

# Electroplated Fe-Ni films prepared from deep eutectic solvents

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Fe-Ni alloy films were prepared by electroplating in a plating bath containing a choline chloride and ethylene glycol based deep eutectic solvent (DES). The Fe content of the electroplated films was found to vary from 0 to 100 at. % and was dependent on the amount of Fe reagent in the plating bath. The composition of the electroplated films could be controlled easily by changing the composition of the bath. We observed bcc or fcc Fe-Ni crystalline phase in the electroplated films by X-ray diffraction and confirmed that magnetically soft Fe-Ni alloy films could be obtained from the DES-based bath. The current efficiency for the plating process was as high as > 88 % over a wide range of the Fe reagent concentrations. Therefore, we conclude that the DES is an attractive solvent for preparing the Fe-Ni alloy films.

*Index Terms*—Soft magnetic films, Electroplating, Permalloy, Deep Eutectic Solvent

## I. INTRODUCTION

Electroplating is one of useful techniques for obtaining thin and thick films, and aqueous solutions are commonly used for the magnetic films in a range of alloy systems such as Fe-Ni, Fe-Co, Fe-Co-Ni, Fe-Pt and Co-Pt [1]-[7]. Recently, we have reported that a plating bath containing a choline chloride and ethylene glycol based deep eutectic solvent (DES) is hopeful for electroplating Fe films [8]. The DESs have many industrial advantages such as wide electrochemical window, extremely low vapor pressure, low cost, high purity, and low toxicity [9]-[11]. Therefore, the DESs are expected as a new solvent for the electroplating bath. Although there have been some reports on magnetic films of Ni, Co, Ni-Co, Ni-Co-Sn, Sm-Co and Co-Pt prepared from DES-based baths [12]-[18], Fe-based materials were rarely reported [19]. It is well-known that Fe-based alloys, such as Fe-Ni, Fe-Al-Si, Fe-Pt and Nd-Fe-B are superior soft or hard magnetic materials and their electroplated films are useful for mass-productive electric devices. In this study, we have focused on soft magnetic Fe-Ni alloys and investigated the structural and the magnetic properties of the Fe-Ni films electroplated in DES-based plating baths with various compositions.

## II. EXPERIMENTAL PROCEDURE

### A. Preparation of electroplated Fe-Ni films

We used a DES base on choline chloride ( $\text{HOCH}_2\text{CH}_2\text{N}(\text{CH}_3)_3\text{Cl}$ ) and ethylene glycol ( $\text{HOCH}_2\text{CH}_2\text{OH}$ ) [8], [17], [20], [21] in the present study. The DES was prepared by stirring the mixture, which consists of 10 g of ethylene glycol and 10 g of choline chloride, at 100 °C until a homogeneous liquid state is obtained.  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  were added into this DES. The weight of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  was altered from 0 to 15 g, and the total weight of the reagents ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O} + \text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ) was kept at 15 g in this

study. We didn't use any smoothing agents. The composition of the plating bath is shown in Table I. 500  $\mu\text{m}$ -thick Ni and Cu plates were used as the anode and cathode electrodes, respectively. The distance between the electrodes was set at 20 mm, and we obtained 75- $\text{mm}^2$  Fe-Ni films on the Cu plate. The bath temperature was kept at 100 °C and no stirring action was taken during the plating. The films were electroplated using a direct current. The current density and the plating time were controlled by a computer-aided dc current source. The plating conditions are shown in Table II.

TABLE I. COMPOSITION OF THE DES-BASED PLATING BATH

Components	Weight (g)
$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	$x$
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	$15 - x$
Choline chloride	10
Ethylene glycol	10

TABLE II. ELECTROPLATING CONDITIONS

Conditions	Value
Bath temperature	100 °C
Current density	67 $\text{mA}/\text{cm}^2$
Deposition time	20 min

### B. Measurements

The thicknesses and the hysteresis loops of the electroplated films were measured with a micrometer (Mitutoyo CPM15-25MJ) and a vibrating sample magnetometer (Tamagawa), respectively. The maximum applied field of approximately 1.6 MA/m was used for the measurement of M-H loops. The saturation magnetization and the coercivity of the electroplated films were determined from the M-H loops. The compositions and the crystal structures of the films were analyzed by EDX (Hitachi High-technologies S-3000) and XRD (Rigaku Rint 2000), respectively. The thickness and the composition of each 75  $\text{mm}^2$ -film were determined by averaging the values obtained for approximately every 9  $\text{mm}^2$  (9 points). The current efficiency was calculated from the actual weight of the electroplated film and the theoretical weight obtained by Faraday's law. For the calculation of the theoretical weight, we used the evaluated film composition.

Manuscript received March 7, 2014. Corresponding author: K. Shiraishi (e-mail: bb52114222 @cc.nagasaki-u.ac.jp).

Digital Object Identifier inserted by IEEE

### III. RESULTS AND DISCUSSION

Figure 1 shows the changes in Fe content and current efficiency of the electroplated Fe-Ni films as a function of amount of the Fe reagent ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) in the bath. The films shown in Fig.1 have almost the same thickness of approximately  $22 \mu\text{m}$ , and we have already confirmed the good homogeneity of the composition in the depth direction for the Fe-Ni films. The Fe content increases linearly with the Fe reagent content, indicating that the composition of the Fe-Ni films can be controlled by adjusting the reagent content in the plating bath. The current efficiency shows high values ( $> 88\%$ ) in a wide range of the Fe reagent content. Therefore, it is found that Fe-Ni films with various Fe compositions could be obtained quite efficiently from the DES-based plating bath.

Figure 2 shows the hysteresis loops of the films electroplated from the bath with various Fe reagent content. As shown in Fig. 2, the saturation magnetizations of the films varied with the amount of the Fe reagent in the DES-based plating bath. In order to investigate the changes in the saturation magnetization systematically, we evaluated the effect of the amount of the Fe reagent on magnetic properties of the films. Figure 3 shows the changes in the saturation magnetization and coercivity of the electroplated Fe-Ni films as a function of the Fe reagent content. The saturation magnetization shows a linear increase with increasing the reagent content. The change in the saturation magnetization could be explained by the Fe content in the films. The coercivity drastically decreases with increasing the Fe reagent from 0 to 5 g followed by a slight increase in the higher amount of the Fe reagent. As shown in Fig.1, the Fe content of the film electroplated in the bath with the Fe reagent of 5 g was approximately 26 at. %. Since both the magnetocrystalline anisotropy and the magnetostriction constants in the Fe-Ni binary system become nearly zero at  $\text{Fe}_{22}\text{Ni}_{78}$ , the drastic decrease in coercivity is attributable to the suppression of the intrinsic magnetic and magneto-elastic anisotropy values.

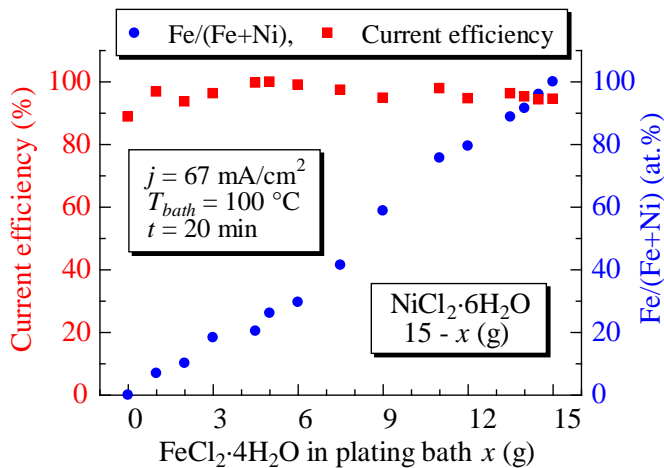


Fig.1 Fe content and current efficiency of the electroplated Fe-Ni films as a function of amount of the Fe reagent ( $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ ) in the DES-based plating bath.

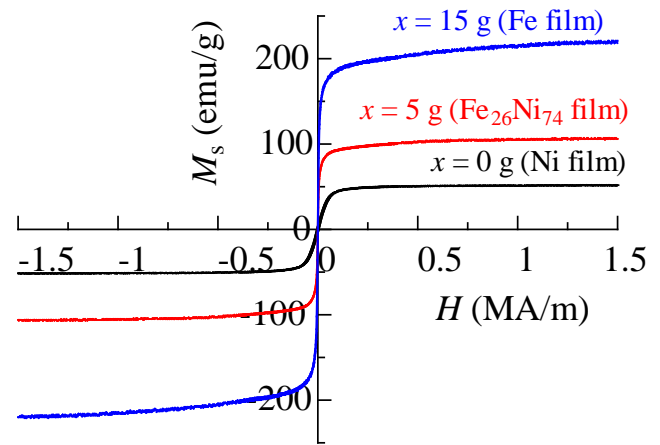


Fig.2 Hysteresis loops of the electroplated Ni,  $\text{Fe}_{26}\text{Ni}_{74}$  and Fe films.

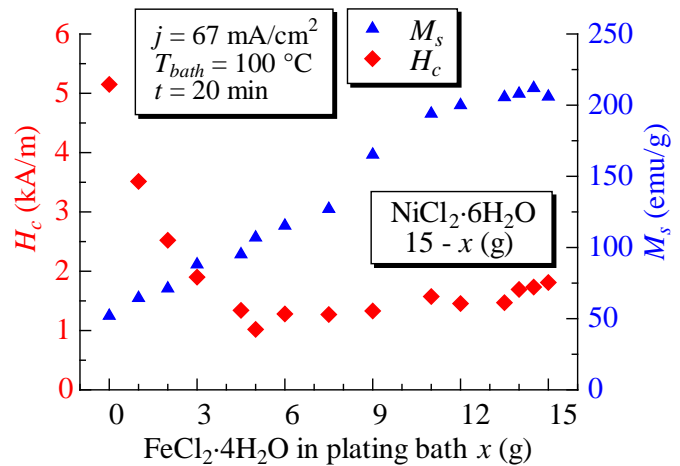


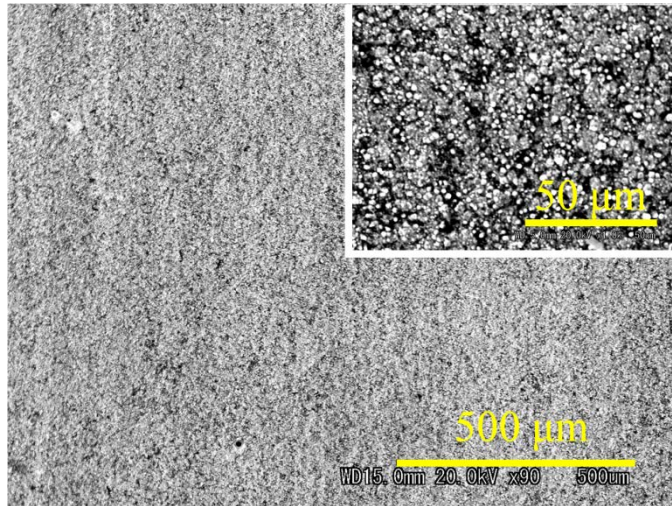
Fig.3 Coercivity  $H_c$  and saturation magnetization  $M_s$  of the electroplated Fe-Ni films as a function of amount of the Fe reagent ( $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ ) in the DES-based plating bath.

Figure 4 shows surface morphologies of the Ni,  $\text{Fe}_{26}\text{Ni}_{74}$  and Fe films. As shown in Fig. 4, the Ni film had a rough surface compared with those for the  $\text{Fe}_{26}\text{Ni}_{74}$  and Fe films. In general, since rough surface prevents magnetic domain wall movement during technical magnetization processes, soft magnetic properties of films with a rough surface are inferior to those for films with a smooth surface. Therefore, we considered that the improvement in the rough surface is one of other reasons for the observed drastic decrease in the coercivity.

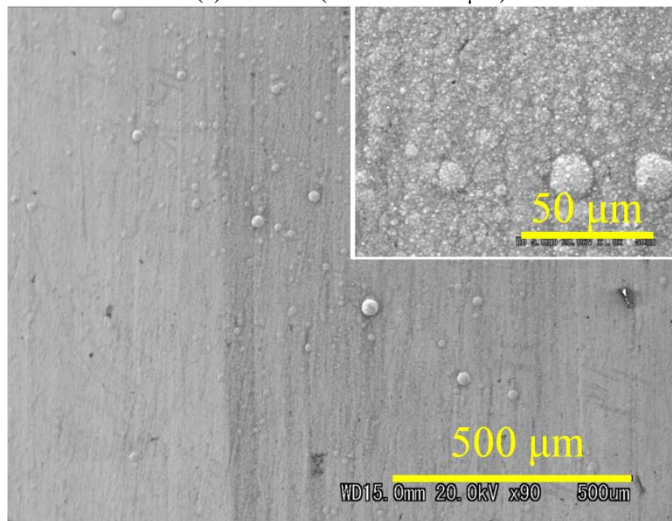
In order to confirm the crystal structures of the Fe-Ni films, we carried out X-ray diffraction experiments for the electroplated films. Figure 5 shows the XRD patterns of the electroplated Fe-Ni films with various Fe contents. The diffraction peaks of fcc or bcc Fe-Ni crystalline phases were observed. The result for the X-ray analysis suggests that that the structure of the films depends on the Fe content. It is well-known that the structure of the Fe-Ni binary system alloy depends on the Fe content [22]. The boundary composition between fcc and bcc structures is approximately  $\text{Fe}_{70}\text{Ni}_{30}$  for the Fe-Ni binary alloy system. As shown in Fig. 5, the boundary was observed between  $\text{Fe}_{52}\text{Ni}_{48}$  and  $\text{Fe}_{76}\text{Ni}_{24}$ , the composition for the phase transformation agrees with that for

the Fe-Ni binary alloy system.

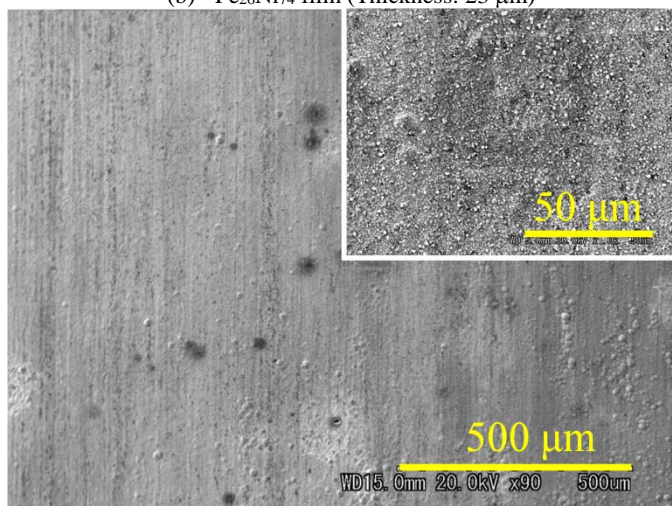
From above-mentioned results, we found that the DES-based bath enables us to obtain Fe-Ni alloy films with high current efficiency.



(a) Ni film (Thickness: 21  $\mu\text{m}$ )



(b)  $\text{Fe}_{26}\text{Ni}_{74}$  film (Thickness: 23  $\mu\text{m}$ )



(c) Fe film (Thickness: 22  $\mu\text{m}$ )

Fig.4 Surface morphologies of the (a) Ni, (b)  $\text{Fe}_{26}\text{Ni}_{74}$  and (c) Fe films.

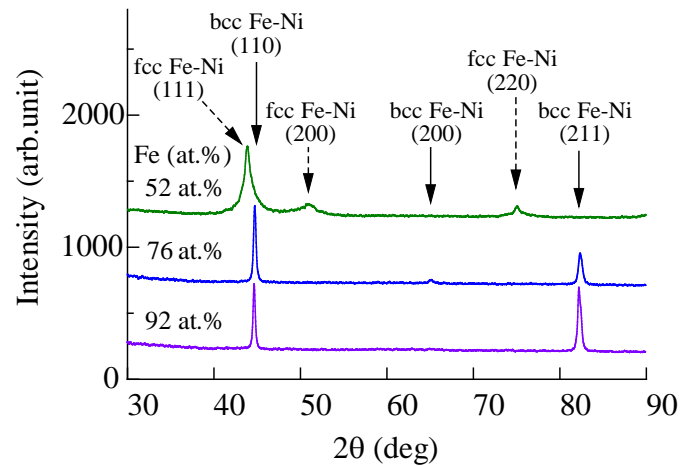


Fig.5 XRD patterns of the films prepared from the DES-based plating bath.

#### IV. CONCLUSION

In this study, we electroplated Fe-Ni films in a DES-based bath and investigated the structural and magnetic properties of the films. The obtained results are summarized as follows:

- (1) The Fe content in the electroplated films depended on the amount of the Fe reagent in the plating bath and adjusting the bath reagent composition is an easy way to control the film composition.
- (2) The current efficiency showed high values of over 88 % in a wide range of the Fe reagent content.
- (3) The saturation magnetization of the film increased proportionally with increasing the Fe reagent, and the coercivity drastically decreases with increasing the Fe reagent from 0 to 5 g. The drastic decrease in the coercivity is attributed to the reduction in the magnetocrystalline anisotropy and the magnetostriction constants of the film.
- (4) Bcc or fcc Fe-Ni crystalline phase was observed in the result for the X-ray analysis, and we confirmed the phase transformation from the fcc structure to the bcc one in the Fe content range from 52 to 76 at.%.

We concluded that the choline chloride-ethylene glycol based DES is one of hopeful solvents for electrodeposition of Fe-Ni alloy films.

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