

Galvanic Corrosion of Zn/Steel Couple in Aqueous MgCl₂

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Galvanic corrosion tests of Zn/steel couples were conducted in 1 M NaCl and 1 M MgCl₂ solutions to investigate the impact of magnesium ion on corrosion behavior of the couples. Two types of Zn/steel couples were used for measurements of open circuit potential (OCP) and galvanic current. From the results of OCP transient of Zn/steel couples, the corrosion potential in 1 M MgCl₂ was a more positive value than that in 1 M NaCl during the sacrificial dissolution of Zn. However, earlier increase of OCP of the couples in 1 M MgCl₂ solution indicates that the sacrificial dissolution rate of Zn in 1 M MgCl₂ was enhanced more than that in 1 M NaCl, agreeing with the results on transients of galvanic current. This result is due to that cathodic reaction on the steel surface of the Zn/steel couple was enhanced in 1 M MgCl₂ by the occurrence of hydrogen evolution reaction.

Keywords: zinc, steel, corrosion product, magnesium ion, galvanic current

1. Introduction

Galvanized steels have been widely used in the engineering fields of automobiles, household appliances and constructions because of great corrosion resistance in atmospheric environments. For further improvement of the corrosion resistance, new galvanized coatings containing Mg were invented and confirmed to have excellent corrosion resistance in atmospheric environments [1]. Some car makers have been trying to utilize the newly-developed Mg-containing galvanized steels to automobile body panels.

So far, many researches have been done to investigate the effect of Mg on corrosion resistance of galvanized coating [2-4]. At a cut edge of a galvanized steel and at a damaged site on the coating, sacrificial dissolution of the galvanized coatings takes place and it can prevent corrosion on exposed steel surfaces. At this time, the corrosion products are formed during the sacrificial dissolution of Zn and Mg and they can bring inhibition of electrochemical reactions on the surface of the exposed steel surface, resulting in corrosion prevention of the galvanized steels. Namely, the excellent corrosion resistance of Mg-containing galvanized coatings is attributed to these complex interactions of electrochemical and chemical reactions. However, the main role of Mg con-

tributing to the excellent corrosion resistance is not fully understood.

In this study, we will investigate galvanic corrosion of Zn/steel couples in the aqueous solution containing Mg²⁺ ions, trying to clarify the effect of Mg²⁺ ions on cathodic reactions taking place on the steel surface during the sacrificial dissolution of zinc. Furthermore, we will discuss galvanic corrosion mechanism of the Zn/Steel couples in aqueous MgCl₂ solutions.

2. Experimental Procedure

In this study, measurements of open circuit potential (OCP) and galvanic current were done with Zn/steel couples shown in Fig. 1. As shown in Fig. 1(a), a galvanic couple of Zn/steel, which has a quasi-coplanar arrangement of a steel substrate and a zinc layer, was used for the OCP measurement. The galvanic couple had the zinc layer of 2 mm in width and 2 μm in thickness, which was electroplated on the center of the steel substrate 15 mm in width. The surface area ratio of the steel to the zinc was 6.5:1. On the other hand, the measurement of the galvanic current was performed with a Zn/steel couple shown in Fig. 1b. As shown in Fig. 1b, a pure Zn plate 1 mm in width and a steel plate 15 mm in width were embedded with a gap of ca. 0.25 mm in epoxy resin. A part of the steel plate was covered with a sealing tape so that the surface area ratio of the steel to the zinc was also 6.5:1.

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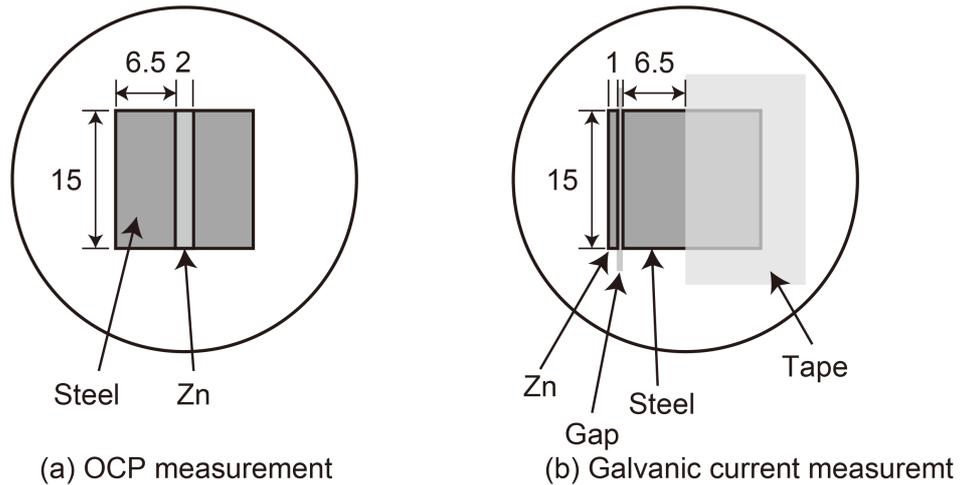


Fig. 1 Schematic drawing of Zn/Steel couples used in this study: (a) for OCP measurement, (b) for Galvanic current measurement.

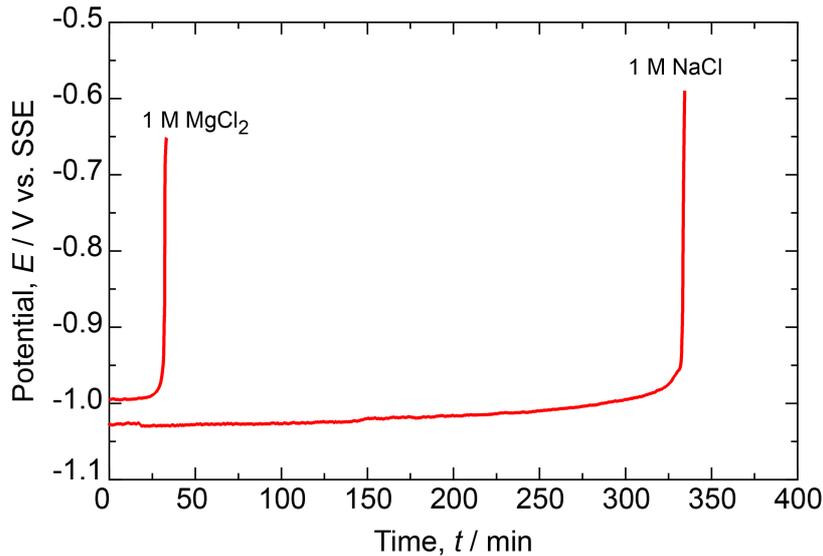


Fig. 2 OCP transients of a Zn/Steel couple measured in 1 M NaCl and 1 M MgCl₂.

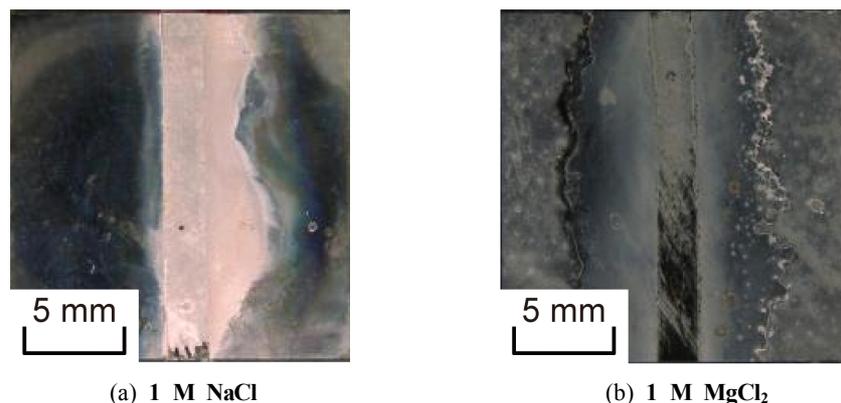
Test solutions used in this study were aqueous solutions of 1 M NaCl and 1 M MgCl₂. The Zn/steel couple was immersed in the test solutions at room temperature (ca. 25 °C) and then the OCP transient or the galvanic current transient was measured. After the OCP measurement, corrosion products formed on the steel were observed by an optical microscope and analysed by an SEM-EDS.

3. Results and Discussion

Fig. 2 shows OCP transients of a Zn/steel couple measured in 1 M NaCl and 1 M MgCl₂. As shown in Fig. 2, the OCP transients are about -1 V (SSE) after im-

mersion in the electrolytes, and after a while they increase abruptly to noble potentials, indicating that sacrificial dissolution of zinc is completed. In the case of 1 M MgCl₂, the OCP indicates a more noble potential than that in 1 M NaCl during the sacrificial dissolution of zinc. On the other hand, the time for the complete dissolution of zinc in 1 M MgCl₂ was about 6 times shorter than that in 1 M NaCl. These results demonstrate that the sacrificial dissolution rate of zinc is enhanced in 1 M MgCl₂ compared to 1 M NaCl.

Fig. 3 shows optical micrographs of Zn/steel couples immersed in 1 M NaCl and 1 M MgCl₂. Corrosion products of zinc form on the steel surface, but the precipitation



(a) 1 M NaCl

(b) 1 M MgCl₂

Fig. 3 Optical micrographs of Zn/Steel couples taken after immersion in (a) 1 M NaCl and (b) 1 M MgCl₂.

morphology of the corrosion products were quite different in both solutions. In the case of 1 M NaCl, the corrosion products precipitated mainly on the steel surface around the center where a zinc layer had been present during the sacrificial dissolution of zinc. SEM-EDS analysis reveals that the corrosion products were composed of Zn, O, and Cl, suggesting that the corrosion products mainly consist of ZnO (including Zn(OH)₂) and/or simonkolleite. On the other hand, in the case of 1 M MgCl₂, the amount of the corrosion products precipitating on the steel surface seemed to be less by comparison with the case of 1 M NaCl. Intriguingly, a boundary around which the precipitation morphology of the corrosion products changed can be seen on the steel surface a few mm away from the center where a zinc layer has been present. SEM-EDS analysis reveals that the corrosion products formed on the steel surface inside the boundary are mainly composed of Zn, O and Cl, which is similar to the case in 1 M NaCl. The corrosion products formed on the steel surface outside the boundary are confirmed to be composed mainly of Mg and O. These results suggest that the corrosion products on the steel in 1 M MgCl₂ consist of ZnO (including Zn(OH)₂) and/or simonkolleite, and MgO (including (Mg(OH)₂), depending on the distance from the zinc layer.

Fig. 4 shows transients of galvanic current of a Zn/steel couple measured in 1 M NaCl and 1 M MgCl₂. The galvanic current density shown in Fig. 4 is evaluated by dividing the galvanic current flowing by the surface area of the steel. In addition, in Fig. 4, the polarity of the galvanic current is positive, meaning that the current flows out from the zinc of the couple into a test solution. In the case of 1 M NaCl, the galvanic current density does not change very much during the immersion of the Zn/steel couple. Furthermore, it was confirmed that the

average potential of the couple does not change at almost the constant of -1.02 V (SSE). On the other hand, in 1 M MgCl₂, the galvanic current density is much higher than that in 1 M NaCl. The average potential of the couple was confirmed to be about -0.99 V (SSE). The average potentials measured in both solutions are in good agreement with the results of the OCP transients shown in Fig. 2. These results demonstrate that cathodic reaction on the steel is enhanced in 1 M MgCl₂ by comparison of 1 M NaCl.

From the results of the OCP measurements and the galvanic corrosion tests, it was found that cathodic reaction on the steel surface was enhanced in 1 M MgCl₂ compared to 1 M NaCl. Judging from the magnitude of the galvanic current densities in 1 M NaCl and 1 M MgCl₂, it can be considered that cathodic reaction on steel surface in 1 M NaCl is mainly oxygen reduction reaction, but that on the steel surface in 1 M MgCl₂ the reduction reaction of water molecules, hydrogen evolution reaction, in addition to oxygen reduction reaction takes place although the average corrosion potential of the Zn/steel couple in 1 M MgCl₂ is more positive than that in 1 M NaCl. In addition, it was found that in 1 M MgCl₂ the corrosion products containing Mg oxides was formed on the steel far away from the surface where a zinc layer has been present, suggesting that Mg²⁺ ions are incorporated into the formation reaction of the corrosion products on the steel. Therefore, it can be drawn from these findings that surface pH on the steel in 1 M MgCl₂ is lower than that in 1 M NaCl due to pH buffering action of Mg²⁺. This means that Mg²⁺ ions can suppress the increment of surface pH due to OH⁻ evolution on oxygen reduction reaction and hydrogen evolution reaction. In this study, Mg²⁺ ions in the aqueous solution are relatively high, and this may also have a large impact on the change in surface pH on the

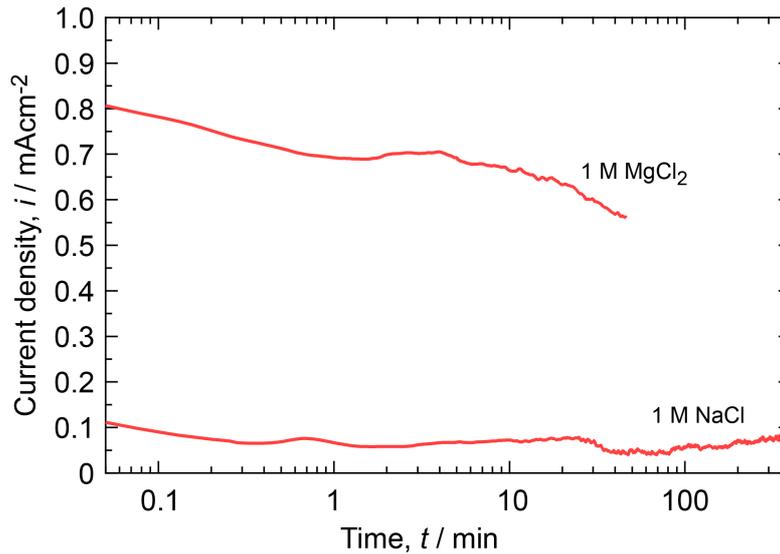


Fig. 4 Transients of galvanic current density of Zn/Steel couples measured in 1 M NaCl and 1 M MgCl₂.

steel. That is why in the case of 1 M MgCl₂ the cathodic reaction taking place on the steel surface, mainly hydrogen evolution reaction, can be accelerated even at more positive corrosion potential by comparison with the case of 1 M NaCl.

4. Summary

In this study, galvanic corrosion behaviours of Zn/Steel couples were investigated in 1 M NaCl and 1 M MgCl₂. From the results of this study, it was found that anodic dissolution of zinc was enhanced significantly in 1 M MgCl₂ by comparison with the case in 1 M NaCl. It was

due to that cathodic reaction on the steel surface is accelerated in 1 M MgCl₂ more than in 1 M NaCl.

References

1. N. C. Hosking, M. A. Ström, P. H. Shipway, and C. D. Rudd, *Corros. Sci.*, **49**, 2669 (2007).
2. R. Kreig, M. Rohwerder, S. Evers, B. Schuhmacher, and J. Schauer-Pass, *Corros. Sci.*, **65**, 119 (2012).
3. M. S. Azevedo, C. Allély, K. Ogle, and P. Volovitch, *Corros. Sci.*, **90**, 472 (2014).
4. P. Volovitch, T. N. Vu, C. Allély, A. A. Aal, and K. Ogle, *Corros. Sci.*, **53**, 2437 (2011).