Electroplated Fe-Ni films prepared from deep eutectic solvents

T. Yanai[1], K. Shiraishi[1], Y. Watanabe[1], M. Nakano[1], T. Ohgai[1], K. Suzuki[2], and H.Fukunaga[1], *Member, IEEE*

[1]Guraduate School of Engineering, Nagasaki University, Nagasaki 852-8521, Japan
[2]Department of Material Engineering, Monash University, Clayton VIC 3800, Australia

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 ($HOCH_2CH_2N(CH_3)_3Cl$) and ethylene glycol ($HOCH_2CH_2OH$) [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. $FeCl_2{\cdot}4H_2O$ and $NiCl_2{\cdot}6H_2O$ were added into this DES. The weight of $FeCl_2{\cdot}4H_2O$ was altered from 0 to 15 g, and the total weight of the reagents ($FeCl_2{\cdot}4H_2O$ + $NiCl_2{\cdot}6H_2O$) 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 μm-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-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.

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

TABLE I. Composition of the DES-based Plating Bath

Components	Weight (g)
$FeCl_2{\cdot}4H_2O$	*x*
$NiCl_2{\cdot}6H_2O$	15 - *x*
Choline chloride	10
Ethylene glycol	10

TABLE II. Electroplating Conditions

Conditions	Value
Bath temperature	100 °C
Current density	67 mA/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 mm^2-film were determined by averaging the values obtained for approximately every 9 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.

[4] T. Osaka, M. Takai, K. Hayashi, K. Ohashi, M. Saito, and K. Yamada, “A soft magnetic CoNiFe film with high saturation magnetic flux density and low coercivity,” *Nature*, vol. 392, pp.796-798, 1998.

[5] G. Zangari, P. Bucher, N. Lecis, P. L. Cavallotti, L. Callegaro,and E. Puppin, “Magnetic properties of electroplated Co-Pt films,” *J. Magn. Magn. Mater.*, vol. 157/158, pp. 256-257, 1996.

[6] Fernand M. F. Rhen, G. Hinds, C. O'Reilly, and J. M. D. Coey, “Electrodeposited FePt Films,” *IEEE Trans. Magn.*, vol. 39, pp. 2699-2701, 2003.

[7] N. Fujita, S. Maeda, S. Yoshida, M. Takase, M. Nakano, and H. Fukunaga, “Preparation of Co-Pt alloy film magnets by electrodeposition,” *J. Magn. Magn. Mater.*, vol. 272-276, pp. e1895-e1897, 2004.

[8] T. Yanai, T. Shimokawa, Y. Watanabe, T. Ohgai, M. Nakano, K. Suzuki, and H. Fukunaga, “Electroplated Fe films prepared from a deep eutectic solvent,” *J. Appl. Phys.*, vol. 115, pp. 17A344 - 17A344-3, 2014.

[9] A.P. Abbott, D. Bothby, G. Capper, D.L. Davies, and R. Rasheed, “Deep Eutectic Solvents Formed between Choline Chloride and Carboxylic Acids: Versatile Alternatives to Ionic Liquids,” *J. Am. Chem. Soc.*, vol. 126, pp. 9142-9147, 2004.

[10] A.P. Abbott, G. Capper, D.L. Davies, R.K. Rasheed, and V. Tambyrajah, “Novel Solvent Properties of Choline Chloride/ Urea Mixtures,” *Chem. Commun.*, vol. 9, pp. 70-71, 2003.

[11] A.P. Abbott, G. Capper, D.L. Davies, K.J. McKenzie, and S.U. Obi, “Solubility of Metal Oxides in Deep Eutectic Solvents Based on Choline Chloride,” *J. Chem. Eng. Data*, vol. 51, pp. 1280-1282, 2006.

[12] E. Gómez, P. Cojocaru, L. Magagnin, and E. Valles, “Electrodeposition of Co, Sm and SmCo from a Deep Eutectic Solvent,” *J. Electroanal. Chem.*, vol. 658, pp. 18-24, 2011.

[13] P. Cojocaru, L. Magagnin, E. Gómez, and E. Valles, “Using deep eutectic solvents to electrodeposit CoSm films and nanowires,” *Mater. Lett.*, vol. 65, pp.3597-3600, 2011.

[14] H. Yang, X. Guo, N. Birbilis, G. Wu, and W. Ding, “Tailoring nickel coatings via electrodeposition from a eutectic-based ionic liquid doped with nicotinic acid,” *Appl. Surf. Sci.*, vol. 257, pp. 9094-9102, 2011.

[15] P. Guillamat, M. Cortés, E. Vallés, and E. Gómez, “Electrodeposited CoPt films from a deep eutectic solvent,” *Surf. Coat. Technol.*, vol. 206, pp. 4439-4448, 2012.

[16] G. Saravanan and S. Mohan, “Structure, composition and corrosion resistance studies of Co–Cr alloy electrodeposited from deep eutectic solvent (DES),” *J. Alloys Comp.*, vol. 522, pp. 162-166, 2012.

[17] Y.H. You, C.D. Gu, X.L. Wang, and J.P. Tu, “Electrodeposition of Ni–Co alloys from a deep eutectic solvent,” *Surf. Coat. Technol.*, vol. 206, pp. 3632-3638, 2012.

[18] J. Vijayakumar, S. Mohan, S.A. Kumar, S.R. Suseendiran, and S. Pavithra, “Electrodeposition of NieCoeSn alloy from choline chloride-based deep eutectic solvent and characterization as cathode for hydrogen evolution in alkaline solution,” *Int. J. Hydrogen Energy*, vol. 38, pp. 10208-10214, 2013.

[19] F. Zhao, S. Franz, A. Vicenzo, M. Bestetti, F. Venturini, and P.L. Cavallotti, “Electrodeposition of Fe–Ga thin films from eutectic-based ionic liquid,” *Electrochimica Acta*, vol. 114, pp. 878-888, 2013.

[20] A.P. Abbott, G. Capper, K.J. McKenzie, and K.S. Rayder, “Electrodeposition of Zinc Tin Alloys from Deep Eutectic Solvents Based on Choline Chloride,” *J. Electroanal. Chem.*, vol. 599, pp. 288-294 2007.

[21] C.D. Gu, Y.H. You, Y.L. Yu, S.X. Qu and J.P. Tu, “Microstructure, nanoindentation, and electrochemical properties of the nanocrystalline nickel film electrodeposited from choline chloride-ethylene glycol,” *Surf. Coat. Technol.*, vol. 205, pp. 4928–4933, 2011.

[22] R.M. Bozorth “Ferromagnetism” *Wiley-IEEE Press*, pp. 102–103, 1993.