Chemistry and Materials

The Center for Science Innovation

Research Article

Chem. Mater. 1 (2) 2022, 61-65

The Effect of Temperature and pH on FeCoNi Film Electrodeposition

Ananda Ico Novtiar Turmiasaputri[1], Erfan Handoko[2], Setia Budi[1*]

[1]Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Jakarta
Jl. Rawamangun Muka, Jakarta 13220, Indonesia

[2]Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Negeri Jakarta
Jl. Rawamangun Muka, Jakarta 13220, Indonesia

*Corresponding author: setiabudi@unj.ac.id

Received
22 March 2022

Received in revised form
21 June 2022

Accepted
21 June 2022

Published online
30 June 2022

DOI
https://doi.org/10.56425/cma.v1i2.25

Abstract

This paper reports the effect of temperature and electrolyte pH on the electrodeposition of FeCoNi film. The FeCoNi electrodeposition was carried out from sulfate solution using the potentiostatic technique. The higher temperature increased deposition rate, thickness of the deposit, and size of the FeCoNi crystallites. The obtained FeCoNi films were characterized by X-ray diffractometer (XRD) and energy dispersive X-Ray (EDX). XRD analysis confirmed typical diffraction patterns of awaruite phase. EDX evaluation indicated that the relative weight increases in pH from 2.5 to 4, the composition of wt% Fe deposited increased from 39.2% to 47.9%, while wt% Co and wt% Ni decreased from 36.2% to 33.5 % and 24.6% to 18.6%.

Keywords: FeCoNi alloy, pH, electrodeposition, temperature

1. Introduction

Nickel, cobalt, iron and their alloys are typical magnetic materials applicable in several fields, such as soft-magnetic and giant-magneto-resistive materials [1]. This is because the ternary FeCoNi alloy has high magnetic saturation and low coercivity, so it can be applied to several magnetic devices such as magnetoresistive sensors, microwave absorbers, and magnetic recording head [2][5]. The magnetic properties of FeCoNi alloys can be improved by making an alloy layer at the nanoparticle scale [6].

Synthesis methods have been introduced to prepare FeCoNi alloys, including physical vapor deposition [7], sputtering, chemical reduction [8], and electrodeposition [2]. However, the use of electrodeposition to synthesize soft magnetic FeCoNi alloys in the form of films or deposits can be considered reliable and versatile, because the method has proven applicable on a large scale. Hence, electrodeposition has become one of the most potential choices for metal and/or alloy fabrication, as it is easy and cost-effective method to fabricate nanostructures of various materials including metal with tailored composition, thickness, and morphology by simply adjusting the electrochemical parameters such as, deposition time, electrolyte pH, current density, and electrolyte composition [2][4][9].

Based on previous research several parameter controls have been studied. The NiCo coating synthesized using the electrodeposition method with a pH from 2.0 to 5.4 resulted in a decrease in the roughness level of the layer from 266.96 nm to 92.93 nm [10], as well as an increase in the pH of the electrolyte from 1.5 to 11.5 resulting in a gradual increase in crystalline size from 8 nm to >100nm. Then controlling another parameter, namely the deposition temperature from 20°C to 60°C resulted in an increase in crystalline size from 5 nm to 91 nm [11]. In this study, the effects of temperatures and electrolyte pH on chemical composition and deposition rate of electro-deposition of FeCoNi films were investigated. The influence of the deposition parameters on crystallite size of the FeCoNi alloy were also discussed.

2. Materials and Method

FeCoNi-based films were electrodeposited on ITO substrates. The FeCoNi films were prepared at room temperature from sulfate electrolyte system containing 0.025 M $CoSO_4.7H_2O$, 0.025 M $FeSO_4.7H_2O$, 0.15 M $NiSO_4.6H_2O$, and 0.4 M H_3BO_4. The electrodeposition was

carried out under various electrodeposition temperature and pH using EDAQ potentiostat of EA163 type in the potentiostatic mode. The solution pH was varied from 2.5 to 4.0 by adding different amount of sodium hydroxide and the deposition temperature was varied from 10℃ to 70℃.

The films were analyzed using PANalytical EMPYREAN X-ray Diffractometer (XRD). The chemical composition of the films was determined by the Energy Dispersive X-ray (EDX).

3. Results and Discussions

3.1 Elemental Analysis

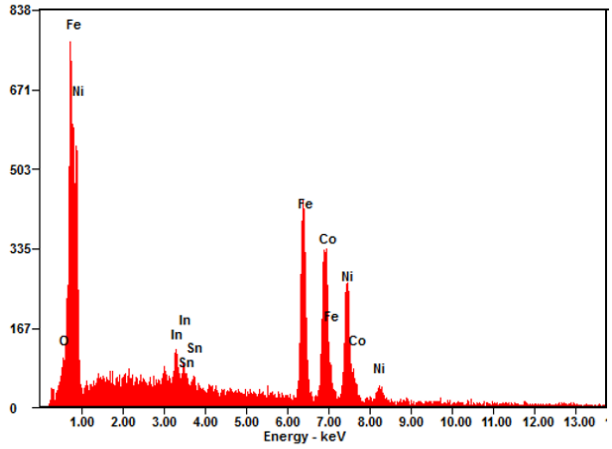

Figure 1. EDX spectrum of FeCoNi

Based on the EDX data of the FeCoNi film shown in Figure 1, the FeCoNi alloy was successfully deposited on the ITO substrate by the electrodeposition method. This is indicated by the appearance of peaks of Fe, Co, and Ni. The peaks In, Sn, and O are associated with the ITO substrate. Table 1 shows that the composition of Fe, Co, and Ni atoms in the deposit are affected by the pH of the electrolyte solution. At a temperature of 10℃ with an increase in pH from 2.5 to 4 the composition of Fe wt.% deposited increased from 39.2% to 47.9% while Co and Ni wt.% decreased from 36.2% to 33.5 % and 24.6% to 18.6%. This result is similar to the previous study, where pH resulted in an increase in Fe content and a decrease in Co, Ni wt. % [1] [2]. This is because the lower pH (pH 2.5) promotes the dissolution of the deposited metal, suppresses the formation, and absorption of metal hydroxyls, so that the deposited Ni content is high [3]. When the pH is higher (pH 4), Fe^{2+} is easily hydrolyzed which will suppress the diffusion of Ni^{2+} due to the absorption of iron hydroxide in the electrolyte [2]. Ni wt. % was deposited less than Co and Fe wt. %. In addition, Fe and Co were deposited first from Ni metal, so that the Ni content was less in the deposit caused by hydrogen evolution due to side reactions of the cathode metal which increased the concentration of hydroxyl ions in the electrolyte solution as shown in Equation 1-4 [1][4].

$$2H_2O + 2e^- \leftrightarrow H_2 + 2OH^- \quad (1)$$

$$M^{2+} + OH^- \leftrightarrow MOH^+ \quad (2)$$

$$MOH^+ \leftrightarrow (MOH)^+_{ads} \quad (3)$$

$$(MOH)^+_{ads} + 2e^- \leftrightarrow M + OH^- \quad (4)$$

Table 1. Chemical compositions of the FeCoNi films

pH	%Wt	T (℃)			
		10	25	50	70
pH 4	Fe	47.9%	33.9%	29.5%	16.1%
	Co	33.5%	34.0%	36.9%	28.1%
	Ni	18.6%	32.1%	33.7%	55.8%
pH 2.5	Fe	39.2%	34.2%	24.5%	17.7%
	Co	36.2%	36.2%	37.0%	31.6%
	Ni	24.6%	29.5%	38.5%	50.7%

3.2 Mass and Deposition Rate Analysis

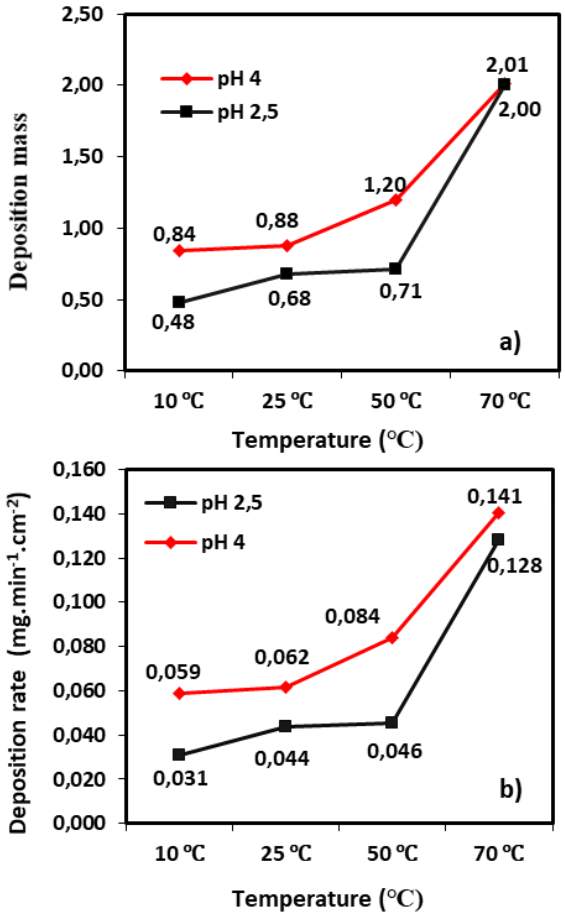

Figure 2. a) Deposition mass of FeCoNi b) Deposition rate of FeCoNi

Based on the data shown in Figure 2, the increase of temperature and pH of the electrolyte solution resulting in an increase in the rate of deposition of FeCoNi thin films. This is because at high temperatures it can reduce the viscosity of the electrolyte solution which encourages the diffusion motion of metal ions in the electrolyte solution to be faster. This promotes an increase in the concentration

of metal ions in the cathode diffusion layer which favors a decrease in cathode polarization [5]. Then the metal electrolyte solution with a low pH supports metal dissolution, suppresses the formation and absorption of metal hydroxyl. This is due to at a low pH the concentration of free hydrogen ions is high and hydrogen evolution is low. Meanwhile, the metal electrolyte solution with a high pH supports the formation and absorption of metal hydroxyl and suppresses the redissolving of the newly deposited metal [3] which causes the deposition rate at pH 4 to be greater than the deposition rate at pH 2.5.

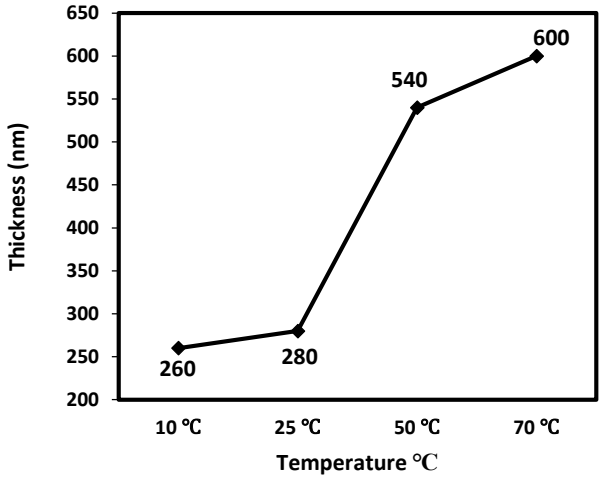

Figure 3. Thickness of FeCoNi

Figure 3 shows that the increase in temperature makes the thickness of the FeCoNi film also increases. The thickness of the Thin Film FeCoNi deposited at a temperature of 10°C is 260 nm, with a flat surface, silver in color, and slightly shiny. While the thickness of the FeCoNi film at a temperature of 70°C is 600 nm where the deposit has a flat, thick, shiny surface, and a few small holes on the deposit surface. Lower temperatures cause grain growth to be less favourable because the diffusion of metal ions deposited in the electrolyte solution moves slowly, so that the surface of the substrate is only covered by small particles [6].

3.3 Phase and Crystallite Size Analysis

Based on the resulting diffractogram on XRD analysis (Figure 4), the diffraction peaks of the awaruite (FeCoNi) phase at 2θ = 44.4°, 51.66 °, 75.81°, 92.02°, and 97.39 ° with a plane (111), (002), (022), (113), (222) which comply with JCPDS 96-900-0090. It is estimated that the crystal structure formed on the synthesized FeCoNi thin film forms the FCC crystal structure. This was confirmed by refinement using the Rietvield method. which obtained lattice parameters a = b = c = 3.576 dan $\alpha = \beta = \gamma$ = 90º. The crystallite size of FeCoNi film was determined using the Rietvield method based on fitting the diffraction curve of the experimental sample with the theoretical diffraction curve obtained from the results of calculations and also calculated using the Scherrer equation [13] [14] [15]. The Scherer equation used to calculate the crystallite size is shown in equation 5, where D is the crystallite size (nm), k is the Scherer constant (k= 0.94), λ is the wavelength (nm), β is the widening of the diffraction line measured at half its maximum intensity (FWHM in radians), and is the peak angle (°) [6].

$$D = \frac{k\lambda}{\beta \cos\theta} \qquad (5)$$

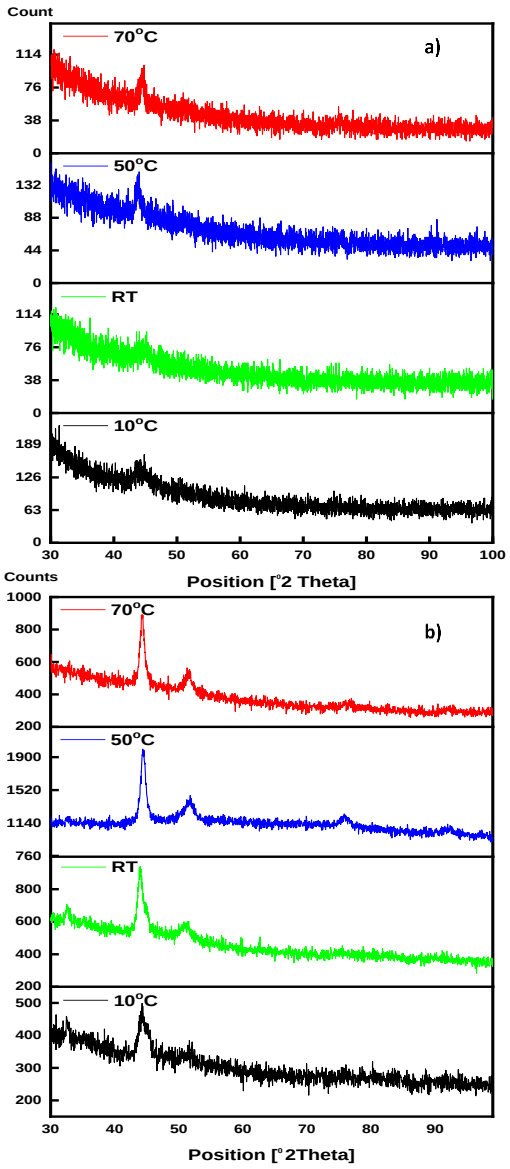

Figure 4. Diffraction pattern of FeCoNi a) pH 2.5 b) pH 4

Figure 5 shows that the FeCoNi crystallite size is in harmony with the analysis of the crystallite size of the FeCoNi alloy thin film. These results are the same as those in previous studies [16]. Then Figure 6 shows that the increase in temperature and pH used in the

electrodeposition process resulted in an increase in the size of the crystallites.

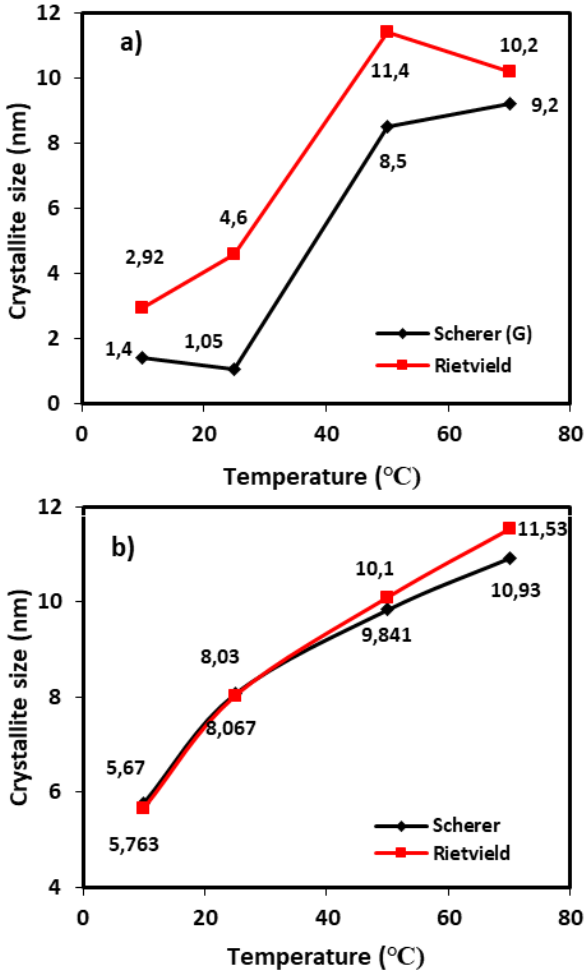

Figure 5. Crystallite size of FeCoNi a) pH 2.5 b) pH 4

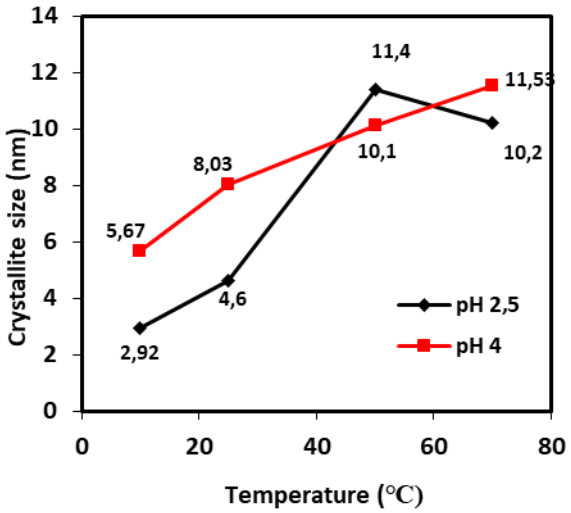

Figure 6. Crystallite size of FeCoNi

This is because the increase in temperature causes the viscosity of the electrolyte solution to decrease which causes an increase in the rate of ion diffusion. The increase in the metal ion diffusion rate causes the supply of ions towards the cathode to increase, which supports a decrease in the cathodic overpotential. The high deposition temperature can also make the adsorption rate of saccharin molecules added to the electrolyte solution decrease [11] [12]. The increase in crystallite size along with increasing pH caused at high pH (pH 4) can encourage the formation and absorption of newly deposited metal hydroxyl. The process that occurs at pH 4 is preceded by an anomaly deposition, which results in a lower Ni metal content due to the absorption of iron hydroxide in the electrolyte [4].

4. Conclusions

The effect of temperature and pH on the characteristics of FeCoNi electrodepositions such as deposition mass, deposition rate, thickness, crystal size and alloy composition has been investigated. By controlling the temperature and pH, FeCoNi alloy nanoparticles with excellent characteristics can be prepared. Higher temperatures and pH of electrolyte solutions can increase the deposition mass, deposition rate, thickness, and crystallite size of a FeCoNi thin film. The higher the pH of the electrolyte solution can increase the amount of Fe and a decrease in the amount of Co, Ni in the precipitate.

Acknowledgements

This work was supported by Universitas Negeri Jakarta and Directorate General of Higher Education (RISTEKDIKTI) Republic of Indonesia through the Research Grant with the contracts No. 41/SP2H/DRPM/LPPM/III/2020.

References

[1] A. Bai. C. Hu. and T. Wen. “Composition control of ternary Fe Ã Co Ã Ni deposits using cyclic v oltammetry.” Electrochim. Acta. vol. 48. pp. 2425–2434. 2003.

[2] H. Kockar et al. “Electrodeposited NiCoFe films from electrolytes with different Fe ion concentrations.” J. Magn. Magn. Mater. vol. 360. pp. 148–151. 2014.

[3] D. H. Riu and S. T. Oh. “Calcination and hydrogen reduction behavior of Fe-Ni and Fe-Co powders from metal nitrates.” Curr. Appl. Phys. vol. 12. no. SUPPL. 2. pp. S188–S191. 2012.

[4] Y. Yang. “Preparation of Fe-Co-Ni ternary alloys with electrodeposition.” Int. J. Electrochem. Sci. vol. 10. no. 6. pp. 5164–5175. 2015.

[5] B.-Y. Zong et al.. “Electrodeposition of granular FeCoNi films with large permeability for microwave applications.” J. Mater. Chem. vol. 21. no. 40. pp. 16042–16048. 2011.

[6] I. Gurrappa and L. Binder. “Electrodeposition of nanostructured coatings and their characterization—

A review." Sci. Technol. Adv. Mater. vol. 9. no. 4. p. 043001. 2008.

[7] A. Mazzi et al. "Materials Science in Semiconductor Processing Physical vapor deposition of mixed-metal oxides based on Fe. Co and Ni as water oxidation catalysts." Mater. Sci. Semicond. Process. pp. 1–4. 2015.

[8] K. Chokprasombat. S. Pinitsoontorn. and S. Maensiri. "Effects of Ni content on nanocrystalline Fe-Co-Ni ternary alloys synthesized by a chemical reduction method." J. Magn. Magn. Mater.. vol. 405. pp. 174–180. 2016.

[9] M. Skompska and K. Zarębska. "Electrodeposition of ZnO Nanorod Arrays on Transparent Conducting Substrates–a Review." Electrochim. Acta. vol. 127. pp. 467–488. 2014.

[10] L. Tian. J. Xu. and S. Xiao. "The influence of pH and bath composition on the properties of Ni-Co coatings synthesized by electrodeposition." Vacuum. vol. 86. no. 1. pp. 27–33. 2011.

[11] H. Natter and R. Hempelmann. "Nanocrystalline copper by pulsed electrodeposition: The effects of organic additives. bath temperature. and pH." J. Phys. Chem. vol. 100. no. 50. pp. 19525–19532. 1996.

[12] W. Fei. L. I. Lei. Q. I. U. Shi-wei. and W. Hua. "Ferronickel preparation using Ni-Fe co-deposition process." J. Cent. South Univ. vol. 23. pp. 3072–3078. 2016.

[13] H. M. M. N. Hennayaka and H. S. Lee. "Structural and optical properties of ZnS thin film grown by pulsed electrodeposition." Thin Solid Films. vol. 548. pp. 86–90. 2013.

[14] P. Christianto. "Analisa Rietveld terhadap Trans-formasi Fasa (α → β) pada Solid Solution Ti-3 at .% Al pada Proses Mechanical Alloying dengan Variasi Milling Time." J. Tek. POMITS. vol. 2. no. 1. pp. 2337–3539. 2013.

[15] M. Sutrisno etal. "The Effects of Aniline Concentration and Deposition Time on Polyaniline Conductance as Substrate in Fe/Ni Electrodeposition." Chem. Mater. vol. 1. no. 1. pp. 12-17. 2022.

[16] M. Karolus and E. Łagiewka. "Crystallite size and lattice strain in nanocrystalline Ni-Mo alloys studied by Rietveld refinement." J. Alloys Compd. vol. 367. no. 1–2. pp. 235–238. 2004.