Effect of electrolyte temperature on composition and phase structure of nanocrystalline Fe–Ni alloys prepared by direct current electrodeposition

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ABSTRACT

Composition and phase structure were analyzed using electron microprobe and X-ray diffraction for a series of Fe–Ni deposits prepared by direct current electrodeposition at four electrolyte temperatures of 298, 313, 333 and 353 K. The well-known anomalous codeposition became less significant with increasing electrolyte temperature, and the deposition eventually shifted to an equilibrium mode in which the electrolyte composition was approximately equal to the deposited one at 353 K. The phase structures of the deposits were affected significantly by the electrolyte temperature. At 298 K, the resultant phases of the deposits were very similar to those of the quenched bulk alloys with the same composition. On the other hand, the 353 K deposits contained phases similar to those of the bulk alloys cooled slowly from high temperatures. The great enhancement of the thermodynamic equilibrium is attributed to the increase of the surface mobility of the adatoms/monovalent intermediates with increasing electrolyte temperature.

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1. Introduction

Fe–Ni alloys have been widely used in the industry due to their unique magnetic and mechanical properties. The initial relative permeability of magnetization is as high as ~10,000 for the alloys having nickel contents around 80 at.%, and the highest saturation magnetization can be obtained in the vicinity of 50 at.% Ni [1]. Moreover, the Fe–36 at.% Ni alloy, known as "invar", possesses almost no thermal expansion at temperatures below ~500 K [2,3]. Recently, Fe–Ni based alloys have been applied as sensing materials in micro electromechanical systems such as position, stress and magnetic microsensors [4,5], as well as in packaging for electronic and micro-electromechanical devices such as radiation sensing MOSFETs and laser diode modules [6–8]. The low thermal expansion of Fe–Ni alloys ensures a good mechanical compatibility with the semiconductor devices, the ceramic substrates and the glass windows on packaging.

Electrodeposition is an attractive process to produce Fe–Ni alloys from μm to mm in size. However, a so-called anomalous codeposition has long been reported [9,10]. The less noble ferrous ions are reduced preferentially over the nickel ions, resulting in a high Fe content in the resultant deposits. Therefore, a slight deviation of the electrolyte composition can make a significant variation of the alloy composition. A hydroxide-based model for the anomalous codeposition was first proposed by Dahms and Croll [11]. This model was modified later by

emphasizing the role of ionized hydrolysis products [12,13]. Recent researches indicated that the electrode kinetics, such as the adsorption of monovalent Fe^+ and Ni^+ intermediates on the electrode, plays a more important role than the chemical reactions in the solution [14–17]. The electrolyte temperature should show a significant effect on the deposit composition due to a strong dependence of the surface adsorption on temperature [18]. However, the effect of the electrolyte temperature on the anomalous codeposition has seldom been examined systematically [10].

Concerning a successful application of the electrodeposited (ED) Fe–Ni alloys, not only the composition but also the microstructure has to be controlled precisely [19]. One of the most important microstructure issues is the phase structure, since both the superior magnetic and thermal expansion properties exist only in alloys having a face-centered cubic (FCC, γ) structure [3]. There are three stable solid phases at temperatures below 620 K: a γ solid solution containing less than 12 at.% Fe, a body-centered cubic (BCC, α) phase having high Fe contents (>95 at.%), and a $FeNi_3$ ordered intermetallic compound having an extended range of composition (10–37 at.% Fe) according to the equilibrium phase diagram [20].

The order–disorder transition of the $FeNi_3$ phase at ~790 K is, however, very sluggish and alloys of high Ni content usually retain the disordered state as cooled from high temperatures. For alloys containing 77 at.% Fe or higher, the γ phase transforms either to a dual-phase (α + γ) structure on slow cooling or to a BCC martensite (α′) on quenching [20]. On the other hand, the high temperature γ phase is stable at room temperature for alloys containing 64 at.% Fe or less. Alloys containing 65–76 at.% Fe were reported, accordingly, to have an α′ + γ, dual-phase structure on cooling to room

temperature [20,21]. The transformation temperatures (M_s, M_f, A_s and A_f) as functions of Fe content are also illustrated as dashed lines in Fig. 1.

The metastable nature of the phase equilibria in the thermally prepared Fe–Ni alloys is in fact inherited by the ED Fe–Ni alloys. The $\alpha/\alpha + \gamma$ phase boundary was found to be extended from ~98 at.% Fe to 50–70 at.% Fe with a narrow two-phase region of 50–60 at.% Fe [22,23] or 60–70 at.% Fe [23–27]. In other words, the two-phase region is very similar to the $\alpha' + \gamma$ one for the thermally prepared alloys. However, there has been no report concerning the effect of the electrolyte temperature on the phase structure of the ED Fe–Ni alloys. The present study, therefore, aims at clarifying the effect of electrolyte temperature on deposit composition and phase structure with additional emphasis on the thermal stability of the deposits.

2. Experimental details

Nanocrystalline Fe–Ni alloys were electrodeposited on brass substrates (30 mm × 100 mm × 0.5 mm) from sulfate-based electrolytes consisting of $FeSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 7H_2O$, ascorbic acid (8 g/L), NH_4Cl (0.3 M), boric acid (0.5 M) and sodium lauryl sulfate (0.1 g/L) at current density of 1–5 A/dm^2. Electrodeposition was performed using a two-electrode cell of 50 mm (W) × 150 mm (L) × 150 mm (H) with a circulation pump and a temperature-control system. The electrolyte was injected into the cell from two nozzles of 5 mm in diameter, which are situated ~5 mm in front of the cathode, and flowed through the anode (a 45 mm × 120 mm Ti basket) to an outlet of the cell. The electrolyte then flowed through a filter and was pumped into the cell again. All the depositions were done under galvanostatic conditions at four electrolyte temperatures, 298 K, 313 K, 333 K and 353 K (with a variation less than +/−0.2 K inside the cell), to obtain deposits from an electrolyte with a $Fe^{2+}/(Ni^{2+} + Fe^{2+})$ ratio (denoted as "electrolyte composition" hereinafter) of 0.5. Additional electrolyte compositions, which varied from 0.07 to 0.3 at 298 K and from 0.5 to 0.73 at 353 K, were used to prepare samples with a total ion concentration of 0.75–1 M. The bath was maintained at pH 2.5 and the deposition charge for all the cases was 3600 C. Each sample was prepared with fresh electrolyte.

The area of the substrate exposed to the electrolyte was 20 mm × 60 mm in size. After electrodeposition, the coated cathode was cleaned with distilled water and dried. Changes in the weight of the cathode were measured to determine the cathode efficiency. The deposits were of about 100 μm thick and then were cut into six coupons (10 mm × 8 mm) from the center of the coated area for

analyses. Five out of the six coupons were annealed in an infrared furnace at temperatures of 473 to 873 K, respectively, for 1 min in a vacuum (~1 × 10^{-5} torr). Thermocouple wires were spot welded at the corner of each coupon prior to annealing to monitor and control the temperature. The heating rate was 3 K/s and the sample was cooled in a vacuum without using any force cooling methods. The cooling rate was higher than 1 K/s as the sample was cooled from the annealing temperature, T, to T − 50 K. Electron microprobe (JEOL, JXA 8900R) operated at 15 kV was employed to determine the chemical composition of the deposits using pure Fe and Ni as standards. The standard deviation of the Fe content of the six coupons cut from the same deposit was always less than 1 at.%, verifying that the compositional homogeneity of the samples is acceptable. The grain size and phase constituent of the deposits in the as-deposited and the annealed states were characterized by X-ray diffraction (XRD). The XRD was carried out on a Siemens D5000 diffractometer, (Cu Kα, 40 kV and 40 mA) equipped with a graphite monochromator. The diffraction pattern was analyzed based on the Stokes–Wilson equation using a TOPAS software to yield the volume-average grain size of the deposits. The phase constituent was also calculated using the TOPAS software.

3. Results and discussion

3.1. Deposit composition and cathode efficiency

Fig. 2 shows the Fe content of the deposits, prepared from an electrolyte containing 0.5 M Fe^{2+} and 0.5 M Ni^{2+} as a function of temperature. It clearly indicates that the Fe content decreases with increasing electrolyte temperature in a higher rate at a current density of 1 A/dm^2, as compared to the 5 A/dm^2 counterparts. The deposits prepared at 1 A/dm^2 thus contain less iron. The electrolyte temperature played an insignificant role on the Fe concentration for deposits prepared from a sulfamate/chloride bath [27]. However, Grimmette et al. [23] reported that an increase in electrolyte temperature from 297 K to 327 K has lessened the anomalous codeposition slightly.

In order to examine the effect of the electrolyte temperature in detail, a series of deposits were prepared from baths having different compositions at 298 K and 353 K, respectively. The current density is maintained at 5 A/dm^2. Fig. 3 shows the deposit composition as a function of the electrolyte composition. Data collected from literatures for Fe–Ni alloys deposited in sulfamate/chloride electrolytes [22,24,27], fluorborate electrolytes [25], chloride electrolytes [26] and sulfate/chloride electrolytes [28] are shown in Fig. 3 as well for
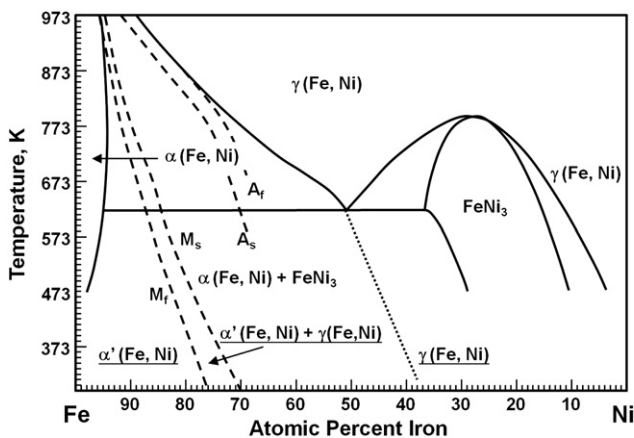

Fig. 1. Equilibrium Fe–Ni phase diagram [14]. The dashed lines are the transformation temperatures of the martensitic transformation as functions of the iron content and the dotted line is the extrapolation of the $\alpha/\alpha + \gamma$ phase boundary. The underlined phases are metastable.
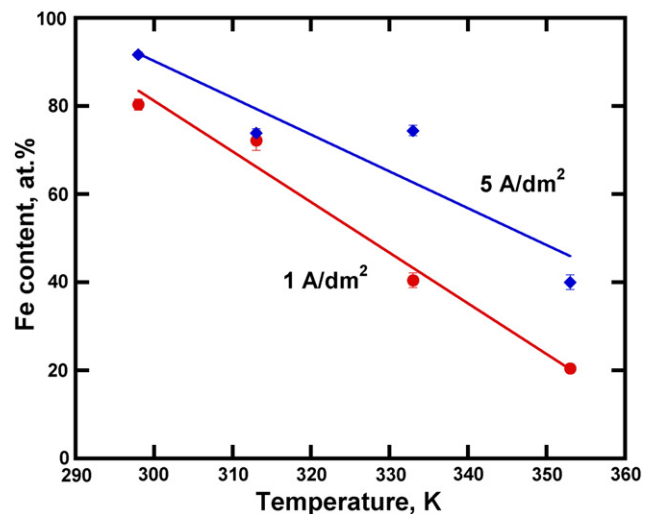

Fig. 2. Fe content of the Fe–Ni deposits as a function of the electrolyte temperature with an electrolyte composition of 0.5.