Effects of Electrolyte Composition and Additives on the Formation of Invar Fe–Ni Alloys with Low Thermal Expansion Electrodeposited from Sulfate Bath

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The effects of solution composition and additives on the formation of electrodeposited invar Fe–Ni alloys with low thermal expansion were investigated. In all solutions, increasing the current density from 10 A·m⁻² significantly decreased the Ni content in the deposits and resulted in anomalous codeposition, in which the electrochemically less noble Fe was preferentially deposited. Further increasing the current density increased the Ni content in the deposits as Fe deposition reached the diffusion limitation of the Fe²⁺ ions. Increasing the concentration of Fe²⁺ ions increased the current density required to initiate an increase in the Ni content in the deposits because of increase in the diffusion-limited current density of Fe. With the increasing concentration of malonic acid, the current density region in which Ni deposition was suppressed was extended, and the potential at which Fe deposition reached the diffusion limitation of the Fe²⁺ ions was shifted to a less noble direction. As a result, the relationship between the Ni content in the deposits and the current density shifted to a higher-current-density region with increasing malonic acid concentration. At malonic acid concentrations above 0.05 mol·dm⁻³, the current efficiency for alloy deposition was greatly reduced owing to the promotion of hydrogen evolution. The Ni content in the deposits was significantly increased with the addition of thiourea. Boric acid somewhat increased the Ni content in the deposits in the lower-current-density region. In solutions containing both boric acid and saccharin, an invar alloy of 36 mass% Ni was obtained in the wider-current-density region.

KEY WORDS: invar alloy; iron-nickel alloys; electrodeposition; anomalous codeposition; polarization curve; partial polarization curve; current efficiency; composition of deposits; malonic acid; boric acid.

1. Introduction

Fe–Ni alloy with a Ni content of 36% by mass exhibits the smallest coefficient of thermal expansion and is known as invar alloy.1–4) In the field of electronic communication devices, such as semiconductor lead frames and the package components of optical fibers, Fe–36 mass% Ni alloy has been widely used as a material with low thermal expansion.5) Invar alloys are produced by melting and casting methods and by rolling, but these manufacturing processes limit the form and accuracy of the dimensions of the products. If invar alloys can be produced by electrodeposition, the range of products that could be formed by deposition will increase and the manufacturing cost will decrease.6) For example, in the vacuum deposition of an organic electroluminescence layer in a smartphone, the metal mask is set between the vapor deposition material and the substrate, and all the metal masks are produced by an etching technology. If the metal mask could be produced by an electrodeposition technique, the size and design of the openings and the thickness of the metal mask could be controlled.

On the other hand, the deposition behavior of Fe–Ni alloys exhibits a typical feature of anomalous codeposition, where the electrochemically less noble Fe is preferentially deposited under most plating conditions.7–19) In order to produce an Fe–Ni invar alloy using electrodeposition, it is essential to establish the electrolysis conditions for the Ni content in deposits of 36 mass%.20–23) Therefore, it is important to understand the effect of the electrolysis conditions on the composition of the Fe–Ni alloy. However, the effects of the composition and additives in the electrolysis solution on the composition of the deposited Fe–Ni alloy have not been evaluated. Therefore, in this study, we varied the composition of the electrolysis solution and selected additives like malonic acid (as a masking reagent of Fe³⁺ ions), saccharin...
(to decrease the stress in the electrodeposits), boric acid (as a buffer for pH), and thiourea (as a brightener). The effects of the composition of the electrolysis solution and the additives on the composition and current efficiency of the deposited Fe–Ni alloy were explained by the change in the total polarization curve and the partial polarization curves for Fe–Ni deposition and hydrogen evolution during Fe–Ni alloy deposition.

2. Experimental

The electrolyte composition and electrolysis conditions for Fe–Ni alloy deposition are listed in Table 1. The electrolytic solution was prepared by dissolving reagent-grade NiSO₄·6H₂O (0.7 mol·dm⁻³), FeSO₄·7H₂O (0.3 mol·dm⁻³), C₃H₄O₄ (malonic acid, 0–0.5 mol·dm⁻³, standard condition: 0.05 mol·dm⁻³), H₃BO₃ (0.5 mol·dm⁻³), C₇H₄NNaO₃S (saccharin sodium, 0.005 mol·dm⁻³), and CH₄N₂S (thiourea, 0.0025 mol·dm⁻³) into pure water. In some experiments, NiSO₄·6H₂O and FeSO₄·7H₂O were dissolved in total amount of 1.0 mol·dm⁻³ without additives. The pH was adjusted to 2.0 using sulfuric acid and sodium hydroxide.

Fe–Ni alloy electrodeposition was performed in unagitated solutions under coulstatic (1.0–2 000 A·m⁻²) and galvanostatic (10–2 000 A·m⁻²) conditions at 40°C. A copper sheet and a titanium sheet plated with platinum, each measuring 2.0 × 1.0 cm, were used as the cathode and the anode, respectively. The deposits were dissolved from the cathode using nitric acid. Both Fe and Ni were quantitatively analyzed using inductively coupled plasma spectroscopy, and the Ni content of the deposits and the cathode current efficiency for Fe–Ni alloy deposition were calculated. The current efficiency for hydrogen evolution was determined by subtracting the current efficiency for Fe and Ni deposition from 100%. The partial current densities for Fe and Ni deposition and hydrogen evolution were calculated by multiplying the total current density by each current efficiency. The current density (A·m⁻²) for each deposit using nitric acid. Both Fe and Ni were quantitatively analyzed using inductively coupled plasma spectroscopy, and the Ni content of the deposits and the cathode current efficiency for Fe–Ni alloy deposition were calculated. The current efficiency for hydrogen evolution was determined by subtracting the current efficiency for Fe and Ni deposition from 100%. The partial current densities for Fe and Ni deposition and hydrogen evolution were calculated by multiplying the total current density by each current efficiency. The cathode potentials during deposition were measured against a saturated Ag/AgCl reference electrode (0.199 V versus NHE, 298 K). In the presented polarization curves, the potentials are plotted with reference to the NHE. The Ni content in the deposits initially decreased with increasing current density, regardless of the solution composition, and reached a minimum before increasing with the further increase of the current density. That is, the curve that represents the relationship between the Ni content in the deposits and the current density had a downward convex shape. If the Ni content in the deposit is greater than the Ni content in the solution, normal codeposition occurs, as the more electrochemically noble Ni is preferentially deposited over Fe. In contrast, if the Ni content in the deposit is less than the Ni content in the solution, anomalous codeposition occurs, as the less noble Fe is preferentially deposited over Ni. The Ni content in the solution was calculated using the following equation:

\[
\text{Ni content in solution (mass%) } = \frac{\text{Ni}^{2+}}{(\text{Ni}^{2+} + \text{Fe}^{2+})} \times 100.
\]

3. Results and Discussion

3.1. Effect of Solution Composition on the Composition and Current Efficiency of the Deposited Alloy

Electrodeposition was first performed using additive-free solutions containing NiSO₄ and FeSO₄ at 1.0 mol·dm⁻³. Figure 1 shows the Ni content in the Fe–Ni alloys deposited at various current densities from solutions of different compositions. The molar ratio of Fe²⁺ ions in each solution was calculated using the following equation:

\[
\text{Molar ratio of } \text{Fe}^{2+} \text{ ions in solution (mol%) } = \frac{\text{Fe}^{2+}}{(\text{Fe}^{2+} + \text{Ni}^{2+})} \times 100.
\]

The Ni content in the deposits initially decreased with increasing current density, regardless of the solution composition, and reached a minimum before increasing with the further increase of the current density. That is, the curve that represents the relationship between the Ni content in the deposits and the current density had a downward convex shape. If the Ni content in the deposit is greater than the Ni content in the solution, normal codeposition occurs, as the more electrochemically noble Ni is preferentially deposited over Fe. In contrast, if the Ni content in the deposit is less than the Ni content in the solution, anomalous codeposition occurs, as the less noble Fe is preferentially deposited over Ni. The Ni content in the solution was calculated using the following equation:

\[
\text{Ni content in solution (mass%) } = \frac{\text{Ni}^{2+}}{(\text{Ni}^{2+} + \text{Fe}^{2+})} \times 100.
\]

![Fig. 1. Ni content in Fe–Ni alloys deposited at various current densities from solutions of different compositions. Total concentration of Fe²⁺ and Ni²⁺: 1.0 mol·dm⁻³, Fe²⁺/ (Fe²⁺+Ni²⁺) × 100 mass%, ○ 10%, ▲ 20%, ● 30%, ◆ 40%, ○ 60%, Ni²⁺/(Fe²⁺+Ni²⁺) × 100 mass%, ● 90%, ▲ 81%, ■ 71%, ◆ 61%, ○ 41%.

Table 1. Standard solution composition and electrolysis conditions.

| Component                        | Concentration (mol·dm⁻³) | Current density (A·m⁻²) | Temperature (°C) | Amount of charge (C·m⁻²) | pH | Cathode   | Anode   |
|----------------------------------|--------------------------|------------------------|-----------------|--------------------------|----|------------|----------|
| NiSO₄·6H₂O                        | 0.7                      | 10–2 000               | 40              | 10³                      | 2.0| Cu (1×2 cm²) | Pt (1×2 cm²) |
| FeSO₄·7H₂O                        | 0.3                      |                        |                 |                          |    |            |          |
| Malonic acid                     | 0.05                     |                        |                 |                          |    |            |          |
| H₃BO₃                            | 0.5                      |                        |                 |                          |    |            |          |
| Saccharin sodium                 | 0.005                    |                        |                 |                          |    |            |          |
| Thiourea                         | 0.0025                   |                        |                 |                          |    |            |          |
| Quiescent bath                   |                          |                        |                 |                          |    |            |          |
When the molar ratio of Fe\(^{2+}\) ions in solution was 10, 20, 30, 40, and 60 mol\%, the Ni content in solution was 90, 81, 71, 61, and 41 mass\%, respectively. With all the solution compositions, the Ni content in the deposits greatly decreased with increasing current density from a low current density of approximately 10 A·m\(^{-2}\) and was less than the Ni content in the solution, indicating anomalous codeposition. Focusing on the current density at which the Ni content in the deposits began to increase, the current density increased with the concentration of Fe\(^{2+}\) ions in solution. As a result, the current density region, at which the Ni content in the deposits almost became constant close to the minimum, broadened with the increasing concentration of Fe\(^{2+}\) ions in the solution. The conditions required to obtain the Fe–36 mass\% Ni alloy were observed in all the solutions except for the 10% molar ratio of Fe\(^{2+}\) ions. In a solution of Fe\(^{2+}\) ions with a molar ratio of 30%, the Ni content in the deposits seemed to be 36 mass\% at two current densities, somewhat above 50 and 500 A·m\(^{-2}\). Therefore, an alloy with a composition of nearly Fe–36 mass\% can be obtained over a relatively wide current density range.

**Figure 2** shows the current efficiency for the deposition of Fe–Ni alloys at various current densities from solutions of different compositions. The current efficiency for Fe–Ni alloy deposition increased with the current density, regardless of the solution composition. The current efficiency increased with the molar ratio of Fe\(^{2+}\) ions from 10% to 30% at all the current densities, but it decreased with increasing the molar ratio of Fe\(^{2+}\) ions to 40% and 60% at low current densities below 100 A·m\(^{-2}\). Although the current efficiency increased with the current density, the increase stagnated at approximately 50 A·m\(^{-2}\) in solutions with a high molar ratio of Fe\(^{2+}\) ions of 40 and 60%. The current efficiency for alloy deposition decreased at a high current density of 2 000 A·m\(^{-2}\) in a solution with a low molar ratio of Fe\(^{2+}\) ions of 10%.

**Figure 3** shows the partial polarization curves for Fe deposition (a), Ni deposition (b), and hydrogen evolution (c) from Fe–Ni alloy solutions of different compositions. The partial polarization curve for Fe deposition closely represented Tafel’s equation at partial current densities of Fe below 100 A·m\(^{-2}\), regardless of the solution composition. However, at partial current densities of Fe above 100 A·m\(^{-2}\), Fe deposition deviated from Tafel’s equation and approached the diffusion limitation of Fe\(^{2+}\) ions. Upon decreasing the concentration of Fe\(^{2+}\) ions in solution, the deviation from Tafel’s equation for Fe deposition particularly increased and the diffusion-limited current density of Fe decreased. On the other hand, the partial polarization curve for Ni deposition polarized from the low-current-density region upon increasing the concentration of Fe\(^{2+}\) ions. At high molar ratios of Fe\(^{2+}\) ions, 40 and 60%, Ni deposition was greatly suppressed by increasing the concentration of Fe\(^{2+}\) ions. At high molar ratios of Fe\(^{2+}\) ions, 40 and 60%, Ni deposition was greatly suppressed in the potential region more noble than −0.65 V, but it increased sharply at approximately −0.65 V. At potentials less noble than −0.8 V, the increase in the current density of Ni stagnated, but the Ni deposition did not seem to approach the diffusion-limited current density. The partial
polarization curve for hydrogen evolution somewhat polarized at the low-current-density region with a molar ratio of Fe$^{2+}$ ions above 10%, but the effect of the molar ratio of Fe$^{2+}$ ions on hydrogen evolution was significantly smaller than that on Ni deposition.

The effect of solution composition on the relationship between the composition and current efficiency of the deposited Fe–Ni alloy and the current density was discussed by considering the changes in the total polarization curve and partial polarization curves for Fe and Ni deposition and hydrogen evolution. Figure 4 shows a schematic diagram of the changes in the polarization curves for the deposition of the Fe–Ni alloy (a) and the current density–alloy composition curves (b) with the increase in the molar ratio of Fe$^{2+}$ ions in solution. There are three regions from the viewpoint of changes in the Ni content of the deposited alloy. When the partial polarization curve for Fe deposition rises at a total current density above $i_{Fe}$, Ni deposition is suppressed by Fe deposition; as a result, the slope of the partial polarization curve for Ni deposition becomes gentler than that for Fe deposition. Therefore, at the total current density region from $i_{Fe}$ to $i_{Ni}$ or $i_{Ni}'$, the Ni content in the deposits decreases with increasing total current density. Iron-group metals such as Fe, Co, and Ni do not inherently initiate deposition at the equilibrium potential, and the following reactions have been reported to occur during the deposition process,17,18) M and the subscript (ad) denote the iron-group metal and adsorption state, respectively.

$$M^{2+} + OH^- → MOH^-$$  \hspace{1cm} (1)

$$MOH^- + e^- → MOH_{ad}$$  \hspace{1cm} (2)

$$MOH_{ad} + e^- = M + OH^-$$ \hspace{1cm} (3)

The deposition of an iron-group metal proceeds through the adsorption of intermediate MOH$_{ad}$, and the rate-determining step is reaction (2). This indicates that the adsorption site of intermediate MOH$_{ad}$ is limited on the cathode. The dissociation constants of FeOH$^+$ and NiOH$^+$ are $5.78 \times 10^{-8}$ and $4.50 \times 10^{-5}$, respectively, indicating that the concentration of FeOH$^+$ in the cathode layer is 1000 times larger than that of NiOH$^+$. Therefore, during Fe–Ni alloy deposition, FeOH$_{ad}$ deprives the adsorption site of NiOH$_{ad}$, and as a result, the reduction of NiOH$^+$, as denoted by Eq. (2), is significantly suppressed. As shown in Fig. 3, with the increase of the molar ratio of Fe$^{2+}$ ions in solution to 20, 40, and 60%, the rise in the partial polarization for Ni deposition is shown to be gentler than that for Fe deposition, which seems to be due to suppression in the reduction of NiOH$^+$ by FeOH$_{ad}$. Since Ni deposition is more suppressed with an increasing molar ratio of Fe$^{2+}$ ions in solution, the curve showing the relationship between the Ni content in the deposits and the current density shifts to the low current density side [see Fig. 4(b)].

At the region where the inclination of the partial polarization curve for Ni deposition is almost identical to that for Fe deposition at a total current density above $i_{Ni}$ or $i_{Ni}'$, the Ni content in the deposits reached a minimum value and became almost constant. The minimum value of the Ni content in the deposits decreases upon increasing the molar ratio of Fe$^{2+}$ ions in solution. The significant increase in the partial current density of Ni is attributed to the release of FeOH$_{ad}$ adsorption sites for NiOH$_{ad}$ due to a decrease in the coverage of FeOH$_{ad}$ because the reduction of Fe$^{2+}$ ions approaches the diffusion limitation of Fe$^{2+}$ and the reduction rate from FeOH$_{ad}$ to Fe increases.

At the total current density region above $i_{Fe}$ or $i_{Fe}'$, since Fe deposition only reaches the diffusion limitation of Fe$^{2+}$ ions but Ni deposition does not reach its diffusion-limited current density, the Ni content in the deposits increases with the current density. With increasing the molar ratio of Fe$^{2+}$ ions in solution or the concentration of Fe$^{2+}$ ions, $i_{Fe}$ increases to $i_{Fe}'$, and as a result, the curve representing the relationship between the Ni content in the deposits and the current density at the high-current-density region shifts to the high current density side. That is, the current density at which the Ni content in the deposits initiates an increase with the current density increases with the concentration of Fe$^{2+}$ ions in solution. With a further increase in the current density, Ni deposition also reaches the diffusion limitation of Ni$^{2+}$ ions, and the Ni content in the deposits increases until it becomes constant at the solution composition [Ni$^{2+} / (Ni^{2+} + Fe^{2+}) \times 100$ mass%]. However, the Ni content in the deposits increases with the current density at the high-current-density region, but it does not reach the solution composition, as shown in Fig. 1, indicating that Ni deposition does not reach the diffusion-limited current density in this study.

On the other hand, when the inclination of the polarization curve for hydrogen evolution is gentler than that for Fe and Ni deposition at the total current density region above $i_{Fe}$, the current efficiency for the deposition of the Fe–Ni alloy increases with the current density. The slow elementary process is present in hydrogen evolution as with the iron-group metal deposition mentioned above, and the adsorption sites for the reaction intermediate, H$_{ad}$, are lim-
3.2. Effect of Malonic Acid on the Composition of the Deposits and Current Efficiency

As shown in Fig. 1, in a solution with a molar ratio of Fe$^{2+}$ ions of 30%, the Ni content in the deposits is expected to be 36 mass% at two current densities somewhat above 50 and 500 A·m$^{-2}$, or the Ni content in the deposits is close to that in invar alloy that can be obtained at a relatively wide range of current densities. Therefore, the following experiments were performed at a molar ratio of Fe$^{2+}$ ions of 30% in order to investigate the effect of additives in the solution.

**Figure 5** shows the Ni content in the Fe–Ni alloys deposited at various current densities from the solutions containing malonic acid of different concentrations. The curve that shows the relationship between the Ni content in the deposits and the current density shifted to the high current density side upon increasing the concentration of malonic acid. Increasing the concentration of malonic acid increased the Ni content in the deposits at the low-current-density region below 500 A·m$^{-2}$ and decreased the Ni content at the high-current-density region above 500 A·m$^{-2}$. The minimum value of the Ni content in the deposits somewhat increased with increasing the concentration of malonic acid.

**Figure 6** shows the current efficiency for Fe–Ni alloy deposition at various current densities from solutions containing malonic acid at different concentrations. The current efficiency for Fe–Ni alloy deposition increased with the current density regardless of the concentration of malonic acid, but it decreased with increasing malonic acid concentration across all current density regions. The current efficiency greatly decreased with increasing the concentration of malonic acid from 0.05 mol·dm$^{-3}$ to 0.1 mol·dm$^{-3}$.

**Figure 7** shows the partial polarization curves for Fe deposition (a), Ni deposition (b), and hydrogen evolution (c) from solutions containing malonic acid at different concentrations. The effect of the addition of malonic acid on the partial polarization curves for Fe deposition (a) was rarely observed at the low-partial-current-density region for Fe below 20 A·m$^{-2}$. However, at the partial current density for Fe above 20 A·m$^{-2}$, increasing the concentration of malonic acid significantly polarized the partial polarization curve for Fe deposition. Focusing on the cathode potential at which Fe deposition reaches the diffusion limitation of Fe$^{2+}$ ions, at malonic acid concentrations of 0, 0.05, 0.1, and 0.5 mol·dm$^{-3}$, the potential was −0.72 V, −0.84 V, −0.92 V, and less than −1.07 V, respectively, indicating that the potential for diffusion limitation of Fe$^{2+}$ ions shifts to a less noble direction with increasing concentration of malonic acid. The partial polarization curve for Ni deposition (b) was rarely affected at partial current densities below 20 A·m$^{-2}$ by the concentration of malonic acid, whereas at partial current densities of Ni above 20 A·m$^{-2}$, polarization increased with the concentration of malonic acid. The partial current density of Ni increased rapidly at approximately −0.65 V in a malonic-acid-free solution, whereas it increased rapidly at approximately −0.97 V in a solution containing 0.5 mol·dm$^{-3}$ malonic acid, indicating that the potential at which the partial current density of Ni begins to
increase rapidly shifts to a less noble direction with increasing concentration of malonic acid. This rapid increase of the partial current density of Ni is attributed to that the coverage of FeOHad decreases due to both approach to the diffusion limitation of Fe²⁺ ions of Fe deposition and increase in reduction rate from FeOHad to Fe, as a result, the adsorption sites for NiOHad deprived by FeOHad are released. Since Fe deposition is polarized with addition of malonic acid, Fe deposition approaches the diffusion limitation of Fe²⁺ ions at less noble potential, resulting that the potential at which the partial current density of Ni begins to increase rapidly shifts to less noble direction.

On the other hand, the partial polarization curve for hydrogen evolution (c) was greatly depolarized with increasing concentration of malonic acid from 0.05 to 0.1 and 0.5 mol·dm⁻³. Since hydrogen evolution during Fe–Ni alloy deposition was expected to be affected by the deposition of Fe and Ni, the polarization curve for hydrogen evolution was measured using an Fe–36 mass% Ni alloy cathode in a pH = 2.0 solution containing only malonic acid, without any Fe²⁺ or Ni²⁺ ions. The result is shown in Fig. 8. The polarization curve for hydrogen evolution was greatly depolarized across the potential region less noble than −0.4 V with the addition of malonic acid.

\[
\text{C}_3\text{H}_4\text{O}_4 = \text{H}^+ + \text{C}_2\text{H}_4\text{O}_4^- \quad \text{(4)}
\]

\[
\text{C}_3\text{H}_4\text{O}_4^- = \text{H}^+ + \text{C}_2\text{H}_4\text{O}_4^{2-} \quad \text{(5)}
\]

Malonic acid dissociates as shown in Eqs. (4) and (5). The dissociation constants for Eqs. (4) and (5) are reported to be 10⁻².6¹ and 10⁻⁵.²⁷,²⁹ respectively. The pH at the cathode layer during Fe–Ni alloy deposition is reported to increase to approximately 6.8 owing to the reduction of H⁺ ions.¹⁷,¹⁸ In solutions containing malonic acid, the malonic acid dissociates according to Eqs. (4) and (5), resulting in an increase in the concentration of H⁺ ions, and as a result, the current efficiency for Fe–Ni alloy deposition decreases owing to the acceleration of hydrogen evolution. Comparing Figs. 7(c) and 8, the partial polarization curve for hydrogen evolution was found to significantly polarize with the existence of Fe²⁺ and Ni²⁺ ions in the solution.

On the other hand, the malonic acid ions form a complex with Fe³⁺ and Ni²⁺ as shown in the following equations:

\[
\text{Fe}^{3+} + \text{C}_3\text{H}_4\text{O}_4^{2-} = \text{FeC}_3\text{H}_4\text{O}_4^+ \quad \text{(6)}
\]

\[
\text{Fe}^{3+} + 2\text{C}_3\text{H}_4\text{O}_4^{2-} = \text{Fe(C}_3\text{H}_4\text{O}_4)_2^2- \quad \text{(7)}
\]

\[
\text{Ni}^{2+} + \text{C}_3\text{H}_4\text{O}_4^{2-} = \text{NiC}_3\text{H}_4\text{O}_4 \quad \text{(8)}
\]

The stability constants of the complexes shown in Eqs. (6), (7), and (8) are reported to be 10⁴.⁷², 10⁷.⁸¹, and 10¹.⁴²,²⁹ respectively. The large polarization of the partial polarization curve of Ni at the high-current-density region with the addition of malonic acid, as shown in Fig. 7, is attributed to the formation of a complex of malonic acid and Ni²⁺ ions. The stability constant of the complex of malonic acid and Fe²⁺ ions is unknown, but the partial polarization curve for Fe deposition is also significantly polarized at the high-current-density region, which is attributed to the formation of a complex between malonic acid and Fe²⁺ ions.
Figure 9 shows a schematic diagram of the changes in the polarization curves for Fe–Ni alloy deposition (a) and the current density–alloy composition and current density–current efficiency curves (b) with increasing malonic acid concentration. Upon increasing the concentration of malonic acid, hydrogen evolution is significantly accelerated and the total polarization curve shifts in a noble potential direction at the low-current-density region. With increasing total current density, the suppression of Fe and Ni deposition increases, resulting in a shift of the total polarization curve to a less noble potential. The total current density, $i_{\text{Ni}}$, where Ni deposition is suppressed, changes to $i'_{\text{Ni}}$ with the addition of malonic acid, and as a result, the curve representing the relationship between the Ni content in the deposits and the current density shifts to a higher current density in the low-current-density region. With increasing the concentration of malonic acid, the current density region where Ni deposition is suppressed increases to approximately $i'_{\text{Fe}}$, but Fe deposition is also simultaneously suppressed, resulting in a slight decrease in the Ni content in the deposits at a current density above $i'_{\text{Ni}}$. On the other hand, the potential at which Fe deposition is limited by the diffusion of Fe$^{2+}$ ions shifts to a less noble direction with increasing the concentration of malonic acid. Therefore, the total current density, $i'_{\text{Fe}}$, where Fe deposition is limited by the diffusion of Fe$^{2+}$ ions, increases to $i''_{\text{Fe}}$ with increasing the concentration of malonic acid. As a result, the curve showing the relationship between the Ni content in the deposits and the current density at the high-current-density region shifts to the high-current-density side with increasing the concentration of malonic acid. On the other hand, the current efficiency for Fe–Ni alloy deposition decreases in all the current density regions with increasing the concentration of malonic acid because the partial polarization curve for hydrogen evolution shifts to the high-current-density region.

Figure 10 shows the SEM images of the surface of the Fe–Ni alloys deposited at various current densities from solutions containing different concentrations of malonic acid. The deposits obtained from the malonic-acid-free solution comprised fine granular crystals, and the size increased somewhat at 50 A·m$^{-2}$. In a solution containing 0.05 mol·dm$^{-3}$ malonic acid, the deposits obtained at low current densities of 20 and 50 A·m$^{-2}$ showed larger granular crystals than those from the malonic-acid-free solution, whereas those obtained at a high current density of 500 A·m$^{-2}$ showed fine crystals with a smooth surface.
Upon increasing the concentration of malonic acid to 0.1 and 0.5 mol·dm$^{-3}$, the deposits obtained at 500 A·m$^{-2}$ partially exhibited granular crystals but showed a smooth surface, except for the spot of granular crystals. The partial polarization curves for Fe and Ni deposition were more polarized at 500 A·m$^{-2}$ with the addition of malonic acid, compared with those without (Fig. 7), indicating an increase in the overpotential for deposition with malonic acid. When the overpotential for deposition increases, the deposits become finer because the nucleation rate of crystals is relatively fast compared to the growth rate.$^{30–33}$ In this study, the overpotential for deposition increased with the addition of malonic acid, and as a result, the deposits seemed to be fine and had a smooth surface.

### 3.3. Effect of Each Additive on the Composition and Current Efficiency of Alloy Deposition

Since the current efficiency for Fe–Ni alloy deposition significantly decreased with increasing the concentration of malonic acid above 0.05 mol·dm$^{-3}$, as shown in Fig. 6, the effect of each additive on the alloy deposition was investigated from solutions containing 0.05 mol·dm$^{-3}$ malonic acid with a molar ratio of Fe$^{2+}$ ions of 30%. Figure 11 shows the Ni content in the Fe–Ni alloys deposited at various current densities from solutions containing different additives. With the addition of thiourea, the Ni content in the deposits significantly increased at current densities less than 300 A·m$^{-2}$. Particularly, at current densities less than 200 A·m$^{-2}$, the Ni content in the deposits was higher than that in solution (71 mass%), indicating a normal codeposition behavior. With the addition of boric acid, the Ni content in the deposits increased somewhat at low current densities below 50 A·m$^{-2}$. With the addition of thiourea, the Ni content in the deposits was somewhat lower than that with the addition of boric acid only. Focusing on the condition where the Ni content in the deposits was 36 mass%, an invar alloy was obtained at a relatively wide range of current densities in the case of the addition of both boric acid and saccharin.

Figure 12 shows the current efficiency for Fe–Ni alloy deposition at various current densities from solutions containing different additives. With the addition of thiourea, the current efficiency for Fe–Ni alloy deposition increased at current densities less than 10 A·m$^{-2}$, but it decreased at current densities above 50 A·m$^{-2}$. With the addition of boric acid, the current efficiency decreased at all current densities. On the other hand, with the addition of both boric acid and saccharin, the current efficiency was somewhat higher at low current densities below 50 A·m$^{-2}$ than with the addition of boric acid only, but it was lower at current densities of 100–1 000 A·m$^{-2}$.

Figure 13 shows the partial polarization curves for Fe deposition (a), Ni deposition (b), and hydrogen evolution (c) from solutions containing different additives. Although the effect of thiourea and boric acid on the partial polarization curve for Fe deposition (a) was rarely observed, with the addition of both of boric acid and saccharin, Fe deposition was somewhat suppressed. The partial polarization curve for Ni deposition (b) was greatly depolarized with the addition of thiourea. With the addition of thiourea, the Ni content in the deposits significantly increased at current densities less than 500 A·m$^{-2}$ (Fig. 11), which is attributed to the acceleration of Ni deposition. With the addition of boric acid, the partial polarization curve for Ni deposition was somewhat depolarized at Ni partial current densities of 10–50 A·m$^{-2}$. As a result, the Ni content in the deposits seemed to increase (Fig. 11). However, with the addition of both boric acid and saccharin, the partial polarization curve for Ni deposition was somewhat more polarized than that with the addition of boric acid only. Therefore, with the addition of both boric acid and saccharin, the Ni content in the deposits seemed to be somewhat lower than that with the addition of boric acid only (Fig. 11). On the other hand, the partial polarization curve for hydrogen evolution (c) was significantly depolarized at low current densities with the addition of thiourea, whereas it was somewhat depolarized with the addition of boric acid and saccharin.
Fig. 14. SEM images of the surface of Fe–Ni alloys deposited at various current densities from solutions containing different additives. Fe²⁺ 0.3 mol·dm⁻³, Ni²⁺ 0.7 mol·dm⁻³, malonic acid 0.05 mol·dm⁻³.

Figure 14 shows the SEM images of the surface of the Fe–Ni alloys deposited at various current densities from solutions containing different additives. Fe²⁺ 0.3 mol·dm⁻³, Ni²⁺ 0.7 mol·dm⁻³, malonic acid 0.05 mol·dm⁻³.

of boric acid only. This trend is identical with the partial polarization curve for Ni deposition (b). As mentioned above, thiourea significantly accelerated Ni deposition and hydrogen evolution, boric acid somewhat accelerated Ni deposition and hydrogen evolution, and saccharin had a somewhat suppressive effect on Fe and Ni deposition and also hydrogen evolution.

Figure 14 shows the SEM images of the surface of the Fe–Ni alloys deposited at various current densities from solutions containing different additives. With the addition of thiourea, the deposits showed granular coarse crystals at all current densities. The partial polarization curve for Ni deposition was significantly depolarized with the addition of thiourea (Fig. 13), showing the decrease in the overpotential for deposition. As a result, the crystal growth rate of the deposits was higher than the nucleation rate, resulting in coarse crystals. With the addition of boric acid, the granular crystals became fine at low current densities of 20 and 50 A·m⁻². On the other hand, with the addition of both boric acid and saccharin, hemisphere-like crystals with smooth surfaces were observed, and these crystals were larger than those formed by the addition of boric acid only.

4. Conclusions

The effects of solution composition and additives on the composition of the electrodeposited Fe–Ni alloys were investigated. In the solutions of all the compositions studied, increasing the current density from a low current density of 10 A·m⁻² significantly decreased the Ni content in the deposits and showed anomalous codeposition in which the electrochemically less noble Fe was deposited preferentially.
Upon increasing the current density further, Fe deposition reached the diffusion limitation of Fe$^{2+}$ ions, and as a result, the Ni content in the deposits increased with the current density. The current density required to initiate an increase in the Ni content in the deposits shifted to a higher-current-density region. With the increasing concentration of malonic acid, the current density in which Ni deposition was suppressed was shifted to a higher-current-density region with the increasing concentration of Fe$^{2+}$ ions because of an increase in the diffusion-limited current density of Fe. With the increasing concentration of malonic acid, the current density required to initiate an increase in the Ni content in the deposits increased with the current density.

The current density range.

An invar alloy of Fe–36 mass% Ni was obtained at a wider region. With the addition of both boric acid and saccharin, deposits somewhat increased in the lower-current-density region. With the addition of boric acid, the Ni content in the deposits significantly increased with the addition of thiourea. With the addition of boric acid and saccharin, an invar alloy of Fe–36 mass% Ni was obtained at a wider current density range.

REFERENCES

1) T. Nagayama, T. Yamamoto and T. Nakamura: J. Surf. Finish. Soc. Jpn., 67 (2016), 140 (in Japanese).
2) H. Saito: Physics and Application of Invar Alloys, Maruzen, Tokyo, (1978), 18.
3) T. Yokoyama and K. Eguchi: Phys. Rev. Lett., 107 (2011), 065901.
4) R. J. Weiss: Proc. Phys. Soc., 82 (1963), 281.
5) H. Saito and H. Fujimori: Bull. Inst. Met., 7 (1968), 263 (in Japanese).
6) H. Ise: Denchu Gizyutsu to Ouyo, Maki Shoten, Tokyo, (1996), 7 (in Japanese).
7) H. Dahms and I. M. Croll: J. Electrochem. Soc., 112 (1965), 771.
8) S. Hessami and C. W. Tobias: J. Electrochem. Soc., 136 (1989), 3611.
9) J. Horkans: J. Electrochem. Soc., 128 (1981), 45.
10) M. Yasuda and N. Koura: J. Met. Finish. Soc. Jpn., 33 (1982), 427 (in Japanese).
11) E. B. Lehman and A. Riesenkampf: Surf. Technol., 11 (1980), 349.
12) W. C. Grande and J. B. Talbot: J. Electrochem. Soc., 140 (1993), 669.
13) K. Y. Sasaki and J. B. Talbot: J. Electrochem. Soc., 142 (1995), 775.
14) M. Matlosz: J. Electrochem. Soc., 140 (1993), 2272.
15) B. C. Baker and A. C. West: J. Electrochem. Soc., 144 (1997), 164.
16) J. Vaes, J. Fransaer and J. P. Celis: J. Electrochem. Soc., 147 (2000), 3718.
17) H. Nakano, M. Matsuno, S. Oue, M. Yano, S. Kobayashi and H. Fukushima: Mater. Trans., 45 (2004), 3130.
18) H. Nakano, M. Matsuno, S. Oue, M. Yano, S. Kobayashi and H. Fukushima: J. Jpn. Inst. Met., 69 (2005), 548 (in Japanese).
19) S. Kawano, T. Ohgai, S. Kobayashi, H. Nakano, T. Tsuru, T. Akiyama, H. Fukushima and K. Harada: Proc. 2nd Int. Conf. on Processing Materials for Properties, TMS, Warrendale, PA, (2000), 769.
20) T. Nagayama, Y. Mizutani, T. Nakamura and N. Shinohara: J. Surf. Finish. Soc. Jpn., 57 (2006), 733 (in Japanese).
21) T. Nagayama, Y. Mizutani, Y. Kato, Y. Kotera, T. Nakamura and N. Shinohara: J. Surf. Finish. Soc. Jpn., 58 (2007), 675 (in Japanese).
22) T. Yamamoto, T. Nagayama, T. Nakamura and Y. Mizutani: J. Surf. Finish. Soc. Jpn., 62 (2011), 702 (in Japanese).
23) T. Nagayama, T. Yamamoto, T. Nakamura and Y. Mizutani: ECS Trans., 50 (2013), No. 52, 117.
24) H. Fukushima, T. Akiyama, M. Yano, T. Ishikawa and R. Kammel: ISIJ Int., 33 (1993), 1009.
25) H. Nakano, T. Ohgai, H. Fukushima, T. Akiyama and R. Kammel: Metall., 55 (2001), 676.
26) J. O'M. Bockris and H. Kita: J. Electrochem. Soc., 108 (1961), 676.
27) H. Nakano, S. Kobayashi, T. Akiyama, T. Tsuru and H. Fukushima: Tetsu-to-Haganè, 49 (2003), 64 (in Japanese).
28) M. Yano, H. Fukushima, H. Nakano and T. Akiyama: Tetsu-to-Haganè, 86 (2000), 176 (in Japanese).
29) D. D. Perrin: Stability Constants of Metal-ion Complexes: Part B Organic Compounds, Pergamon Press, Oxford, (1979), 98.
30) S. Haruyama: Hakumaku Zairyo no Kiso to Ohyo, The Japan Institute of Metals, Sendai, (1987), 37 (in Japanese).
31) H. Nakano, S. Oue, T. Miiek, S. Kobayashi and H. Fukushima: ISIJ Int., 46 (2006), 106.
32) H. Nakano, S. Oue, Y. Hamaguchi, S. Kobayashi and H. Fukushima: ISIJ Int., 49 (2009), 1769.
33) H. Nakano: Trans. Nonferr. Met. Soc. China, 19 (2009), 835.