

## Electrodeposition Characteristics and Magnetic Properties of CoFeNi Thin Film Alloys

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**Abstract :** Various compositions of CoFeNi alloys have been electrodeposited in chloride bath and in sulfate bath, and evaluated for electrodeposition characteristics and magnetic properties. For electrodeposited CoFeNi thin film alloys, the increase of Fe content in the deposits from sulfate bath was considerably faster than those from chloride bath. The current efficiencies in sulfate bath showed observable decrease from 75% to 50% while those in chloride bath showed no significant decrease. From the low coercivity of 3 Oe in the minimum and the higher squarenesses of the alloys from sulfate bath than those from chloride bath, the alloy at Co, Fe, and Ni contents of 80 wt.%, 10 wt.%, and 10 wt.% can be considered to be the best CoFeNi alloy in this research for the soft magnetic material.

**초 록 :** 다양한 조성의 CoFeNi 합금이 chloride bath와 sulfate bath에서 전해도금 되어졌고, 합금의 도금 특성과 자기특성이 관찰되어졌다. CoFeNi 합금 박막의 전해도금에 있어서 Fe조성의 증가는 chloride bath에서보다 sulfate bath에서 빠르게 증가하였다. 전류효율은 큰 변화가 보이지 않는 chloride bath와 달리 sulfate bath에서는 75%에서 50%로 큰 폭으로 감소하였다. Co, Fe, Ni 조성이 80%, 10%, 10%되는 CoFeNi 합금이 이번 실험에서 가장 우수한 연자성 재료로 평가 되었으며, 그때의 Coercivity는 3 Oe이고 높은 squareness값을 보였다.

**Key words :** CoFeNi alloy, electrodeposition, coercivity, squarenesses, magnetic property

### 1. Introduction

Enhancements of the electrodeposition of iron group metals, such as Ni, Fe, and Co, enabled thin-film recording heads to become technologically viable. General requirements for thin-film recording heads were reviewed by Andriacos and Robertson.<sup>1)</sup> These include: 1) high magnetic saturation ( $B_s \gg 1T$ ), 2) low coercivity ( $H_c < 1$  Oe), 3) optimal anisotropy field ( $H_k$ ) for high permeability ( $\mu$ ), 4) close to zero magnetostriction ( $\lambda$ ), 5) high electrical resistivity ( $\sigma$ ) and 6) good corrosion resistance.

There have been various researches on electrodeposition of iron group metals. Anomalous codeposition behaviors of binary iron group alloys depending on bath pH, complexing agents, and buffering agents have been studied.<sup>2-4)</sup> Also, there have been studies about the morphology and the other characteristics of the deposited films.<sup>5,6)</sup> For practical applications, the electrodeposited Ni80Fe20 (Permalloy) has been used as a soft magnetic film since 1979.<sup>7,8)</sup> Liao and Tolman reported that electrodeposited CoFe alloys, especially 90Co10Fe, have promising magnetic properties including high magnetic saturation (1.9 T), low coercivity (1 Oe), and near-zero magnetostriction.<sup>9)</sup> High performance NiFe(45/55) film for writing head was investigated Robertson, Hu and Tsang.<sup>10)</sup>

Many researchers investigated properties of the soft magnetic CoNiFe alloy electrodeposited from the bath containing saccharin as the additive.<sup>11-13)</sup> Also, the electrodeposited CoNiFe ternary alloy films using saccharin and thiourea as additives have been investigated,<sup>14,15)</sup> and a CoNiFe soft magnetic film with 1.7T by incorporating 3-4 atom% S in the film was successively prepared using a thiourea additive bath.<sup>15)</sup> Subsequently, a study was made of the CoNiFe film with no S inclusion, which was electrodeposited from no SCA (sulfur containing additive excluding surfactant) bath. The film from the bath without saccharin or thiourea was found to have desired soft magnetic characteristics with  $B_s > 2.0$  T,  $H_c < 2.0$  Oe, and  $1s < 10^{-5}$  in the compositional region of FCC-BCC phase boundary.<sup>16,17)</sup>

It is also found that ethylenediamine greatly increase the Ni/Fe ratio of the deposit when the bath is chloride-based. Ion microprobe analysis indicates that ethylenediamine is incorporated in the deposit during electrodeposition.<sup>18)</sup> The effect of diethylenetriamine (DET) was also investigated to find that the magnetic properties increased as a function of DET concentration.<sup>19)</sup> A supportive model of iron-group electrodeposition, which expands upon the one-dimensional diffusion model by including the effects of competitive adsorption, site blockage by hydrogen atoms, and a variance in the number of adsorption sites within the kinetics is proposed. A main contribution of this model is the inclusion of hydrogen adsorption and its effects on electrodeposition.<sup>20)</sup>

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The addition of a relatively small quantity of nitrate to a cobalt deposition bath results in the electrochemical formation of black cobalt film, instead of white cobalt, which is formed in the absence of nitrate. The black cobalt deposit is more dispersed and less smooth than the white cobalt.<sup>21)</sup>

Even though there are many studies on electrodeposited iron-group alloys, there is a lack of systematic studies relating properties of electrodeposited iron group thin films including NiFe, CoNi, CoFe and their ternary alloys with deposit composition, magnetic property, and crystal structure. In this paper, we investigated and compared the effects of solution compositions and electrodeposition parameters on the film compositions and resulting structures and properties of iron group alloys such as microstructure, magnetoresistances and other magnetic properties, and corrosion resistances. Particular emphasis was on the effect of magnetic properties according to different anions, since it is important consideration for producing enhanced recording materials.

## 2. Experimental

NiCoFe alloys were electrodeposited from various plating solutions. Table 1 gives the plating solution compositions investigated. Two different solutions (chloride or sulfate electrolytes) were used to compare the differences in anionic environments. Saccharin is used to reduce deposit stress and L'ascorbic acid to minimize  $\text{Fe}^{+2}$  oxidation. Solution pH was adjusted to 3.0 by adding HCl,  $\text{H}_2\text{SO}_4$  or NaOH; experiments were conducted at room temperature with no stirring.

The depositions of ternary composition of Ni, Co, and Fe were conducted with fixed  $\text{Ni}^{+2}$  concentration of 0.2 M and fixed  $\text{Co}^{+2}$  concentration of 0.15 M and variable concentrations of  $\text{Fe}^{+2}$  from 0.005 to 0.16 M. The deposited contents of Co, Fe, and Ni were examined by dissolving the deposits with 30% nitric acid and measuring with Atomic Absorption Spectrometer(AAS).

Brass plates were used as substrates at the cathode and Ni were used as the soluble anodes. Current density and total charge were set at  $10 \text{ mA cm}^{-2}$  and  $10 \text{ C cm}^{-2}$ , respectively. Magnetic properties of electrodeposited films were measured with a vibrating sample magnetometer (Model 1660 ADE Tech.).

## 3. Results and Discussion

Electrodeposition of NiFe, CoNi, and CoFe alloys has been characterized as "anomalous codeposition". That is individual electrodeposition of  $\text{Ni}^{+2}$  is faster than  $\text{Fe}^{+2}$ , but during codeposition the rates are reversed.<sup>22)</sup> The degree of "anomalous codeposition" decreased in the order,  $\text{CoNi} > \text{NiFe} > \text{CoFe}$ .<sup>23,24)</sup>

The NiCoFe films were deposited in sulfate and chloride

solutions (Solution A and B, Table 1). Figure 1 shows the deposit Fe content as a function of  $\text{Fe}^{+2}$  concentration. Deposit Fe content increased with increasing  $\text{Fe}^{+2}$  concentration in both of the solutions. The increase of deposit Fe content in sulfate bath was considerably faster than that in chloride bath. In sulfate bath, the cross-over between the Co and Fe content was observed at 0.12 M  $\text{Fe}^{+2}$  concentration, however, the cross-over was not found in chloride bath even when the concentration of  $\text{Fe}^{+2}$  is higher than that of  $\text{Co}^{+2}$ . The contents of Ni in the deposits were about 10% which was expected in anomalous codeposition and keep slowly decreasing as  $\text{Fe}^{+2}$  concentration increase. Ni contents were slightly higher in sulfate bath than in chloride bath where the Co content is higher instead. As shown in Figure 2, current

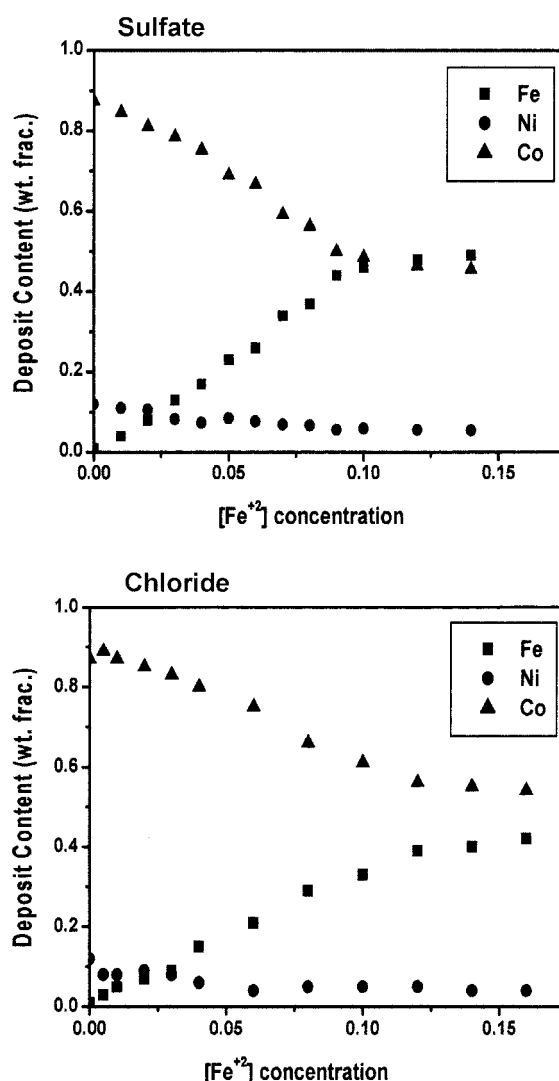


Figure 1. Dependence of Fe, Co, and Ni deposit content on  $\text{Fe}^{+2}$  solution concentration: in chloride bath and sulfate bath,  $10 \text{ mA cm}^{-2}$ , unstirred,  $[\text{Co}^{+2}] = 0.15 \text{ M}$  and  $[\text{Ni}^{+2}] = 0.2 \text{ M}$ .

Table 1. Solution compositions for electrodeposition of CoFeNi alloy.

A. NiCoFe (Chloride)	0.2 M $\text{NiCl}_2$ + 0.15 M $\text{CoCl}_2$ + X M $\text{FeCl}_2$ + 0.7 M NaCl + 0.4 M $\text{H}_3\text{BO}_3$ + 0.0075 M saccharin + 0.05 M L'ascorbic acid
B. NiCoFe (Sulfate)	0.2 M $\text{NiSO}_4$ + 0.15 M $\text{CoSO}_4$ + X M $\text{FeSO}_4$ + 0.7 M NaCl + 0.4 M $\text{H}_3\text{BO}_3$ + 0.0075 M saccharin + 0.05 M L'ascorbic acid

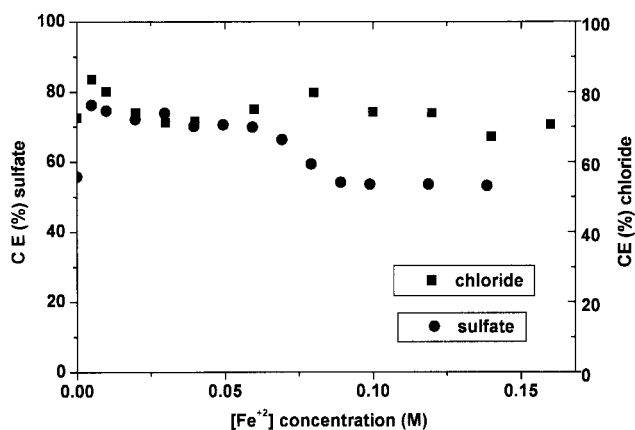


Figure 2. Dependence of current efficiency on  $\text{Fe}^{2+}$  solution concentration: in chloride bath and sulfate bath,  $10 \text{ mA cm}^{-2}$ , unstirred,  $[\text{Co}^{+2}] = 0.15 \text{ M}$  and  $[\text{Ni}^{+2}] = 0.2 \text{ M}$ .

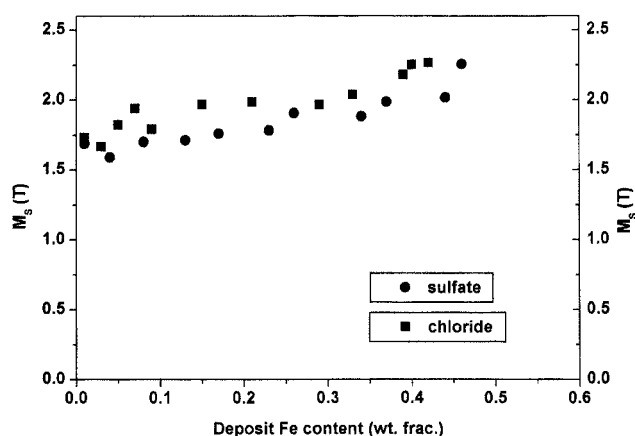


Figure 3. Dependence of magnetic saturation of electrodeposited CoFeNi on Fe content: in chloride bath and sulfate bath,  $10 \text{ mA cm}^{-2}$ , unstirred,  $[\text{Co}^{+2}] = 0.15 \text{ M}$  and  $[\text{Ni}^{+2}] = 0.2 \text{ M}$ .

efficiencies from chloride solutions (75%) were independent to the  $\text{Fe}^{2+}$  concentrations, while those from sulfate solutions were considerably decreasing from 75% to 50% as  $\text{Fe}^{2+}$  increase. The decrease of current efficiencies in sulfate bath seemed to be related with the fast decrease of Co content in the deposits, i.e., the activities of  $\text{Co}^{+2}$  were reduced in the sulfate bath so that both the current efficiency and the Co content would decrease. In both chloride and sulfate baths, current efficiencies were independent of  $\text{Fe}^{2+}$  concentrations when the  $\text{Fe}^{2+}$  is lower than 0.05 M, although current efficiencies in chloride baths were higher by about 20% in  $\text{Fe}^{2+}$  rich condition. Horkans studied hydrogen gas evolution in  $\text{Na}_2\text{SO}_4$ ,  $\text{NaCl}$  and  $\text{NaClO}_4$  and observed higher limiting currents of  $\text{H}^+$  reduction in  $\text{Na}_2\text{SO}_4$  than in either  $\text{NaCl}$  or  $\text{NaClO}_4$ . The differences in limiting currents were attributed to different diffusion coefficients.<sup>25,26</sup> She observed a significant decrease in the overpotential of Ni, Fe and NiFe in chloride baths and suggested that chloride catalyses deposition of Ni, Fe and NiFe through the formation of an ion bridge between the electrode and the metal ion being discharged. Higher current efficiency in chloride baths com-

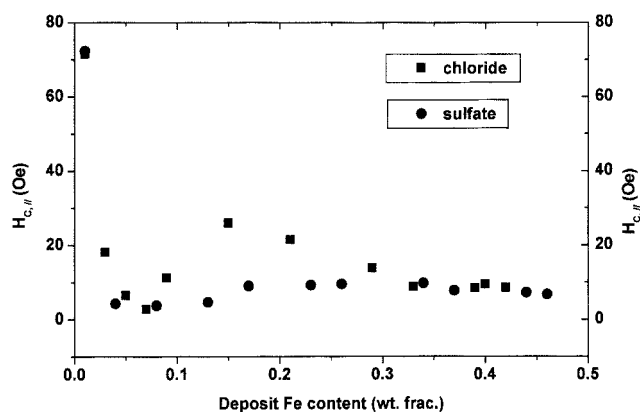


Figure 4. Dependence of coercivities of electrodeposited CoFeNi on Fe content: in chloride bath and sulfate bath,  $10 \text{ mA cm}^{-2}$ , unstirred,  $[\text{Co}^{+2}] = 0.15 \text{ M}$  and  $[\text{Ni}^{+2}] = 0.2 \text{ M}$ .

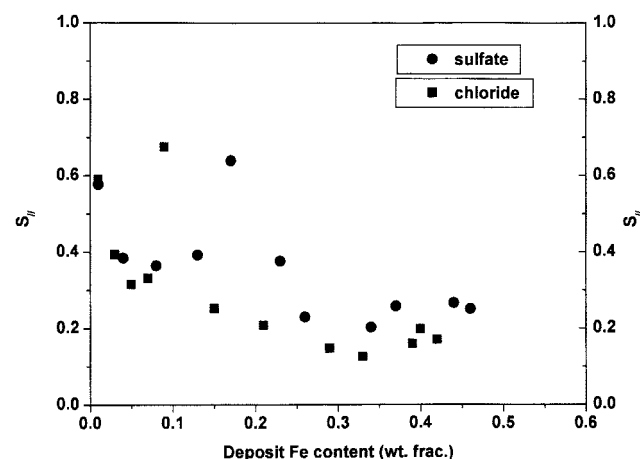


Figure 5. Dependence of squarenesses of electrodeposited CoFeNi on Fe content: in chloride bath and sulfate bath,  $10 \text{ mA cm}^{-2}$ , unstirred,  $[\text{Co}^{+2}] = 0.15 \text{ M}$  and  $[\text{Ni}^{+2}] = 0.2 \text{ M}$ .

pared to sulfate baths in our experiments may be due to a lower  $\text{H}_2$  limiting current in chloride baths than in sulfate bath.

Figure 3 compares the magnetic saturation ( $M_s$ ) of electrodeposited NiCoFe films in chloride and sulfate bath, which start at 1.7 and keep increasing as Fe content increase. As expected from the intrinsic nature of magnetic saturation, magnetic saturations of electrodeposits showed no significant difference between anions.

Figure 4 and 5 showed the coercivity and squareness of electrodeposited NiCoFe from chloride and sulfate baths, respectively. Coercivities in chloride and sulfate baths showed similar pattern with different magnitude. Coercivities of electrodeposited CoFeNi decreased steeply from 70 to 3 Oe as the deposit Fe wt.% increases from 0 to 8%. Both of the deposits from chloride bath and sulfate bath showed minimum coercivity at low Fe contents of about 5-8%. Osaka and others studied the crystal structure of the ternary alloys of Co, Fe, and Ni, and it was reported that the crystal structures were changed at about 5% of Fe content,<sup>15-17</sup> which is related with the minimum of coercivities in this study. As

deposit Fe wt.% increase higher than 8%, coercivities increase higher than 20 Oe in chloride solution while they increase up to less than 10 Oe in sulfate solution. Squarenesses of the CoFeNi deposits showed similar patterns between two solutions of chloride and sulfate anions. The squarenesses in both solutions showed continuously decreasing tendency from 0.6 at 0 Fe wt.% to 0.2 in sulfate bath and 0.1 in chloride bath at high Fe content. A sharp peaks was observed at 10 Fe wt.% in chloride bath and 15 Fe wt.% in sulfate bath were observed.

The low coercivities of 3 Oe at the minimum at Fe content of 8 wt.% and higher squarenesses of the alloys from sulfate bath than those from chloride bath after the minimum of coercivity suggest that at Co, Fe, and Ni contents of about 80 wt.%, 10 wt.%, and 10 wt.%, respectively, it can be considered to be the best CoFeNi alloys in this research for the soft magnetic material.

#### 4. Conclusions

The contents of Fe in the deposits were increasing faster in sulfate bath than in chloride bath, and the content of Co in the deposits were decreasing faster in sulfate bath than in chloride bath.

Current efficiencies from chloride solutions (75%) were independent to the  $\text{Fe}^{+2}$  concentrations, while those from sulfate solutions were significantly decreasing from 75% to 50% as  $\text{Fe}^{+2}$  increase. .

Coercivities of electrodeposited NiCoFe decreased steeply from 70 to 3 Oe as deposit Fe wt.% increase from 0 to 8%. As deposit Fe wt.% increase higher than 8%, coercivities increase higher than 20 Oe in chloride solution while they increase below 10 Oe in sulfate solution.

The squarenesses in both solutions showed continuously decreasing tendency from 0.6 at 0 Fe wt.% 0.2 in sulfate bath and 0.1 in chloride bath with a sharp peak at 10% Fe content in sulfate bath and 18% Fe content in chloride bath.

From the low coercivity of 3 Oe in the minimum and the higher squarenesses of the alloys from sulfate bath than those from chloride bath, the alloy at Co, Fe, and Ni contents of 80 wt.%, 10 wt.%, and 10 wt.% can be considered to be the best CoFeNi alloy in this research for the soft magnetic material.

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