Electrodeposition of Zn–Zr Oxide Composite from Dispersed-Particle-Free Solution*

Hiroaki Nakano¹, Yosuke Hara², Satoshi Oue¹ and Shigeo Kobayashi³

¹Department of Materials Science & Engineering, Kyushu University, Fukuoka 819–0395, Japan

²Department of Materials Process Engineering, Kyushu University, Fukuoka 819–0395, Japan

³Department of Applied chemistry and Biochemistry, Kyushu Sangyo University, Fukuoka 813–8503, Japan

Electrodeposition of Zn–Zr oxide composite from an unagitated sulfate solution containing Zn^{2+} and Zr ions was investigated at pH 1–2 and at 313 K under galvanostatic conditions. The Zr content was higher in deposits formed from the solution at pH 2 than in those formed from the solution at pH 1 and initially decreased with increasing current density; however, when the current density was increased further, the Zr content in the deposits increased. This increase in Zr content was attributed to the acceleration of the hydrolysis of Zr ions by an increase in hydrogen evolution in the solution in the vicinity of cathode. In solutions containing Zr ions, Zn deposition was substantially polarized because of the electric resistance of film of the Zr oxide formed by the hydrolysis of Zr ions. The pH in the vicinity of the cathode, as measured using an Sb microelectrode, was approximately 2.2, which is similar to the critical pH for the formation of ZrO_2 . Scanning electron microscopy and energy-dispersive X-ray spectroscopy point analysis of the deposits revealed that granular Zr oxide was deposited at the surfaces of the Zn platelet crystals and in the voids between the crystals. Polarization curves in 3 mass% NaCl solution revealed that the corrosion potential of the deposited Zn–1.1 mass% Zr oxide films was more noble than that of Zn films and that the corrosion current density of the Zn–1.1 mass% Zr oxide films was lower than that of Zn films. [doi:10.2320/matertrans.M2016084]

(Received March 4, 2016; Accepted April 7, 2016; Published May 13, 2016)

Keywords: electrodeposition, zinc, zirconium oxide, polarization curve, corrosion potential, corrosion current density, antimony microelectrode, oxide composite, hydrolysis

1. Introduction

The deposition of composites can result in materials with functional properties such as good abrasion resistance,^{1,2)} good lubricating ability,^{3,4)} and good corrosion resistance.^{5,6)} In composite deposition, fine particles are generally suspended in the electrolyte as dispersion materials and are subsequently incorporated into the deposits during electrodeposition. Because the fine particles are likely to aggregate in the electrolyte and at the cathode layer, they are difficult to codeposit as fine particles in matrix materials. In addition, numerous problems arise in manufacturing processes because of settling of aggregated particles in electrolyte solutions.⁷⁾

By contrast, in the electrodeposition of less-noble metals such as Zn, the pH in the cathode layer generally increases as a result of the evolution of hydrogen. Therefore, when metal ions that hydrolyze at low pH values are added to electrolytes as secondary elements, these metal ions can codeposit with Zn as oxides or hydroxides as a result of the hydrolysis reaction.^{8–11)} Because this deposition accompanied by a hydrolysis reaction can be performed in an electrolyte containing only metal ions and not suspended particles, extremely fine nanometer-scale particles are expected to codeposit with Zn, potentially resulting in materials with new functional properties and solving the problems associated with manufacturing of conventional composites.

Steel sheets are typically coated with Zn via hot-dip galvanization or electroplating processes. Investigations of Zn alloy films produced by hot-dip galvanization and dry-process coating have shown that alloying elements less noble than Zn, such as Mg, Al, and Ti, improve the corrosion resistance of

the resulting Zn alloy films.^{12–15)} Zr (standard electrode potential of Zr^{4+}/Zr $E^0 = -1.53$ V vs. NHE) is a considerably less noble metal than Zn ($E^0 = -0.76$ V); therefore, Zr oxide codeposited with Zn is expected to improve the corrosion resistance of Zn composite films. However, the literature contains very few studies on the codeposition of Zr oxide with Zn. Therefore, in this study, we added Zr^{4+} , which hydrolyzes at a lower pH than Zn^{2+} , to the electrolyte to investigate the deposition behavior of the resulting Zn and Zr oxide composite. The distribution of Zr oxide in the composite and the polarization properties of the deposits were also examined.

2. Experimental

Table 1 shows the solution composition and electrolysis conditions. The electrolytic solution was prepared by dissolving fixed amounts of high-grade $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ($0.52 \text{ mol} \cdot \text{dm}^{-3}$) and $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ ($0.1 \text{ mol} \cdot \text{dm}^{-3}$) in distilled deionized water. The pH was adjusted to 1 or 2 with sulfuric acid. The electrodeposition was conducted in un-agitated solutions under coulostatic ($10^5 \text{ C} \cdot \text{m}^{-2}$) or galvanostatic conditions of $10\text{--}5000 \text{ A} \cdot \text{m}^{-2}$ at 313 K. Sheets of Cu and Pt measuring $2 \text{ cm} \times 1 \text{ cm}$ were used as cathodes and anodes, respectively.

Table 1 Electrolysis conditions.

Bath composition	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	$0.52 \text{ mol} \cdot \text{dm}^{-3}$
	$\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$	$0.1 \text{ mol} \cdot \text{dm}^{-3}$
	pH	1, 2
Operating conditions	Current density	$10\text{--}5000 \text{ A} \cdot \text{m}^{-2}$
	Amount of charge	$10^5 \text{ C} \cdot \text{m}^{-2}$
	Temperature	313 K
	Cathode	Cu ($2 \text{ cm} \times 1 \text{ cm}$)
	Anode	Pt ($2 \text{ cm} \times 1 \text{ cm}$)
	Quiescent bath	

*This Paper was Originally Published in Japanese in J. Japan Inst. Met. Mater. **80** (2016) 151–156.

The deposits were dissolved from the cathode using nitric acid. Both Zn and Zr were quantitatively analyzed by inductively coupled plasma (ICP) spectroscopy, and the Zr content of the deposits, the cathode current efficiency, and the partial current density for Zn deposition were calculated. The cathode potentials during deposition were measured against a saturated Ag/AgCl reference electrode (0.199 V vs. NHE, 298 K). In the presented polarization curves, the potentials are plotted with reference to the NHE.

The surfaces and cross-sectional morphologies of the deposits were analyzed on the basis of secondary electron images and backscattered electron images collected at an ultra-low accelerating voltage using scanning electron microscopy (SEM); the distributions of Zn, Zr, and O were visualized by energy-dispersive X-ray analysis (EDX). The backscattered electron images were collected using an energy-selective backscatter electron detector. The crystal orientation of the deposited Zn was determined using the method developed by Wilson and Rogers¹⁶⁾; an X-ray diffraction intensity of 0002 to the 11 $\bar{2}$ 2 reflection was used. To study the hydrolysis behavior of the hydrated metal ions in the solutions, pH titrations were performed using NaOH. A 5.0 mol·dm⁻³ NaOH solution was added to a 0.05 mol·dm⁻³ ZnSO₄ and/or a Zr(SO₄)₂ solution using a burette. The concentrations of Zn²⁺ and Zr⁴⁺ ions in the mixed solution were measured by ICP during the pH titrations. A Sb microelectrode¹⁷⁾ was fabricated to measure the pH change in the vicinity of the cathode during Zn–Zr oxide composite deposition accompanied by hydrogen evolution. Under a galvanostatic condition of 300 A·m⁻² in unagitated solutions, the potential of the Sb electrode attached to a micrometer was measured at various distances between the cathode and Sb electrode. The distance between the capillary of the reference electrode and the Sb microelectrode was approximately 2 mm, and the distance between the capillary of the reference electrode and the cathode was identical to that between the Sb microelectrode and the cathode. Using a pH–potential calibration curve constructed in advance, we determined the pH profile near the cathode during electrolysis. The corrosion resistances of the deposited Zn–Zr oxide composite films were evaluated by polarization curves. Potentiodynamic polarization curves were collected by polarizing from a less-noble potential than the corrosion potential toward the anodic-potential direction using a potential sweep method at 1.0 mV·s⁻¹ in an oxygen-saturated 3 mass% NaCl solution at 313 K.

3. Results and Discussion

3.1 Chemical state and equilibrium potential of Zr

Figure 1 shows the potential vs. pH diagram for the Zr–H₂O system. The concentration of Zr in the solution and the activity coefficient of the Zr ions are assumed to be 0.1 mol·dm⁻³ and 1, respectively. The thermodynamic data are quoted from Pourbaix.¹⁸⁾ As is evident in Fig. 1, Zr exists in the form of ZrO²⁺ or Zr⁴⁺ ions in the electrolyte with pH values less than 1.74; however, at pH values greater than 1.74, ZrO₂ is formed as a result of the hydrolytic reaction of Zr ions. In the electrodeposition of Zn from aqueous solution, the pH in the cathode layer increases as a result of the evolution of hydrogen. When the pH in the cathode layer reaches

Fig. 1 Potential–pH diagram for the Zr–H₂O system at 298 K. ($a_{\text{Zr}} = 0.1$).

Fig. 2 Effects of current density and pH on Zr content of deposits.

the critical pH value for the hydrolysis of Zr ions, Zr ions are expected to be converted into an oxide such as ZrO₂. However, no precipitation was observed in electrolytes of pH 2 in this study. We assumed that the activity coefficient of Zr ions becomes less than 1.0 because of the high concentration of the electrolyte; consequently, the critical pH values for the hydrolysis of Zr ions increase to above 2.0.

3.2 Codeposition behavior of Zr oxide

Figure 2 shows the effects of current density and pH on the Zr content in deposits. The Zr content in deposits in this study was calculated from the masses of Zr and Zn in the deposits using the following equation:

$$\text{Zr content (mass\%)} = [\text{mass Zr} / \text{total mass (Zn + Zr)}] \times 100.$$

In solutions of pH 1 or 2, the Zr content in the deposits decreases with increasing current density from 10 A·m⁻², whereas it gradually increases with increasing current density above 100 A·m⁻². The Zr contents in the deposits obtained at all of the investigated current densities are higher in the pH 2 solution than in the pH 1 solution. The increase in Zr content with increasing current density in the high-current-density re-

Fig. 3 Effects of current density, Zr ions, and pH on current efficiency for Zn deposition.

gion is attributable to an increase in the hydrolysis reaction of Zr ions as a result of the pH increasing in the vicinity of cathode; the increase in pH is, in turn, a result of an increase in the rate of hydrogen evolution with increasing current density. Similarly, the hydrolysis reaction of Zr ions is more likely to occur in a pH 2 solution; as a result, the Zr content in deposits increases in the pH 2 solution.

Figure 3 shows the effects of the current density and the pH on the current efficiency of Zn during Zn–Zr oxide composite deposition. In this study, Zn–Zr oxide composite deposition is accompanied by the reduction reaction of H^+ ions to hydrogen gas. In both the pH 1 and 2 solutions, the current efficiency initially increases with increasing current density from $10 \text{ A} \cdot \text{m}^{-2}$, reaches a maximum, and then decreases as the current density increases further. The increase in current efficiency with increasing current density in the lower-current-density region is attributable to the increase in the overpotential for Zn deposition; by contrast, the decrease in current efficiency with increasing current density in the higher-current-density region is caused by reaching the diffusion limitation of Zn^{2+} ions.

With respect to the effect of Zr ions, in the high-current-density region beyond $1000 \text{ A} \cdot \text{m}^{-2}$ in the pH 2 solution and in the low-current-density region below $50 \text{ A} \cdot \text{m}^{-2}$, the current efficiency of Zn is slightly lower in the presence of Zr ions than in their absence. In the current density region below $1000 \text{ A} \cdot \text{m}^{-2}$, the current efficiency of Zn is slightly lower in the pH 1 solution than in the pH 2 solution. At low current densities, the Zr content in the deposits increases with decreasing current density at pH 1 and 2, as shown in Fig. 2; this increased Zr content is a consequence of the decrease in the current efficiency of Zn with decreasing current density, as shown in Fig. 3.

Figure 4 shows the partial polarization curves for Zn deposition from solutions of pH 1 and 2 containing Zn^{2+} and Zr ions. The partial polarization curve in the Zr-ion-free solution was also collected to elucidate the effect of Zr ions on the deposition behavior of Zn–Zr oxide composites. A comparison of the partial polarization curve from the solution containing Zr ions with that from the Zr-ion-free solution reveals that the cathode potential was polarized by Zr ions in the current density region above $200 \text{ A} \cdot \text{m}^{-2}$. This tendency is re-

Fig. 4 Effects of Zr ions on partial polarization curve for Zn deposition.

Fig. 5 pH titration curves for Zn–Zr solution and concentrations of Zr^{4+} and Zn^{2+} in Zn–Zr solutions. [●Zn only, ▲Zr only, ■Zn–Zr, ○ Zr^{4+} concentration, △ Zn^{2+} concentration, initial pH: 2.0 (Zn only), 1.2 (Zr only, Zn–Zr)].

markable in the case of the pH 2 solution. This large polarization in the presence of Zr ions above $200 \text{ A} \cdot \text{m}^{-2}$ appears to result from an increase in resistance overpotential caused by Zr oxide films formed by hydrolysis of Zr ions on the cathode. As is evident in Figs. 3 and 4, Zn deposition reaches the diffusion limitation of Zn^{2+} ions at approximately $1000 \text{ A} \cdot \text{m}^{-2}$, except in the case of the Zn–Zr solution of pH 2, where it reaches the diffusion limitation at approximately $500 \text{ A} \cdot \text{m}^{-2}$. This decrease in the diffusion limitation current density of Zn in the Zn–Zr solution of pH 2 is attributable to the diffusion of Zn^{2+} ions being suppressed by the Zr oxide films formed by the hydrolysis of Zr ions.

During deposition from the solution containing both Zr ions and Zn^{2+} , the pH in the vicinity of the cathode increased because of hydrogen evolution, which resulted in the formation of a metal oxide via hydrolysis. The critical pH value for ZrO_2 formation was calculated to be 1.9 on the basis of the solubility product of ZrO_2 [$10^{-25.5}$ (298 K)]¹⁸⁾ in the solution containing $0.05 \text{ mol} \cdot \text{dm}^{-3} \text{ ZrO}^{2+}$. Similarly, the critical pH value for $Zn(OH)_2$ formation was calculated to be 6.3 on the basis of the solubility product of $Zn(OH)_2$ [2×10^{-17} (298 K)]¹⁹⁾ in the solution containing $0.05 \text{ mol} \cdot \text{dm}^{-3} \text{ Zn}^{2+}$. Figure 5 shows the pH titration curves measured for a solution containing Zn^{2+} and Zr ions titrated with $5.0 \text{ mol} \cdot \text{dm}^{-3} \text{ NaOH}$. In the solution containing only Zn^{2+} , the increase in pH stagnates and the solution begins to exhibit suspension formation as a result of the formation of precipitates at a pH

of approximately 6.5. In the solution containing only Zr ions, the initial pH is 1.2, and the increase in pH stagnates in the initial stages of the titration. The solution begins to exhibit suspension formation as a result of the formation of precipitates at a pH of approximately 2.2; subsequently, the pH begins to increase. In the case of the solution containing both Zn^{2+} and Zr ions, the increase in pH stagnates at pH levels of approximately 1.2–2.2 and 5–6.5, similar to the results obtained by the superposition of the two pH titration curves obtained from the solutions containing only Zn^{2+} and only Zr ions. However, the second stagnation (pH 5–6.5) of pH rise begins from a slightly lower pH in the solution containing both Zn^{2+} and Zr ions than that in the solution containing only Zn^{2+} . The pH values at which stagnation occurs are similar to the critical pH levels necessary for the formation of ZrO_2 and Zn(OH)_2 , as calculated from each solubility product. Because the critical pH value for ZrO_2 formation is lower than that for Zn(OH)_2 formation, ZrO_2 should preferentially form in the solution in the vicinity of cathode. Furthermore, Fig. 5 shows the concentrations of Zn^{2+} and Zr ions measured during the NaOH titration of the solution containing both ions. At a pH of approximately 2.2, the concentration of Zr ions decreases, and, at a pH of approximately 5, the concentration of Zn^{2+} ions decreases. These results demonstrate that the precipitations of ZrO_2 and Zn(OH)_2 occurred at pH values of 2.2 and 5, respectively. Thus, although no precipitation of ZrO_2 occurred in the pH region from 1.2 to 2 during the initial titration of the solution containing Zr ions, the pH values stagnated. Because reaction (1) reaches equilibrium at a pH of -1.03 ,¹⁸⁾ Zr ions are thermodynamically assumed to exist in the form of ZrO^{2+} at pH 1 and 2:

However, because the pH values stagnated despite a lack of formation of ZrO_2 in the pH region from 1.2 to 2, a fraction of the Zr ions are assumed to exist in the form of Zr^{4+} , allowing hydrolysis reaction (1) to occur at pH 1.2–2.

The pH in the vicinity of the cathode was measured using a Sb microelectrode in both an un-agitated solution containing Zn^{2+} and Zr ions at pH 1.6 and a solution containing only Zn^{2+} at pH 2. Figure 6 shows the pH in the vicinity of the cathode during deposition at $300 \text{ A}\cdot\text{m}^{-2}$. The pH of the cathode surface increases to 5.6, which is substantially higher

Fig. 6 pH profiles in vicinity of cathode during Zn–Zr and Zn deposition at $300 \text{ A}\cdot\text{m}^{-2}$.

than the pH of the bulk solution containing only Zn^{2+} ; by contrast, the pH increases to only 2.2 in the solution containing both Zn^{2+} and Zr ions. In the solution containing only Zn^{2+} , the pH appears to increase to the critical pH necessary for the formation of Zn(OH)_2 because of hydrogen evolution during electrolysis. By contrast, in the solution containing both Zn^{2+} and Zr ions, the pH stagnates at a pH lower than the critical pH for the formation of Zn(OH)_2 , which is attributable to buffer action by the hydrolysis of Zr ions at a pH of approximately 2.2. As previously mentioned, during deposition from the solution containing both Zn^{2+} and Zr ions, the pH in the vicinity of cathode increases because of hydrogen evolution; however, the pH does not reach the critical pH for formation of Zn(OH)_2 because of buffer action by the hydrolysis of Zr ions, resulting in the formation of ZrO_2 only at the cathode. Generally, Zn^{2+} ions are reduced to Zn via the formation of Zn(OH)_2 intermediate, but in the solution containing Zr ions, Zn^{2+} ions seem to be directly reduced to Zn. Since ZrO_2 is formed at the cathode during deposition, Zn^{2+} ions should transport from the solution to cathode through ZrO_2 films. We hypothesize that Zn^{2+} ions are reduced to Zn via the ZrO_2 layer without the formation of Zn(OH)_2 intermediate and that ZrO_2 is subsequently incorporated into the resulting deposits. In this study, because the distance from the capillary of the reference electrode to the cathode was identical to that from the Sb electrode to the cathode, the error induced by the IR drop during measurements of potential using the Sb microelectrode was assumed to be small.

3.3 Structure of deposits

Figure 7 shows SEM images and EDX spectra of Zn and Zn–Zr oxide composites deposited at $5000 \text{ A}\cdot\text{m}^{-2}$. The deposited Zn consist of layers of large Zn platelet crystals with hexagonal close-packed (hcp) structures; the edges of the platelet crystals are clear, and numerous steps are observable on the smooth platelet in Fig. 7(a). The SEM images of the Zn–Zr oxide composite show layers of large Zn platelet crystals, similar to deposited Zn; however, the edges of the platelet crystals changed irregularly and become gear-like. Granular crystals are observable on the smooth platelets [Fig. 7(b) ①] and in the voids between the Zn platelet crystals [Fig. 7(b) ②]. These granular crystals shown in Fig. 7(b) ① and ②.

Fig. 7 SEM images and EDX spectra of deposits obtained at $5000 \text{ A}\cdot\text{m}^{-2}$ from solutions of pH2 with and without Zr^{4+} ions. [(a) Zn, (b) Zn–Zr oxide, (c) EDX of ①, (d) EDX of ②].

Fig. 8 Backscatter electron images of deposits obtained at $5000 \text{ A}\cdot\text{m}^{-2}$ from solutions of pH2 with and without Zr^{4+} ions. [(a) Zn, (b) Zn–Zr oxide].

Fig. 9 Crystal orientation of Zn in deposits obtained at $5000 \text{ A}\cdot\text{m}^{-2}$ from solutions of pH2 with and without Zr^{4+} ions. [●(0002), ▲(10 $\bar{1}$ 3), ■(10 $\bar{1}$ 2), ◆(10 $\bar{1}$ 1), ○(10 $\bar{1}$ 0), △(11 $\bar{2}$ 2)].

were analyzed by EDX; as a result, Zr and O were detected in addition to Zn, as shown in Figs. 7(c) and 7(d), indicating that Zr codeposited onto the smooth Zn platelet crystals and in the voids between the Zn platelet crystals in the form of a granular oxide. The gear-like edges of the platelet crystals of the Zn–Zr oxide composites indicate that the lateral growth of basal plane {0001} of the Zn platelet crystals does not occur normally. Zr oxide deposited on smooth Zn platelet crystals possibly suppresses the lateral growth of Zn.

Figure 8 shows the backscatter electron images of cross-sections of Zn and Zn–Zr oxide composite deposits obtained at $5000 \text{ A}\cdot\text{m}^{-2}$. Clear steps formed by numerous micro steps of platelet crystals are observable on the surface of the Zn deposits, whereas no clear steps are observable on the surface of the Zn–Zr oxide composite deposits because of their random morphology. These morphologies correspond to those assumed on the basis of the SEM surface morphologies shown in Fig. 7. The crystals of the Zn deposits grew large, whereas growth of the crystals of Zn–Zr oxide composite deposits was suppressed.

Figure 9 shows the crystal orientations of the Zn and Zn–Zr oxide composite deposits obtained at $5000 \text{ A}\cdot\text{m}^{-2}$. The preferred orientations of the pure Zn are {0001} and {10 $\bar{1}$ 3}. The inclination of the {10 $\bar{1}$ 3} to the {0001} basal plane of hcp is smaller than those of the other planes to {0001}. That is, the preferred orientation of the {0001} and {10 $\bar{1}$ 3} planes of deposited Zn means that the basal plane of Zn platelet crystals is likely to be parallel to the substrate; such an orientation is consistent with the SEM images in Fig. 7(a). By contrast, the preferred orientation of Zn in the Zn–Zr oxide composites is

Fig. 10 Polarization curves in 3 mass% NaCl solution for Zn (a) and Zn–1.1 mass% Zr oxide (b) obtained at $5000 \text{ A}\cdot\text{m}^{-2}$ from solutions of pH2.

the {10 $\bar{1}$ 2} plane, and the orientation of the {10 $\bar{1}$ 3} and {0001} planes is smaller than that of the Zn. This result indicates that the basal plane of the Zn platelet crystals grew at an incline to the substrate. Pangarov calculated the relative values of two-dimensional nucleation work on various crystal planes.^{20,21} By assuming that the two-dimensional nuclei with the smallest nucleation work were formed at a given crystallization overpotential, he showed the overpotential dependence of the preferred orientation of various metals deposited from aqueous solutions. According to Pangarov, the preferred orientations of hcp Zn are shifted from {0001} Zn to {10 $\bar{1}$ 1}, {10 $\bar{2}$ 0}, and {10 $\bar{1}$ 0} Zn (in this order) with increasing overpotential for Zn deposition. In the case of Zn–Zr oxide composite deposition in this study, we attributed the significant decrease in orientation of the {0001} and {10 $\bar{1}$ 3} planes to an increase in overpotential for Zn deposition due to codeposition of Zr oxide, as shown in Fig. 4.

3.4 Polarization properties of deposits

Figure 10 shows the polarization curves of Zn and Zn–1.1 mass% Zr oxide composite deposits in 3 mass% NaCl solution. The corrosion potential of the Zn–1.1 mass% Zr oxide composites is more noble than that of the Zn deposit. Because the anodic polarization curves for Zn dissolution are shifted toward the noble direction by codeposition of Zr oxide, the corrosion potential of the deposits shifts toward the noble direction. The anodic reaction was more suppressed in Zn–1.1 mass% Zr oxide composite deposits than that in Zn; as a result, the corrosion current density was lower in the Zn–1.1 mass% Zr oxide composite deposits. We attributed this result to an extremely low conductivity of Zr oxide.

4. Conclusion

Zn–Zr oxide composites were electrodeposited from a sulfate solution containing Zn^{2+} and Zr ions to investigate the deposition behavior, structure, and polarization properties of the deposits. The Zr content was higher in the deposits formed in the pH 2 solution than in those formed in the pH 1 solution and initially decreased with increasing current density; however, when the current density was increased further, the Zr contents in the deposits increased. This increase in the Zr

contents of the deposits was attributed to the acceleration of the hydrolysis of Zr ions by an increase in hydrogen evolution in the cathode layer. In solutions containing Zr ions, Zn deposition was substantially polarized because of the electric resistance of film of the Zr oxide formed by the hydrolysis of Zr ions. The pH in the vicinity of the cathode, as measured using a Sb microelectrode, was approximately 2.2, which is similar to the critical pH for the formation of ZrO_2 . SEM and EDX point analyses of the deposits revealed that the granular Zr oxide deposited on the surfaces of the Zn platelet crystals and in the voids between the crystals. The polarization curves in 3 mass% NaCl solution revealed that the corrosion potential of the deposited Zn–1.1 mass% Zr oxide films was more noble than that of the Zn films and that the corrosion current density of the Zn–1.1 mass% Zr oxide films was lower than that of the Zn films.

Acknowledgement

This work was supported by a JSPS Grant-in-Aid for Scientific Research (B), Grant Number 26289274.

REFERENCES

- 1) S. Ishimori, M. Shimizu, S. Honda, S. Otsuka and M. Toyoda: *J. Met. Finish. Soc. Jpn.* **28** (1977) 508–512.
- 2) E.C. Kedward and K.W. Wright: *Plating Surf. Finish.* **65** (1978) 38–41.
- 3) Y. Umeda, Y. Sugitani, M. Miura and K. Nakai: *Tetsu-to-Hagane* **67** (1981) 1377–1386.
- 4) S.S. Tulsi: *Trans. Inst. Metal Finishing* **61** (1983) 142–149.
- 5) Y. Shiohara, A. Okabe, M. Abe and M. Sagiya: *Tetsu-to-Hagane* **77** (1991) 878–885.
- 6) K. Nishimura, Y. Miyoshi and T. Hada: *J. Met. Finish. Soc. Jpn.* **38** (1987) 217–222.
- 7) H. Enomoto, N. Furukawa and S. Matsumura: *Fukugo Mekki*, (Nikkan Kogyo Shinbunsha, Tokyo, 1989) pp.161–164.
- 8) S. Oue, H. Nakano, S. Kobayashi, T. Akiyama, H. Fukushima and K. Okumura: *J. Surf. Finish. Soc. Jpn.* **53** (2002) 920–925.
- 9) H. Nakano, S. Oue, S. Kobayashi, H. Fukushima, K. Okumura and H. Shige: *Tetsu-to-Hagane* **90** (2004) 801–806.
- 10) H. Nakano, S. Oue, D. Kozaki, S. Kobayashi and H. Fukushima: *ISIJ Int.* **48**(2008) 506–511.
- 11) H. Nakano, S. Oue, Y. Annoura, T. Nagai, N. Oho and H. Fukushima: *ISIJ Int.* **54** (2014) 1906–1912.
- 12) J. Kawafuku, J. Katoh, M. Toyama, H. Nishimoto, K. Ikeda and H. Satoh: *Tetsu-to-Hagane* **77** (1991) 995–1002.
- 13) K. Nishimura, H. Shindo, H. Nomura and K. Kato: *Tetsu-to-Hagane* **89** (2003) 174–179.
- 14) Y. Morimoto, M. Kurosaki, K. Honda, K. Nishimura, A. Takahashi and H. Shindo: *Tetsu-to-Hagane* **89** (2003) 161–165.
- 15) T. Shimizu, F. Yoshizaki, Y. Miyoshi and A. Ando: *Tetsu-to-Hagane* **89** (2003) 166–173.
- 16) K.S. Willson and J.A. Rogers: *Tech. Proc. American Electroplaters Soc.* **51** (1964) 92–95.
- 17) H. Fukushima, T. Akiyama, J.H. Lee, M. Yamaguchi and K. Higashi: *J. Met. Finish. Soc. Jpn.* **33** (1982) 574–578.
- 18) M. Pourbaix: *Atlas of Electrochemical Equilibria*, (Pergamon Press, New York, 1966).p.225.
- 19) A. J. Bard, translated by Y. Matsuda and K. Ogura: *Chemical Equilibrium* (in Japanese, Kagaku Dojin, Kyoto, 1993), p198.
- 20) N.A. Pangarov: *J. Electroanal. Chem.* **9** (1965) 70–83.
- 21) N.A. Pangarov: *Electrochim. Acta* **7** (1962) 139–146.