Mechanism of Anomalous Type Electrodeposition of Fe-Ni Alloys from Sulfate Solutions

Hiroaki Nakano¹, Masayuki Matsuno², Satoshi Oue¹, Masaaki Yano³,
Shigeo Kobayashi² and Hisaaki Fukushima¹

¹Department of Materials Science & Engineering, Kyushu University, Fukuoka 812-8581, Japan

²Department of Industrial Chemistry, Kyushu Sangyo University, Fukuoka 813-8503, Japan

³Department of Materials Science and Engineering, Kurume National College of Technology,
Kurume 830-8555, Japan

The electrodeposition of Fe-Ni alloys was performed galvanostatically in the sulfate solutions of pH 1–3 at 40°C and the alloy deposition behavior was compared with that of Zn-iron-group metal alloys to investigate their codeposition mechanism. The deposition behavior of Fe-Ni alloy showed a typical feature of the anomalous codeposition, in which electrochemically less noble Fe deposits preferentially under most plating conditions. The anomalous codeposition behavior in Fe-Ni alloy deposition was evidently dependent on the pH buffer capacity of the solutions. This can be explained in terms of the preferential adsorption of FeOH on the deposition sites of more noble Ni due to the extremely smaller dissociation constant of FeOH⁺ than NiOH⁺ in the multi-step reduction process of hydrated iron-group metal ions.

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1. Introduction

Electrodeposited Fe-Ni alloys have been widely used for the thin film head of magnetic recording because of their high magnetic permeability and small coercive force.^{1,2)} In recent years, the application of Fe-Ni alloy films to the stress sensor of magnetostriction type has been expected. This type of stress sensors detect the tension, torque, stress and weight loaded to the subject by using the reverse magnetostrictive effect that their magnetic property changes depending on the strain applied to magnetic substances.³⁾ It has been well known that the deposition behavior of Fe-Ni alloys showed a typical feature of anomalous codeposition, in which electrochemically less noble Fe deposits preferentially under most plating conditions.^{4–13)} Since the magnetic properties of Fe-Ni alloy change greatly depending on its composition, the alloy of fixed composition should be deposited stably to keep the desired properties. Therefore, it is important to make clear the mechanism of anomalous deposition of Fe-Ni alloys. The hydroxide suppression model⁴⁾ and the mathematical model⁵⁾ have been proposed so far to explain the anomalous codeposition of Fe with Ni. The hydroxide suppression model⁴⁾ explained that noble Ni deposition was strongly suppressed in the presence of Fe(OH)₂ preferentially formed and adsorbed on the cathode, while the mathematical model⁵⁾ was based on the great difference in the dissociation constant between FeOH⁺ and NiOH⁺. However, no mechanism explaining completely for the anomalous codeposition has been reported.

On the other hand, the deposition of Zn-iron-group metal alloys is one of the best-known examples of anomalous codeposition and Zn hydroxide suppression mechanism^{14–16)} is accepted widely for the anomalous deposition. In this study, the deposition of Fe-Ni alloys was performed under various plating conditions and the alloy deposition behavior was compared between Fe-Ni and Zn-Ni systems to investigate the mechanism of anomalous type deposition of Fe-Ni alloys.

2. Experimental

Electrolytic solutions for Fe-Ni alloy deposition were prepared by dissolving the reagent grade FeSO₄·7H₂O and NiSO₄·6H₂O (1.0 mol/L in total metal ion concentration) in water purified by distillation and ion exchange. The pH was adjusted with sulfuric acid to 1, 2 or 3 (standard condition: 3). Besides the sulfate solutions, the chloride solutions were used in some experiments. Electrolytic solutions for Zn-iron-group metal alloy deposition were also prepared by dissolving the reagent grade metal sulfate (1.0 mol/L in total) and the pH was adjusted with sulfuric acid to 1 or 3 (standard condition: 3). The deposition was performed in un-agitated solutions under coulstatic (10⁵ C/m²) and galvanostatic conditions at 40°C. Copper sheet and platinum sheet of 1 × 2 cm² were used as the cathode and the anode, respectively. An H-section cell where catholyte was separated from anolyte by sintered glass was used for performing electrolysis. A small amount of Ar gas was injected consistently during electrolysis into the cell to prevent oxidation of Fe²⁺. The deposited alloys were dissolved from the cathode with nitric acid. Each metal was quantitatively analyzed by ICP, and the alloy composition, the cathode current efficiency and the partial current density for each metal deposition were calculated. The cathode potentials were measured during the alloy deposition using a saturated Ag/AgCl reference electrode (0.199 V vs NHE, 25°C). In the presentation of polarization curves, the potentials were plotted with reference to NHE.

Using Sb microelectrode technique,¹⁴⁾ the pH in the vicinity of the cathode was evaluated during the alloy deposition. Under galvanostatic condition, the potential of Sb electrode attached to a micrometer was measured at various distance between the cathode and Sb electrode. Using the pH-potential calibration curve measured in advance, the pH profile near the cathode was determined.

To study the hydrolysis behavior of the aqua metal ions in the solutions, the pH titration curves were measured. The

0.2–0.8 mL of 0.01–5 N NaOH solution was added into 0.2 mol/L of FeSO_4 or NiSO_4 solution every 30 min. The measurement was performed in the sealed type cell and $10^{-3} \text{ m}^3/\text{min}$ of Ar gas was consistently injected to prevent oxidation of Fe^{2+} .

To confirm the mechanism of Fe-Ni alloy deposition, pulse plating was also performed in the sulfate solution containing 0.5 mol/L of Fe^{2+} and Ni^{2+} . The plating was kept during the on-time period of the pulse current (T_{on}) and was interrupted during the subsequent off-time period (T_{off}). The duty cycle given by $T_{\text{on}}/(T_{\text{on}} + T_{\text{off}})$ was fixed at 0.01, 0.1 and 1. The peak current density was changed from 10 to 10^4 A/m^2 .

3. Results and Discussion

3.1 Electrodeposition behavior of Fe-Ni and Zn-iron group metal alloys

Figure 1 shows the relationship between the content of Ni, which is more noble than other constituent in the deposited Fe-Ni and Zn-iron group metal systems, and the composition of the solutions. The CRL in the figure expresses the composition reference line which shows when the mass-percentage composition of the alloy just equals the metal-percentage of the solution. In the case in which Ni content of the alloys is higher than the CRL, alloy deposition of normal type occurs, indicating the preferential deposition of more noble Ni. As shown in Fig. 1, on the contrary, Ni content of the alloys was lower than the CRL in the whole composition range of the solutions. This indicates that anomalous codeposition was proceeding during the deposition of both Fe-Ni and Zn-iron-group metal alloys. The cathode current efficiency for Fe-Ni and Zn-iron-group metal alloy deposition shown in Fig. 1 was from 80 to 90%.

Figure 2 shows the current density-dependence of Ni content of Fe-Ni and Zn-Ni alloys deposited from the sulfate solutions of various pH's. Ni content of the alloys was higher than the CRL at small current densities. With increasing the current density, Ni content markedly decreased to the alloy composition region below the CRL. Further increase in the current density resulted in the gradual increase in Ni content toward CRL. The curves of Ni content thus showed a

Fig. 2 Effect of current density on the composition of Fe-Ni alloy (a) and Zn-iron group metal alloy (b) electrodeposited from sulfate solutions of different pH. (a) Fe^{2+} 0.2 mol·L $^{-1}$, Ni^{2+} 0.8 mol·L $^{-1}$, (b) Zn^{2+} 0.5 mol·L $^{-1}$, Ni^{2+} 0.5 mol·L $^{-1}$.

common feature that the normal codeposition at small current densities, the transition of the alloy deposition behavior to the anomalous type with increasing the current density and the gradual increase in Ni content toward the CRL at large current densities occurred.

The current density at which the deposition behavior of the alloys changes from a normal to an anomalous type is called the transition current density.¹⁵⁾ Figure 2 showed that Ni content curves were shifted to larger current density region as the pH of the solution lowered. This indicates that the transition current density for Fe-Ni and Zn-Ni alloy deposi-

Fig. 1 Effect of solution composition on the alloy composition of Fe-Ni alloys (a) and Zn-iron group metal alloys (b) electrodeposited from sulfate solutions at $1000 \text{ A}\cdot\text{m}^{-2}$. Metal-percentage of Ni = [mass Ni/total mass (Fe+Ni)]100.

Fig. 3 Partial polarization curves for Fe, Ni and Zn deposition from the solution containing each metal sulfate alone and from the alloy solution containing both metal sulfates. (a) Fe-Ni, (b) Zn-Ni.

tion was increased and therefore the alloy deposition of a normal type proceeded in a larger range of current density when the acidity of the solutions was increased.

Figure 3 shows the partial polarization curves for Fe, Ni and Zn deposition from the solution containing each metal sulfate alone (below simply referred to as metal single solution) and also from the alloy plating solution containing both metal sulfates. As shown in Fig. 3(a), the partial polarization curve for Fe deposition in Fe-Ni alloy plating solution was almost identical to that in Fe single solution. On the contrary, the polarization curve for Ni deposition was markedly polarized in the presence of Fe^{2+} in the alloy plating solution. This suggests that the anomalous deposition of Fe-Ni alloys was not caused by the depolarization of Fe deposition in the alloy plating solution but caused by the suppression of Ni deposition due to the codeposition of Fe. In Zn-Ni alloy deposition, the partial polarization curve for Ni deposition was markedly polarized in the presence of Zn^{2+} in the solution as shown in Fig. 3(b), showing the same feature as Ni-Fe alloy deposition.

3.2 Mechanism of the anomalous type alloy deposition proposed so far

In the anomalous type alloy deposition of Fe-Ni and Zn-Ni systems, as described above, the deposition of more noble Ni is suppressed in the presence of less noble metal ions in the alloy plating solutions. This indicates that a certain inhibitory substance containing less noble Fe or Zn ion should be formed to decrease the deposition rate of more noble Ni. The anomalous codeposition occurred easier in the solutions of higher pH, as shown in Fig. 2, implying that H^+ or OH^- ion is also closely related to the formation of the inhibitor.

The mechanism of anomalous type Zn-iron group metal alloy deposition has been studied well so far. At present, the hydroxide suppression mechanism^{15,16)} is accepted widely. According to this mechanism, Zn(OH)_2 was formed on the cathode due to the increase in pH in the cathode layer and the deposition rates of iron-group metals were suppressed greatly by the inhibitory Zn(OH)_2 adsorbed on the cathode. In this case, the pH in the cathode layer does not reach the critical value for iron-group metal hydroxide precipitation because of

an extremely large pH buffer capacity of the solution due to Zn(OH)_2 precipitation. This mechanism can explain well the characteristic alloy deposition behavior shown in Fig. 2(b) that the transition current density was increased when the pH of the solution lowered. In the sulfate solutions used in this work, the dissociation of HSO_4^- to SO_4^{2-} ($\text{pK} = 1.99$) is the major buffering reaction and therefore the pH buffer capacity of the solution increases greatly when the pH of the solution lowers less than 2. In the solutions having larger buffer capacity, the transition current density should be increased because the larger current density for hydrogen evolution is needed to reach the critical pH for Zn(OH)_2 precipitation in the cathode layer.

On the other hand, the hydroxide suppression mechanism, in which Fe(OH)_2 was considered to act as an inhibitor, has been also proposed in the anomalous type Fe-Ni alloy deposition.⁴⁾ According to this mechanism, the alloy deposition behavior shown in Fig. 2(a) also seems to be explicable in the same manner as Zn-Ni alloy deposition. In Zn-Ni alloy plating solutions, the solubility product¹⁷⁾ of Zn(OH)_2 (2.0×10^{-17}) is smaller enough in than that of Ni(OH)_2 (1×10^{-15}), resulting in the preferential precipitation and subsequent adsorption of inhibitory Zn(OH)_2 on the cathode. However, in Fe-Ni alloy plating solutions, the solubility product¹⁷⁾ of Fe(OH)_2 is 2.2×10^{-15} which is almost identical to that of Ni(OH)_2 . The critical pH values calculated from these solubility constants are 7.0 and 6.8 for the precipitation of Fe(OH)_2 and Ni(OH)_2 , respectively. Therefore, both metal hydroxides are considered to precipitate almost simultaneously when the pH of the cathode layer increases during the alloy deposition. Consequently, the Fe(OH)_2 suppression mechanism seems to be invalid for Fe-Ni alloy deposition.

Hessami and Tobias⁵⁾ proposed another mechanism of Fe-Ni alloy deposition. They assumed that the deposition of iron-group metals proceeds with preceding formation of metal hydroxide ions as expressed by following reactions.

Fig. 4 Effect of pH in the solution on the partial polarization curves of Fe (a) and Ni (b) during the electrodeposition of Fe-Ni alloys. (Fe^{2+} $0.2 \text{ mol}\cdot\text{L}^{-1}$, Ni^{2+} $0.8 \text{ mol}\cdot\text{L}^{-1}$).

In above reactions, M expresses iron-group metals. Since the dissociation constants⁵⁾ of FeOH^+ and NiOH^+ are 5.78×10^{-8} and 4.50×10^{-5} , respectively, the hydroxide ion concentration is almost thousand times smaller in FeOH^+ than NiOH^+ in the cathode layer. As a result, Fe deposits preferentially under most plating conditions. However, the reason why Ni deposition rate was suppressed in Fe-Ni alloy solution cannot be explained by the mechanism of Hessami and Tobias. Even if the concentration of NiOH^+ are markedly smaller than that of FeOH^+ , Ni deposition rate in Fe-Ni alloy solution should be equal to that in Ni single solution because the concentration of NiOH^+ is low in both solutions and FeOH^+ has no effect on the Ni deposition. However, Fig. 3 showed that Ni deposition was suppressed only in the codeposition with Fe, indicating that the mechanism proposed by Hessami and Tobias also cannot be accepted.

3.3 Estimation of the mechanism of anomalous type Fe-Ni alloy deposition

Figure 4 shows the partial polarization curves of Fe and Ni during the alloy deposition from the solutions of various pH's. The figure indicated that the polarization curves of both Fe and Ni were depolarized with the increase in pH of the solution, suggesting that the deposition rates of both Fe and Ni were promoted when the condition accelerated the formation of such intermediate species as MOH^+ presented in the reactions of (1) and (2).

The increase in pH in the cathode layer was confirmed by directly measuring the pH using Sb microelectrode technique during Fe-Ni alloy deposition. Figure 5 shows the pH profiles near the cathode during the alloy deposition at the current density of 10 or 50 A/m^2 , which is smaller or larger than the transition current density. The pH in the cathode layer increased slightly from the pH value of bulk solution at 10 A/m^2 . On the other hand, the pH increased considerably to reach 6.8 at 50 A/m^2 . Then the concentration of each metal hydroxide ion formed at pH 6.8 was calculated using the dissociation constants given by Hessami and Tobias.⁵⁾ The result showed that the concentration of the metal hydroxide ion was 0.21 mol/L for Fe and 10^{-3} mol/L for Ni. This indicates that NiOH^+ is scarcely formed but FeOH^+ is

Fig. 5 pH profiles in the vicinity of cathode during Fe-Ni alloy deposition. (Fe^{2+} $0.2 \text{ mol}\cdot\text{L}^{-1}$, Ni^{2+} $0.8 \text{ mol}\cdot\text{L}^{-1}$).

formed in the cathode layer when the current density is increased to permit the anomalous codeposition.

Figure 6 shows the pH titration curves measured in Fe single or Ni single solution containing 0.2 mol/L of its sulfate using NaOH solution. In the figure, the titration curves are presented in the region where the pH began to increase abruptly due to the hydrolysis of each metal ion. With an addition of NaOH solution, the titration curve of Ni single solution increased directly toward the critical pH for Ni(OH)_2 precipitation¹⁷⁾ and no stagnation of pH due to NiOH^+ formation was observed. On the other hand, the titration curve of Fe single solution showed the distinct shoulder at the pH range between 6.3 and 7.0 before reaching the critical pH for Fe(OH)_2 precipitation. This indicated the formation of FeOH^+ as predicted by theoretical calculation described above. In the anomalous type Fe-Ni alloy deposition, therefore, the FeOH^+ must be formed in preference to NiOH^+ .

It is well known that the iron-group metal has the inherent

Fig. 6 pH titration curves of the sulfate solution containing Ni^{2+} or Fe^{2+} ion. (FeSO_4 $0.2 \text{ mol}\cdot\text{L}^{-1}$, NiSO_4 $0.2 \text{ mol}\cdot\text{L}^{-1}$).

property of not beginning to deposit at its equilibrium potential but requiring a deposition overpotential. The minimum overpotential needed for beginning iron-group metal deposition is attributed to a rate-determining step in the multi-step reduction of iron-group metal ions. A series of reactions described below has been proposed for the deposition process of iron-group metals.¹⁸⁾ In the reactions, M expresses iron-group metal and subscription “ad” for adsorbed state.

According to above reactions, the deposition of iron-group metals proceeds with preceding formation of adsorbed intermediate MOH_{ad} and the reaction (4) is rate-determining. This means that the number of adsorption sites for MOH_{ad} is limited on the cathode. Since the concentration of FeOH^+ formed in the cathode layer is, as mentioned previously, overwhelmingly higher than NiOH^+ , the adsorption sites for NiOH_{ad} should be occupied by the FeOH_{ad} in the Fe-Ni alloy deposition. Consequently, the reduction of NiOH^+ , shown in the reaction (4), is markedly suppressed in the alloy plating solution. Therefore, only in the case that Ni codeposits with Fe, Ni deposition is suppressed, resulting in the anomalous codeposition.

According to the discussions presented above, it can be concluded that the inhibitor is $\text{Zn}(\text{OH})_2$ in the anomalous type Zn-Ni alloy deposition, while in the Fe-Ni alloy deposition, FeOH_{ad} acts as an inhibitor which decreases the deposition rate of more noble Ni.

3.4 Confirmation of the mechanism proposed above

The effects of chloride ion and pulse plating on the deposition behavior of Fe-Ni alloys were studied to confirm the mechanism proposed above. Figure 7 shows the current density-dependence of Fe-Ni alloy composition in the chloride solutions of various pH's. The trend of the alloy deposition behavior with respect to the current density was

Fig. 7 Relationship between the alloy composition and the current density for Fe-Ni alloy deposition in the chloride solutions of different pH. (Fe^{2+} $0.2 \text{ mol}\cdot\text{L}^{-1}$, Ni^{2+} $0.8 \text{ mol}\cdot\text{L}^{-1}$).

quite identical to those in the sulfate solutions shown in Fig. 2(a). However, the Ni content curves were shifted upwards in the chloride solutions when compared to the sulfate solutions, indicating the decrease of the anomaly. It was reported that the deposition of iron-group metals in the chloride solutions was performed with smaller deposition overpotential than in the sulfate solutions, because the deposition of iron-group metals in the chloride solutions proceeded with preceding formation of intermediate MCl_{ad} which could be much more easily discharged than MOH_{ad} .¹⁹⁾ Consequently, in Fe-Ni alloy deposition from the chloride solution, Ni deposition proceeded faster through NiCl_{ad} whose adsorption sites were less limited, resulting in the decrease of the anomaly.

Figure 8 shows the relationship between the composition of deposited Fe-Ni alloys and the peak current density during pulse plating in the sulfate solution. The figure showed that Ni content curves were shifted to larger current density region as the duty cycle of the pulsed current was decreased. This indicated that the transition current density for Fe-Ni

Fig. 8 Effect of duty cycle in the pulse plating on the Fe-Ni alloy composition. (Fe^{2+} $0.5 \text{ mol}\cdot\text{L}^{-1}$, Ni^{2+} $0.5 \text{ mol}\cdot\text{L}^{-1}$, pulse time 100 ms).

alloy deposition was increased and therefore the current density region where the normal type alloy deposition occurred was broadened in pulse plating than in direct current plating.

In the pulse plating, the alloy is deposited during the on-time period of the pulsed current (T_{on}). During the subsequent off-time period (T_{off}), species depleted in the cathode layer due to the electrochemical reactions are supplied from the bulk solution. Since the duty cycle of pulsed current is given by $T_{\text{on}}/(T_{\text{on}} + T_{\text{off}})$, the increase in pH in the cathode layer is expected to retard when the duty cycle becomes smaller, because enough amounts of H^+ ions are supplied from the bulk solution during longer off-time period to prevent the increase in pH in the cathode layer. Therefore, the formation rate of inhibitory FeOH_{ad} is decreased, resulting in the preferential deposition of more noble Ni in wider range of current density.

As discussed above in detail, the effects of chloride ion and pulse plating on the deposition behavior of Fe-Ni alloys suggested that the degree of anomaly was decreased under the conditions which decreased the suppression effect by inhibitory FeOH_{ad} formed on the cathode. These results demonstrate the validity of the anomalous type Fe-Ni alloy deposition mechanism proposed in this study that Ni deposition is suppressed to permit the preferential deposition of less noble Fe because the adsorption sites for intermediate NiOH_{ad} are occupied by the inhibitory FeOH_{ad} preferentially formed and subsequently adsorbed on the cathode.

4. Conclusion

Deposition of Fe-Ni alloys was performed under various plating conditions in the sulfate solutions and the deposition behavior was compared with that of Zn-iron-group metal alloys. The results obtained are described as follows.

(1) The deposition behavior of Fe-Ni alloy showed a typical feature of the anomalous codeposition, in which electrochemically less noble Fe deposits preferentially under most plating conditions. This anomalous codeposition was caused by the suppression of Ni deposition due to the codeposition of Fe.

(2) The anomalous codeposition behavior in Fe-Ni alloy deposition was evidently dependent on the pH buffer capacity

of the solutions. This can be explained in terms of the preferential adsorption of FeOH on the deposition sites of more noble Ni due to the extremely smaller dissociation constant of FeOH^+ than NiOH^+ in the multi-step reduction process of hydrated iron-group metal ions.

(3) The degree of the preferential deposition of less noble Fe was decreased under the plating conditions that the formation of FeOH_{ad} retarded.

(4) The formation of FeOH^+ in the cathode layer during the anomalous codeposition was confirmed by directly measuring the pH profiles near the cathode and by measuring the pH titration curves of the single Fe solution.

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