Role of Metal Cations on Corrosion of Coated Steel Substrate in Model Aqueous Layer

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To elucidate the role of Zn$^{2+}$ on corrosion of coated steel, the effects of metal cations on the corrosion of carbon steel in the concentrated Cl$^-$ aqueous solutions were studied by immersion tests, surface analysis and electrochemical tests. Among the examined metal cations, Zn$^{2+}$ showed the significant effect on corrosion inhibition of carbon steel in the Cl$^-$ aqueous solution at high concentration. XPS analysis results elucidated that Zn$^{2+}$ can remain on the steel surface after immersed in the solutions with Zn$^{2+}$. In addition, AFM results showed lower roughness of specimen immersed in the solution with Zn$^{2+}$ than other solutions with metal cations. EIS measurements showed higher impedance in the solution with Zn$^{2+}$ than other solutions, and the results suggested that Zn$^{2+}$ reduced the defect points in the thin oxide film by forming a metal cation layer. Based on the experimental results, Zn$^{2+}$ may form a layer on the oxide film that protects the Cl$^-$ attack in the solution. The findings demonstrated that the formation of Zn layer on the oxide film is one of the main reasons for showing high and long-time corrosion resistance of Zn coated steel substrate.

KEY WORDS: metal cation; carbon steel; chloride ion; SEM; AFM; XPS.

1. Introduction

Coated steels are extensively used as various constructional materials due to low cost and good mechanical and anti-corrosion properties than other steels. Zinc coated steel is one of the most common materials and has wide applications in automobiles, buildings, bridges, marine platforms and port docks.1–4) In the environment that contains Cl$^-$, main factors of steel corrosion are the concentration and corrosive nature of the Cl$^-$, and the passive film is generally destroyed by this ion in aqueous environment.5–8) It is well known that the Cl$^-$ concentration reaches a high level on the steel surface during drying situation of atmospheric environment. There are many studies have been carried out about the corrosion of zinc coated steel in the Cl$^-$ aqueous environment at high concentration.9–13)

Sun et al.14) reported that ZnO and Zn(OH)$_2$ are produced as corrosion products when zinc coated steel is exposed in aqueous environment and corrosion protective ability is attributed by these corrosion products. Tsuru15) proposed that Zn$^{2+}$ is dissolves from the corrosion products and adsorbs onto the steel and prevent further corrosion of the steel substrate. Same phenomena occur when carbon steel is exposed in the aqueous solution with Zn$^{2+}$.16) The cation adsorbs as hydroxides onto the steel substrate and suppress the corrosion reactions of steel. There are many researchers reported that metal cations (Zn$^{2+}$ and Al$^{3+}$) can reduce the corrosion of carbon steel by adsorbing onto the steel substrate in aqueous solution.16–20) Islam et al.16) reported that Zn$^{2+}$ effectively inhibits the corrosion of mild steel in 10 mM Cl$^-$ aqueous solution. They also clarified the mechanism in which metal cation inhibits the corrosion of mild steel. Otani et al.17,18) investigated the effects of metal cations (Zn$^{2+}$ and Al$^{3+}$) on mild steel corrosion in model fresh water and explained that metal cations make a layer on the passive film that inhibits the corrosion reactions in the solution. They also reported that Zn$^{2+}$ effectively improve the corrosion inhibition ability of gluconates in model fresh water.19) In some nuclear power reactors, Zn$^{2+}$ are also added into the working fluid for suppressing corrosion of the reactor component materials.20)

Zinc coated steel is protected by the galvanic reactions or sacrificial anodic reaction of Zn.21) However, the zinc coating on steel is not fully corrosion protected or sufficient for long time protection of steel in the environment that contains Cl$^-$ at high concentration. Because, once the coating is consumed by the sacrificial anodic reaction in presence of aggressive Cl$^-$, severe corrosion happens on the steel surface. Therefore, it is needed to clarify the role of Zn$^{2+}$ on carbon steel corrosion in such environment that contains Cl$^-$ at high concentration. In this experiment, the effects of Mg$^{2+}$ and Al$^{3+}$ have also been carried out, because some of the coated layer of steel contains Mg and Al.

In the present study, the effect of metal cations on the corrosion of carbon steel in the Cl$^-$ aqueous solution at high concentration were investigated by immersion tests with mass change measurement and electrochemical impede-
2. Experimental Procedures

2.1. Specimens
A carbon steel sheet was cut into 7×7×0.7 mm in size and were used as specimens. The chemical composition (wt.%) of specimen used for all the experiments as follows: C = 0.02; Mn = 0.18; P = 0.015; Si = 0.01; S < 0.01, and balance Fe. Prior to the experiments, the specimens were abraded with #240 to #4000 grit size of SiC abrasive paper and then was ultrasonically cleaned with ethanol and in highly purified water.

2.2. Test Solutions
Three different salt solutions of 0.1 mM MgCl₂ (Mg₅₀₀), 0.1 mM ZnCl₂ (Zn₅₀₀) and 0.1 mM AlCl₃ (Al₅₀₀) were prepared and their Cl⁻ concentration was adjusted to 0.5 M by NaCl, and were used as the tests solutions. In this experiment, 0.5 M NaCl (Na₅₀₀) was used as a reference solution. Highly purified water was used to prepare the experimental solutions. The pH of the solutions was adjusted to 5.8 by 0.1 M NaOH. The measurements of the pH were carried out using the pH meter (Eutech Instruments Pte. Ltd., CyberScan 6000). All chemicals used in this study were special analytical grade and obtained from Kanto Chemical Co. Ltd.

2.3. Immersion Tests
Immersion tests were carried out at 25°C for 3 d in stagnant condition. During the immersion, the solutions were open to the air. The appearances of specimens and solutions were observed by a digital camera (Nikon D80). Before and after the tests, the specimens were cleaned in ethanol and then in highly purified water using ultrasonic bath. The mass of the specimens was measured using a micro-balance (METTLER TOLEDO MX5, Pro FACT), and the corrosion rates were calculated from the mass change.16)

2.4. Surface Characterizations
The surface morphological changes due to immersion in the solutions were observed by scanning electron microscope (SEM, JEOL Ltd., JSL6510-LA). The surface roughness was measured by atomic force microscope (AFM, SPA400; cantilever: SI-DF40). The surface of the immersed specimens was analyzed by X-ray photoelectron spectroscope (XPS, JEOL Ltd., JPS-9200) using a monochrome Al Kα X-ray source (1486.6 eV). Before the surface characterizations, the immersed specimens were cleaned ultrasonically by ethanol and then in highly purified water.

2.5. Electrochemical Tests
Electrochemical measurements were carried out in a three-electrode cell using a potentiostat (Pocketstat, IVIUM TECHNOLOGIES). Open-circuit potential (OCP) was measured for 1 h at room temperature and the potentiodynamic measurements were carried out in the cathodic and anodic direction with a scan rate of 1 mV/s. A platinum plate and an Ag/AgCl electrode (SSE) immersed in a saturated KCl solution were used as counter and reference electrodes, respectively. EIS measurements were carried out at OCP in the frequency range from 10 kHz to 1 mHz, and a modulation amplitude of 10 mV. Reproducible data were obtained in all electrochemical measurements.

2.6. Corrosion Inhibition Efficiency of Metal Cations
The corrosion inhibition efficiency of metal cations was calculated from the mass loss by Eq. (1).

\[
\text{Corrosion inhibition efficiency (\%)} = \frac{\text{Na}_\text{ms} - \text{CAT}_\text{ms}}{\text{Na}_\text{ms}} \times 100
\]

where Na_ms is the mass loss of specimen immersed in Na₅₀₀ and CAT_ms is the mass loss of specimen immersed in Mg₅₀₀, Zn₅₀₀ and Al₅₀₀. The corrosion inhibition efficiency of metal cations was also calculated from the EIS by Eq. (2).

\[
\text{Corrosion inhibition efficiency (\%)} = \frac{\text{CAT}_\text{ct} - \text{Na}_\text{ct}}{\text{Na}_\text{ct}} \times 100
\]

where Na_ct is the charge transfer resistance (R_ct) of specimen immersed in Na₅₀₀ and CAT_ct is the R_ct of specimen immersed in Mg₅₀₀, Zn₅₀₀ and Al₅₀₀. From Eqs. (1) and (2), the corrosion inhibition efficiency of Na⁺ is zero.

3. Results

3.1. Immersion Tests
Figure 1(a) shows the appearance of solutions and specimens at the starting time of immersion, and (b) shows the appearance of solutions and specimens after the immersion tests at 25°C for 3 d. After the immersion, brown-red color corrosion products are observed in all the solutions. Less amount of brown-red color corrosion products is observed in the case of Zn₅₀₀ as compared to the other solutions. The solution color also different in Zn₅₀₀ as compared to the other solutions. The corrosion rates were calculated from the mass change during the immersion. Several researchers16–19) introduced the hardness of metal cation, X to explain the effect of metal cations on corrosion loss of steel in fresh water and in Cl⁻ aqueous solution. The X is not suitable corrosion indicator regarding corrosion of mild steel in fresh water and in Cl⁻ aqueous solution.16,17) However, mass losses or corrosion rates were plotted as a function of X to find out the relation between them in the environment that contains Cl⁻ at high concentration in this study. Figure 2 shows the corrosion rate as a function of X (hardness of metal cation). Each of the solution shows different corrosion rate and Zn₅₀₀ shows the lowest corrosion rate among other solutions. The correlation coefficient is ~0.32 indicating that corrosion rate is not closely related with X. The results of immersion tests indicate that Zn₅₀₀ has the better corrosion inhibition effect on carbon steel as compared to the other solutions used in this study.
3.2. Surface Characterizations

The corrosion rates of specimens immersed in the solutions are different in each solution of metal cation. The surface of the specimens may be affected by the metal cations. To clarify this matter, the surface morphological changes were observed by SEM. Figure 3 shows the surface SEM images of specimens and different surface morphologies are observed for the different solutions. SEM images represent the clear grain boundaries and pits in the case of Na$_{sol}$, Mg$_{sol}$, and Al$_{sol}$ that reflect the severe corrosion. A few numbers of pits are observed on the specimen immersed in Zn$_{sol}$. The results suggest that the corrosion of carbon steel may be affected with the metal cations in the solutions and Zn$^{2+}$ may formed hydroxides with the OH$^{-}$ of the oxide film that inhibited the corrosion reactions.$^{16,17}$ These results correspond well with the corrosion rate.

The surface roughness was measured by atomic force microscopy and the 3D images are shown in Fig. 4. Different surface roughness is observed for different solutions with metal cations. The average roughness factor ($R_a$) was calculated$^{22,23}$ from the respective 3D images to enumerate the surface roughness. The calculated $R_a$ values are listed in the Table 1. The specimen immersed in the Zn$_{sol}$ shows the lowest $R_a$ among other solutions. These results correspond well to the surface observation by SEM.

For better consideration of the effects of different metal cations on the oxide film, the specimen surfaces were analyzed by XPS after the immersion tests. Figure 5 shows the XPS wide spectra of specimen immersed in the solutions with metal cations. This figure clearly shows the peaks of Zn2p1/2 and Zn2p3/2 after immersion in the Zn$_{sol}$. Figure 5 also includes the narrow spectra of Zn 2p3/2. XPS analysis results show that there is no peak of Na 1 s, Mg 1 s and Al2p3/2 on the specimen after immersed in the respective solution signifying that Na$^+$, Mg$^{2+}$ and Al$^{3+}$ cannot form
chemical bond with the oxide film on the carbon steel surface in the solution. Clear peak of Zn$^{2+}$ among all experimental metal cations meaning that only Zn$^{2+}$ remains on the carbon steel after immersion in the solution, and Zn$^{2+}$ may form a chemical bond with the oxide film. Previous paper demonstrated that Zn$^{2+}$ formed a chemical bond with the oxide film that lead to the formation of a layer which inhibited the corrosion reactions, and protected the dissolution of metal.\textsuperscript{16-18} The results obtained from XPS analysis were good agreement with corrosion rate and surface images.

### 3.3. Electrochemical Tests

The open circuit potentials (OCP) of specimen measured in the solutions with metal cations are shown in Fig. 6. All the measured values of OCP are decreased with time. However, the OCP reached almost a stable value after around 3000 s of immersion in the solution. Slight difference can be noticed in which the Na$_{sol}$ shows the most negative open-circuit potential and Zn$_{sol}$ shows the most positive one.

Potentiodynamic polarization curves are shown in Fig. 7. From the cathodic polarization curves (Fig. 7(a)), it is found that Zn$_{sol}$ shows lower current density as compared to the other solutions. From the anodic polarization curves (Fig. 7(b)), passivation region is not observed. However, the current density around the immersion potential is not high as the active state. Therefore, it is assumed that the iron oxide film partially remained and was affected by metal cations in the solutions. Zn$_{sol}$ shows (Fig. 7(b)) lower current density as compared to the other solutions. Na$_{sol}$ shows the highest current density among used solutions both in cathodic and anodic polarization curves. In other word, Zn$_{sol}$ acts as both cathodic and anodic inhibitor as compared to the other solutions.

Figure 8 shows the Bode diagram of (a) impedance and (b) phase shift in the solutions with metal cations after immersion for 1 h. The fitted lines calculated by Randle’s equivalent circuit model\textsuperscript{24-26} are also shown in Figs. 8(a), 8(b), and the used equivalent circuit model is shown in Fig. 8(c). The fitted lines correspond well to the experimental data. The equivalent circuit model consists of solution resistance ($R_{sol}$), charge-transfer resistance ($R_{ct}$), and constant phase element ($Q$). Among experimental solutions, Zn$_{sol}$ shows the highest impedance at low frequency (Fig. 8(a)). Higher phase shift is also observed in Zn$_{sol}$ (Fig. 8(b)) than other solutions. The magnitude of impedance at low frequencies in Bode diagram indicates the corrosion resistance of specimen in the solutions.

### Table 1. Surface roughness of specimen obtained by AFM after immersion in the solutions with different metal cations at 25°C for 3 d.

<table>
<thead>
<tr>
<th>Solutions</th>
<th>Average surface roughness, R$_a$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before immersion</td>
</tr>
<tr>
<td>Na$_{sol}$</td>
<td>4.53</td>
</tr>
<tr>
<td>Mg$_{sol}$</td>
<td>4.56</td>
</tr>
<tr>
<td>Zn$_{sol}$</td>
<td>4.65</td>
</tr>
<tr>
<td>Al$_{sol}$</td>
<td>4.62</td>
</tr>
</tbody>
</table>

Fig. 6. Open circuit potential of specimen immersed in the solutions.

Fig. 5. XPS wide spectra (inset XPS narrow spectra of Zn 2p3/2) of specimens after the immersion tests.
Table 2. The calculated mean values of EIS parameters of carbon steel immersed in the solutions for 1 h.

<table>
<thead>
<tr>
<th>Solutions</th>
<th>$R_{\text{sol}}$ ($\Omega \cdot \text{cm}^2$)</th>
<th>$R_{\text{ct}}$ (k$\Omega \cdot \text{cm}^2$)</th>
<th>$Q$ ($\mu$A$^{-1} \cdot \text{cm}^{-2}$)</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Na}_{\text{sol}}$</td>
<td>17.16</td>
<td>3.03</td>
<td>206.67</td>
<td>0.83</td>
</tr>
<tr>
<td>$\text{Mg}_{\text{sol}}$</td>
<td>18.5</td>
<td>3.22</td>
<td>193.33</td>
<td>0.83</td>
</tr>
<tr>
<td>$\text{Zn}_{\text{sol}}$</td>
<td>18.16</td>
<td>4.74</td>
<td>154.00</td>
<td>0.82</td>
</tr>
<tr>
<td>$\text{Al}_{\text{sol}}$</td>
<td>17.66</td>
<td>3.64</td>
<td>180.00</td>
<td>0.85</td>
</tr>
</tbody>
</table>

The electrochemical impedance parameters are calculated using the Eq. (3).\textsuperscript{27–30} The calculated values of electrochemical impedance parameters are listed in the Table 2.

\[
Z = R_{\text{sol}} + \frac{R_{\text{ct}}}{1 + (j\omega)^n Q R_{\text{ct}}} \quad \text{(3)}
\]

High $R_{\text{ct}}$ means that the specimen has high corrosion resistance in the corresponding solution. From Table 2, $\text{Zn}_{\text{sol}}$ shows the highest $R_{\text{ct}}$ than other solutions. $\text{Zn}_{\text{sol}}$ also shows the lowest value of $Q$ than other solutions of metal cation (Table 2). The $Q$ represents the structure of solution/metal interface and the area of defects in the passive film on the surface.\textsuperscript{19,31} Islam et al.\textsuperscript{16} and Otani et al.\textsuperscript{17} reported that the decrease in $Q$ indicates that $\text{Zn}^{2+}$ can decrease the defect points in the passive film on the carbon steel. This result indicates that relatively perfect oxide film is formed on the specimen immersed in $\text{Zn}_{\text{sol}}$. Therefore, the results obtained from EIS tests suggest that the specimen immersed in the $\text{Zn}_{\text{sol}}$ has the high corrosion resistance due to formation of perfect film compare to the other solutions used in this study.

It is considered that the mass loss of specimen is directly related to the charge transfer resistance ($R_{\text{ct}}$). If the $R_{\text{ct}}$ of solution is high, the mass loss of specimen should be low. To clarify this matter, the relationship between mean values of both parameters have been examined. Figure 9 shows the relationship between charge transfer resistance ($R_{\text{ct}}$) and mass loss of specimen immersed in the solutions. The correlation coefficient is $-0.99$ indicates that $R_{\text{ct}}$ and mass loss are closely related to each other, and $\text{Zn}_{\text{sol}}$ shows the highest $R_{\text{ct}}$ and lowest mass loss among other solutions. The results of electrochemical tests well correspond with the immersion
3.4. Corrosion Inhibition Efficiency of Metal Cations

From the above experimental results, it has been confirmed that metal cations have an effective inhibitory influence on carbon steel corrosion in the solutions and Zn$^{2+}$ shows the highest corrosion inhibition effect among other metal cations used in this study. To elucidate the corrosion inhibition effect, the efficiency of corrosion inhibition of metal cations was calculated depending on the immersion tests and electrochemical tests. Figure 10(a) shows the corrosion inhibition efficiency of metal cations based on the immersion tests in which mean values of mass losses have been used. Figure 10(b) also shows the corrosion inhibition efficiency of metal cations based on the electrochemical tests in which mean values of charge transfer resistances ($R_{ct}$) have been used. In both case, Zn$^{2+}$ shows the highest corrosion inhibition efficiency than other metal cations used in this study.

4. Discussions

From the experimental results, it has been confirmed that Zn$^{2+}$ remains on the steel surface after the immersion tests. It is assumed that Zn$^{2+}$ forms a chemical bond with the
oxide film and make a layer that decrease the defect points in the film. Whereas, the other metal cations used in this study cannot remain on the surface or unable to make such kinds of bond with the oxide film. Figure 11(a) shows the schematic images of the corrosion process on carbon steel in the solution with metal cations (M²⁺ = Na⁺, Mg²⁺ and Al³⁺). The metal cations (M²⁺ = Na⁺, Mg²⁺ and Al³⁺) cannot make layer on the defect site of the oxide film. Therefore, Cl⁻ destroy the film easily at the defect point, and then corrosion occurred resulting the formation of grain boundaries and huge numbers of pits on the immersed specimen as shown in the Fig. 3. Figure 11(b) shows the schematic images of the corrosion inhibition process of carbon steel by Zn²⁺ in the solution. Zn²⁺ forms a chemical bond with the OH⁻ of the oxide film and make a metal cation layer. The metal cation layer decreases the defect points on the oxide film. From this reason, the specimen immersed in the Zn sol would have the less defect points in the oxide film as compared to the other solutions. Therefore, Zn²⁺ layer has good protective ability against the Cl⁻ attack in the solutions.

From the above discussions, it can be proposed that the high and longtime corrosion resistance of Zn coated steel substrate is attributed to the formation of Zn layer on the oxide film of steel.

5. Conclusions

(1) The corrosion behavior of carbon steel is changed in the solutions with metal cations, however, it is not closely related with the hardness of metal cation, X.

(2) The surface morphologies dependent on the metal cations (Na⁺, Mg²⁺, Zn²⁺ and Al³⁺) contained by 0.5 M Cl⁻ aqueous solution are observed by SEM and AFM. The surface of specimen immersed in the solution containing Zn²⁺ (Zncl) shows the lowest roughness as compared to the others.

(3) Zn²⁺ is detected by XPS on the specimen surface after immersion in the Zncl and, however, Na⁺, Mg²⁺ and Al³⁺ do not exist in the surface after the immersion in respective solutions.

(4) It is assumed that Zn²⁺ forms a chemical bond with the OH⁻ of oxide film, and then forms a protective layer that decreased the defect points in the film. Therefore, the Zn layer acts as a barrier for the corrosion reactions.

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