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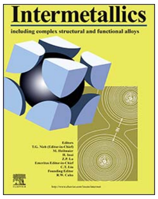

Effects of thermal annealing on microstructure and magnetic properties of electrodeposited Co-Fe alloys

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ABSTRACT

Thermal annealing could potentially serve as important instrument for controlling and improving the properties of the soft magnetic films. A systematic investigation is carried out in this study to determine and analyze the effects of low-temperature heat treatment on the microstructure and magnetic properties of CoFe films of different chemical compositions. The coercivity of the alloys is found to be critically influenced by surface roughness and uniaxial anisotropy, which is in turn affected by thermal annealing. The saturation magnetization on the other hand is controlled mainly by chemical compositions.

1. Introduction

Thin films with good soft magnetic properties, comprising high saturation magnetization and low coercivity, play an important role in various advanced magnetic applications, such as micro- and nano-electrochemical systems, electronic sensors and magnetic recording head cores. Several material systems, containing nickel, iron and cobalt, have been explored as candidates for effective soft magnetic films [1–4]. These include NiFe alloys, which received strong attention in the past 50 years, and CoFe and CoFeNi alloys developed with enhanced properties in the more recent time. While soft magnetic films can be produced by various methods [1–6], electroplating is by far considered a practical approach for mass scale production with efficient quality control. A CoFe soft magnetic film with relatively high saturation magnetization of 24 kG and fairly low coercivity of 9 Oe has been fabricated with the electroplating process [7,8].

Prior studies have determined that several electroplating parameters control the compositions and microstructure of the alloys, which in turn influence the materials' soft magnetic properties. For example, increasing of current density leads to refinement of grain size and hence decrement of the coercivity of CoFe alloys [9,10]. Furthermore, the chemical composition and the content of additives in the plating baths influence the composition and morphology of CoFe deposits, which subsequently affect both saturation magnetization and coercivity [11,12].

Additionally, a post thermal treatment conducted on soft magnetic alloys may also influence their magnetic properties. Depending on the temperature ranges and soaking durations, thermal annealing could help reduce internal stress and alter crystallographic orientation and microstructural details of the alloys [13–15]. This subsequently may affect the films' magnetic responses, which are known to be dictated by interactions between magnetic domains and the films structural features. For examples, the coercivity of $Co_{50}Fe_{50,}$ and $Co_{60}Fe_{20}B_{20}$ films is increased by annealing at a temperature of about 400 °C, and grain growth and texture development were noted to be the main attributors [16,17]. On the other hand, applying thermal treatment to $Co_{50}Fe_{50}$ alloy at 700–850 °C leads to a decrease of coercivity, despite enlargement of grain size [18]. To date, a systematic study that aims to gain an understanding on the influences of thermal annealing on the characteristics and hence the magnetic properties of soft magnetic films, including CoFe alloys, is however very limited.

In this work, we extend the prior studies by systematically assessing the effects of thermal annealing applied on CoFe alloys of a broad range of compositions. Furthermore, through the investigation of microstructural transformations and corresponding magnetic properties of the alloys, their structure-property relationships are established. The understanding gained from the study could serve as a basis to explain the behavior of related soft magnetic alloys undergone thermal

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Table 1
The formulations of the plating baths for Co-Fe electrodeposition.

Chemicals	Concentration (mol/L)
$CoSO_4 \cdot 7H_2O$	0.05, 0.09, 0.12, 0.15, 0.18
$FeSO_4 \cdot 7H_2O$	0.31, 0.28, 0.24, 0.21, 0.18
NH_4Cl	0.50
H_3BO_3	0.50
saccharin	0.006

treatment, and shed light on how annealing can be effective instrument for improving the properties of the soft magnetic films.

2. Experimental procedures

CoFe alloy films were fabricated by electroplating the alloys on copper substrates (32 × 10 mm) using acidic sulfate baths (300 mL) controlled at 25 °C. The copper substrates were polished to mirror finish with measured roughness of about 10 nm. The concentrations of Co and Fe salts in the electrolyte were systematically varied to achieve the range of film compositions, as listed in Table 1. Boric acid, ammonium chloride, and saccharin were introduced to the solution for pH buffering, Co-Fe complex formation, and stress and grain size controls, respectively [19–21]. The depositions were carried out for 4 h using applied direct current with current density of 0.03 A/cm^2 (Dynatronix DuPR10-3-6 rectifier). Platinum was used as an anode. The baths were controlled in a nitrogen atmosphere to prevent Fe oxidation and magnetically stirred at 400 rpm. After plating, the samples were annealed for 1 h either at 200 °C or 300 °C in a tube furnace under a nitrogen atmosphere.

The structural and phase analysis were performed on the CoFe samples by means of X-ray diffractometry (XRD, Rigaku TTRAX III). The thickness and the chemical compositions of the films were determined with X-ray fluorescence spectroscopy (XRF, Fischerscope XRAY XUV-773). Films' roughness was measured using atomic force microscopy (AFM, Asylum Research MFP-3D). Grain size was determined by both XRD and AFM. Vibrating sample magnetometer (VSM) was employed to determine in-plane magnetization properties of the samples as a function of magnetic field. Hysteresis loops were generated to determine the films' saturation magnetization and coercivity, from which the films' susceptibility and uniaxial anisotropy could be determined.

3. Results

3.1. Magnetic properties

The specific saturation magnetization (σ_s) and coercivity (H_c) of the CoFe specimens were determined from hysteresis loops obtained from the VSM measurement. The saturation intensity of magnetization (M_s) could be calculated, according to [22]:

$$M_s = \sigma_s \rho \tag{1}$$

where, ρ is film density. Subsequently, the saturation magnetization (B_s) of the films for a given applied magnetic field (H) was determined by:

$$B_s = H + 4\pi M_s \tag{2}$$

Fig. 1 shows representative hysteresis loops obtained in the study. A similarity of hysteresis loops, obtained from 2 in-plane measurements with a magnetic field applied perpendicular to one another, suggests that the films are magnetically isotropic and domain magnetization orients randomly [23].

The saturation magnetization and coercivity of the CoFe deposits are shown in Fig. 2(a) and (b) respectively. In general, the saturation magnetization of the specimens follows the same trend, progressively decreasing with the increase of Fe content in the films, regardless of thermal annealing. On the other hand, the coercivity of the alloys appears to be affected by annealing temperatures (Fig. 2(b)). The coercivity of the as-deposited specimens ranges from about 20 Oe to 30 Oe as the Fe content is reduced from 80 to 57 wt.%. Reductions of the coercivity to below 20 Oe occurred when the films were annealed at 200 °C. An increment of the annealing temperature to 300 °C results in the increase of the coercivity to about 40 Oe for all chemical compositions examined.

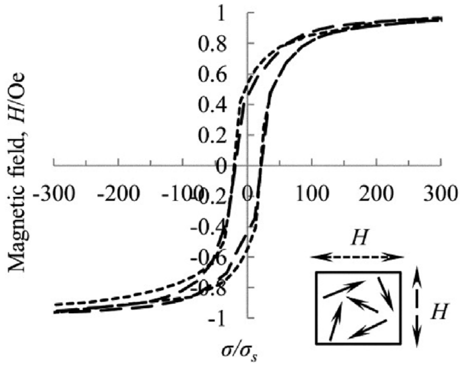

Fig. 1. In-plane magnetic hysteresis loops of as-deposited 74.8 wt.%Fe film measured by applying magnetic field of VSM in two orthogonal directions, representing magnetic isotropy property of the CoFe films.

3.2. Films' physical characteristics

As illustrated in the AFM images in Fig. 3, all fabricated specimens under investigation exhibit a uniform coating layer without crack formation.

The roughness of the specimens of all compositions considered falls in a nano-scale regime, as exhibited in Fig. 4(a). Slight differences of surface roughness levels are observed in the specimens annealed at different temperatures, suggesting some influence of heat treatment on the development of films' morphology. According to the XRF measurements, the thickness of the as-deposited and as-annealed is approximately 1.8 μm and 1.4 μm, respectively.

The XRD profiles confirm a presence of bcc CoFe alloys in all deposits, as exemplified in Fig. 5 for the 57% and 80% Fe specimens. Furthermore, the profiles suggest that texture of the alloy depends strongly on the alloy composition. Particularly, the films with low Fe and high Fe contents are preferentially oriented in (110) and (200) planes, respectively. The relationship (110) texture coefficient and weight fraction of iron in the CoFe films are illustrated in Fig. 4(b). Except for the low Fe alloy, the crystallographic orientation is not significantly affected by thermal annealing.

3.3. Grain size and exchange length

Confirming the observation under AFM, grain sizes of the alloys, as determined by XRD, are found to be in the nano-range and vary with the alloy content (Fig. 4(c)). The exchange length and domain wall width, on the other hand, can be calculated by Ref. [22]:

$$L_{ex} = \sqrt{A/K_u} \tag{3}$$

K_u is the uniaxial anisotropy constant, to be discussed in the next section, and A is the exchange stiffness, estimated by Ref. [24]:

$$A = nJS^2/a \tag{4}$$

where n is the number of atoms in unit cell (for BCC, $n = 2$), S total spin of electron (assuming 1 for CoFe), a is the XRD lattice constant, J is exchange integral, which can be estimated for CoFe as follows [3]:

$$J = 0.15kT_c \tag{5}$$