Letters

Electrodeposition of Zn-Mg Alloy from Trimethyl Propylammonium Bis(trifluoromethylsulfonyl)imide Ionic Liquid

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1. Introduction

We have studied about the electrodeposition of Zn-Mg alloy, which shows very high corrosion resistance, from the baths using 1-ethyl-3-methylimidazolium bromide (EMIB) ionic liquid^{1)~4)}. In order to obtain basic metal, Mg, with Zn, the EMIB based baths must be dehydrated thoroughly, and the constant potential electrodepositions must be conducted at near the potential where the reduction of EMI^+ cation occurred^{1)~3)}. Constant current electrodeposition at high current density causes the reduction of EMI^+ cation. Trimethyl propylammonium bis(trifluoromethylsulfonyl)imide (TMPATFSI) is one of the ionic liquids which have wide electrochemical potential windows and hydrophobic property^{5)~8)}. This TMPATFSI appears to be preferable to EMIB for the electrodeposition of Zn-Mg alloy. We have already reported about the electrodeposition of Zn from TMPATFSI based bath as a previous step to Zn-Mg alloy electrodeposition⁹⁾. In this paper, the electrodeposition of Zn-Mg alloy from the bath using TMPATFSI was investigated.

2. Experimental

We previously reported about the electrodeposition of Zn-Mg alloy from ethylene glycol (EG) added EMIB baths¹⁾ or glycerin (G) added EMIB baths³⁾. Mg contents in the electrodeposits obtained from EG-added baths were 0.3-2.5 mol% and those obtained from G-added baths were 0.48-25 mol%⁴⁾. The addition of G seems to be effective for Zn-Mg alloy electrodeposition. However, Zn-Mg alloy plated steel containing more than 2.5 mol%Mg showed high corrosion resistance independently of Mg content and Zn-Mg alloy plating containing more than 20 mol%Mg obtained from G-added baths had a tendency to have a lot of cracks and peel off from the substrate. Thus, the electrodeposition of Zn⁹⁾ and Zn-Mg alloy from EG-added TMPATFSI baths were investigated. Zn (TFSI)₂ (Sanko Chemical Industry Co., water ≤ 0.

1%) was dehydrated under vacuum at 373 K for 72 h before use. Zn(TFSI)₂, EG (Kanto Chemical Co., purity > 99.5%, water ≤ 0.2%), and TMPATFSI (Sanko Chemical Industry Co., water ≤ 0.2%) were weighed in the composition of TMPATFSI-Zn (TFSI)₂-EG (48 : 12 : 40 mol%) and mixed. This mixture was dehydrated under vacuum again to prepare the Zn plating bath. Mg ion was introduced into the bath by anodic dissolution under constant current density of 50 Am⁻² at 393 K using a copper cathode (purity : 99.99%, 0.3' mm × 30 mm × 5 mm) electropolished in orthophosphoric acid and a magnesium anode (purity : 99.97%, 0.3' mm × 30 mm × 5 mm) degreased by acetone. These substrates were exchanged every passed charge of 50 C. Concentration of Mg ion and Zn ion in the bath was measured by ICP analysis (Seiko Instruments Inc., SPS-4000) to calculate the composition of the bath. The electrodeposition of Zn-Mg alloy was conducted on the copper substrate in TMPATFSI-(Zn, Mg)(TFSI)₂-EG (48 : (12-x : x) : 40 mol%) bath under constant current density of 50 Am⁻² for 2.5 × 10⁵ Cm⁻² at 393 K. After washing with acetone and water, and drying, the electrodeposits were examined by XRD (Rigaku, RINT-2200) and EPMA (JEOL, JXA-8900 R). Preparation of bath and electrodeposition were conducted in Ar gas filled glove box (MIWA MFG, DB 0-1-W).

3. Results and discussion

The electrodeposition of Zn-Mg alloy was conducted in the TMPATFSI-(Zn, Mg)(TFSI)₂-EG (48 : (6 : 6) : 40 mol%) bath under constant current density of 50 Am⁻² for 2.5 × 10⁵ Cm⁻² at 393 K. The obtained electrodeposit was analyzed by XRD and the result is shown in Fig. 1 (a). XRD peaks corresponding to the Cu substrate, Zn, and CuZn₅, which was considered to be formed between the Cu substrate and the Zn deposit, were detected. In addition, the weak peaks suggesting the deposition of Zn-Mg alloy, Mg₂Zn₁₁, were observed in Fig. 1 (a). Since the XRD peaks of Mg₂Zn₁₁ was very weak, the component elements of

the electrodeposit were analyzed by EPMA to confirm the co-electrodeposition of Mg. **Figure 2** shows the SEM image and EPMA mapping images of Zn and Mg of the surface of the electrodeposit. This result indicates that the electrodeposit contains Zn element and Mg element, and Mg exists almost uniformly in the electrodeposit. Mg content in this specimen measured by EPMA quantitative analysis was about 5 mol%. According to the equilibrium phase diagram of the Mg-Zn binary system, Mg is hardly solid-soluted in Zn¹⁰. From these results, it seems that Mg in the electrodeposit exists as Mg₂Zn₁₁ and/or supersaturated solid solution in Zn in nonequilibrium state. In order to verify the state of Mg in the electrodeposit, the electrodeposition of Zn-Mg alloy under the same condition as mentioned above was conducted on the W substrate so as not to form intermetallic compound between the substrate and the electrodeposit, and it was heat-treated at 573K for 10.8ks. **Figure 1 (b)** and **(c)** show the XRD patterns of the electrodeposit on the W substrate before and after heat treatment, respectively. The XRD pattern of **Fig. 1 (b)** is almost the same as **Fig. 1 (a)**. The lattice constant (Å) of Zn in Zn-Mg alloy electrodeposit calculated from the XRD peaks at high angles is (a, c) = (2.671, 4.955) whereas that of pure Zn is (a, c) = (2.665, 4.947)¹¹. It is possible that Mg is solid-soluted in Zn. As shown in **Fig. 1 (c)**, the XRD peaks corresponding to Mg₂Zn₁₁ are sharpened and much clear after heat treatment. These result suggests the possibility that Mg exists as supersaturated solid solution in Zn in the Zn-Mg

electrodeposit obtained from the TMPATFSI-(Zn, Mg)(TFSI)₂-EG (48 : (6 : 6) : 40 mol%) bath under constant current density of 50 Am⁻² for 2.5×10⁵ Cm⁻² at 393 K.

Figure 3 shows the Mg contents of the electrodeposits obtained from TMPATFSI-(Zn, Mg)(TFSI)₂-EG (48 : (12-x : x) : 40 mol%) baths under constant current density of 50 Am⁻² for 2.5×10⁵ Cm⁻² at 393 K. As the concentration of Mg ion in the bath increased within the limit of 0≤x≤6, Mg content in the electrodeposit increased. The maximum Mg content was about 5 mol% in the electrodeposit obtained from the TMPATFSI-(Zn, Mg)(TFSI)₂-EG (48 : (6 : 6) : 40 mol%) bath as mentioned above. The structure of Zn-Mg alloy electrodeposit in this study is almost the same as that obtained from EMIB based baths in previous study^{1),3)}. We have already reported that the corrosion resistance of Zn-Mg alloy plated steel containing more than 2.5mol% of Mg is about 20 times higher than that of Zn plated steel in 5mass% NaCl aqueous solution at 308 K⁴⁾. Thus Zn-5mol%Mg alloy plating prepared in this study is also expected to show high corrosion resistance.

As mentioned above, the electrodeposition of Zn-Mg alloy from EMIB based bath was conducted at near the potential where the reduction of EMI⁺ cation occurred in order to obtain Zn-Mg alloy at high current densities^{1)~3)}, because Zn-Mg alloy whose Mg was dispersed uniformly in the electrodeposit could not be obtained at low current densities²⁾. However, it was obtained at low current density of 50 Am⁻² in this study. Further investigation including the electrochemical measurements such as cathodic polarization curves and cyclic voltammograms, the activities of ionic species, and the electrodeposition at high current

Fig. 1 X-ray diffraction patterns of the electrodeposits obtained from the TMPATFSI-(Zn, Mg)(TFSI)₂-EG (48 : (6 : 6) : 40 mol%) bath under the constant current density of 50 Am⁻² with passed charge of 2.5×10⁵ Cm⁻² at 393 K on (a) Cu and (b, c) W substrate. (c) shows the XRD pattern of the specimen after heat treatment at 573 K for 10.8 ks. ○ : Zn, ■ : Cu, □ : W, ▲ : CuZn₅, and △ : Mg₂Zn₁₁.

Fig. 2 a) SEM image and EPMA mapping images of b) Zn and c) Mg of surface of the electrodeposit obtained from the TMPATFSI-(Zn, Mg)(TFSI)₂-EG (48 : (6 : 6) : 40 mol%) bath under the constant current density of 50 Am⁻² with passed charge of 2.5×10⁵ Cm⁻² at 393 K.

Fig. 3 Mg content in the electrodeposits as a function of Mg concentration in the TMPATFSI-(Zn, Mg)(TFSI)₂-EG (48 : (12- x : x) : 40 mol%) bath. Electrodeposition was conducted at 50 Am^{-2} with passed charge of $2.5 \times 10^5 \text{ Cm}^{-2}$ at 393 K.

densities in TMPATFSI-(Zn, Mg)TFSI₂-EG baths are necessary to discuss the effects of structure and properties of TMPATFSI on the electrodeposition of Zn-Mg alloy.

4. Conclusions

The electrodeposition of Zn-Mg alloy from the bath using trimethyl propylammonium bis(trifluoromethylsulfonyl)imide (TMPATFSI) was investigated. Zn-Mg alloy containing about 5 mol%Mg was obtained

from the TMPATFSI-(Zn, Mg)(TFSI)₂-EG (48 : 6 : 6 : 40 mol%) bath under the constant current density of 50 Am^{-2} for $2.5 \times 10^5 \text{ Cm}^{-2}$ at 393 K. The electrodeposit consists of Zn and Mg₂Zn₁₁, and Mg was electrodeposited as Mg₂Zn₁₁ and/or supersaturated solid solution in Zn.

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