Electrodeposition of Zn-Mg Alloy from 1-Ethyl-3-Methylimidazolium Bromide Organic Molten Salt

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The electrodeposition of Zn-Mg alloy from 1-ethyl-3-methylimidazolium bromide (abbreviated to EMIB) organic molten salts was investigated. The Zn-Mg alloy deposits were obtained from EMIB-(Zn, Mg)Br_2 molten salts with ethylene glycol (EG) or glycerin (G) at 120 or 140□, respectively. The Mg content of Zn-Mg alloy obtained from the EMIB-(Zn, Mg)Br_2-EG (18:6:4:72 mol%) bath and the EMIB-(Zn, Mg)Br_2-G (25.5:8.5:6.5:59.5 mol%) bath were 2.5 mol% and 20 mol%, respectively. The corrosion tests in the 5 mass% NaCl aqueous solution at 35°C showed that the Zn-Mg plated steel (independently of Mg content) has about 20 times higher corrosion resistance than the Zn plated steel.

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1. Introduction

Zinc plating is widely utilized as a rust preventive surface treatment for steel plates for automobiles, building materials, and so on. In order to improve the corrosion resistance of the zinc plating, many kind of zinc alloy plating has been studied and developed. Kawafuku *et al* [1]. reported that the first red rust generation time of the Zn-Mg alloy plated steel prepared by vacuum vapor deposition in the salt spray test was about 20 times longer than that of Zn plated steel. The zinc and zinc alloy platings such as Zn-Ni, Zn-Fe, and Zn-Co can be obtained from aqueous solutions. The Zn-Mg alloy plating, however, must be carried out in a non-aqueous solution such as molten salts so that less noble Mg co-electrodeposit with zinc without H_2 generation.

Steel for automobile is produced via a series of heat treatment to increase its mechanical strength. If the electrodeposition of Zn-Mg alloy is conducted onto steel in the usual molten salt (inorganic molten salt) at elevated temperature, the strength of the substrate steel obtained by the heat treatment will reduce. We have paid attention to 1-ethyl-3-methylimidazolium bromide (EMIB), one of the organic molten salts (organic ionic liquid), as a bath for the electrodeposition of metals and alloys. The suitable conditions for Zn plating from the EMIB-$ZnBr_2$ and the effect of additives such as ethylene glycol and glycerin have been already clarified[2-5]. In this paper, the electrodeposition of Zn-Mg alloy from EMIB-(Zn, Mg)Br_2 based organic molten salt and the corrosion test in the 5 mass% NaCl aqueous solution were investigated.

2. Experimental

2-1 *Preparation of baths*

The electrolytic baths used in this study were composed of EMIB(Sanko Chemical Co.), $ZnBr_2$, ethylene glycol (abbreviated to EG), glycerin (abbreviated to G), and Mg(II) ions. Before use, EMIB was dried at 80°C under vacuum using a rotary oil pump for 259.2 ks, $ZnBr_2$ was dried at 180°C for 1.8 ks, and EG and G were dehydrated by molecular sieve (0.3 nm). EMIB and $ZnBr_2$ were mixed, heated to 120°C, and dehydrated under vacuum for 86.4 ks. Prescribed amount of EG or G was added to the EMIB-$ZnBr_2$ bath. Mg(II) ion was introduced by the chemical displacement of Zn(II) ion in the EMIB-$ZnBr_2$-EG or EMIB-$ZnBr_2$-G baths with Mg metal (grain size 1-5 mm, purity>99.9%). The concentration of Mg(II) in the baths were measured by ICP analysis. The preparations of the baths were conducted in an Ar gas filled glove box.

2-2 *Electrodeposition of Zn-Mg alloy*

The schematic illustrations of the electrolysis cell and the reference electrode are shown in Fig. 1. The electrochemical behaviors of Zn ion and Mg ion were studied by measuring the cathodic polarization curves with a scan rate of 0.05 Vs^{-1} using a copper cathode (purity: 99.99%, 0.2 mm thickness) and a glassy carbon anode. The reference electrode used in the electrochemical measurements was a Zn wire immersed in a separate glass tube containing the EMIB-$ZnBr_2$-EG (45:10:45 mol%) or the EMIB-$ZnBr_2$-G (40.3:17.2:42.5 mol%) with frit glass at its bottom.

Zn-Mg alloys were electrodeposited from the EMIB-(Zn, Mg)Br_2-EG bath at 120°C and the EMIB-(Zn, Mg)Br_2-G bath at 140°C using a copper cathode (purity: 99.99%, 0.2 mm thickness) and a zinc anode (purity: 99.99%, 0.2 mm thickness). The electrodeposition of Zn-Mg alloys were conducted at constant potentials of -0.6 V or -0.8 V. The electric charge passed was 2.5×10^5 Cm^{-2} of the cathode substrate. EPMA analysis and X-ray diffraction analysis were used to identify the electrodeposits, and the Mg contents in the electrodeposits were measured by ICP analysis.

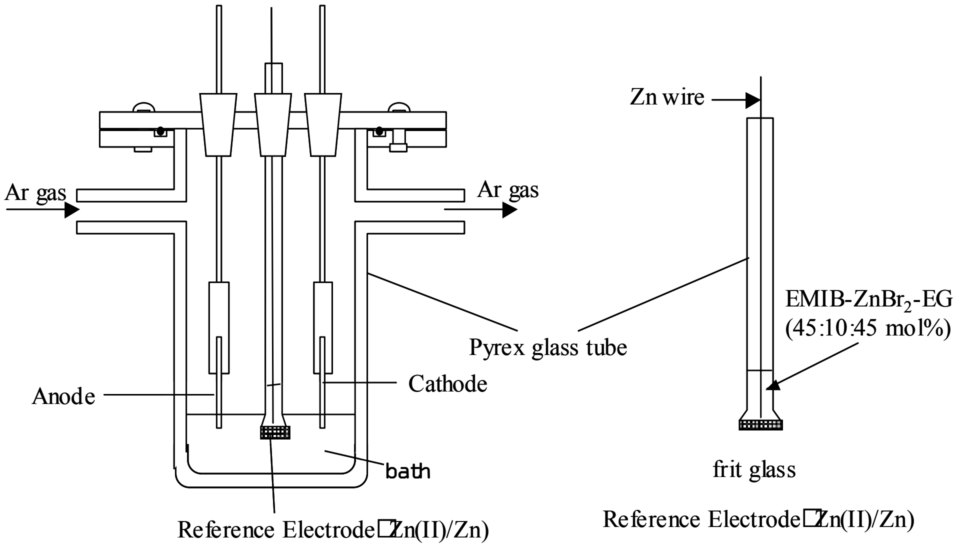

Fig. 1 Schematic illustrations of the electrolysis cell and the reference electrode.

2-3 *Corrosion test*

The corrosion evaluation test for the Zn-Mg alloy platings was conducted in the 5 mass% NaCl aqueous solution at 35°C. Zn-Mg alloys were electrodeposited on the steel for automobiles in the conditions as mentioned above. The non-plating area of the steel was masked by an epoxy resin. The Zn-Mg alloy plated steel was immersed in the NaCl aqueous solution and the corrosion resistance was evaluated by observing the surface and measuring the first red rust generation time. The corrosion products were identified by X-ray diffraction analysis.

3. Results and Discussion

3-1 *Electrodeposition of Zn-Mg alloy*

3-1-1 *Electrochemical behavior in EMIB-(Zn, Mg)Br_2-EG bath*

Figure 2 shows the cathodic polarization curves measured in (a) EMIB, (b) EMIB-$ZnBr_2$-EG (18:10:72 mol%), and (c) EMIB-(Zn, Mg)Br_2-EG (18:(6:4):72 mol%) which was prepared from bath (b) by the chemical displacement of Zn(II) ions with Mg metal. Figure 2 (a) shows that the reduction of EMI^+ cation occurs at the potential of -0.8 V. The reduction current starting at the potential of 0.2 V in bath (b) corresponds to the reduction of Zn(II) ion to Zn metal and the Zn plating was obtained from this bath[3]. On the other hand, an increase in reduction current of bath (c) is observed at about 0 V. It is thought that this is due to the over potential caused by the electrodeposition of Mg as Zn-Mg alloy. The oscillation of the current at about -0.8 V can be attributed to the reduction (decomposition) of EMI^+ cation.

3-1-2 *Electrodeposition of Zn-Mg alloy from EMIB-(Zn, Mg)Br_2-EG*

Constant potential electrolysis was conducted in the EMIB-(Zn, Mg)Br_2-EG (18:(6:4):72 mol%) at a potential of -0.6 V for 2.5×10^5 Cm^{-2} to obtain the Zn-Mg alloy. This potential was the one that the maximum cathodic current without the decomposition of EMI^+ cation (it occurs at the nobler potential than -0.8 V) was available. Figure 3 shows results of EMPA analysis for a cross section of the specimen. It shows that the specimen contains Zn and Mg elements, and Mg element was uniformly distributed in the specimen. Figure 4 (b) shows an X-ray diffraction pattern of the specimen. For reference, the X-ray diffraction pattern of the Zn electrodeposit obtained from bath (b) at 300 Am^{-2} is shown in Fig. 4 (a). The diffraction peaks of Cu (substrate), Zn, and $CuZn_5$ which is considered to be the intermetallic compound formed at the interface of the substrate Cu and the electrodeposited Zn were detected as shown in both Fig. 4 (a) and Fig. 4 (b). Furthermore, small and broad X-ray peaks corresponding to Mg_2Zn_{11} were detected in Fig. 4 (b). It is thought that Mg in the specimen was electrodeposited as fine and/or amorphous-like Mg_2Zn_{11}. Figure 5 shows the variation in Mg content in the platings obtained from the EMIB-(Zn, Mg)Br_2-EG bath with Mg(II) concentration. The maximum Mg content was 2.5 mol% in the plating obtained from the EMIB-(Zn, Mg)Br_2-EG (18:(6:4):72 mol%) bath. As the Mg(II) concentration in the bath became more than 4.0 mol%, the Mg content in the plating decreased. It is considered that Mg(II) ions can not be electrodeposited without Zn(II) ions from the EMIB-based organic molten salt. Since Mg(II) ion was introduced by the chemical displacement in this study and as a result the concentration of Zn(II) ion decreased as the concentration of Mg(II) ion increased, the co-electrodeposited Mg content is considered to be decreased in proportion to the concentration of Zn(II) ion.

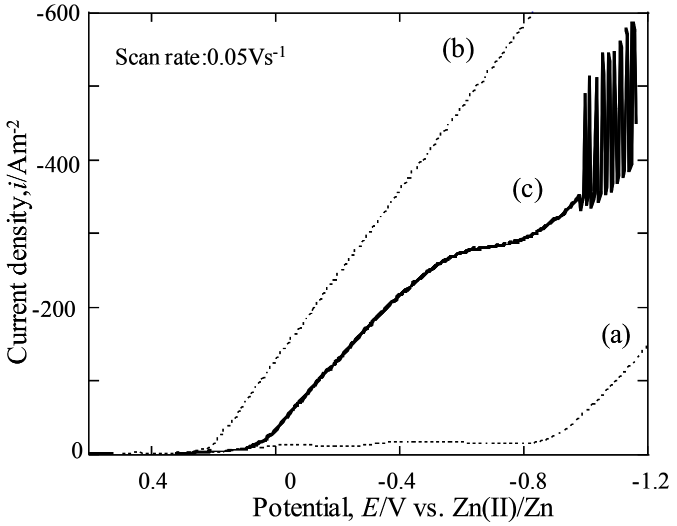

Fig. 2 Cathodic polarization curves measured in (a) EMIB, (b) EMIB-ZnBr$_2$-EG (18:10:72 mol%), and (c) EMIB-(Zn, Mg)Br$_2$-EG (18:(6:4):72 mol%) at 120°C.

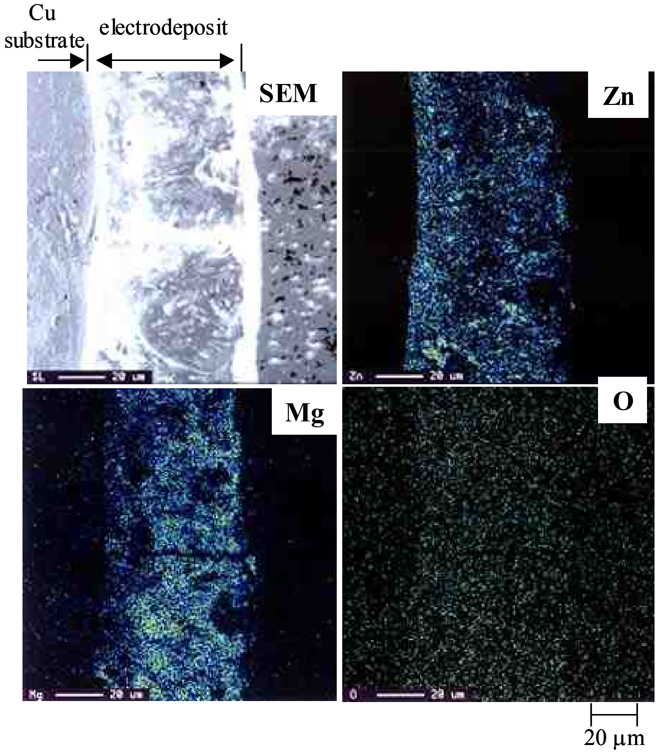

Fig. 3 EPMA image mappings of a cross section of a deposit obtained from the EMIB-(Zn, Mg)Br$_2$-EG(18:(6:4):72 mol%) at -0.6 V vs. Zn(II)/ Zn at 120°C.

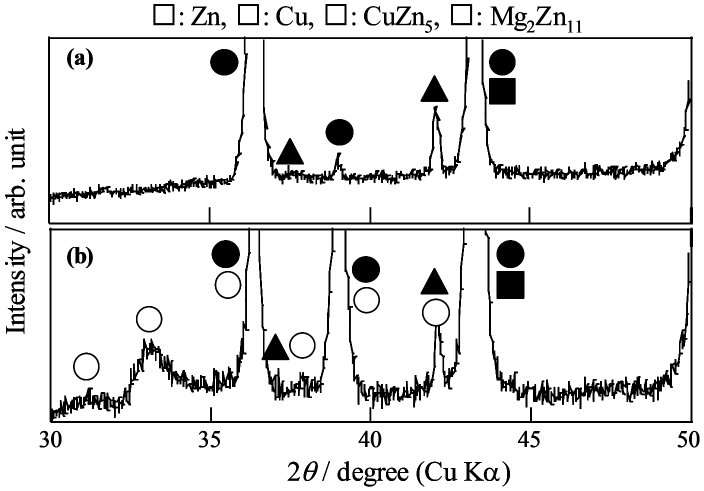

Fig. 4 X-ray diffraction patterns of the specimens obtained from (a) EMIB-ZnBr$_2$-EG (18:10:72 mol%) at 300 Am^{-2} and from (b) EMIB-(Zn,Mg)Br$_2$-EG (18: (6: 4): 72 mol%) at -0.6 V vs. Zn(II)/Zn at 120°C.

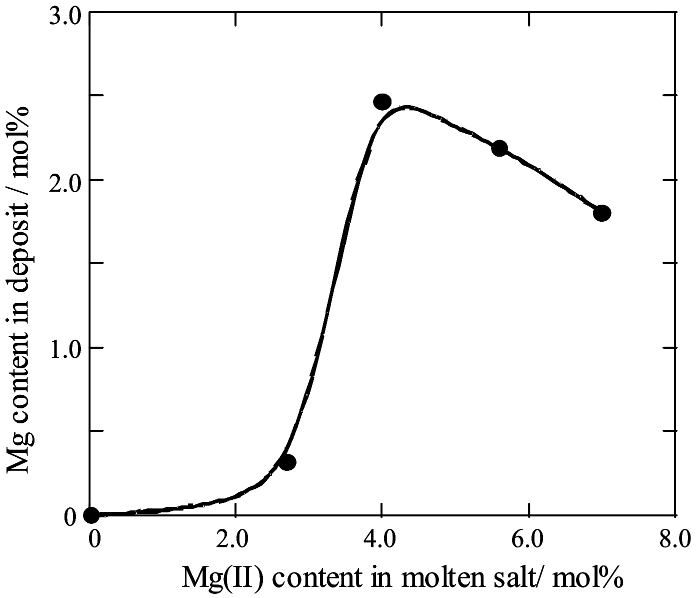

Fig. 5 Variation in Mg content in the plating with Mg(II) content in the molten salt. The electrolysis was conducted in the EMIB-(Zn, Mg)Br$_2$-EG baths at -0.6 V vs. Zn(II)/Zn at the temperature of 120°C.

3-1-3*Electrochemical behavior in EMIB-(Zn, Mg)Br$_2$-G*

A small amount of ethylene glycol evaporates during the electrolysis in the EG added bath at 120°C. The vapor pressure of G is much lower than that of EG and therefore the electrolysis at an elevated temperature of 140°C is possible without evaporation of G. Figure 6 shows cathodic polarization curves measured in (a) EMIB, (b) EMIB-ZnBr$_2$-G (25.5:15:59.52 mol%), and (c) EMIB-(Zn, Mg)Br$_2$-G (25.5:(8.5:6.5):59.5 mol%) which was prepared from bath (b) by the chemical displacement. Figure 6 (a) shows the reduction of EMI$^+$ cation was occurred at about -1.0 V. The reduction current at the potential of 0 V in bath (b) corresponds to the reduction of Zn(II) ion to Zn metal$^{4)}$. On the other hand, the reduction current of bath (c) is observed at about 0.15 V. It is thought that this was caused by the same reason as mentioned above.

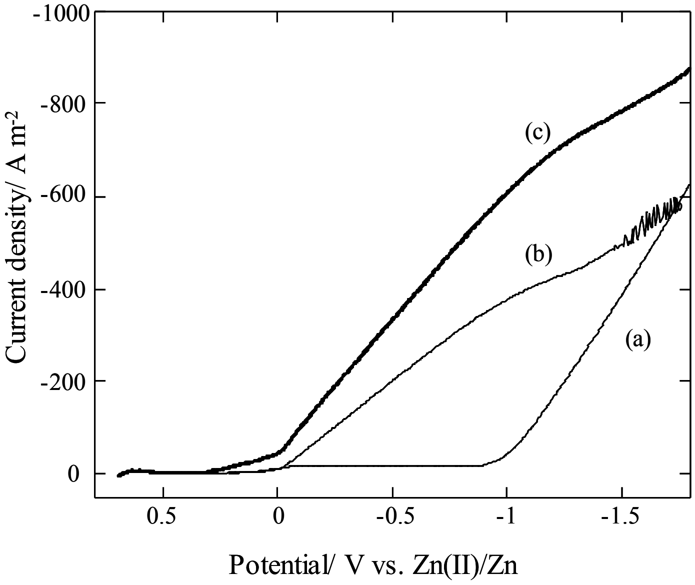

Fig. 6 Cathodic polarization curves measured in (a) EMIB, (b) EMIB-ZnBr$_2$-G (25.5:15:59.5 mol%), and (c) EMIB-(Zn, Mg)Br$_2$-G (25.5:(8.5:6.5):59.5 mol%) at 140°C.

3-1-4 *Electrodeposition of Zn-Mg alloy from EMIB-(Zn, Mg)Br_2-G*

Constant potential electrolysis was conducted in the EMIB-(Zn, Mg)Br_2-G (25.5:(8.5:6.5):59.5 mol%) at a potential of -0.8 V for 2.5×10^5 Cm^{-2} to obtain the Zn-Mg alloy. This potential was the one that the maximum cathodic current without the decomposition of EMI^+ cation (nobler than -1.0 V) was available. The results of EMPA analysis and the X-ray diffraction pattern of the specimen is shown in Fig.7 and Fig.8 (a), respectively. These figures show that the Zn-Mg alloy was composed of Zn and Mg_2Zn_{11}, and also Mg element was uniformly distributed in the specimen. However, the X-ray peaks corresponding to Mg_2Zn_{11} were small and broad. In order to confirm the electrodeposition of Mg as Mg_2Zn_{11}, the electrodeposit was heat-treated at 300°C for 10.8 ks. Figure 8 (b) shows the X-ray diffraction pattern of the specimen after the heat treatment. The sharp and definite X-ray peaks for Mg_2Zn_{11} were detected. Table 1 shows the Mg contents in the platings obtained from the EMIB-(Zn, Mg)Br_2-G bath. It shows that the Zn-Mg alloys contain 12~25 mol%Mg. The maximum Mg content was 25 mol% in the plating obtained from the EMIB-(Zn, Mg)Br_2-G (25.5:(8.4:6.6:59.5 mol%) bath. Thus it was found that the Zn-Mg alloy plating was possible in the EMIB-(Zn, Mg)Br_2-G bath at 140°C and the Mg content in the plating obtained from G-added bath was higher than that of the EG-added bath. The Zn-Mg alloy platings containing more than 25 mol% Mg had a tendency to have a lot of cracks and peel off from the substrate.

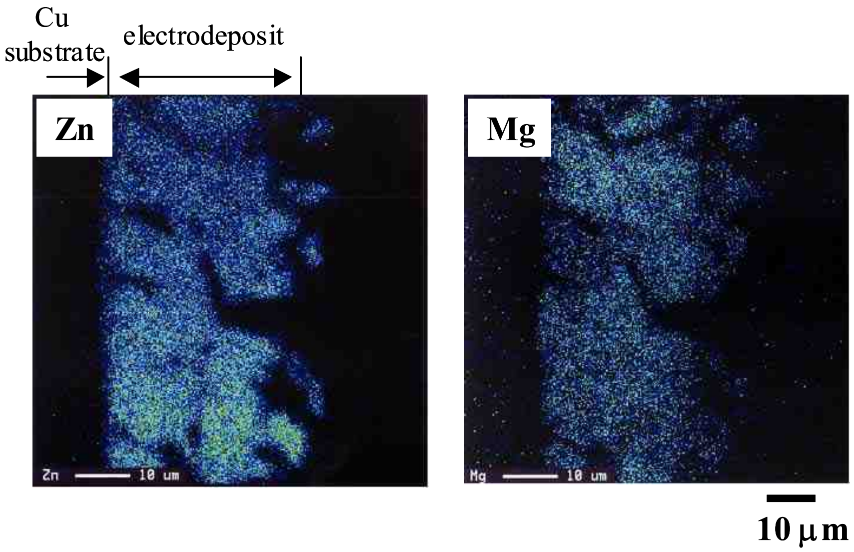

Fig. 7 EPMA image mappings of a cross section of deposit obtained from EMIB-(Zn, Mg)Br$_2$-G(25.5:(8.5:6.5):59.5 mol%) at -0.8 V vs. Zn(II)/ Zn at 140°C.

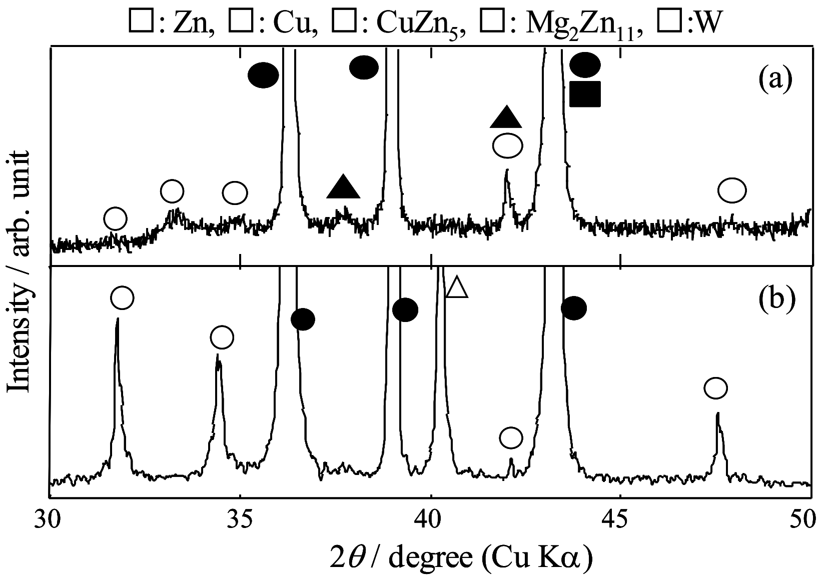

Fig. 8 X-ray diffraction patterns of the specimens obtained from (a) EMIB-(Zn,Mg)Br$_2$-G (25.5:(8.5:6.5):59.5 mol%) at -0.8 V vs. Zn(II)/Zn at 140°C and (b) specimen on W after heat treatment at 300°C for 10.8 ks (b).

Table 1 the Mg contents in the platings obtained from the EMIB-(Zn, Mg)Br_2-G bath

Mg content in the bath / mol%	Mg content in deposit / mol%
6.0	12
6.5	20
6.6	25

3-2 *Corrosion test*

The corrosion resistance of the Zn plated steel and the Zn-Mg plated steel was estimated by measuring the first red rust generation time in the 5 mass% NaCl aqueous solution at 35°C. The Zn plated steel was prepared by the electrodeposition of Zn on steel at a current density of 300 Am^{-2} from the EMIB-$ZnBr_2$-EG(18:10:72 mol%) bath at 393 K. The Zn-2.5 mol%Mg alloy plated steel and the Zn-20 mol%Mg alloy plated steel were prepared by the electrodeposition of Zn-Mg on steel under the condition mentioned above. Figure 9 shows the results of the corrosion test. The time of first red rust occurrence for the Zn-plated steel was about one week. On the other hand, that for the Zn-Mg plated steels was about 20 weeks independently of Mg content. This test revealed that the Zn-Mg alloy plating has a very high corrosion resistance (about 20 times higher corrosion resistance than the Zn-plated steel).

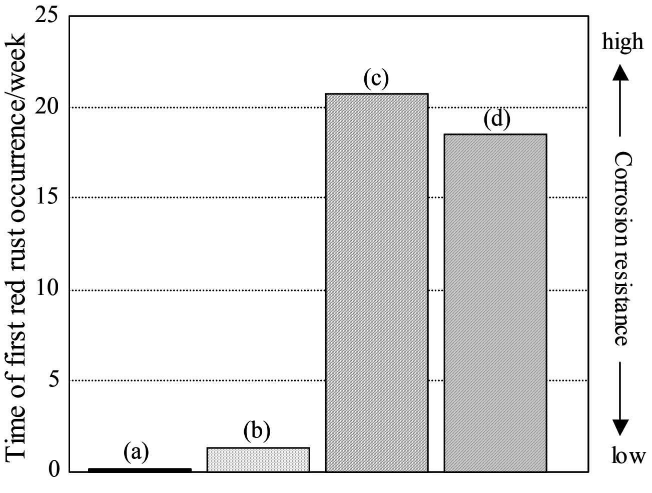

Fig. 9 Time of first red rust occurrence for (a) steel, (b) Zn-plated steel, (c) Zn-2.5 mol%Mg alloy plated steel, and (d) Zn-20 mol%Mg alloy plated steel.

Figure 10 shows the change in the rest potential for (a) the Zn plated steel and (b) the Zn-2.5 mol%Mg alloy plated steel in the 5 mass% NaCl aqueous solution at 35°C. As for (a), the rest potential of the Zn plated steel at the beginning of the corrosion test was about -1.05 V vs. SCE. It began to move to nobler potential after 3 days, and reached -0.6 V vs. SCE after 10 days. The X-ray diffraction patterns of the Zn plated steels after the corrosion tests of (a) 2 days (at -1.07 V vs. SCE), (b) 5 days (at -0.92 V vs. SCE), and (c) 10 days (at -0.60 V vs. SCE) are shown in Fig. 11. From this results, it is considered that the corrosion process of the Zn plated steel is as follows: (i) In the initial stage of the corrosion, $ZnCl_2$□$4Zn(OH)_2$ which was an insulating corrosion product was formed on the Zn plated steel. (ii) ZnO which has conductivity was formed and as a result the rest potential moved to nobler potential. (iii) The plating material on the steel was dissolved and steel was corroded. On the other hand (Fig. 10 (b)), the rest potential of the Zn-Mg alloy plated steel at the beginning of the corrosion test was almost the same as that of the Zn plated steel. However, it moved very slowly to nobler potential, and it was about -0.9 V vs. SCE even after 35 days. Figure 12 shows the X-ray diffraction patterns of the Zn-Mg plated steels after (a) 10 days (at -0.95 V vs. SCE) and (b) 35 days (at -0.90 V vs. SCE) in the corrosion test. The initial corrosion product□$ZnCl_2$□$4Zn(OH)_2$ was detected in Fig. 12 (a). ZnO which has conductivity and causes the acceleration of corrosion was formed just after 35 days. Therefore, we consider that the excellent corrosion resistance of the Zn-Mg plating is due to the fact that Mg ion suppress the process (i) to (ii) and/or (ii) to (iii), and as a result the effect of sacrificial protection of the Zn-Mg alloy for steel continues for a long time.

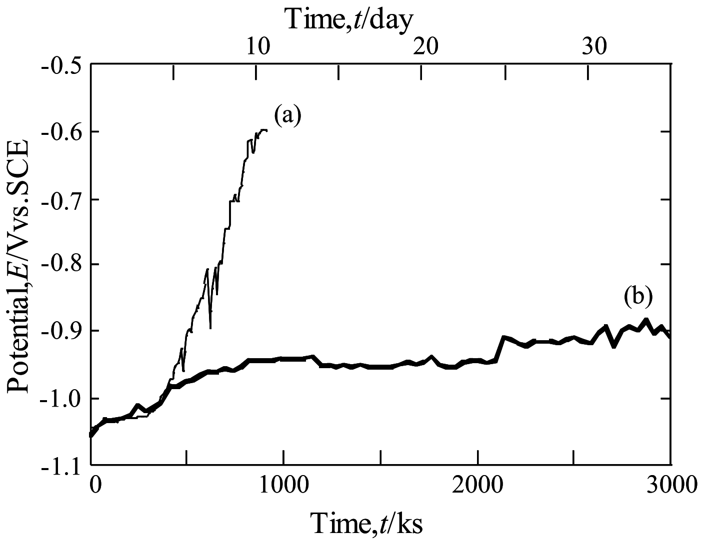

Fig. 10 Rest potential changes of the Zn-plated steel (a) and the Zn-2.5 mol%Mg alloy plated steel (b) in 5 mass% NaCl aqueous solution at 35°C.

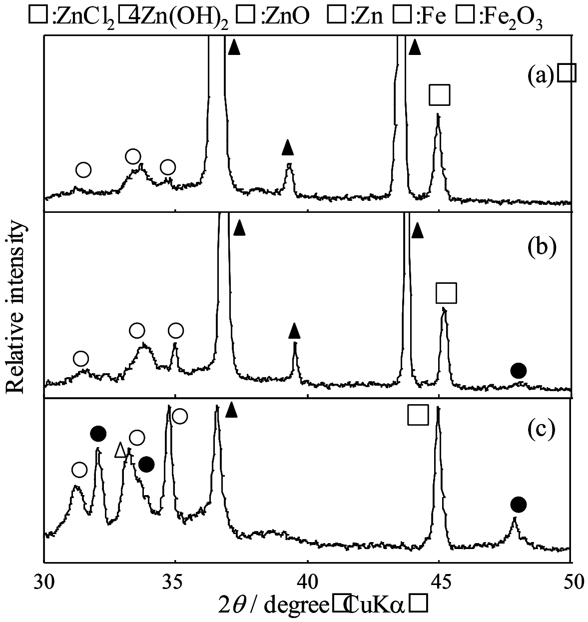

Fig. 11 X-ray diffraction patterns of the Zn plated steel after (a) 2 days, (b) 5 days, and (c) 10 days in the corrosion test.

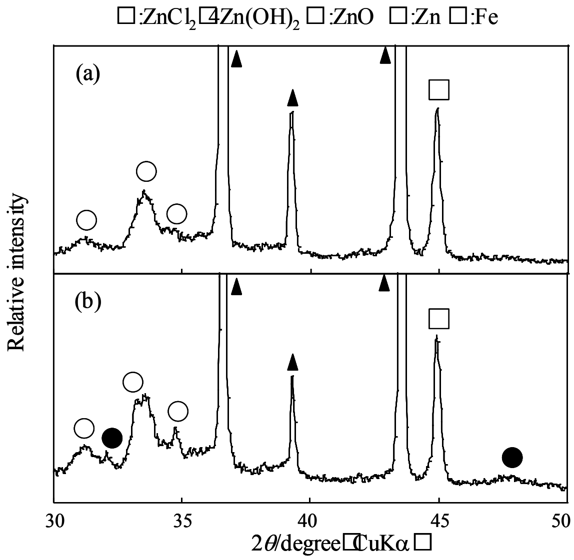

Fig. 12 X-ray diffraction patterns of the Zn-Mg plated steel after the corrosion tests of (a) 10 days and (b) 35 days.

4. Conclusion

The electrodeposition of the Zn-Mg alloy was investigated using the 1-ethyl-3-methylimidazolium bromide organic molten salts. The Zn-Mg alloy deposits were obtained from the EMIB-(Zn, Mg)Br_2 molten salts with ethylene glycol (EG) or glycerin (G) at 120 or 140□, respectively. Mg was electrodeposited as Mg_2Zn_{11}. The Mg content of the Zn-Mg alloy obtained from the EMIB-(Zn, Mg)Br_2-EG (18:6:4:72 mol%) bath at -0.6 V vs. Zn(II)/Zn and the EMIB-(Zn, Mg)Br_2-G (25.5:8.5:6.5:59.5 mol%) bath at -0.8 V vs. Zn(II)/Zn were 2.5 mol% and 20 mol%, respectively. The corrosion tests in the 5 mass% NaCl aqueous solution at 35°C showed that the Zn-Mg alloy plating has about 20 times higher corrosion resistance than the Zn-plated steel.

5. Reference

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