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# Analysis of Fe–Ni Thin Films Using the Phenomenological Theory of Electrodeposition

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Fe–Ni thin films electrodeposited using rectangular pulse voltages over a megahertz frequency range were investigated through scanning electron microscopy-energy dispersive X-ray spectroscopy and X-ray diffraction. The Ni content of the Fe–Ni thin films increased with the cathode potential; further, it significantly changed at resonant frequencies when the cathode potential was equal to the Fe<sup>2+</sup> or Ni<sup>2+</sup> potential barrier, and became constant, which was consistent with the phenomenological theory of electrodeposition. The Fe<sup>2+</sup> and Ni<sup>2+</sup> potential barriers were determined to be 1.48 and 2.22 V, respectively. The Fe–Ni thin films comprised a body-centred cubic crystal structure, namely,  $\alpha$ -Fe, and an amorphous structure FeNi<sub>0.832</sub> phase (corresponding to the stoichiometric molar ratio of Fe–Ni thin films containing 29.8 at% Ni). The Fe–Ni films had smooth surfaces, which indicated that they were formed by layer-by-layer growth and not by island growth.

**Keywords:** Fe–Ni thin film; Phenomenological theory of electrodeposition;  $\alpha$ -Fe; FeNi<sub>0.832</sub>; Smooth surface

## **1. INTRODUCTION**

Conventional Fe–Ni thin films have attracted the attention of researchers because of their excellent magnetic properties for micromagnetic devices [1–3], low thermal expansion known as invar alloys [4], and high strength for micro electro-mechanical systems [5, 6].

According to the Fe–Ni phase diagram [7], stable solid phases of Fe–Ni alloys are dependent on the Ni content at 473 K: body-centred cubic (BCC) crystal structure  $\alpha$ –Fe for < 2 at% Ni; co-phases comprising  $\alpha$ -Fe and FeNi<sub>3</sub> between 2 and 72 at% Ni; FeNi<sub>3</sub> between 72 and 89 at% Ni; and FeNi<sub>3</sub> and the face-centred cubic (FCC) structure  $\gamma$ –Fe between 89 and 96 at % Ni. Hence, the precise control of the Ni content is the most important issue.

Electrodeposition is an attractive method for the fabrication of Fe-Ni alloys. However,

electrodeposition of iron-group elements has been reported to cause a so-called "anomalous codeposition" [8, 9], in which the less notable Fe (standard electrode potential [10] Fe/Fe<sup>2+</sup>, -0.447V) than Ni (Ni/Ni<sup>2+</sup>, -0.257 V) is preferentially reduced within a framework of thermal equilibrium. Consequently, it is difficult to control the composition of the Fe-Ni thin films. However, the standard electrode potentials, which are true for thermal equilibrium, cannot always account for the nonequilibrium phenomena associated with electrodeposition.

Recently, a phenomenological theory of electrodeposition described not by thermodynamic variables, but by the cathode potential, potential barrier, and resonant frequencies was proposed [11, 12]. According to the phenomenological theory of electrodeposition, the potential barrier affects the probability of atomization from  $Fe^{2+}$  and  $Ni^{2+}$  ions to Fe and Ni atoms, and the compositions of Fe–Ni thin films can be controlled by the cathode potential and frequencies under the given Ni and Fe contents of the solutions.

The surface morphology of electrodeposited Fe–Ni thin films has been reported to be porous or rough [13–15]. This is because of the surface growth mechanism not by layer-by-layer [16], but by islands. The smooth surface is a key to planar technology. This study demonstrates that Fe–Ni thin films had smooth surfaces formed by layer-by-layer growth.

The aims of the present study are to demonstrate that the Ni content of Fe–Ni thin films was consistent with the phenomenological theory of electrodeposition, Fe–Ni thin films had smooth surfaces, and comprised a BCC crystal structure  $\alpha$ -Fe and amorphous structure FeNi<sub>0.832</sub> phase.

### 2. EXPERIMENTAL SETUP

An aqueous solution containing the following chemical compounds was prepared:  $FeSO_4 \cdot 7H_2O$  (0.627 mol L<sup>-1</sup>), NiSO<sub>4</sub> · 6H<sub>2</sub>O (0.323 mol L<sup>-1</sup>), and KNaC<sub>4</sub>H<sub>4</sub>O<sub>6</sub> · 4H<sub>2</sub>O (1.06 mol L<sup>-1</sup>).

A  $30 \times 10 \text{ mm}^2$  copper plate and  $50 \times 40 \text{ mm}^2$  carbon plate were used as the cathode and anode, which were placed parallel to each other in an electrochemical cell filled with the aqueous solution.

The rectangular pulse voltages in the range of 0.4–1.2 MHz frequency were supplied to the cell by a function generator. A 22  $\Omega$  metal film resistor was connected in series with the electrochemical cell to measure the current flowing to the cell. The impedance of the metal film resistor was independent of the frequency under 80 MHz. The rectangular pulse currents carried in the electrochemical cell were calculated from the voltage drop across the metal film resistor, which was measured with a digital storage oscilloscope.

The cathode potential (defined as the voltage drop across the electric double layer) was determined as follows: Fe–Ni thin films were electrodeposited at 300 K on the Cu plate immersed to a depth of 15 mm in the solution. As the area of the C plate was approximately 27 times larger than the deposited area of the Cu plate, the impedance of the electric double layer at the C plate in the solution can be neglected. The impedance between the cathode and anode can also be ignored because of the highly concentrated solution. Hence, the cathode potential is obtained from the amplitude of the rectangular pulse voltage minus the mean voltage measured across the 22  $\Omega$  metal film resistor.

Figure 1 shows typical rectangular pulse voltages measured across the metal film resistor when rectangular pulse voltages with an amplitude of 2 V and a frequency of 1 MHz were applied to the cell. As the mean amplitude is 0.501 V in Fig. 1, the cathode potential is calculated as 1.499 V.



Figure 1. Voltage drops measured across a 22  $\Omega$  resistor when rectangular pulse voltages with an amplitude of 2 V and a frequency of 1.0 MHz were applied to the cell.

After deposition, the Fe–Ni thin films electrodeposited on the Cu plate were rinsed with distilled water and dried in a vacuum chamber. The Fe–Ni thin films were weighed to a precision of 0.1 mg with an electric balance to calculate their film thickness.

The compositions of Fe–Ni thin films on the Cu plate were investigated using scanning electron microscope-energy dispersive X-ray (SEM-EDX) spectroscopy (Hitachi TM3030). The crystallographic structure of the Fe–Ni thin films was determined by X-ray diffraction (XRD) (Rigaku Ultima) using a diffractometer (Rigaku Ultima) with carbon-monochromator-filtered CuKα radiation

### 3. RESULTS AND DISCUSSION

## 3.1 Schematic diagram of the Ni content in Fe and Ni co-electrodeposition

The dependence of the Ni content of Fe–Ni thin films on the cathode potential,  $V_c$  is illustrated in a schematic diagram in Fig. 2 according to the phenomenological theory of electrodeposition [11–12]. When  $V_{bNi^{2+}} > V_{bFe^{2+}}$  and  $V_c < V_{bFe^{2+}}$  where  $V_{bNi^{2+}}$  and  $V_{bFe^{2+}}$  are the potential barriers of Ni<sup>2+</sup> and Fe<sup>2+</sup>, respectively, the Ni content increases with  $V_c$ . At  $V_c = V_{bFe^{2+}}$ , the Fe content significantly changes at resonant frequencies of Fe<sup>2+</sup>. The arrows at  $V_c = V_{bFe^{2+}}$  in Fig. 2 show a change in the Ni content at the resonant frequencies of Fe<sup>2+</sup>.



**Figure 2.** Ni content diagram of Fe–Ni thin films when  $V_{bNi}^{2+} > V_{bFe}^{2+}$ .

Furthermore, with an increase in  $V_c \ge V_{bFe^{2+}}$ , as the Fe mass electrodeposited on the Fe–Ni thin films becomes constant, the discontinuity of the slope of the Ni content curve occurs as shown in Fig. 2. When  $V_{bFe^{2+}} < V_c < V_{bNi^{2+}}$ , the Ni content increases with  $V_c$ . When  $V_c = V_{bNi^{2+}}$ , the Ni content significantly oscillates at resonant frequencies of Ni<sup>2+</sup>, as indicated by the arrows shown in Fig. 2. For  $V_c > V_{bNi^{2+}}$ , the Ni content becomes constant because the Fe and Ni masses electrodeposited on the Fe–Ni thin films become constant.

### 3.2 Dependence of the Ni content on $V_c$

Figure 3 shows the dependence of the Ni content of Fe–Ni thin films on  $V_c$  at frequencies of 0.4, 0.45, and 0.5 MHz. The Ni content of the Fe–Ni thin films increases with  $V_c < 1.48 V$  and shows a large change with the frequencies at  $V_c = 1.48 V$ , at which point, the arrows show the difference in the Ni content. The change in the Ni content is attributed to a change in the Fe content at  $V_c = V_{bFe^{2+}}$ . The value of  $V_{bFe^{2+}}$  is determined to be 1.48 V. The Ni content remains slightly stagnant around,  $V_c = 1.86 V$  and the discontinuity of the slope of the Ni content curve occurs.

Furthermore, the Ni content increases with  $V_c < 2.22 V$  and shows a large change in the Ni content at  $V_c = 2.22 V$ , at which point, the arrows show the difference in the Ni content. The value of  $V_{bNi^{2+}}$  is determined to be 2.22 V in a similar way to that of  $V_{bFe^{2+}}$ . Additionally, with an increase in  $V_c$ , the Ni content tends to become constant irrespective of the frequencies and  $V_c$ .

The dependence of the Ni content on  $V_c$  is consistent with that in Fig. 2.



**Figure 3.** Dependence of the Ni content of Fe–Ni thin films on  $V_c$  in a range of 0.4–0.5 MHz. The arrows show large changes in the Ni content at  $V_c = V_{bi}$  (i=Fe<sup>2+</sup> or Ni<sup>2+</sup>).

# 3.3 Dependence of the Fe content or the Ni content on the frequency at $V_c = V_{bFe^{2+}}$ or $V_{bNi^{2+}}$

Figure 4 shows the dependence of the Fe content on the frequency at  $V_c=1.48$  V ( $V_{bFe^{2+}}$ ). The Fe content of the Fe–Ni thin films changes in a range of 68.3–72.7 at%.



Figure 4. Frequency dependence of the Fe content of Fe–Ni thin films electrodeposited at  $V_c = 1.48 V$ .

The Fe content has local maxima at resonant frequencies of 0.5, 0.65, 0.75, 0.9, and 1.15 MHz. The mean resonant frequency spacing between the neighbouring resonant frequencies is 0.163 MHz.

The observed resonant frequency spacing is related to the multi-quantized rotational energy [17] of Fe<sup>2+</sup> in FeSO<sub>4</sub>. Electrons in the Cu plate at the Fermi level can transfer to the multi-quantized rotational energy levels at  $V_c = V_{bFe^2+}$ [15]. Hence, multiple resonant frequencies are observed in this study.



Figure 5. Frequency dependence of the Ni content of Fe–Ni thin films electrodeposited at  $V_c = 2.22 V$ .

Figure 5 shows the dependence of the Ni content on the frequency at  $V_c=2.22 \text{ V}(V_{bNi^{2+}})$ . The Ni content of Fe–Ni thin films changes in a range of 29.8–39.9 at%. The Ni content has local maxima at resonant frequencies of 0.45, 0.65, 0.8, 0.95, and 1.1 MHz. The mean resonant frequency spacing between the neighbouring resonant frequencies is 0.163 MHz, which is equal to the mean resonant frequency spacing of Fe<sup>2+</sup>. This indicates that the multi-quantized rotational levels of Fe<sup>2+</sup> are approximately equal to those of Ni<sup>2+</sup>. The mean resonant frequency spacing of Ni<sup>2+</sup> in Ni[SO<sub>3</sub>NH<sub>2</sub>]<sub>2</sub> was reported to be 0.2 MHz [17].

### 3.4 Crystalline structure of Fe–Ni thin films

Figure 6 shows XRD charts of 1.8 µm-thick Fe–Ni thin films formed (a) at  $V_c$ =1.48 V and 0.9 MHz, and (b) at  $V_c$ =2.22 V and 0.8 MHz. The frequencies, 0.9 and 0.8 MHz, at which the lowest and highest Ni content, 27.5 and 39.9 at% were produced, respectively (shown in Figs. 4 and 5) were produced, respectively, were selected. The diffraction peaks from the Fe–Ni thin films in Figs. 6 (a) and (b) are identified as the ones from the (110) crystallographic planes of the  $\alpha$ -Fe phase. No other diffraction peaks are observed. The Fe–Ni thin films have the (110)  $\alpha$ -Fe crystallographic plane parallel to the Cu plate.



Figure 6. XRD charts of Fe–Ni thin films: (a)  $V_c = 1.48 V$ , 0.9 MHz, and 27.5 at% Ni and (b)  $V_c = 2.22 V$ , 0.8 MHz, and 39.9 at% Ni.

According to the Fe–Ni phase diagram [7], Fe–Ni alloys comprise a BCC crystal structure, namely,  $\alpha$ –Fe and an FCC crystal structure, namely, FeNi<sub>3</sub> phase in the range of 2–72 at% Ni. However, in this study, the FCC crystal structure of the FeNi<sub>3</sub> phase was not identified. Hence, using an element mapping technique of SEM-EDX, the distributions of the  $\alpha$ –Fe and FeNi<sub>3</sub> phases in Fe–Ni thin films grown at an initial stage were investigated.

### 3.5 Stoichiometric molar ratio, x of $Fe_x N_{1-x}$

Figure 7 shows the element mapping of the Fe–Ni thin films at a deposition time of 10 s,  $V_c$ =2.22 V, and 0.4 MHz. The film thickness of the Fe–Ni thin film was estimated to be 4 nm and the Ni content was 29.8 at%. The blue and yellow colours denote Fe and Ni element, respectively. In Fig. 7 (a), the Fe and Ni regions are clearly divided into two regions each other. In Fig. 7 (b), the deep blue and light blue regions are shown. The deep blue regions correspond to the  $\alpha$ –Fe phase and show no island shapes, but band shapes.



Figure 7. Fe and Ni element mapping of Fe–Ni thin films electrodeposited at a deposition time of 10 s,  $V_c = 2.22 V$ , and 0.4 MHz: (a) mapping of Fe and Ni, and (b) mapping of Fe.

The Ni and Fe elements co-exist in the gap regions between the  $\alpha$ -Fe band shape phases as shown in Fig.7 (b). The gap regions correspond to Fe-Ni electrodeposits. To determine the stoichiometric molar ratio, x of  $Fe_x N_{1-x}$ , Fig. 7 (a) was converted to the binary image as shown in Fig. 8. The black area, which shows  $\alpha$ -Fe phases, covers 33.3 % of the total area. If the density of  $Fe_x N_{1-x}$ ,  $\rho_{Fe_x Ni_{1-x}}$  is interpolated from the densities of  $\alpha$ -Fe and FeNi<sub>3</sub>, it is given as

$$\rho_{Fe_xNi_{1-x}} = 7.87 + \frac{8.57 - 7.87}{1 - 0.25} (1 - x) = 8.803 - 0.933x,\tag{1}$$

where the densities of  $\alpha$ -Fe and FeNi<sub>3</sub> are 7.87 [10] and 8.57  $gcm^{-3}$  [18], respectively, and  $0.25 \le x \le 1$ .

As the Fe–Ni thin film in Fig. 7 contained 70.2 at% Fe, the following equation is obtained,

$$\frac{\frac{A_{Fe}\rho_{Fe}}{M_{Fe}} + \frac{(1-A_{Fe})\rho_{Fe_{\chi}Ni_{1-\chi}x}}{M_{Fe}}}{\frac{A_{Fe}\rho_{Fe}}{M_{Fe}} + \frac{(1-A_{Fe})\rho_{Fe_{\chi}Ni_{1-\chi}x}}{M_{Fe}} + \frac{(1-A_{Fe})\rho_{Fe_{\chi}Ni_{1-\chi}(1-\chi)}}{M_{Ni}}} = 0.702,$$
(2)

where  $\rho_{Fe}$  is the density of Fe,  $A_{Fe}$  denotes the deep blue area ratio of  $\alpha$ -Fe in Figs. 7 (a) and (b) or the black area in Fig. 8, and  $M_i$  is the atomic weight (i=Fe or Ni). The numerator and denominator indicate the number of Fe atoms and the summation of the number of Fe and Ni atoms in the Fe–Ni thin film, respectively. Substituting Eq. (1) and values of  $A_{Fe}$ ,  $M_i$ , and  $\rho_{Fe}$  into Eq. (2), we have

 $0.2295x^2 - 2.318x + 1.197 = 0.$ 

Equation (3) gives x = 0.546. Hence, the chemical formula of the amorphous structure Fe–Ni electrodeposits is determined to be  $FeNi_{0.832}$ . The obtained molar ratio is the Ni content in the Fe and Ni co-existing area in the Fe–Ni thin film.

(3)



**Figure 8.** Binary image of α–Fe band shapes converted from Fig. 7 (a).

The molar ratio deviates significantly from the stoichiometric ratio of  $FeNi_3$  in the thermal equilibrium phase diagram [7]. This implies that the formation of  $FeNi_3$  requires a much longer time duration, more than a microsecond, as shown in Fig.1.

### 3.6 Morphology of Fe-Ni thin films



Figure 9. SEM snapshot images of Fe-Ni thin films electrodeposited at  $V_c = 2.22 V$ , 0.4 MHz, and a deposition time: (a) 10 s, (b) 30s, (c) 60 s, and (d) 300 s.

Figure 9 shows SEM snapshot images of Fe-Ni thin films electrodeposited at a deposition time of 10, 30, 60, and 300 s. In particular, the Fe-Ni thin film at a deposition time of 300 s has a mirror-like appearance. The surface morphology shows not islands, but the layers that comprise steps, terraces, and kinks. The surface growth follows the Burton, Cabrera, and Frank (BCF) growth mechanism [16], that is, layer-by-layer growth. The BCF growth mode is useful for application in planar technology.

### **4. CONCLUSIONS**

Electrodeposited Fe–Ni thin films were investigated using SEM-EDX and XRD. SEM-EDX analyses demonstrated that the dependence of the Ni content on the cathode potential was consistent with the phenomenological theory of electrodeposition and the Fe<sup>2+</sup> and Ni<sup>2+</sup> potential barriers were determined to be 1.48 and 2.22 V, respectively. EDX and XRD analyses revealed that the Fe–Ni thin films comprised a BCC crystal structure  $\alpha$ -Fe and amorphous structure FeNi<sub>0.832</sub> phase, in which the stoichiometric molar ratio was determined for Fe–Ni thin films containing 29.8 at% Ni. The smooth SEM surface images of the Fe–Ni thin films showed that the surface growth mode was the layer-by-layer growth.

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