ABSTRACT

Fe-Co-Ni thin films were electrodeposited using a potentiostatic technique. Phase and structure studies showed that the synthesized deposit was a crystalline phase of a Fe-Co-Ni alloy. The deposit was composed of Fe-Co-Ni nanoparticles, which produces comparable morphologies throughout the surface. Different alloy compositions were obtained with different electrodeposition times, and the content of iron and cobalt decreased with increasing deposition time, in contrast to that of nickel. The anomalous electrodeposition of Fe, Co and Ni characteristics was found to decrease at longer deposition times. This technique was successfully employed to deposit iron, cobalt and nickel homogeneously over the substrate to produce a compact film with a uniform morphology.

Keywords: time-dependent composition, potentiostatic electrodeposition, FeCoNi alloy, thin film.

INTRODUCTION

Ferromagnetic Fe-Co-Ni alloys are known to have potential uses in numerous communications and electronic devices including sensors [1, 2], magnetic writing heads [1, 3] and microwave noise filter [4, 5]. The wide applications of this transition metal-based alloys is attributed to its remarkable soft magnetic properties [6, 7], good corrosion resistance [8] and thermal stability [3, 9]. These excellent properties of the alloy have been the main factors driving research on the development of fabrication methods of Fe-Co-Ni in its most applicable form, namely, a thin layer or film [4, 6, 10].

Among synthesis techniques, electrodeposition has demonstrated advantages in synthesizing metal alloy films without the need for post-treatment [11 - 14]. The properties of the electrodeposited alloy have been found to depend on its microstructure and chemical composition which can be controlled by applied current [15, 16] or potential [17, 18], additives such as cetyltrimethylammonium bromide (CTAB)[19] and saccharin [6, 20] and the chemical composition of the electrolyte [11, 21].

However, to the best of our knowledge from the literature review, no studies on the influence of deposition time on chemical composition the Fe-Co-Ni alloy have been reported, even though deposition time should be among the important parameters for alloy electrodeposition [22, 23]. This is due to the fact that most of the previous investigations were conducted using a laboratory-scale cells. In such kinds of electrochemical cells, the electrodeposition process of metals is generally carried out using inert anodes such as platinum or graphite that make the system reliant solely on the electrolyte as a metal ion source. This condition should cause the gradual decrease of the metal ion concentration during the deposition process. In addition, some metals are nobler than others, making the deposition rate of one metal differ from another. Hence, the decrease in different metals from the same system might vary. This condition could result in a change in the metal deposition rate along the deposition process, which should further...
alter the metal atomic ratio in the deposit over time [24]. In addition, the electrodeposition of iron metal group-based alloys that are known to be anomalous [20, 25]. Hence, controlling the alloy composition has become an interesting challenge. Because the properties of metal alloy films depend on their chemical composition, it is important to investigate the change of the chemical composition ratio of the alloy in the timespan of the deposition.

In this study, the influence of deposition time on the Fe-Co-Ni composition was investigated. The FeCoNi samples were electrodeposited by a potentiostatic technique from a sulfate electrolyte system. The obtained Fe-Co-Ni films were further investigated in order to understand their structure and morphology.

**EXPERIMENTAL**

The electrodeposition processes were performed in an electrolyte containing 0.005 M FeSO$_4$.7H$_2$O, 0.025 M CoSO$_4$.7H$_2$O and 0.170 M NiSO$_4$.6H$_2$O. Boric acid (H$_3$BO$_3$) was added to the electrolyte up to a concentration of 0.400 M. All of the chemicals used in this work were ACS-grade purchased from Merck. All the electrolytes were freshly prepared for each day work using double distilled water.

A three-electrode cell was used to conduct all of the electrochemical studies, along with a computer-controlled eDAQ potentiostat ER466. A platinum wire and Ag/AgCl were used as a counter and a reference electrode, respectively. Indium tin oxide (ITO)-coated polyethylene (PET) with a sheet resistance of 10 Ω sq$^{-1}$ was used as a substrate for a working electrode. Prior to deposition, ITO-PET substrate was cleaned with ethanol and double-distilled water.

Electrodeposition of the Fe-Co-Ni film was then carried out by means of potentiostatic technique on the ITO-PET substrate at a co-deposition potential of -1.100 mV vs. Ag/AgCl. To investigate the effect of deposition time on the film composition, the electrodeposition processes were performed with different durations: 10, 60, 90, and 300 s. The phase and structure of the electrodeposited films were analysed with a diffractogram in the 2θ range of 20 - 90°, obtained using a PANalytical EMPYREAN X-ray diffractometer (XRD) with Cu Kα radiation. The composition of the FeCoNi alloy was quantitatively measured with a Shimadzu atomic absorption spectrophotometer (AAS). The morphology of the electrodeposited film was studied using an FEI INSPECT F50 field emission scanning electron microscope (FESEM). A cross-sectional analysis was also carried out by the FESEM to determine the thickness of the Fe-Co-Ni film. A microanalysis of the observed layer was performed out using an energy dispersive X-ray spectrometer (EDX) coupled to the FESEM to qualitatively differentiate between the deposit and the substrate. To understand the distribution of iron, cobalt and nickel throughout the electrodeposited film, an EDX coupled to a SEM (JEOL, JSM-6510LA) was employed to conduct elemental mapping studies.

**RESULTS AND DISCUSSION**

The Fe-Co-Ni thin film was successfully electrodeposited onto the ITO-PET substrate using a potentiostatic technique with different deposition times. To confirm the formation of a FeCoNi deposit, XRD analysis was carried out on the obtained deposit. Due to the film’s thickness, the XRD measurement was conducted on the sample electrodeposited with a deposition time of 300 s. From the XRD pattern (Fig. 1), three diffracted peaks at 2θ of 44.41°, 51.73° and 76.11° were identified. An analysis performed with HighScore Plus software using the Rietveld refinement approach showed that the XRD pattern match with the Crystal Open Database card no. 96-900-0090 for a Fe-Co-Ni alloy showing diffracted peaks at 2θ of 44.22°, 51.52°, and 75.85° as the diffraction from the planes of (111), (002) and (022), respectively. The observed peaks were also in good agreement with those of a FeCoNi deposit on copper-beryllium strips [26]. This result indicates

![Fig. 1. XRD pattern of the Fe-Co-Ni film obtained with electrodeposition time of 300 s.](image)
that the electrodeposited film consisted of a Fe-Co-Ni crystalline phase.

Fig. 2 shows the morphology of the Fe-Co-Ni film as observed by FESEM. On the micrograph of the Fe-Co-Ni deposit prepared at a deposition time of 90 s, fine particles of Fe-Co-Ni were found to have grown uniformly throughout the substrate (Fig. 2(a)). It was seen that the particles agglomerated and created connections with others to form a dense deposit. However, a vacant area was still clearly observed over the deposit. At a deposition time of 300 s, a more compact deposit (Fig. 2(b)) was formed with no vacant area observed, indicating that the deposit covered the substrate thoroughly. In this case, the longer deposition time resulted in more deposit growth. An FESEM analysis was also conducted on the cross-section of the FeCoNi deposit to measure the thickness of the film. The micrograph showed that the film was constructed of a layer with a thickness range of 145 - 160 nm (Fig. 3(a)).

A microanalysis of the observed layer was carried out using an EDX coupled to an FESEM to qualitatively differentiate between Fe-Co-Ni deposit and the substrate. Based on the spectrum shown in Figs. 3b and 3c, each layer showed an obviously different chemical composition. The observed peaks from the EDX spectrum confirmed that the first layer was the electrodeposited Fe-Co-Ni film. Peaks with no attribute were those of a gold and palladium coating that had been coated onto the film surface prior to the FESEM analysis. While the second analysed layer was the PET substrate, composed of carbon and oxygen, no deposited metals were detected at this location. To further investigate the distribution
of the elements throughout the electrodeposited film, an EDX coupled to an FESEM was employed to conduct the elemental mapping of Fe, Co and Ni over the deposit. The three elements are indicated by yellow, red and green dots, respectively (Fig. 4). It can be seen that all three transition metals were distributed uniformly throughout the electrodeposited film, reflecting solid solution formation and a homogeneous film, which was formed successfully in the present approach. The current findings confirmed the advantage of electrodeposition in producing a chemically homogenised film. In this technique, a deposit grown through ion reduction offer the opportunity of the metals to co-deposit all at once.

A quantitative analysis from the EDX measurement of the deposit obtained at a deposition time of 300 s showed that the film contained 9.74 wt. % Fe, 40.80 wt. % Co and 47.58 wt. % Ni. This result is in agreement with the quantitative analysis conducted using AAS, as shown in Table 1. The ratio of Fe:Co: Ni in the deposit was 1:4.83:5.24, which was different from the ratio of the metal ions in the electrolyte (1:5:34). This result indicates that co-deposition of Fe, Co, and Ni takes place anomalously. Anomalous electrodeposition is seen when a less noble metal (Fe) is preferentially electrodeposited from the system over a more noble metal, in this case Ni. It is well known that alloys co-deposition of iron-group metals are commonly found as anomalous co-deposition. In this work, anomalous co-deposition may have occurred due to the adsorption of metal monohydroxide ions over the working electrode surface [27, 28]. The metal monohydroxide ions compete with each other to diffuse, reaching the substrate surface site as adsorbed species before being reduced as deposited metals. In this case, the adsorption preference of the monohydroxide ion of Fe, Fe(OH)$^+$, was greater than that of the monohydroxide ion of Co (Co(OH)$^+$) and Ni (Ni(OH)$^+$)[29,30].

For the purpose of understanding the influence of deposition time on deposit composition, AAS measures were conducted on the Fe-Co-Ni electrodeposited at different electrodeposition times. The composition shown in Fig. 5 indicated that the mass fraction of iron, cobalt and nickel were controlled by the deposition time. From the figure, the mass fraction of the three metals in the films that were electrodeposited at different deposition times are summarised. The content of Fe decreased with increasing of deposition time. This was in contrast to the very high Ni content. The lower initial concentrations of Fe (0.005 M) in the electrolyte system compare to that of Ni (0.170 M) and Co (0.025 M) caused a lack of availability of the ion sources at longer deposition times. This condition might have gradually decreased the formation of Fe(OH)$^+$ ions as a preferred species to

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<th>Alat</th>
<th>Composition (wt. %)</th>
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<tr>
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<td>Fe</td>
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<td>EDX</td>
<td>9.74</td>
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<td>AAS</td>
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Fig. 4. Elemental mapping of the Fe-Co-Ni film electrodeposited with deposition time of 300 s.
be absorbed on the substrate, which suppressed Fe deposition. On the other hand, since the deposition process was controlled at fix potential, the decrease of Fe(OH)\(^+\) ion in the bulk solution would reduce the competing species for Co(OH)\(^+\) and Ni(OH)\(^+\) hence escalating mass transport of both ions toward the substrate surface. This condition has progressively increased Co and Ni deposition at longer deposition times. As a result, a relatively high content deviation between Fe and the more noble metals (Co and Ni) was observed at 300 s. In this case, the obtained composition shows that the anomalous co-deposition diminished at longer deposition time.

**CONCLUSIONS**

An electrodeposition technique was employed to synthesize a Fe-Co-Ni film. The electrodeposited film was composed of a crystalline phase of the Fe-Co-Ni alloy that formed a thin deposit with a homogeneous morphology throughout the film’s surface. A compact film was obtained after a relatively longer deposition time, in this case at 300 s. The Fe-Co-Ni electrodeposition was found to be an anomalous process in which a less noble metal (Fe) was deposited preferentially over a more noble metal (Ni). From the study of the effect of electrodeposition time on chemical composition, it was found the Ni content increased gradually at longer deposition times. This means that the anomalous characteristic decrease along the deposition process can be attributed to a continuous decline of the Fe(OH)\(^+\) ions as a competing species for Ni(OH)\(^+\) ions to be absorbed on the substrate as an intermediate stage prior to metal deposition.


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