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Regular Article

Electrochemical production of Fe-Cu films: determination of the deposition potentials and their effect on microstructural and magnetic properties

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Abstract. Fe-Cu alloys were grown on polycrystalline titanium substrates after determining the suitable deposition potentials. Based on the results obtained from cyclic voltammetry curves, a potential region between –1.8 V and –2.3 V vs. saturated calomel electrode (SCE) was selected. During growth, the electrochemical characterizations of the films were made by recording the current-time transients. The structure of films becomes more brittle with the increase of the deposition potential over –2.3 V vs. SCE due to extreme hydrogen liberation from cathode surface. The structural analysis by the X-ray diffraction demonstrated that the films have a typical body centered cubic of α-Fe preferentially grown in the (211) direction. The grain sizes, lattice parameters and interplanar spacings were also calculated. Energy dispersive X-ray spectroscopy measurements demonstrated that the ratio of Fe:Cu was almost the same. The magnetic analysis by vibrating sample magnetometer indicated that the coercivity of the films was slightly affected by the deposition potential.

PACS. 75.50.Bb Fe and its alloys – 75.70.Ak Magnetic properties of monolayers and thin films – 75.70.Kw Domain structure – 82.45.Aa Electrochemical synthesis

1 Introduction

Since magnetic films present important applications in data storage, actuator and sensor technology, such films have mostly been produced using thermal evaporation, sputtering, molecular beam epitaxy and electrodeposition [1–4]. Electrodeposition is an electrochemical process by which metal is deposited on a substrate by passing a current through an electrolyte. Besides, it does not require high vacuum system and so can provide the production of high quality films in a cheaper and simpler way at room temperature and pressure [1,5].

The properties of electrodeposited Fe-Cu alloys are affected by a lot of factors, including the deposition potentials [6,7]. Nevertheless, it has been undertaken a lot of efforts to grow Fe-Cu alloys by electrodeposition since Cu has highly noble character with respect to Fe [8]. Therefore, difficulties always occurred during the production and characterization of the electrodeposited Fe-Cu alloys.

In this study, the proper deposition potentials for Fe-Cu films were obtained, and their effect on microstructural and magnetic properties was studied. It was seen that the properties of films were observed to be slightly affected by deposition potential.

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2 Experimental

The electrodeposition system which was used in this work consists of a potentiostat/galvanostat (EGG model 362) with three electrodes and an electrochemical cell. Polycrystalline titanium (Ti) substrates are used as cathodes, a platinum (Pt) plate as the anode. The reference electrode was a saturated calomel electrode (SCE). All potentials were referred to SCE. All experiments were carried out at room temperature. Prior to deposition, Ti substrates were polished with emery paper mechanically and cleaned in the distilled water. Afterwards, the polished surface was covered with electroplating tape, except for the area to be deposited. Finally, substrate was rinsed, in turn, in distilled water, 10% H_2SO_4 and then distilled water. After deposition, all films were stored in desiccators until characterization.

The cyclic-voltammogram (CV) curve of the electrolyte was taken to estimate the suitable deposition potentials with a potential scan rate of 20 mV/s. The scans were performed on a Pt wire electrode with an area of $\sim$0.02 cm^2 in the cathodic direction from +1.0 V to –1.8 V. During the growth process, the current was recorded as a function of time.

The structural analysis of the films was achieved using the X-ray diffraction technique (XRD, Rigaku – rint

2200) with Cu-K_α radiation. The analysis of surface morphology and compositional analysis were done by the scanning electron microscope (SEM, Zeiss Supra 50 Vp) and energy dispersive X-ray spectroscopy (EDX) in SEM, respectively. The magnetic measurements were performed with a commercial vibrating sample magnetometer (VSM, ADE Technologies EV9) at ±10 kOe.

3 Results and discussion

3.1 Determination of the deposition potentials

The Fe-Cu alloys were electrodeposited on a hexagonal closed packed polycrystalline Ti substrates from the electrolyte composed of 1 M $FeSO_4{\cdot}7H_2O$, 0.01 M $CuSO_4{\cdot}5H_2O$, 0.1 M H_3BO_3 and its pH was 2.8 ± 0.2. The EDX measurements showed that the Cu ratio in the films was between 2.3 ± 0.1 wt.% and 2.5 ± 0.1 wt.%.

Before deposition of the films, the CV curves of the electrolytes were obtained to study the electrochemical characterizations of Fe and Cu ions. Figure 1 indicates the CV curve of the solution used to deposit Fe-Cu alloy and the solution containing Cu ion only. In Figure 1a, there is a slight deposition until around –1.2 V. After this point, the cathodic current begins to flow and continuously increases to around –1.8 V. After the reversal of the scan direction, the current follows almost the same potential dependence up to about –0.8 V. In Figure 1b, which is the CV curve of the electrolyte containing only 0.01 M $CuSO_4{\cdot}5H_2O$, it was seen that a slight current occurred between anode and cathode confirming small amount of Cu in the electrolyte. When the electrolyte is void of Fe ion, the current almost remains zero until the deposition of Cu (–0.7 V). According to results obtained from the polarization curve, the deposition potentials for Fe-Cu should be higher than –1.2 V. Therefore, the films can be grown at the potential of over –1.2 V.

The current-time transients of the films produced at the –1.8 V, –2.0 V and –2.3 V for the first 30 s of deposition period were shown in Figure 2. As seen from the figure, at the beginning of the applied potentials, a high cathodic current is seen for a short time of ~2 s compared to the deposition of ~200 s. Then, the current rapidly decreases, due to the depletion of metal ion concentrations close to the electrode surface, and hence reaches a stable value. As the cathode potential is increased the current also increases. It is seen that Fe-Cu alloys which deposited at the different cathode potentials have the same type of growth mode and the films were deposited correctly and orderly with the constant current values.

To clearly see the surface morphology of the films, SEM images were obtained. The SEM image of the film produced at –2.5 V was illustrated in Figure 3. It was shown that the film has so many splits and a brittle structure as opposite to the films grown at the potential region of –1.8 V and –2.3 V, see Table 1. This may be due to extreme hydrogen liberation from cathode surface. The film was quite hard to handle for microstructural and magnetic measurements. All of the films were generally in grey color as in [9], and the increase of the deposition potential makes the film morphology more brittle and split structure. Also surface of the film looks like a cauliflower structure as similar to the other films produced in this study. On the other hand, when the deposition potential was under the –1.2 V the deposition of the films did not occur due to the fact that this potential value is lower than the potential required for the Fe deposition. This result agrees with CV curve for the electrolyte. The observed features of films were presented in Table 1. Based on the results obtained from the CV curves, current – time transients

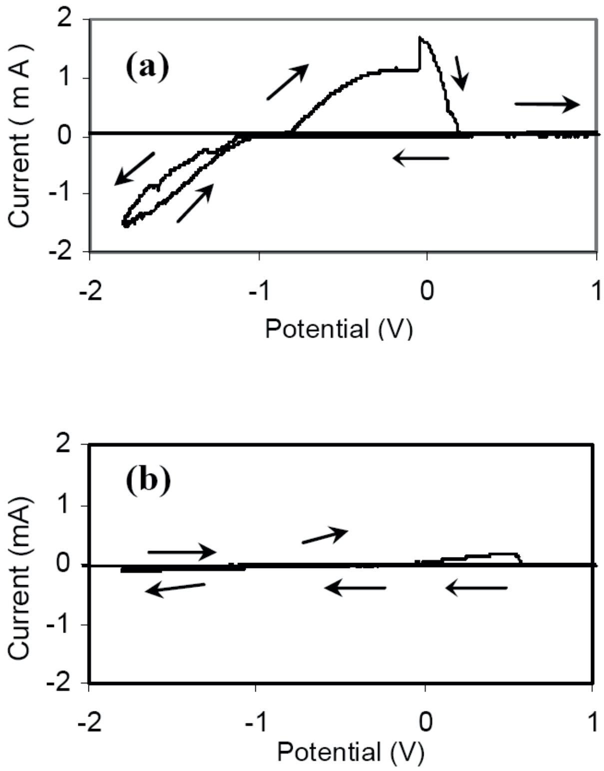

Fig. 1. (a) CV curve for the electrolyte used to deposit Fe-Cu alloys (1 M $FeSO_4{\cdot}7H_2O$, 0.01 M $CuSO_4{\cdot}5H_2O$ and 0.1 M H_3BO_3); (b) CV curve for the electrolyte without Fe ion.

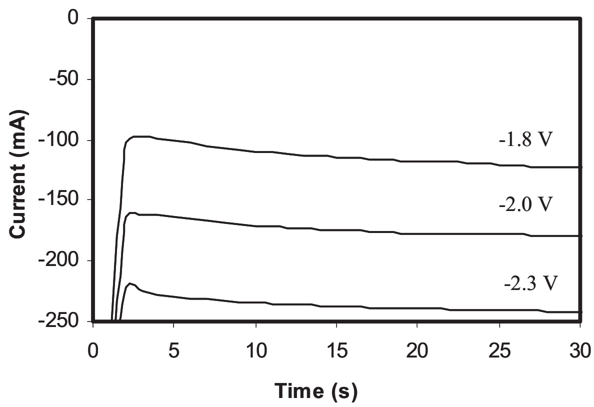

Fig. 2. Current-time transients for Fe-Cu alloys deposited at –1.8 V, –2.0 V and –2.3 V.

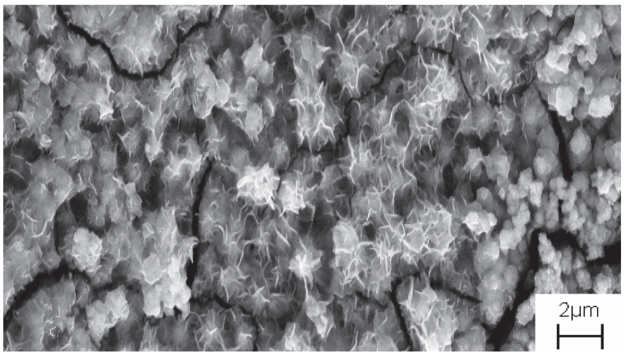

Fig. 3. SEM image of the Fe-Cu alloy produced at the –2.5 V.

Table 1. Physical appearances of the film formation at different potentials.

Deposition Potentials (V)	Physical appearances	Film Formation
–0.7	Orange/Patchy and quite thin	No
–1.2	Dark orange/Quite brittle and thin	No
–1.8	Gray/Slightly brittle	Yes
–2.0	Gray/Slightly brittle	Yes
–2.3	Grayish/Slightly brittle	Yes
–2.5	Dark gray/Quite brittle	No

and the films produced (see Tab. 1) a potential region between –1.8 V and –2.3 V was selected for the production of Fe-Cu alloys.

3.2 Characterizations

In order to understand the effect of deposition potentials on the properties of the Fe-Cu films, the lowest (–1.8 V) and the highest (–2.3 V) deposition potentials were used to investigate the films. Figure 4 shows the XRD trace for Fe-Cu alloys produced at –1.8 V and –2.3 V, respectively. Both films give a strong Bragg diffraction peak confirming the presence of a polycrystalline α-Fe phase and the films have a typical body centered cubic (bcc) crystal structure. The peaks labelled as Fe-Cu (110), Fe-Cu (200), Fe-Cu (211), Fe-Cu (220), correspond to the main Bragg reflections for (110), (200), (211) and (220) planes of Fe-Cu, respectively. Also it is clearly seen that these peaks absent from the reflection of face centered cubic (fcc) Cu planes. The compositional analysis of the films produced at the low and high deposition potentials indicated that the all of the films consisted of less than 3 wt.% Cu. This probably may happen from too small reflection on Cu planes due to the quite low amount of Cu (less than 3%) in the films as confirmed by EDX measurements. The crystalline structure of Fe-Cu films are verified with the compositional analysis as indicated that the composition regions of a bcc phase for 0–70 at.% Cu and a fcc phase for 73–100 at.% Cu are seen [10] and also Fe-rich Fe-Cu alloys crystallize in the α-Fe bcc phase [11]. The preferential orientation was found from intensities of the peaks in the XRD pattern as

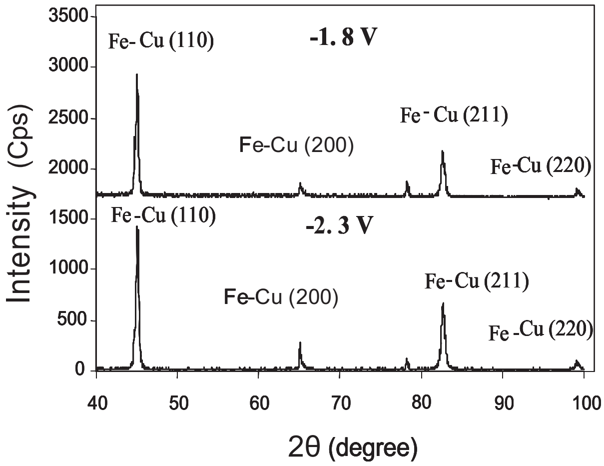

Fig. 4. XRD patterns of the films deposited at low and high cathode potentials.

indicated in [12]. It was understood that the Fe-Cu alloys textured preferentially in the (211) direction.

The data obtained from the XRD was also used to calculate the lattice parameters, grain sizes and interplanar spacings, $d_{(hkl)}$. The lattice parameters were calculated as about 0.2866 ± 0.0002 nm by using the least squares technique. There was a slightly change in lattice parameters, which were in the error limits. The grain sizes were calculated as 28.9 nm and 24.5 nm for film produced at –1.8 V and –2.3 V respectively by using the Scherrer formula [13]. The $d_{(hkl)}$, from the positions of Fe-Cu (110), Fe-Cu (200) and Fe-Cu (211) peaks were calculated. They were 0.2012 nm, 0.1432 nm, 0.1167 nm at –1.8 V and 0.2012 nm, 0.1429 nm, 0.1167 nm at –2.3 V, respectively. It is thus noted that the change in deposition potential resulted in a slightly change in the microstructure of the films. The results can be verified by the fact that the films have nearly the same composition as indicated in EDX results.

Figure 5 shows the hysteresis loops of the films produced at –1.8 V and –2.3 V in the film plane. In the case of the film produced at –1.8 V, the saturation magnetization, M_s is 1630 emu/cm^3, while 1240 emu/cm^3 was obtained in the film produced at –2.3 V. The coercivity, H_c values remain almost constant irrespective of deposition potential and are 24 Oe and 25 Oe at –1.8 V and –2.3 V, respectively. Including the same Cu ratio at the low and high deposition potentials did not cause a considerable change in the microstructural and magnetic properties.

4 Conclusions

There have been a lot of efforts to grow Fe-Cu alloys by the electrodeposition technique since Cu shows a highly noble character with respect to Fe. The proper film structures can be formed under the potential of –1.8 V to –2.3 V. Therefore, the films for characterization reason were produced at the potential region of –1.8 V and –2.3 V.

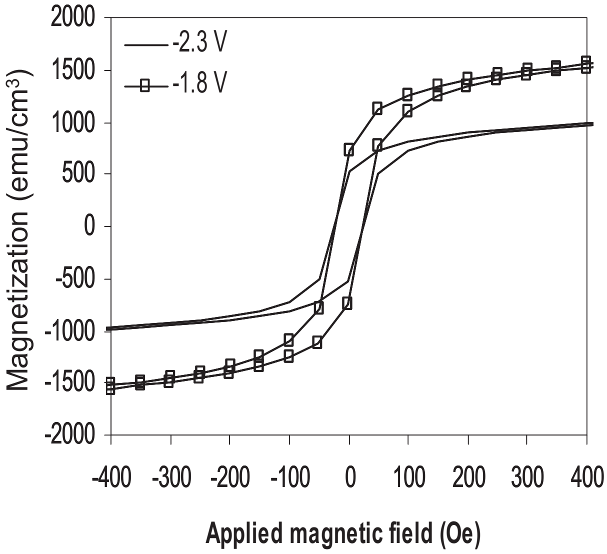

Fig. 5. The hysteresis loops of the films produced at –1.8 V and –2.3 V.

The films were generally burn-like deposits and so brittle at over –2.3 V. It was found that the films exhibit bcc crystalline structure of α-Fe and preferentially grown in the (211) direction. The lattice parameters, grain sizes, the $d_{(hkl)}$, the H_c and the composition of films were slightly affected by the deposition potentials caused by quite a small change of Cu ratio in the films according to the EDX analysis. This work provides a good specimen for the possible production Fe-Cu alloys when considering the potential applications of magnetic sensors and actuators.

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