Study on Anomalous Codeposition Phenomenon of CoNi Magnetic Films

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CoNi alloy films prepared from electrolytes with various concentrations of cobalt ions were studied in the paper. Influences of different cobalt ions concentrations on electrochemistry processes, components, microstructures, surface morphologies and magnetic properties of CoNi films were investigated. It was found that CoNi film plating was a kind of anomalous codeposition process. The percentage of cobalt content in CoNi films was higher than that of in the electrolyte. Moreover, with the rise of cobalt ions concentrations, the percentage of cobalt content in the samples increased gradually. CoNi films possessed crystal structures with four stronger diffraction peaks. However, CoNi films prepared from bath with higher cobalt ions possessed hcp structures which contributed to dendrite structures resulting in the increase of coercivity.

Keywords : CoNi films, anomalous codeposition, Coercivity

1. Introduction

Magnetic thin films play a significant role in the field of microelectronic systems, which could be widely used in micro-switches, sensors, magnetic heads and so on [1-5]. Cobalt and nickel possess optimal magnetic and mechanical properties. Magnetic properties of CoNi alloys derive from exchange of 3d electrons. High melting point of CoNi alloys contribute directly to great mechanical properties [6-8]. Many investigations have been done so far about CoNi alloy thin films. For example, Aubry studied effects of Ni concentration on structure and magnetic properties of CoNi alloys [9]. Surface texture properties of CoNi alloys formed with unipolar and bipolar plating were investigated by Vazquez [10]. CoNi and FeNi alloy nanoparticles were synthesized by Solanki [11]. CoNi alloys with chain-like microstructures were fabricated by Dan [12]. Many ways could be utilized to prepare CoNi alloy thin films, such as electrodeposition, physical vapor deposition, chemical vapor deposition, molecular beam expitaxy and so on. Each kind of preparation technology possesses the advantage and disadvantage. However, when it comes to the aspects of economy and efficiency, electrodeposition technology is considered as a kind of very effective and cheap approach to fabricate alloy films, which does not need too much equipment, but offers highly selective and conformal coatings. Therefore, some works have been done so far about obtaining CoNi alloy films by the electrodeposition technology [13-19]. It was found out that CoNi plating process belonged to anomalous codeposition which indicated that composition of alloy films was different from that of in electrolyte composition. 3d transition metal ferromagnet, such as Fe, Co and Ni usually exhibits anomalous phenomenon during codeposition process. Mechanism of anomalous codeposition is complicated. Many theories have been done to study anomalous codeposition, such as hydroxide colloid theory, underpotential deposition and so on. Composition of CoNi alloys could be affected because of the anomalous codeposition phenomenon which contributed directly to magnetic and mechanical properties. Therefore, anomalous codeposition phenomenon of CoNi alloys based on hydroxide colloid theory was studied in the paper to investigate its influences on electrochemistry mechanism, composition, structure, surface morphology and magnetic performance of CoNi alloy films.

2. Experimental

Electrodeposition process of CoNi alloy films was carried out based on the traditional three electrodes system by Princeton 2273. Meanwhile, copper sheet with 1×1 cm^2 was chosen as working electrode while platinum sheet with 2×2 cm^2 was utilized as counter electrode. In order

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Table 1. Bath composition and electrodeposition parameters.

Bath composition and condition	Value
NiSO$_4$	0.05~0.09 mol/L
CoSO$_4$	0.01~0.05 mol/L
H$_3$BO$_3$	0.5 mol/L
pH	3
Temperature	303 K
Deposition time	1800 s
Current density	2 A/dm^2

to make the data more precisely, saturated calomel electrode (SCE) was chosen as the reference electrode. Codeposition phenomenon would occur when deposition voltages of two metals were similar. Standard deposition voltage of nickel and cobalt was –0.23 V and –0.28 V respectively. Therefore, it was possible to obtain CoNi alloy films in the solution with cobalt and nickel ions. The electrolyte composition and electrodeposition conditions were listed in Table 1.

As shown in Table 1, NiSO$_4$ and CoSO$_4$ were used as source of nickel and cobalt ions. Boric acid was served as buffering agent during electrodeposition process. A polish machine (MP-1A) was utilized to polish the surface of copper substrate before the experiment to make the data more precisely. At last, the copper substrate was immerged into 100 ml acid electrolyte to perform electrodeposition for half an hour at 303 K. Princeton 2273 electrochemistry station was used to research electrochemical process of CoNi codeposition. Quartzmicrobalance (QCM25) was utilized to monitor the deposition mass on cathode. It is known that the quartzmicrobalance possesses extremely sensitive sensors which are capable of measuring mass changes in μg/cm^2.

3. Results and Discussion

3.1. Electrochemistry process of CoNi codeposition

In order to study the electrochemistry process of CoNi codeposition, cyclic voltammetry curves combined with quartzmicrobalance were investigated. The typical cyclic voltammetry curve of CoNi codeposition process at 20 mV/s scan rate in the solution of 0.05 M Co^{2+} and 0.05 M Ni^{2+} was shown in Fig. 1.

As seen in Fig. 1, cathode current and deposition mass were nearly equal to zero when the scanning voltage increased from 0 to –1.0 V$_{SCE}$ (position a) which indicated that there was no CoNi codeposition in this range. However, with the scanning voltage moved more negative than –1.0 V$_{SCE}$, cathode current and deposition mass increased gradually. Larger scanning voltage intended to get stronger cathode polarization that contributed directly to the increase of cathode current and deposition mass. According to Fig. 1 (b), when scanning voltage arrived at position b (–2.5 V$_{SCE}$), CoNi coating with mass of 120 μg could be obtained. No typical reduction peaks were detected from position a to b. This phenomenon could determine that CoNi deposition process basically belonged to electrochemistry controlling mechanism. Electrochemical reaction on the surface of electrode during electrodeposition process is considered as two kinds of limiting mechanisms: electrochemistry and diffusion controlling. If the diffusion rate of species is faster than reaction rate in the plating system, the electrodeposition system is controlled by electrochemistry. However, during the plating process, if diffusion rate of species is slower than reaction rate, the electrodeposition system is controlled by diffusion. Oxidization peaks of cobalt and nickel were obviously observed when the scanning voltage moved from position a to e. Oxidization peaks of cobalt
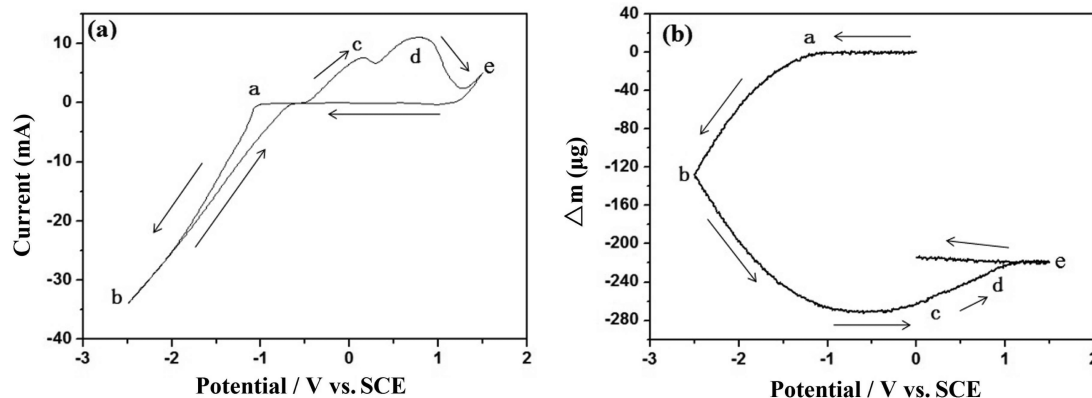

Fig. 1. Cyclic voltammogram of CoNi plating process (working electrode: 1.37 cm^2 Au disc of QCM; counter electrode: 2 × 2 cm^2 platinum sheet; reference electrode: SCE; 0.05 M NiSO$_4$ + 0.05 M CoSO$_4$ with scan rate 20 mv/s).
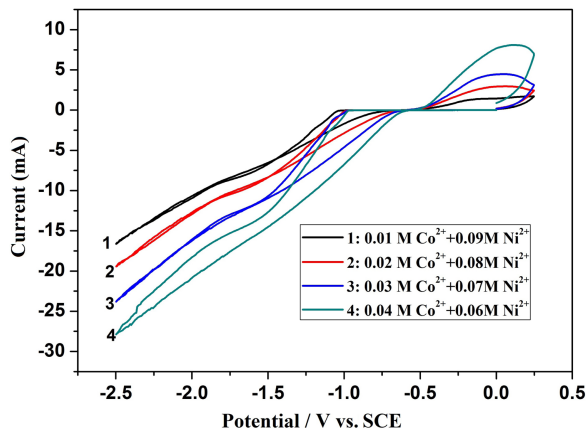
Fig. 2. (Color online) Cyclic voltammogram of CoNi plating process (working electrode: 1×1 cm^2 copper sheet; counter electrode: 2×2 cm^2 platinum sheet; reference electrode: SCE; scan rate 20 mv/s).

Fig. 3. (Color online) Compositions of CoNi films obtained from baths with different concentrations of nickel and cobalt ions.

and nickel were observed respectively at position c and d. It was found out that oxidization peak of cobalt was more negative that nickel which meant that nickel possessed better corrosion resistance than cobalt. Standard deposition potential of nickel was more positive than that of cobalt. According to the deposition theory, nickel is easier to be deposited than cobalt. However, during the codeposition process of CoNi, it was found that cobalt content in CoNi alloys deposited from bath with same amount of cobalt and nickel ions was higher than that of nickel. This phenomenon was considered as anomalous codeposition. Cyclic voltammetry curves of electrolytes with different concentrations of cobalt and nickel ions were investigated to study the anomalous codeposition process shown in Fig. 2.

According to Fig. 2, obvious cathode polarization current was observed at the potential of about −0.8 V$_{SCE}$. In addition, with the scanning voltage moved more negative, stronger polarization phenomenon was detected. No typical reduction peaks were found and the conspicuous oxidization peak appeared at about 0 V$_{SCE}$. The cathode current increased gradually with the rise on concentration of cobalt ions in the bath. Higher concentration of cobalt ions in the electrolyte contributed directly to the increase of cathode current that resulted in improvement of cobalt electrodeposition rate. Moreover, cobalt possessed poorer corrosion resistance than nickel. Plating bath with higher cobalt ions tended to obtain CoNi films with higher cobalt composition which could result in the increase of oxidization current when scanning voltage moved more positive. Detail information about composition of CoNi alloy films obtained from baths with different concentrations of cobalt and nickel ions was shown in Fig. 3.
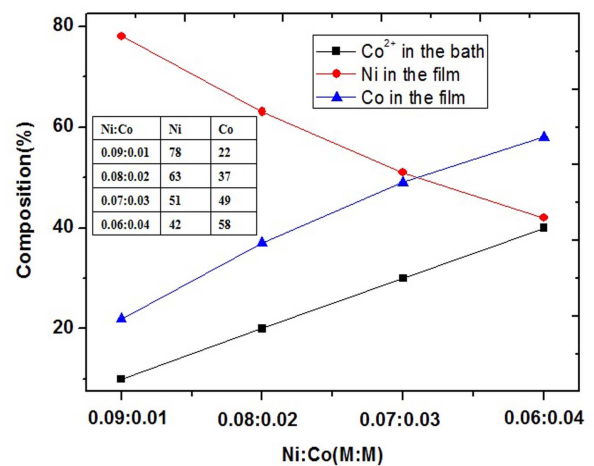
The amounts of nickel decreased from 78% to 42%, but cobalt contents increased from 22% to 58% as the mole ratio of Ni^{2+} and Co^{2+} ranged from 0.09:0.01 to 0.06:0.04. From the data shown in Fig. 3, it was obvious that the percentage of cobalt content in CoNi films was higher than that of in the electrolyte, which indicated a kind of anomalous codeposition process. The phenomenon of anomalous codeposition was found and reported [20, 21]. Meanwhile, the hydroxide colloid theory was accepted by most researchers. During plating process, metal ions and hydrogen ions were extremely consumed near cathode, resulting in the rise on pH value that attributed directly to formation of hydroxide colloid. It is believed that Ksp value (solubility product constant) of Co(OH)$_2$ is smaller than Ni(OH)$_2$. Therefore, compare to Ni(OH)$_2$, Co(OH)$_2$ is favored to be absorbed in aqueous solution.

$$CO^{2+} + 2OH^- \Leftrightarrow Co(OH)_2 \qquad (1)$$
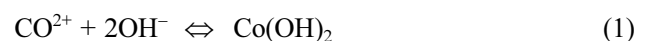
The Co(OH)$_2$ colloids absorbed on the surface of cathode inhibited the transportation of nickel ions. However, Co(OH)$^+$ could transport through Co(OH)$_2$ colloids to reduce into cobalt. Therefore, the absorption Co(OH)$^+$ and Co(OH)$_2$ restrained the deposition process of nickel resulting in the different of cobalt percentage in coatings and electrolytes. All in all, the anomalous codeposition phenomenon was caused by the absorption of Co(OH)$^+$ and Co(OH)$_2$. Detail information about hydroxide colloid theory and changing of pH values during plating process was studied by many researchers [22-25].

3.2. Microstructure and surface morphology of CoNi alloy films

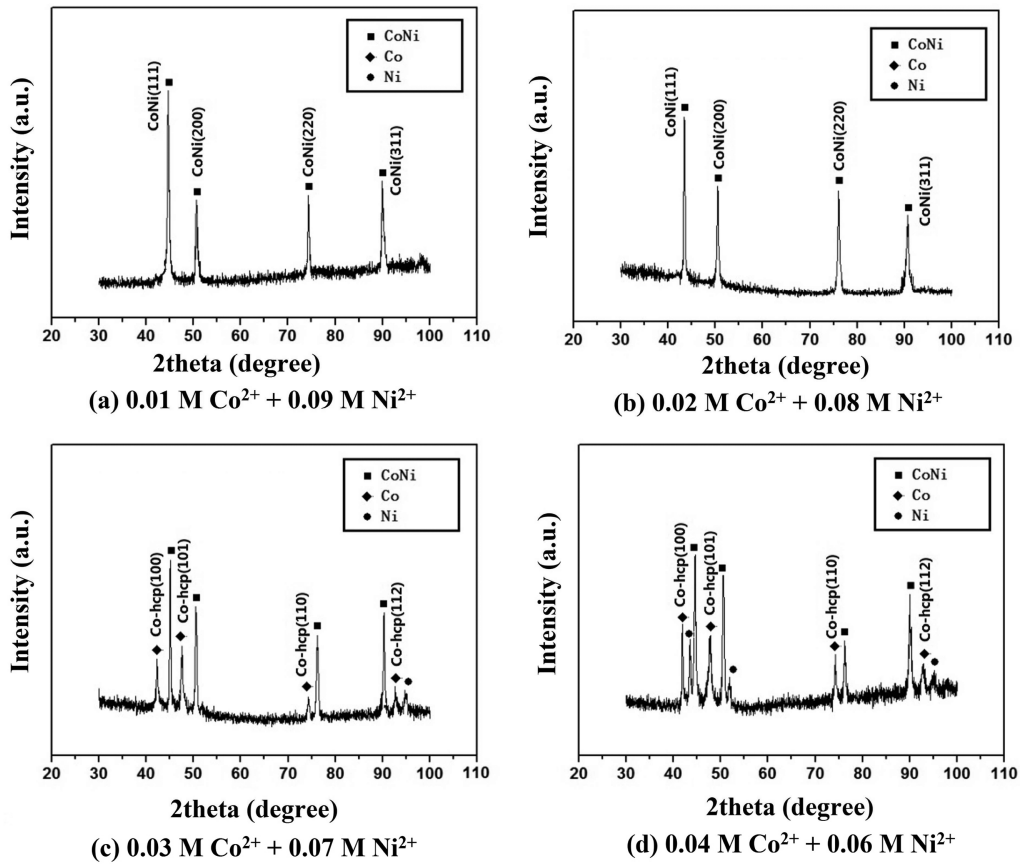Microstructures of CoNi alloy films were shown in Fig.

Fig. 4. XRD patterns of CoNi films obtained from baths with different concentrations of cobalt and nickel ions.

4. As seen in Fig. 4, CoNi samples possessed four strong diffraction peaks with CoNi(111), CoNi(200), CoNi(220) and CoNi(311). The diffraction intensities were conspicuous and strong which indicated that electrodeposited films possessed the crystalline CoNi alloy. With the increase of cobalt contents in the electrolyte, Co-hcp (cobalt with hcp structure) could be observed in the XRD pattern. Moreover, electrolyte with higher cobalt contents tended to prepare CoNi films with stronger Co-hcp diffraction peaks.

Surface morphology of CoNi films obtained through electrolytes with different concentrations of cobalt and nickel ions was shown in Fig. 5. CoNi films were a kind of typical nodular structure. With the increase of cobalt ions in the bath, different surface morphologies were detected. The films transferred from nodular structures to dendrite structures. CoNi films prepared from bath with higher cobalt ions possessed Co-hcp which contributed to dendrite structures. In addition, CoNi films with smaller and denser dendrite structures could be observed with the increase of cobalt ions in the bath. This phenomenon was in accord with some results reported by others [26-28].

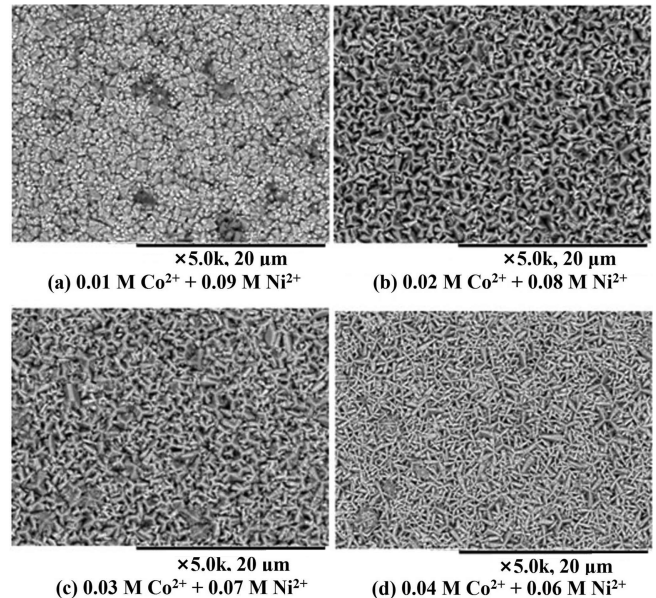Magnetic properties of CoNi films were investigated by

Fig. 5. Surface morphology of CoNi films obtained from baths with different concentrations of cobalt and nickel ions.

VSM curves. Regarding to Fig. 6, it was clear that, CoNi films obtained from the electrolyte with higher cobalt
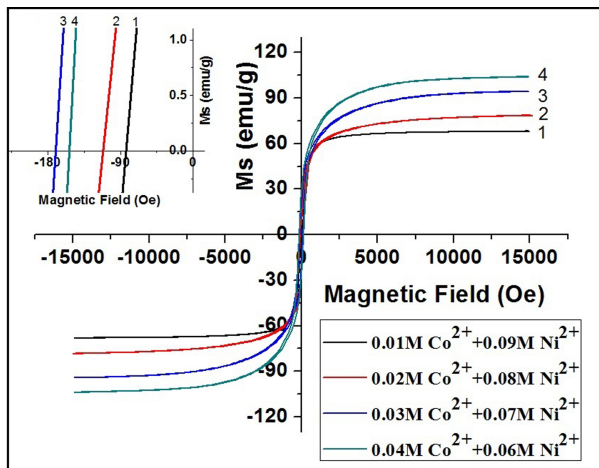
Fig. 6. (Color online) Magnetic performance of CoNi films fabricated from baths with different concentrations of cobalt and nickel ions.

concentraiton possessed better coercivity and saturation magnetization. With the increase of cobalt ions from 0.01 M to 0.04 M, coercivity of samples changed from 58 to 139 Oe while the saturation magnetization improved from 64 to 101 emu/g. CoNi films prepared from the bath with higher concentration of cobalt ions possessed Co-hcp structures which might enter into the crystal lattice to hinder domain wall displacement resulting in the increase of coercivity.

4. Conclusion

CoNi alloy films prepared from baths of different cobalt concentrations were investigated. Effects of cobalt ions concentrations on components, microstructures, surface morphologies and magnetic properties of CoNi films were studied. The conclusions were as followings:

1. During the codeposition process of CoNi, it was obvious that the percentage of cobalt content in CoNi films was higher than that of in the electrolyte, which indicated a kind of anomalous codeposition process. In addition, higher concentration of cobalt ions in the electrolyte contributed directly to the increase of cathode current that resulted in improvement of cobalt contents in the samples.

2. CoNi samples possessed four strong diffraction peaks with CoNi(111), CoNi(200), CoNi(220) and CoNi(311). With the increase of cobalt contents in the electrolyte, cobalt with hcp structures could be observed in the XRD pattern. CoNi films obtained from the electrolyte with higher cobalt concentration possessed higher coercivity and saturation magnetization. With the increase of cobalt ions from 0.01 M to 0.04 M, coercivity of samples increased

from 58 to 139 Oe while the saturation magnetization improved from 64 to 101 emu/g.

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