Composition controlling of Co–Ni and Fe–Co alloys using pulse-reverse electroplating through means of experimental strategies

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Abstract

The optimal plating settings in the pulse-reverse electroplating mode for the non-anomalous plating of Co–Ni deposits (i.e., the metal composition of deposits is equal to that of the plating solutions) from chloride solutions were approached by using experimental strategies including fractional factorial design (FFD), path of steepest ascent and central composite design (CCD) coupled with the response surface methodology (RSM). The potentials and time period of pulse-plating were the key factors affecting the composition of Co–Ni deposits in the FFD study. The two variables were the path of the steepest ascent investigation to approach the optimal conditions for non-anomalous plating of Co–Ni deposits. The effects of pulse-plating potential and pulse-plating time on the compositions of Co–Ni deposits were further examined using a regression model in the CCD study.

The variable Ni contents of Co–Ni deposits are caused by metal hydroxide on the deposit surface. After anodic dissolution process, the increasing pulse-plating time and lower pulse-plating potential can remove metal hydroxide and improve Ni ion deposition ratio on the fresh deposit.

All Fe–Co deposits were equal to the composition metal ratio of plating bath while pulse-reverse-plating potential included the anodic dissolution process.

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1. Introduction

Cobalt–nickel (Co–Ni) and cobalt–iron (Fe–Co) electroplating are a one-step process for the production of magnetic films used in electronic materials. This deposition technique attracts industrial consideration because of the low cost and the deposition capability on almost geometry[1]. Co–Ni and Fe–Co deposits are mainly employed in soft ferromagnetic alloy, computer memory elements, printed circuit board (PCB), some aviation industries, some anti-corrosion materials as well as some medical instruments[2–4]. Nano-cristalline soft ferromagnetic of Fe–Co have highly desirable materials for high temperature applications like magnetic bearings for high-speed motor, flywheels, gas turbine engines, etc.[2–6]. The Co–Ni alloy with some Ru, Ir and Pd has more active catalysts than the crystalline material in the oxygen evolution[7–8]. Because of different application purposes, different compositions and specificities of Co–Ni and Fe–Co alloys were required, which were significantly affected by the plating temperature, agitation conditions, ionic characteristics, pH, pulse-plating current, reverse-plating current and additives, etc. Accordingly, several studies considered the electroplating mechanisms as well as the textural characteristics of iron alloy deposits[9–14].

According to Brenner’s definition[15], the codeposition of iron-group metals (e.g., Fe, Co, and Ni) is widely recognized as an anomalous electroplating type since the less noble
adsorption ability is Ni(OH)+ < Co(OH) + < Fe(OH) + [12]. This increase in the concentration of hydroxyl ion led to the formation and adsorption of metal hydroxide ions on cathode surface, favoring the anomalous deposition of iron-group alloys. Due to the sequence of metal hydroxide ions with respect to increase the adsorption of metal hydroxide ions on cathode surface, favoring the anomalous deposition, the hydrogen evolution of the iron-group alloys depleted protons and resulted in increasing the local concentration of hydroxyl ions [9–14,16]. This increase in the concentration of hydroxyl ions led to the formation and adsorption of metal hydroxide ions. The reaction mechanism is generally proposed as following [14,16–20]:

\[
\begin{align*}
2\text{H}_2\text{O} + 2\text{e}^- & \rightarrow \text{H}_2 + 2\text{OH}^- \\
\text{M}^{2+} + \text{OH}^- & \rightarrow \text{M(ОН)}^+ \\
\text{M(ОН)}^+ & \rightarrow \text{M(ОН)ads}^+ \\
\text{M(ОН)ads}^+ + 2\text{e}^- & \rightarrow \text{M} + \text{OH}^- 
\end{align*}
\]

where \( \text{M} \) indicates nickel, iron and cobalt atoms. Although many attempts have been made to explain the anomalous codeposition of alloys, there is still no universally accepted theory.

According to the above plating mechanism, the pulse-reverse-plating is believed to be powerful way to solve the anomalous plating and to easily control the compositions of Co–Ni and Fe–Co deposits. Free metal ions in the plating bath can be deposited under mass-transfer control during the pulse-plating period; meanwhile, the adsorbed metal hydroxide ions formed during pulse-plating period are dissolved during the reverse-plating period. This concept is further supported by the fact that an improvement of the anomalous phenomenon was generally found for the pulse-reverse-plating of Co–Ni and Fe–Co alloys [17–19]. Moreover, the pulse-reverse-plating has been deemed as a better deposition mode than dc electroplating [21], since the relaxation time period during the reverse potential and/or rest enables larger currents to be applied during the pulse-plating period without the concentration depletion of reactants.

The experimental strategy is a sequential procedure to reach the optimal operation conditions of interest [22–24]. This strategy assumes that the response variable(s) (e.g., the Ni and Co content in the Co–Ni and Fe–Co alloys, respectively) is a function of the quantitative control variables. Moreover, the starting point of experimental conditions is usually remote from the optimum, while there may be many factors influencing the response(s) of interest. Thus, screening experiments are employed to find the key factors affecting the responses. To efficiently find the key variables affecting the response variable(s), the fractional factorial design (FFD) is often employed [22–24], because a system or process is likely to be driven primarily by some of main effects and low-order interactions. Hence, the response variable(s) against the key factors near the starting point in the system can be suitably modeled as a first-order model. When the key factors have been screened out in the FFD experiments, the methodology of the steepest ascent path is used to approach the vicinity of the optimal conditions on the basis of the relationship between response variable(s) and key control variables deduced from the FFD results. Finally, the central composite design (CCD) is used to model the apparent curvature of response variable(s) against the key factors at the vicinity of optimum.

Since mathematic models of the response variable(s) against the control variables can be represented as contour lines or a plane in graphs, this method is called a response surface methodology (RSM).

The purpose of this work is to search the optimal electroplating conditions to produce Co–Ni and Fe–Co deposits with the same compositions of the plating solutions (denoted as non-anomalous codeposition) since the composition of plating baths is easily controlled. The key variables affecting the composition of Ni and Co atomic percentage in the Co–Ni and Fe–Co deposits, respectively, were screened out by FFD [22–24]. These variables were subjected to the steepest ascent investigation to approach the optimal conditions for the non-anomalous codeposition of Co–Ni and Fe–Co deposits. The CCD coupled with RSM [23,24] was used to examine the relationship between the composition and the plating variables around the optimal conditions of the equilibrium plating of Co–Ni and Fe–Co deposits.

2. Experimental

Cobalt–nickel and cobalt–iron deposits were deposited onto commercial pure (99.5%) 1 cm × 2 cm copper plates. These copper plates were first cleaned with trichloroethylene, rinsed with pure water, and then anodized at 30 mA cm⁻² in a 0.1 M NaOH solution for 5 min. After anodizing, the plated samples were cathodically polarized at 75 mA cm⁻² in another 0.1 M NaOH solution for 10 s, vibrated in an ultrasonic bath for 5 min. After cleaning, the Cu substrate was vertically placed at a three-compartment cell. The exposed geometric area of each Cu substrate was about 1 cm², while the other surface area were insulated by means of a polytetrafluoroethylene (PTFE) coating before deposition. An Ag/AgCl electrode [Argenthal, 3 M KCl, 207 mV versus a standard hydrogen electrode (SHE) at 25 °C] was used as the reference while a piece of platinum gauze wire with an exposed area equal to 4 cm² was employed as the counter electrode. A Luggin capillary, whose tip was set at a distance of about 1–2 mm from the surface of working electrode, was placed at a distance of about 1–2 mm from the surface of working electrode.
used to minimize errors due to internal (iR) drop in the electrolytes.

Two kinds of plating bath were prepared: 0.1 M CoCl₂·6H₂O and 0.1 M NiCl₂·4H₂O were mixed to make the Co–Ni series, and 0.1 M CoCl₂·6H₂O and 0.1 M FeCl₂·4H₂O to make the Fe–Co series, respectively. The pH of all the mixtures was adjusted by 1 M HCl to 2 or 3, according to the design of FFD. All solutions were prepared with pure water produced by a reagent water system (Milli-Q SP, Japan) at 18 MΩ·cm and all reagents were Merck, GR. In addition, the plating solutions were used to plate the alloys were degassed with purified nitrogen gas for 15 min before plating and nitrogen was passed over the solution during the measurements. Solution temperature was maintained at 25 °C with an accuracy of 0.1 °C by means of a water thermostat (Haake DC3 and K20). The wave signals of pulse-reverse-plating were performed by means of an electrochemical analyzer system, Jiehan 5000 (Electrochemical Workstation, Taiwan) in a three-component cell. The total electroplating time for every deposit was equal to 20 min.

The average composition of deposits was measured using an energy-dispersive X-ray (EDX) spectroscope with standard at three points coupled with a scanning electron microscope (SEM, JEOL JSM35). The mean error of this EDX analysis is ca. ±1.5 at%.

3. Results and discussion

The simple chloride baths are employed in this work since the Ni and Co content in the Co–Ni and Fe–Co deposits was proposed to be relatively lower when they were plated from the chloride solutions in comparison with the sulfate solutions [1,25]. In our previous work [26–28,30], the anomalous codepositions of iron-group alloys were inhibited by cyclic voltammetry (CV) when the potential region of CV includes the anodic dissolution process. In addition, this anodic process has been attributed to the dissolution of freshly deposit, removing the simultaneous metal hydroxides formed during the cathodic deposition process. CV is a complicated mode for explaining the controlling mechanism of dynamic current and potential. On the contrary, the pulse-reverse-plating is an easy way to realize the deposition mechanism. Accordingly, pulse-reverse-plating is proposed to replace the CV plating for non-anomalous codeposition of Co–Ni and Fe–Co alloys.

The behaviors of cyclic voltammetry were examined in the plating solution should support some important information to determine the operation parameters of the pulse-reverse electroplating (e.g., the potential and time period of pulse-plating, the potential and time period of reverse-plating, pH and stirring affection, etc.)

Typical CV curves for the non-anomalous codeposition of a Co–Ni and Fe–Co deposits are shown in Fig. 1a and b, respectively. Those CV curves could be divided into three reaction sections (i.e., the cathodic deposition, double-layer response and anodic dissolution processes). Because the anodic dissolution current of Co–Ni is insignificant in the Fig. 1a, the anodic dissolution process of Co–Ni deposit is shown as Fig. 1b. Note that cathodic section, the deposition of iron alloys occurs in the section. During potential range from −800 to −1100 mV, the cathodic currents on the positive sweep are larger than that on the negative sweep, indicating the nucleation of the Co–Ni and Fe–Co deposits occurs during this potential region. Therefore, in the FFD study, the pulse-plating potential has to adjust more negative than −1100 mV to structure nucleation for depositing iron-group deposit. In the non-reaction section, metal ions take place concentration diffusion in the bulk solution. During the anodic section, Fe(OH)+, Co(OH)+ and Ni(OH)+ are expected to dissolve into the plating solutions due to the dissolution of surface metal atoms, which are seriously affected by pH of the plating solutions [21,27]. Hence, the non-anomalous plating of Co–Ni and Fe–Co deposits can be deposited by controlling the time period and potentials of the pulse- and reverse-plating as well as the pH of plating solutions.

3.1. Fractional factorial design for Co–Ni composition

To screen the key variables affecting the Ni and Co atomic percentage in the Co–Ni, the FFD is used to screen out these key variables. This experiment design can research the influences of each preparation parameter at a variety of other variable levels, as well as the interactions among these variables on the composition of Ni.

Fig. 2 shows a typical wave signal of the pulse-reverse-plating. There are four variables, including the potentials of pulse- and reverse-plating (i.e., Eᵦ and Eᵦ) and the time periods of pulse- and reverse-plating (i.e., tᵦ and tᵦ). Observing the red curve in the Fig. 2, the red curve indicates the response current was caused by the wave signal. In addition, the red response current includes the cathodic and anodic current in every duty cycle. Note that the pulse-reverse-plating
of the highest-order interaction ABC, identifying its plus and minus levels with the plus and minus signs by writing down a basic design matrix consisting of a full $2^5$ factorial design. The fixed levels of these five variables are listed in Table 1, and the $2^{5-1}$ design matrix with the experimental data is shown as Table 2.

$2^{5-1}$ fractional factorial design matrix can be constructed by writing down a basic design matrix consisting of a full $2^{5-1}$ factorial design and then adding the 4th factor by identifying its plus and minus levels with the plus and minus signs of the highest-order interaction ABC... (k−1). For example, the $2^{5-1}$ fractional factorial design has the defining relation $I = ABCDE$ (introduced by Box et al [22–24]).

$$I = E \cdot A \cdot BCDE = ABCDE = ABCD = E \quad (5)$$

Therefore, the $2^{5-1}$ fractional factorial design is obtained by writing down the full $2^5$ factorial as the basic design and then equating factor E to the ABCD interaction [22–24]. According to Eq. (5), the combination of observations used to estimate the effect of the main factor E (reverse-plating potential) is identical to that used to estimate the four-factor interaction effect of the aliases A (pulse-plating time), B (reverse-plating time), C (pulse-plating potential), and D (pH). Thus, the main effect of factor E and the interaction effect of ABCD are confounded [22–23]. From the principle of the sparsity of effects, a system is likely to be driven primarily by main factor and low-order interaction effects. Effects of the high-order (e.g., three and greater order) interactions are assumed to be negligible. Thus, the main effect of factor E can be isolated from the confounded effects by this FFD experiment.

In Table 2, the low and high levels of A, B, C, D, and E were denoted as “−” and “+”, respectively. From an examination of the results in Table 2, the composition of Co–Ni deposits is ranged from 12.9 to 45.5 at.%, although these deposits were prepared from the plating solutions with the same composition of Co and Ni ions. Accordingly, analysis of variance (ANOVA) was carried out on the basis of the data shown in Table 2 and the result of the statistical analysis is summarized in Table 3. Note that ANOVA is derived from a partitioning of total variability (SST) into its component parts (i.e., model sum of square, $SS_{model}$, and error sum of square, SSE), which can be calculated on the basis of the following equations:

$$SST = \sum_{i=1}^{2^k} (y_i - \bar{y})^2 \quad (6)$$

$$SS_0 = \frac{(C_i)^2}{2^{k-1}} \quad (7)$$

$$SSE = SST - SS_{model} \quad (8)$$

where $y_i$ and $\bar{y}$ are indicative of the ith response and the grand average of all the observations, respectively. Note that $C_i$ is indicative of the contrast of factor (or interaction) $i$, which is the sum of multiplying the observations (i.e., $y_i$) with the plus-
Statistical significance is defined as the SS model. The quantities MS$_i$ = SS$_i$/d.f.$_i$ and MSE = SSE/d.f. error are defined as the mean squares of factor (or interaction) $i$ and the mean square of error, respectively. The d.f. and d.f. error indicate the degree of freedom for factor $i$ and error, respectively. In Table 3, the test statistics, $F_i$ defined as MS$_i$/MSE, are employed to test the statistical significance of each factor and the two-factor interactions. If the calculated value of $F_i$ is greater than that in the $F$ table at a specific probability level, a statistically significant factor or interaction is obtained. After the test, factors A and C, interactions BD, CD, AC and AE exhibit statistically significant effects on the composition of Co–Ni deposits. However, the calculated $F$ values of interaction factors BC and AD are between 3.59 (i.e., $F_{0.05}(1, 7) = 5.59$; $F_{0.1}(1, 7) = 3.59$) and 5.59 [i.e., $F_{0.05}(1, 7) = 5.59$, $F_{0.05}(1, 8)$] and 5.59, indicating that these interaction effects are not as important as the other six effects. Therefore, factors BC and AD may be not considered in the steepest ascent study. However, from previous studies for the electroplating of iron-group alloys [20,29–30], pH of the plating bath has been proposed to be an important variable influencing their quality as well as compositions, and the rates of nickel and iron plating are increased with increasing the solution pH. Based on the results of ANOVA table, pH (factor D) is not considered in the path of the steepest ascent study set factor D at the best condition (high level) in pH of 3. The multiple correlation coefficient, $R^2 = 1 − (SSE/SST)$, is the proportion of SST (sum of squares of total variances) explained by the fitted equation. An $R^2$ value close to 1 means a good fit to the experiment data ($R^2 = 0.928$ if factors BC and AD are significant). From the calculated $F$ values in Table 3, the sequence of factors or interactions with respect to decreasing the statistical significance is: A > CD > BD > AC > AE > C > BC > AD. The other effects (including the main factor B, D, E and other two-factor interactions) are pulled into the error since they do not have statistical significance. Calculation of the estimates for main factors and two-factor interactions follows the procedure recommended by Box et al. [22,23] which is equal to C$_{ij}^2/2$. The results of the main factors A–E and the two-factor interactions with statistical significance are respectively shown in Fig. 3a and b. In Fig. 3a, the main factors A, B, C, D, and E, especially the pulse-plating time (factor A), possess obvious effects on the composition of Co–Ni deposits. The effects of factor B, D, and E are negligible since those are statistically insignificant. Factor A has the largest effect, indicating the fact that the pulse-plating time has the largest influence on the composition of Co–Ni deposits prepared from the pulse-reverse-plating mode. Since this effect is positive, the time period of pulse-plating should be adjusted to more large values to increase the Ni content in the Co–Ni deposits. This concept is also applicable for factors C, although factors B, D and E exhibit positive effects on the Ni content in the Co–Ni deposits.

From the ANOVA results shown in Table 3, several effects of two-factor interactions are larger than the main effects, e.g., AE > C, indicating that these interaction effects are statistically significant.
are not negligible and need to be further analyzed, which are shown in Fig. 3b. In this figure, a longer time period of the pulse-plating (high level of factor A) increases the Ni content in the Co–Ni deposits when factor E is under the high level (reverse-plating potential at 100 mV), while the effect of factor A becomes negligible when factor E is under the low level. This phenomenon reveals the existence of a strong interaction between factors A and E. Similar phenomena are visible for AC, BD and CD interactions. Accordingly, a combination of the positive adjustment in factors A, B, D, and E meanwhile the negative adjustment in factor C should obviously increase the Ni content in the Co–Ni deposits. In other words, Co–Ni deposition may be changed from the anomalous plating to the non-anomalous plating if factor C is moved in the negative direction with factors A, D, and E being simultaneously moved in the positive directions. From these results and discussions, the composition of Co–Ni deposits is not only dependent on time period of the pulse-plating but also on the applied potentials of pulse-plating. The positive effect of factor A indicates that a longer pulse-plating time increases the deposition rate of nickel content after removing the iron metal hydroxide, Fe(OH)₃. This effect results in the simultaneous dissolution of CoOH₃⁺ and NiOH₃⁺, forming the adsorption of adsorbed M(OH)⁺ layer during the reverse-plating process (anodic dissolution section). This effect is consistent with the finding that a higher reverse current density favors the active dissolution of both metals. The negative effect of factor C indicates that an increase in Ni content occurs at a more negative pulse-plating potential on the fresh deposit. This effect is reasonably attributed to the fact that the fresh substrate can deposit equilibrium deposition potential of Ni ion is less negative than that of Co ion from plating solution. Accordingly, under lower deposition overpotential, a higher deposition rate of Ni should be deposited onto the substrate since the Co²⁺ is very likely under the electroneutral control. This phenomenon was also found for the deposition of Co–NiNi alloys through means of potentiostatic conditions. The positive effect of factor D indicates that increasing pH of the plating baths depressed the anomaly of Co–Ni codeposition. This effect has also been found previously and was attributed to a lower overpotential of the Co–Ni electroplating in a plating solution of a higher pH. However, the strong effects of the pulse-plating potential pH and reverse-plating time pH interactions indicate that the influence of pH on the formation and disappearance of the adsorbed M(OH)⁺ layer in the pulse-reverse-plating mode should be very complicated and is probably unpredictable. Thus, the employment of experimental strategies for searching the optimal plating settings of Co–Ni non-anomalous codeposition is expected to be a powerful and efficient methodology. The positive effect of factor E suggests that an increase in the potential of reverse-plating must increase the dissolving rate of both nickel and cobalt metals, which should decrease the coverage of adsorbed M(OH)⁺. Therefore, the anomaly of Co–Ni electroplating is significantly depressed by a longer time period of the reverse-plating.

3.2. Path of steepest ascent for Co–Ni composition

From the analysis of variance and regression analysis of the results shown in Table 2, a fitted polynomial model can be generated. This model, quantitatively elucidating the effects of all plating variables with statistical significance, is expressed in the following:

\[ y = 30.65 + 4.65x_A + 2.45x_C + 3.25x_Ax_C + 2.62x_Ax_D 
- 4.44x_{TD} - 4.6x_{CD} \]  

where \( x_i \) are the coded variables for factor \( i \) (i.e., A and C). The coded variables, \( x_i \), are defined in the standardized form as following [15]:

\[ X_{i,HIGH} = \frac{X_{i,MEAN} - X_{i,LOW}}{X_{i,HIGH} - X_{i,LOW}} \]  

\[ X_{i,LOW} = \frac{X_{i,MEAN} - X_{i,LOW}}{X_{i,HIGH} - X_{i,LOW}} \]  

\[ X_{i,MEAN} = \frac{X_{i,HIGH} + X_{i,LOW}}{2} \]  

\[ S_i = \frac{X_{i,HIGH} - X_{i,LOW}}{2} \]  

where \( X_{i,HIGH} \) and \( X_{i,LOW} \) are the high and low levels of factor \( i \), respectively. Note that factors A and C are considered in the steepest ascent study from the results and discussion in the FFD section. From Eq. (5), the sign of coefficients for factors A is positive while that of factor C is negative. On the other hand, from the results and discussion for Fig. 3b, a synergistic effect on increasing the Co content in the Co–Ni deposits should occur when factors A and C are simultaneously moved in the positive and negative direction, respectively. In addition, it is very possible that Co–Ni deposition is changed from the anomalous plating to the equilibrium/non-anomalous deposition if factor A, D and E is moved in the positive direction with factors C being simultaneously moved in the negative directions. However, the main purpose of this work is to search the suitable deposition conditions for the equilibrium/non-anomalous electroplating of Co–Ni alloys. The transformation from anomalous deposition to normal deposition has to be avoided. Moreover, it is worthy noting that the effects of factors B, D and E are under the high level, indicating that the composition of Co–Ni deposits will be not sensitive to the electroplating variable (e.g., potential and time of reverse-plating and pH) when pH is equal to 3. Accordingly, both factors A is moved the positive direction while factor C is moved in the negative direction to reach the optimal conditions for the equilibrium/non-anomalous electroplating of Co–Ni deposits. If the equilibrium/non-anomalous plating of Co–Ni deposits can be reached by employing the above steepest ascent study, the composition of Co–Ni alloys should be not a stiff function of the electroplating variables and very stable plating settings for the equilibrium deposition of Co–Ni alloys can be obtained.
the direction of the steepest ascent path should be simulta-
neously moved $+4.65$ in the $X_A$ direction. However, the pulse-
plating time complicated interactions with the potentials of
pulse-plating the FFD study. Moreover, the composition of
Co–Ni deposits is expected to be not sensitive to the elec-
troplating variable when pH is under the high level ($pH$ 3,
see Fig. 3b) while strong influences of these variables were
found when factor $A$ is under the high level. Accordingly, the
step size of factor $A$ (i.e., $S_A$) is diminished to $+1.0$ to find
the stable deposition conditions for the equilibrium plating
of Co–Ni deposits. Typical points on the path of the steep-
est ascent study with the corresponding results are shown in
Table 4. From an examination of Table 4, the experimental
settings of run 4 are suitable for the central composite design study coupled
with the response surface method [22,23]. It is worthy noting
these results support the statements proposed in previous
sections. First, the Ni content in the Co–Ni deposits is a
smooth function of the pulse-plating time and pulse-plating
potentials. Second, the anomalous codeposition of Co–Ni al-
loys can be changed to the non-anomalous plating by con-
sequent runs in this CCD study is equal to $2^k + (2 \times 2)^n = 11$. The equal distance from the experimental points to the
central points is constant ($\sqrt{2}$). A design with this property
will leave a constant variance of the response variable at all
experimental points when the design is rotated around the
center. The design matrix with the corresponding results in
the CCD study is shown in Table 5. Note that experiments on
the original (central) point are repeated three times in order to
evaluate the pure error between each experiment. The regression
analysis and ANOVA for the data shown in Table 5 were
carried out, and the resultant second-order model represent-
ing the dependence of the Ni content of Co–Ni deposits on
factors $A$ (pulse-plating time) and $C$ (pulse-plating potential)
was generated

$$y = 48.9 + 2.52x_1 + 1.44x_2 - 9.72^2 - 6.5x_1^2 + 0.5x_1x_2$$

(14)

where $y$, $x_1$, and $x_2$ are indicative of the Ni content, the pulse-
plating time, and the pulse-plating potential, respectively. The
contour plots for the dependence of the Ni content on factors
$A$ and $C$ were constructed by using the regression model (i.e.,
Eq. (14)), and a typical contour diagram is shown in Fig. 4.

Note that the Ni content in the deposits increases slowly when
the electroplating variables are simultaneously moved in the
directions to the central point. In addition, a non-anomalous
plating (i.e., the composition of Co–Ni deposits is equal to
that of the plating solutions) is approximately reached when
the experimental settings are close to that of the central point.

3.3. Central composite design for Co–Ni composition

The purpose of the central composite design is to provide
real samples to fit the second-order model, correlating the
electroplating variables and the composition of Co–Ni de-
posits. Since the composition of a deposit prepared from the
experimental settings of run 4 in Table 4 is approximately the
same as that of the plating bath, the original (central) point
of the CCD is set at run 4. Note that factor $D$ is neglected
in this study since it is not very important from the ANOVA
results (Table 3). The pH of the plating bath was kept pH

<table>
<thead>
<tr>
<th>Run</th>
<th>Factor A (pulse-plating time)</th>
<th>Factor C (pulse-plating potential)</th>
<th>Ni (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5400</td>
<td>-1200</td>
<td>38.2</td>
</tr>
<tr>
<td>2</td>
<td>6120</td>
<td>-1200</td>
<td>44.1</td>
</tr>
<tr>
<td>3</td>
<td>6840</td>
<td>-1200</td>
<td>45.2</td>
</tr>
<tr>
<td>4</td>
<td>7560</td>
<td>-1200</td>
<td>49.8</td>
</tr>
<tr>
<td>5</td>
<td>8280</td>
<td>-1200</td>
<td>43.1</td>
</tr>
<tr>
<td>6</td>
<td>9000</td>
<td>-1300</td>
<td>43.5</td>
</tr>
<tr>
<td>7</td>
<td>9720</td>
<td>-1320</td>
<td>39.1</td>
</tr>
<tr>
<td>8</td>
<td>10440</td>
<td>-1340</td>
<td>38.2</td>
</tr>
</tbody>
</table>

On the basis of the steepest ascent methodology [22,23],
the direction of the steepest ascent path should be simulta-
neously moved $+4.65 S_A$ in the $X_A$ directions, respectively,
for every $-2.45 S_C$ in the $X_C$ direction. However, the pulse-
plating time complicated interactions with the potentials of
pulse-plating the FFD study. Moreover, the composition of
Co–Ni deposits is expected to be not sensitive to the elec-
troplating variable when pH is under the high level ($pH$ 3,
see Fig. 3b) while strong influences of these variables were
found when factor $A$ is under the high level. Accordingly, the
step size of factor $A$ (i.e., $S_A$) is diminished to $+1.0$ to find
the stable deposition conditions for the equilibrium plating
of Co–Ni deposits. Typical points on the path of the steep-
est ascent study with the corresponding results are shown in
Table 4. From an examination of Table 4, the experimental
settings of run 4 are suitable for the central composite design study coupled
with the response surface method [22,23]. It is worthy noting
Fig. 1. According to the Co–Ni results, the pH to 3.0 is the respectivestimated from the windows in a dotted line of plating. Time period of pulse- and reverse-plating are still reference points to design the potential of pulse- and reverse- upper and lower potential limit of CV curve were set as the close pH values are existed two different non-anomalous tion. In our pre-work[26–28,30] , the best pH value to struc-

suitable preparation value to deposit non-anomalous Co–Ni deposits with different compositions.

3.4. Fractional factorial design for Fe–Co composition

To efficiency find the key variables affecting the Co at.% in Fe–Co deposits, the fractional factorial design is introduced to screen out these key variables. According to Fig. 1, the upper and lower potential limit of CV curve were set as the reference points to design the potential of pulse- and reverse-plating. Time period of pulse- and reverse-plating are still respectively estimated from the windows in a dotted line of the Fig. 1. According to the Co–Ni results, the pH to 3.0 is the suitable preparation value to deposit non-anomalous Co–Ni deposition meanwhile the pulse-plating procedure includes the anodic dissolution response current in reverse-plating section. In our pre-work[26–28,30], the best pH value to structure the non-anomalous alloy of Fe–Ni deposit is 2.8. Hence, the close pH values are existed two different non-anomalous deposits, Co–Ni and Fe–Co alloy, that indicate the suitable pH for the pulse-reverse-plating is between 2.8 and 3. Hence, the pH for Fe–Co alloy is set at 3.0 by using pulse-reverse-plating with anodic dissolution process. Therefore, the effects of the following electroplating variables were investigated in the FFD study: (A) pulse-plating time; (B) reverse-plating time; (C) pulse-plating potential; and (D) reverse-plating potential. The fixed four variables are listed in Table 6 meanwhile the 2⁴−1 design matrix with the experimental data.

In the Table 6, the compositions of Fe–Co deposits are ranged from 48.1 to 51.2 Co at.% although these deposits were prepared in the different plating parameters. The composition ratio of Co and Fe ions is 1:1 meanwhile the total concentration of Fe–Co plating bath is 0.1 M. According to experimental data in the FFD, the composition ratio of Fe–Co deposits are very close to the concentration ratio of Fe–Co bath meanwhile the preparation means of pulse-reverse-plating contains anodic dissolution process. Further, those results make sure the anomalous Fe–Co deposit is cause by the metal mono-hydroxide cover the deposit surface. In addition, the anodic dissolution response current could easy remove metal hydroxide from the deposit surface and get fresh deposit which were proved the FFD data (see Table 6).

Comparison the composition of Fe–Co and Co–Ni deposit in the FFD, the composition ratio of Fe–Co deposits has the less different than those Co–Ni deposits with the concentration ratio of plating baths. The result indicates that the Fe(OH)⁺⁺ and Co(OH)⁺ ions are more active in the cathodic deposition section and easier to remove during the anodic dissolution processes. In the other word, the Fe(OH)⁺⁺/Co(OH)⁺ ions are easier to desorb than Co(OH)²⁺/Ni(OH)⁺ ions during anodic dissolution section. Further, the Fe–Co deposit is easier to form non-anomalous plating than the Co–Ni deposit when the pulse-reverse-plating contain anodic dissolution process. Dissolution effect of reverse-plating could be provided by the weight loss of Fe–Co deposit in the pulse-reverse-plating with/without through anodic dissolution process. This deposition bath of Fe–Co and Co–Ni deposits were not in the mass transport control. Because the deposition re-

sponse current could be increased with the increasing low overpotential limit of CV plating and the increasing pulse-plating potential. In addition, the stirring race of plating bath didn’t affect the compositions of Co–Ni and Fe–Co deposits. The loading weight of Co–Ni deposit was increased from 2.75 to 2.99 mg meanwhile the stirring rate of Co–Ni plating bath was adjusted from 100 to 200 rpm from the solution contained 0.05 M CoCl₂ 6H₂O and 0.05 M NiCl₂ 6H₂O at 20mV s−¹ with 60 segments by using CV plating with anodic dissolution process. Further, the composition ratio of Co–Ni deposit is equal to the plating bath ratio. When the Co–Ni deposit was prepared by using CV plating without anodic dissolution process, the deposit contain 6.38 mg and anomalous codeposition. The oxygen contents of anomalous and non-anomalous Co–Ni deposits were 11.4 and 5.4 at %, respectively. Due to the oxygen contents were cause by the metal hydroxide cover on the deposit surface, those oxygen content could be seem as the metal hydroxide concentration on the deposit surface. Consequently, metal hydroxide is main
The design matrix and experiment data of the Co content in Fe–Co deposit in FFD with the defining relation $I = ABCD$

<table>
<thead>
<tr>
<th>Run</th>
<th>Pulse-plating time (ms)</th>
<th>Reverse-plating time (ms)</th>
<th>Pulse-plating potential (mV)</th>
<th>Reverse-plating potential (mV)</th>
<th>Co (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3600</td>
<td>600</td>
<td>−1300</td>
<td>−250</td>
<td>49</td>
</tr>
<tr>
<td>2</td>
<td>7200</td>
<td>600</td>
<td>−1300</td>
<td>−250</td>
<td>49.5</td>
</tr>
<tr>
<td>3</td>
<td>3600</td>
<td>1200</td>
<td>−1300</td>
<td>−300</td>
<td>51.2</td>
</tr>
<tr>
<td>4</td>
<td>7200</td>
<td>1200</td>
<td>−1300</td>
<td>−250</td>
<td>49.7</td>
</tr>
<tr>
<td>5</td>
<td>3600</td>
<td>600</td>
<td>−1100</td>
<td>−250</td>
<td>48.1</td>
</tr>
<tr>
<td>6</td>
<td>7200</td>
<td>600</td>
<td>−1100</td>
<td>−300</td>
<td>49.4</td>
</tr>
<tr>
<td>7</td>
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<td>−1100</td>
<td>−300</td>
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</tr>
<tr>
<td>8</td>
<td>7200</td>
<td>1200</td>
<td>−1100</td>
<td>−250</td>
<td>51.1</td>
</tr>
</tbody>
</table>

factor to control the deposition rate of Co–Ni and Fe–Co deposit.

Three kinds of electroplating baths, Co, Fe, and Fe–Co, are employed to prepare Co, Fe and Fe–Co deposits by using different pulse-reverse-plating models. In model 1, the parameters of the pulse-reverse-plating without through anodic dissolution process to prepare the Co, Fe, and Fe–Co deposits are set as that the pulse-plating potential is at $−1260 \text{ mV}$; the reverse-plating potential is at $−800 \text{ mV}$; the pulse-plating time is $7560 \text{ ms}$; and reverse-plating time is $1200 \text{ ms}$. The response current of pulse-reverse-plating of model 1 is shown as Fig. 5. During model 2, the parameters of the pulse-reverse-plating with through anodic dissolution process to prepare the Co, Fe, and Fe–Co deposits are set as that the pulse-plating potential is at $−1260 \text{ mV}$; the reverse-plating potential is at $−800 \text{ mV}$; the pulse-plating time is $7560 \text{ ms}$; and reverse-plating time is $1200 \text{ ms}$. The response current of pulse-reverse-plating of model 2 is displayed in Fig. 6. In addition, total concentration of plating baths is $0.1 \text{ M}$ with pH 3 at $25^\circ \text{C}$. Moreover, the Fe–Co plating bath for pulse-reverse-plating contains equal ion ratio.

Observing the Co pulse-reverse-plating response current in the Fig. 5, the response current of pulse- and reverse-plating are close to $−0.03$ and $−0.0025 \text{ A}$, respectively. The response current of pulse- and reverse-plating are close to $−0.015$ and $−0.0025 \text{ A}$ for preparation Fe deposit, respectively. Comparison the response current of pulse-plating for Co and Fe deposits, the Co deposit have higher deposition rate than Fe deposit in the pure metal deposition bath. Because the nucleation over potential for Fe deposit ($−0.44 \text{ V}$) is more negative than the Co nucleation over potential ($−0.27 \text{ V}$), the pure Fe deposit needs much energy to nucleate. Then, the pure Fe gets less pulse-plating response current. In addition, response current of pulse- and reverse-plating are close to $−0.035$ and $−0.0025 \text{ A}$ for Fe–Co deposit. Moreover, the composition of anomalous Fe–Co deposit is $\text{Fe} \text{Fe}_{0.3} \text{Co}_{0.7}$, meanwhile the pulse-reverse-plating miss anodic dissolution process. By the theory, the increasing pulse-plating response current is cause by the increasing deposition rate. Accordingly, the phenomenon indicates that increasing current for the Fe–Co deposit is caused by the metal hydroxide leading to anomalous electroplating. Consequently, anodic dissolution section of pulse-reverse-plating is confirmed as a key factor to deposit non-anomalous deposit, because the metal hydroxides, Fe(OH)$_{3 \text{ad}}^+$ and Co(OH)$_{3 \text{ad}}^+$, could be removed from the deposit.

The pulse-reverse-plating response current curves of Co, Fe, and Fe–Co with anodic dissolution process are shown as Fig. 6a–c, respectively. In the Fig. 6, the three kinds of pulse-plating response current curves are close to $−0.02 \text{ A}$. Fig. 5. Response current for potentiostatic pulse-reverse-plating of (a) Co, (b) Fe and (c) Fe–Co deposits. The square waveform is the applied potentials, $−0.8$ and $−1.26 \text{ V}$, while the reverse-plating is not across anodic dissolution process.
Equal pulse-plating response current indicate that the three kinds of deposits have the same deposition rate. In addition, composition of the Fe–Co deposit is Fe:Co = 51:49. Accordingly, this result confirms the anodic dissolution of pulse-reverse-plating could remove the metal hydroxide form the Fe–Co deposit surface. The equal pulse-plating response current indicates that Fe and Co ions have fair chance to deposit on the fresh deposit. Consequently, any composition ratios of Fe–Co deposits can be prepared by controlling the concentration ratios of plating bath during the anodic dissolution process.

The atomic ratios of Fe:Co in solutions 1–4 are 8:2, 6:4, 4:6 and 2:8, respectively, while the total concentration of Fe and Co ions in the plating are 0.1 M. The Co content in the Fe–Co deposits are plated from solutions 1–4 are 20.6%, 40.8%, 61.1% and 82.2 at.%, respectively. Consequently, any composition ratios of Fe–Co deposits can be deposited from the same Fe–Co ion ratio in the plating bath by using pulse-reverse-plating with anodic dissolution process.

4. Conclusions

Using the sequential experiment strategies (i.e., the fractional factorial design, the path of steepest ascent, and the central composite design coupled with response surface methodology), the optimal deposition settings of the pulse-reverse-plating for the equilibrium/non-anomalous electroplating of Co–Ni deposits were clearly demonstrated. The experimental settings, pH of 3, the pulse-plating potential of −1260 mV, the reverse-plating potential of +100 mV, the pulse-plating time of 7560 ms and the reverse-plating time of 1200 ms, for the equilibrium plating of Co–Ni deposits were applicable for the deposition baths with different compositions. Based on the optimal settings of the pulse-reverse-plating proposed in this work, the composition of Co–Ni alloys can be precisely controlled through means of adjusting the composition of the plating baths.

Any composition ratio of Fe–Co deposit can be prepared by using the pulse-reverse-plating with anodic dissolution process.

Those variable Ni contents in Co–Ni deposit are cause by the metal hydroxide cover on the deposit surface. In the pulse-reverse-plating with anodic dissolution process, we find the increasing pulse-plating time and shifting lower potential limit can easy to remove metal hydroxide and deposit equilibrium/non-anomalous Fe–Co and Co–Ni alloys.

Acknowledgments

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References