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The Effects of Deposition Time on Phase and Structure of FeCoNi Films

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Abstract

This study aims to determine the effects of deposition time on the phase and structure of FeCoNi. FeCoNi was prepared by electrodeposition method at room temperature. X-ray diffraction measurement shows the formation of a single phase of FeCoNi at 5 and 10 minutes of deposition, while at 20, 35, and 50 minutes, a new phase was formed, namely CoNi. The obtained FeCoNi and CoNi show a crystal plane at $2\theta = 44.05°$ (111); 51.33° (002); and 75.59° (022) in all different deposition times, indicating the face centered cubic crystal structure. The effect of deposition time on the chemicals composition shows an anomalous co-deposition because Fe has a larger ratio than Co and Ni. The deposition rate and the value of current efficiency were found to be optimum at FeCoNi synthesized for 20 minutes, namely 0.00214 mg/cm^{2}s and 97.00%.

Keywords: FeCoNi, phase, structure, current efficiency, deposition rate

1. Introduction

FeCoNi alloys have excellent soft magnetic properties due to low coercivity, good magnetic saturation [1], and high permeability [2]. In addition, FeCoNi also has good microwave absorption and thermal stability [3], high corrosion resistance, good microstructural hardness [4], and good electrocatalytic activity [5]. Based on these properties, FeCoNi potential to be used as magnetic data storage devices [6], micromagnetic sensors [7], strong coatings [4], flexible electronic devices [8], fuel cell [5], and absorber or shielding of electromagnetic interference [9].

This has led to the development of various methods to synthesize FeCoNi alloys, such as chemical vapor deposition [10], ball milling [11], sputtering [12], electrospinning [13], impregnation [5], and electrodeposition [1]. Among the available methods, electrodeposition is a promising method in the synthesis of thin film nanostructured FeCoNi due to a low-cost process and good results [14][15].

The structure of FeCoNi can be influenced by temperature, pH, deposition time, and additives [16]. Based on previous work, FeCoNi deposited with the addition of saccharin produces a smooth, uniform surface, and has a very low coercivity of 1.6 A/m [8]. The structure and phase of the formed FeCoNi will affect its physical and chemical properties. As reported by Park et al., 2012, the phase change from -FeNi with a face centered cubic (FCC) crystal structure to -CoFe with a body centered cubic (BCC) crystal structure which affects the coercivity from 530 Oe to 512 Oe. In this paper, the phase changes and structures of FeCoNi prepared using electrodeposition method with different deposition time are reported.

2. Materials and Method

The electrolyte used in this study was prepared using analytical grade chemicals, namely iron(II) sulphate heptahydrate ($FeSO_4.7H_2O$), cobalt(II) sulphate heptahydrate ($CoSO_4.7H_2O$), nickel(II) sulphate hexahydrate ($NiSO_4.6H_2O$), boric acid (H_3BO_3), and sodium saccharin ($C_7H_4NNaO_3S$). FeCoNi films were electrodeposited onto indium tin oxide (ITO) substrate. The electrodeposition of FeCoNi thin films was performed in a three-electrode cell. A platinum wire and an Ag/AgCl were used as counter and reference electrodes, respectively. All electrochemical experiments were controlled by eDAQ 163 potentiostat, which were carried out in the potential range −1.3 V versus Ag/AgCl with different deposition time: 5, 10, 20, 35, and 50 minutes. This experiment was carried out in the room temperature. The chemical composition of FeCoNi deposit was determined using an atomic absorption spectrophotometer (AAS, Shimadzu AA-7000). The cristalinity of deposit was characterized by X-ray diffractometer (XRD, PANalytical).

3. Results and Discussion

Figure 1 shows the comparison of the atomic compositions of Fe, Co, and Ni in different deposition time. Based on these results, it is known that the number of Fe atoms decreases with the increasing times from 5 to 50 minutes. This is due to the formation of Fe cations complexes with saccharinate anions so that the adsorption of Fe cations is inhibited. The complex formed between saccharin and Fe cations is $[Fe(C_7H_4NO_3S)_2(H_2O)_4].2H_2O$, where iron is bound to the N atom in saccharin. This is due to a smaller electronegativity of N atom compared to O atom in the saccharinate ion and the hydroxyl ion, so that the N atom more easily gives its free electrons to Fe to form a complex. The iron-saccharin complex which is adsorbed to the active site has a neutral charge so that the competition of Fe with Co and Ni is reduced because the positive species will be attracted to the cathode more than the Iron-saccharin complex species which have a neutral charge [17]. The complex structure between metal (Fe) and saccharin is shown in Figure 2.

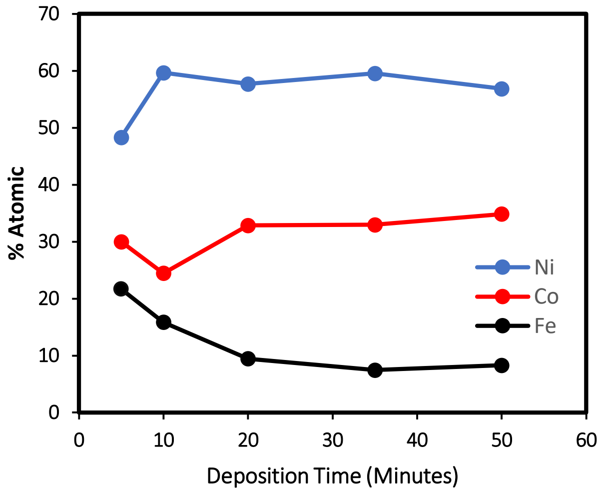

Figure 1. The effect of deposition time on the composition of FeCoNi alloy

The formation of the iron-saccharin complex is easier than that of cobalt-saccharin or nickel-saccharin. This is due to the lower affinity of iron compared to that of cobalt and nickel. The low affinity of iron is due to the larger atomic radius of iron that make the atom has lower effective nuclear charge. This causes iron ions to be more easily polarized than nickel and cobalt. The saccharinate ion has a large molecular size so it is easy to polarize as well. According to the Hard Soft Acid Base theory, soft acids prefer to bind to soft bases and strong acids prefer to bind to strong bases. Metal ions that are easily polarized are soft acids, so Fe ions are soft acids. Ligands that are easily polarized are soft bases, so that the saccharinate ion is a soft base. Therefore, the iron-saccharin complex will be more easily formed than cobalt-saccharin and nickel-saccharin.

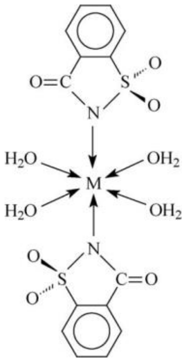

Figure 2. Complex structure between metal and saccharin

The Ni composition significantly increased at 5 to 10 minutes of the deposition time. Then the amount of Ni fluctuated at 20, 35, and 50 minutes. The increase of Ni composition is due to the decrease in Fe atoms which are inhibited in the deposition process; so that Ni, which is a nobler metal, is deposited first [18]. While the number of Co atoms decreased from 5 to 10 minutes. Then the Co composition was continuously increased from 20 to 50 minutes due to the anomalous co-deposition, where the Co deposition was hampered by Fe deposition. Then the increase in Co composition was due to the inhibition of Fe metal being deposited because it formed a complex with saccharin so that Co which competed with Fe could be adsorbed and deposited first. In addition, the metal adsorption ability of metal hydroxide according to Bai et al, 2003 is $Ni(OH)^+ < Co(OH)^+ < Fe(OH)^+$, so that Co is adsorbed more after Fe. The increase in the composition of Ni and Co is because Ni and Co are nobler metals than Fe based on their standard potential values so that Ni and Co are more easily deposited [19].

From this AAS data can also be obtained Composition Ratio Value (CRV) data. The CRV is a value that shows the ratio of the mass percent of Fe, Co, and Ni deposited in the FeCoNi alloy to the total mass percent of Fe, Co and Ni contained in the electrolyte solution. From the CRV, it can be seen the co-deposition behavior of the formed FeCoNi alloy. The CRV is determined by using Equation 1.

$$\text{CRV} = \frac{\%\, Mass\ of\ Fe(Co,Ni)\ in\ deposit}{\%\, Mass\ Fe(Co,Ni)\ in\ electrolyte} \qquad (1)$$

Based on Figure 3, Fe undergo an increase in the composition ratio at all different deposition times. This occurs because of the anomalous co-deposition where the less noble atoms are more easily deposited. The drastic decrease in the ratio of Fe composition was due to the presence of an additive in the form of saccharin which formed a complex with Fe thereby inhibiting the Fe atom deposition process. At more than 20 minutes, the CRV Fe value was close to 1.0, indicating that the Fe ratio in the deposit was almost the same as the ratio in the solution. This is due to the limited number of Fe ions in the solution because low concentrations of FeCoNi were used in the synthesis process.

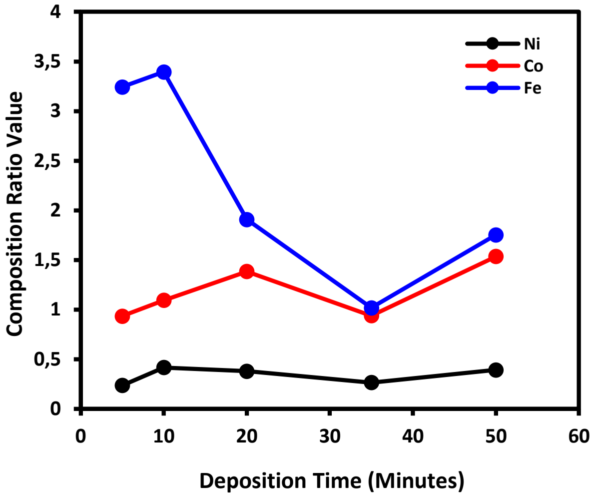

Figure 3. The effect of deposition time on CRV

Metal Co undergo a slight increase and decrease in the deposit ratio with a CRV. The decrease in the ratio was due to anomalous co-deposition in which Fe atoms inhibited Co atomic deposition. The increase in CRV up to 20 minutes indicates that the Co ratio has increased due to Fe atoms inhibited by saccharin by forming a complex, so that the Co atoms are more easily adsorbed to the substrate. This happens because Co is a less noble metal than Ni. Ni experienced a decrease in the composition ratio, which has a CRV value of only 0.24-0.42. This occurs because of the anomalous co-deposition where nickel deposition is inhibited by the Fe or Co co-deposition.

The current efficiency (CE) of FeCoNi electrodeposition was determined to evaluate the effectiveness of the electric current used in electrochemical reactions in the electrodeposition process. The effect of changes in deposition time on the CE value is shown in Figure 4. The resulting CE value increases at 5 to 20 minutes. This was due to the H^+ concentration which increased with increasing deposition time, because H^+ was prevented from migrating around the cathode. Therefore, the reduction of H^+ ions will not occur at the same reaction rate as the formation of H^+ ions which causes hydrogen evolution to be limited and the current used is smaller than that required for metal deposition, so that the CE at the cathode increases during the electrodeposition process [20].

Meanwhile, at 35 and 50 minutes, the CE values decreased. This is because the metal cations in the electrolyte solution form a complex with saccharin, leading the metal charge to become neutral and stable, thereby inhibiting the reduction of monohydroxy metal ions to become metal, so that the CE value decreases. In addition, the evolution of hydrogen that occurs forms hydrogen gas bubbles which hinders the deposition process.

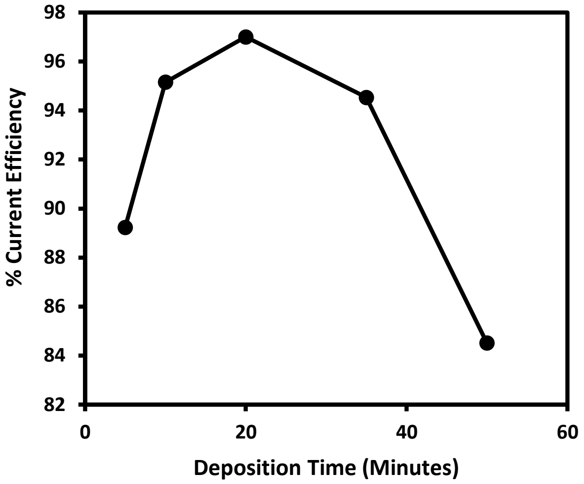

Figure 4. The effect of deposition time on CE

Figure 5 shows the results of the FeCoNi alloy deposition rate at different times. From the data, it can be seen that the deposition rate increased from 5 to 20 minutes. This increase in deposition rate was because the mass transport of metal ions in the electrolyte solution had not been disturbed by saccharin. The increasing concentration of H^+ ions with increasing deposition time also contributed. Therefore, the reduction of H^+ ions will not occur at the same reaction rate with the formation of hydrogen ions. It is encourage results in limited hydrogen evolution and the current required to reduce H^+ ions is smaller than that required for metal deposition, so that the deposition rate increases [20]. When deposition time longer than 20 minutes, deposition rate was found to decrease. This is because the ions in the solution have started to decrease due to deposition so that the mass transport of the metal ions becomes slower which affects the decrease in the deposition rate. In addition, the presence of saccharin in the solution causes metal ions to be inhibited in the deposition process because the longer the time used, more metal ions will form complex and stable, thus inhibiting the deposition process.

Figure 6 shows the diffraction pattern of FeCoNi synthesized with different deposition times. Based on the diffractogram, the diffraction peaks were appeared at 2θ 44.00°, 51.50°, and 76.00°. The peaks are in accordance with the FeCoNi database (COD-96-900-0090) with diffraction peaks at 2θ = 44.22°; 51.52°, and 75.84°. At 20, 35, and 50 minutes, there was a slight shift in peak at 2θ ~44.00° to ~44.40°.

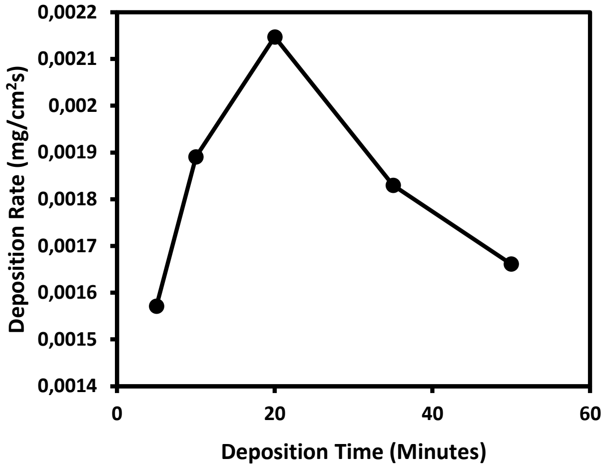

Figure 5. The effect of deposition time on deposition rate

The asymmetrical shape of the peak also indicates the presence of another peak, namely CoNi (ICSD-98-062-4443) which has a diffraction peak at 2θ 44.42°; 51.75°; and 75.84°. The appearance of high peaks at 2θ ~31.50° at 20, 35, and 50 minutes come from the ITO substrate (ICSD-98-005-0847).

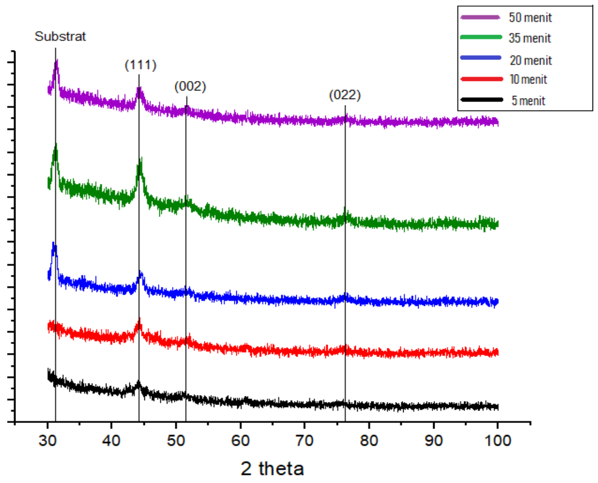

Figure 6. XRD pattern of FeCoNi synthesized at different times deposition

Based on the diffraction pattern, the number of phases, crystal structure, and crystallite size were evaluated using Rietveld method. Table 1 shows the phases formed in the FeCoNi deposits. These results indicate that at deposition times of 5 and 10 minutes only one phase is formed, namely FeCoNi, while at deposition times more than 10 minutes a new phase is formed, namely CoNi. The formation of the CoNi phase was due to the inhibition of the Fe ion deposition process because it formed a complex with saccharin.

HighScore Plus software was used to evaluate XRD pattern and determine the crystallite size. Figure 7 shows the crystallite size obtained from both line profile analysis and Rietvield method.

Table 1. The effect of deposition time on phases composition of of FeCoNi deposits

Time	% Phase	
(minutes)	FeCoNi	CoNi
5	100	-
10	100	-
20	58.8	41.2
35	32.7	67.3
50	46.7	53.3

The longer deposition time, the larger crystallites formed. This is in accordance with Faraday's law which states that the precipitate formed is directly proportional to the synthesis time, so that the larger crystallite size is due to the large number of atoms of Fe, Co, and Ni being deposited [21]. In the measurement using the line profile analysis method, the crystallite size was obtained from 4.58-16.91 nm, while the Rietvield method obtained a crystallite size from 6.17-14.69 nm. The increase in the size of the crystallites formed is due to the increased efficiency at the working electrode due to the low hydrogen evolution rate, so that the current used for metal deposition is less [20].

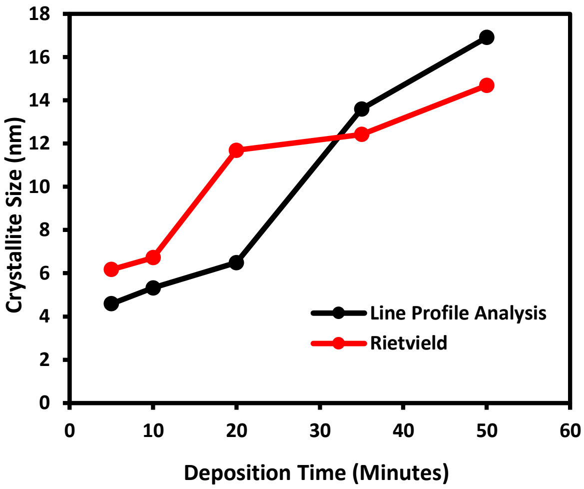

Figure 7. The effect of deposition times on crystallite size

4. Conclusions

The FeCoNi films were prepared with different electrodeposition times. The formation of a single phase of FeCoNi was achieved at 5 and 10 minutes. At longer than 10 minutes, FeCoNi and CoNi phases were formed due to the inhibition of the Fe ions deposition process. The deposits are found to have face FCC structures with fine crystallite size.

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