Iron Rust Occurrence Behavior of Galvanic Specimen

The galvanic specimens are tested in the SST using NaCl solution, MgCl\textsubscript{2} solution and artificial seawater. For a corrosion evaluation of the galvanic specimen, the starting time of iron rust propagation on the coating from the edge of exposed Fe is measured. Figure 5 shows that the iron rust starts to propagate at 196 h in both 0.85 M NaCl and 0.085 M MgCl\textsubscript{2} SST. On the other hand, the iron rust starts to propaga-
tioned below.

Next, the relationship between the width \( x \) of Fe electrode and the galvanic current is investigated. Figure 6 shows that the current has been almost constant since the current was increased. For the other condition, the current has been almost constant since current increased. Therefore, the mean of galvanic current was evaluated between 20 to 24 h when the galvanic current was stable. From the results, Fig. 7 shows the galvanic current was increased as the width \( x \) of Fe was increased in 0.85 M NaCl SST. It is suggested that the cathodic protection works within width \( x = 10 \text{ mm} \), and cathodic reaction on Fe controls the corrosion reaction. On the other hand, the galvanic current is suppressed regardless of the width \( x \) of Fe in 0.425 M MgCl\(_2\) SST. It is suggested that the coverage by corrosion products suppresses the cathodic reaction on Fe within the range of cathodic protection. Further details on this point are mentioned below.

4. Discussion

It is clarified that the corrosion rate of coating near cut edge is accelerated by galvanic action in NaCl SST, and it is suppressed in MgCl\(_2\) SST. Here, to clarify the corrosion mechanisms on corrosion suppression in MgCl\(_2\) SST, the cathodic reaction on substrate Fe exposed in cut edge was focused. In particular, the evaluation by cathodic polarization curve on Fe, the prediction of corrosion products by numerical analysis and verification by analysis are achieved.

4.1. Behavior of Cathodic Polarization Curve

First, Fig. 8 shows the cathodic polarization curves of Fe electrodes without corrosion test in 0.85 M NaCl solution and 0.425 M MgCl\(_2\) solution. In each solution, the current density is constant in \(-1.0 \text{ to } -0.7 \text{ V vs. SCE}\). It was confirmed that these current densities are the diffusion limiting current density of oxygen by the cathodic polarization curve on copper.

Next, the galvanic electrode was tested in the SST for 24 h, of which the lead wires of AZ and Fe electrodes were connected to each other. After that, it was moved into the same concentration solution immediately to measure the polarization curve on Fe. After 180 s immersion, the cathodic polarization curve was measured (Fe/AZ, \( t = 24 \text{ h} \)). In addition, after Fe was tested alone in the SST for 24 h, the cathodic polarization curve was measured (Fe w/o AZ, \( t = 24 \text{ h} \)). Furthermore, for the AZ electrode without SST, anodic polarization curve was measured in 1.0 mV s\(^{-1}\) (AZ anode). Figure 9 shows the results of using 0.85 M NaCl for spray test solution and measuring solution, and Fig. 10 shows the results of using 0.425 M MgCl\(_2\).

Further, the rest potentials of the galvanic couple, of which the lead wires of the AZ and Fe electrodes were connected, were measured in NaCl and MgCl\(_2\) solutions. The potentials were between \(-0.9 \text{ to } -1.0 \text{ V vs. SCE}\) in both solutions. In this potential range, it is considered that the corrosion is controlled by cathodic reaction shown in Fig. 8. From now, the current density has been evaluated in the range of \(-0.9 \text{ to } -1.0 \text{ V vs. SCE}\).

These figures show that the cathodic current density of the Fe electrode after NaCl SST (Fe/AZ, \( t = 24 \text{ h} \)) was increased in comparison with that without SST (as) in the range of \(-0.9 \text{ to } -1.0 \text{ V vs. SCE}\); on the other hand, for MgCl\(_2\), it was suppressed. It is suggested that MgCl\(_2\) forms a film on Fe electrode with the suppression effect of reaction or that of species transformation. On the other hand, when the Fe was tested alone in SST, the cathodic current density was increased (Fe w/o AZ, \( t = 24 \text{ h} \)). It is suggested that this phenomenon of increased current is caused by the
In other words, the cathodic reaction is suppressed on the Fe electrode of the galvanic electrode in MgCl₂ SST. This corresponds with the corrosion suppression of the coating near the cut edge of the galvanic specimen in MgCl₂ SST shown in Fig. 5. Furthermore, if the galvanic corrosion progresses with the current density of the intersection between the anodic current of AZ electrode (AZ anode) and the cathodic current of Fe shown in Fig. 9 and Fig. 10, the galvanic corrosion is suppressed in MgCl₂. This phenomenon corresponds with the galvanic current suppression in MgCl₂ shown in Fig. 5.

In summary, it is suggested that the cathodic reaction is suppressed by formation of the film when protected cathodically using MgCl₂. In addition, the cathodic current density on Fe is suppressed with the film after MgCl₂ SST, but it is not suppressed without MgCl₂ SST shown in Fig. 8. This phenomenon suggests that the film precipitates on Fe in MgCl₂ SST and suppresses the cathodic reaction, but it is hard to precipitate on Fe while measuring the cathodic polarization curve.

4.2. Numerical Analysis

As mentioned above, it is shown that the cathodic reaction on Fe is suppressed by the film formed when protected cathodically in MgCl₂ SST. Therefore, to clarify the mechanisms for suppressing the cathodic reaction, the film formation was investigated by the numerical analysis for galvanic corrosion considering ions transportation and precipitation reactions. Here, the anodic reactions of both Al and Zn for AZ electrode are to be considered, but the modeling of Al anode is not accomplished. In the initial stage, the anodic reaction of Zn is a major reaction, so Zn/Fe model was investigated.

Figure 11 shows the results of the precipitation distribution by the numerical analysis after 100 s test started. The results are within the conditions of (a) 0.85 M NaCl, (b) 0.425 M MgCl₂, and (c) 0.00425 M MgCl₂. In 0.85 M NaCl, ZnCl₂·4Zn(OH)₂ was precipitated on only Zn. In 0.425 M MgCl₂, furthermore, Mg(OH)₂ was precipitated on Fe. It is explained that the environmental Mg²⁺ is used to neutralize OH⁻, which is formed by the cathodic reaction of reduction of oxygen on Fe electrode. In other words, in NaCl, no precipitation is formed on Fe because of the high solubility of NaOH. On the other hand, in MgCl₂, the precipitation of Mg(OH)₂ is formed on Fe. It is confirmed by the numerical analysis.

For reference, Fig. 11(c) shows the results of precipitation distribution in 0.00425 M MgCl₂ that was diluted to 1/100. The major precipitation on Zn electrode was Zn(OH)₂. On Fe electrode, Mg(OH)₂ was formed near interface to Zn, Fe(OH)₂ was formed over 2 mm from the interface. Here, the cathodic protection distance is ca. 13 mm in the 0.1 mm thickness film of 0.85 M NaCl solution, and it is ca. 1.5 mm in the concentration of 1/100. In other words, the whole Fe surfaces in Figs. 11(a) and 11(b) are protected cathodically, Fe in Fig. 11(c) is protected within ca. 1.5 mm from Fe/Zn interface. Therefore, it is suggested that Mg(OH)₂ is formed on Fe when the pH rises on Fe by cathodic reaction, and then Fe is protected cathodically and Fe is not dissolved anodically.

From the numerical analysis, it is suggested that Mg(OH)₂ formed on Fe contributes corrosion suppression, from the results there is more suppression in MgCl₂ SST than that in NaCl SST, in which the corrosion of
4.3. Verification of Corrosion Mechanisms by Corrosion Products Analysis

It is predicted that the Mg(OH)$_2$, as a contribution substance for corrosion suppression, is formed on Fe in MgCl$_2$ SST, which suppresses the cathodic reaction on Fe by the electrochemical analysis and the numerical analysis. To verify this, the analysis of corrosion products on Fe is achieved by FTIR. The results are shown in Fig. 12. Figure 12(a) shows $\alpha$-FeOOH, $\gamma$-FeOOH and Zn(OH)$_2$ were detected after 24 h NaCl SST. Figure 12(b) shows Mg(OH)$_2$, and Zn(OH)$_2$ were detected after 24 h MgCl$_2$ SST. Furthermore, during the galvanic action, the reason why iron rusts ($\alpha$-FeOOH and $\gamma$-FeOOH) are formed is as follows: Although the fine particles of solution are sprayed in SST, the water film is not uniformly formed and the galvanic reaction doesn’t spread over the entire of Fe. Therefore, corrosion occurs independently and iron rusts are formed on Fe out of the range of the protection distance.

On the other hand, when the Fe is tested alone in MgCl$_2$ SST, it is confirmed that Mg(OH)$_2$ is not formed but $\alpha$-FeOOH and $\gamma$-FeOOH are formed shown in Fig. 12(c). Furthermore, the infrared spectra of reference specimens are shown in Figs. 12(d)–12(g).

The results above correspond to the precipitations predicted by the numerical analysis. The reason for suppression of corrosion is that Mg(OH)$_2$ is an insulator, therefore, it is the barrier against the electron transportation and suppresses the cathodic reaction on Fe.

The ‘electro-coating’ is widely known that a film is formed on the steel structure when applying cathodic current externally in seawater or river-water, and the film is formed of CaCO$_3$ and Mg(OH)$_2$ because of the increasing pH on the steel surface.$^{18}$ The formation of Mg(OH)$_2$ on Fe exposed in the shear cut edge is a similar phenomenon in our study. New knowledge are obtained, however, that the film is formed by the galvanic corrosion of coating and substrate Fe, the film controls the reduction reaction of oxygen and it suppresses the corrosion of coating near the shear cut edge significantly.

The result of accelerated corrosion test using 5 mass% NaCl SST doesn’t correspond to that in the actual environment. Therefore, recently, the test method using artificial seawater has been proposed,$^7$ or the differences between corrosion test and the actual environment have been studied from the point of view of the water film thickness caused by salt composition.$^6$ The new knowledge obtained from our study proposes to discuss the film formation and its protection effects on the cathodic site. This phenomenon widely occurs in anode/cathode separation system without limited in corrosion near the shear cut edge in our study.

5. Summary

The corrosion mechanisms of the environmental cation are investigated on the corrosion of the hot dip 55mass% Al–Zn alloy coated steel sheet near shear cut edge in comparison with that of NaCl. As a result, new knowledge is obtained as follows:

(1) The corrosion of the 55mass% Al–Zn coating near the shear cut edge is significantly suppressed by the artificial seawater or MgCl$_2$ in comparison with NaCl. This phenomenon is confirmed by measuring the galvanic current of AZ/Fe galvanic electrode.

(2) The cathodic reaction on Fe of AZ/Fe galvanic electrode is significantly suppressed after MgCl$_2$ SST.

(3) From the results of the prediction for precipitations by numerical analysis, Mg(OH)$_2$ is formed on Fe. On Fe of AZ/Fe electrode, both OH$^-$ formation and the increase of pH by cathodic reaction and the decrease of Fe$^{2+}$ by anodic resolution form the Mg(OH)$_2$ in the galvanic corrosion condition.

(4) From the results of FTIR analysis, the corrosion products formed on Fe in MgCl$_2$ SST are confirmed to consist mainly of Mg(OH)$_2$. In NaCl SST, main corrosion products are $\alpha$-FeOOH, and $\gamma$-FeOOH.

(5) The formation of Mg(OH)$_2$ on Fe is formed by neutralizing with OH$^-$ formation by reduction reaction of oxygen. Precipitation of Mg(OH)$_2$ on Fe suppresses the cathodic reaction and suppresses the corrosion of coating near the shear cut edge. In other words, in the corrosion of anode/cathode separation system, OH$^-$ formation on the cathodic site is neutralized with the cation, that is formed by the anodic resolution and supplied from the environment. In this condition, the result of competition of that from anodic resolution and that from environment, the cation from environment takes precedence over that from resolution to be neutralized with OH$^-$.

REFERENCES

1) D. J. Blickwede: Tetsu-to-Hagané, 66 (1980), 821.
2) H. E. Townsend and A. R. Borzillo: Mater. Perform., 4 (1996), 30.
3) M. Matsumoto: CAMP-ISIJ, 10 (1997), 601.
4) M. Murakami et al.: Proc. 50th Japan Conf. Materials and Environments, JSCE, Tokyo, (2003), 321.
5) M. Matsumoto, M. Kimoto, A. Sakoda and T. Kudo: Tetsu-to-Hagané, 91 (2005), 700.
6) W. Oshikawa, T. Shinohara and S. Motoda: Zairyo-to-Kankyo, 52 (2003), 293.
7) e.g. Proc. 131th Symp. Corros. Eng., JSCE, Tokyo, (2001), 28. Proc. 143th Sympo.Corros. Eng., JSCE, Tokyo, (2003), 33.
8) N. Okada, M. Matsumoto, M. Kimoto and T. Kudo: CAMP-ISIJ, 21 (2008), 552, CD-ROM.
9) N. Okada, M. Takebayashi, M. Matsumoto, M. Kimoto and T.
10) N. Okada, M. Matsumoto, M. Kimoto and T. Kudo: Proc. of Galvat-ech '07 7th Int. Conf. on Zinc and Zinc Alloy Coated Steel Sheet, ISIJ, Tokyo, (2007), 624.

11) J. Newman and K. E. Thoma-Alyea: Electrochemical System, 3rd ed., John Willey & Sons, Inc., (2004), 275.

12) A. Sakoda, N. Usuki, S. Wakano and M. Nishihara: J. Surf. Finish. Soc. Jpn., 40 (1989), 164.

13) S. Hashimoto: J. Surf. Finish. Sci. Soc. Jpn., 22 (2001), 128.

14) W. Feitknecht: Chem. Ind., 36 (1959), 1102.

15) Handbook of Chemistry, 5th ed., CSJ, Maruzen, Tokyo, (2004).

16) K. Nishihara, M. Matsumoto, M. Kimoto, T. Kudo, H. Uchida, Y. Haruyama, K. Kanda and S. Matsui: Zairyo-to-Kankyo, 56 (2007), 314.

17) I. Suzuki, N. Masuko and N. Hisamatsu: Corros. Eng. (Jpn.), 23 (1974), 141.

18) e.g. Handbook of Metal Corrosion Protection, 1st ed., Nikkan Kogyo Shinbun, Tokyo, (1972), 580.