An Electrodeposition Process for Producing Ductile Bulk Nanocrystalline Ni-Fe Alloys in a Wide Current Density Range

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Current distribution become nonuniform as the shape becomes more complicated, following the edge effect. In creating complex shapes with near net shapes by an electrodeposition, it is required to obtain the same characteristics from a wide current density range. In this study, we prepared bulk samples of Ni-Fe alloys by an electrodeposition with different current densities of 10–150 mA/cm², and their microstructure, mechanical properties, and magnetic properties were examined. In the current density range of 25–150 mA/cm², a relatively constant Fe content of 17–20 at% was observed. X-ray diffraction analysis showed that these alloys had a similar microstructure, which was a strong (200) texture and an average grain size of 17 nm. Tensile tests of these alloys also showed a constant tensile strength of 1.8–1.9 GPa and elongation of 10%. Furthermore, the constant saturation magnetic flux density of 1.2–1.3 T and coercivity of 67–74 A/m were observed. The results of this study indicated the high compatibility of the developed electrodeposition process for Ni-Fe alloys with complicated shape forming.

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1. Introduction

Electrodeposition processes for Ni and its alloys have been used in the industry to improve wear and corrosion resistance.¹⁾ Ni-Fe electrodeposition is used to decrease the production cost^{2,3)} and also provide soft magnetic properties, good electrical conductivity, or special optical properties.⁴⁾ Ni-Fe electrodeposition is also developed as a one-step process for production of nanocrystalline Ni-Fe alloys.^{5–8)} Electrodeposited nanocrystalline Ni-Fe alloys exhibit high strength and good ductility.^{9–11)} These electrodeposited alloys can be in the form of thick coatings and free-standing foils, plates, or tubes, and can be considered to be bulk structural materials.¹²⁾ They have, therefore, attracted much attention with respect to their potential application to micro-electro-mechanical systems (MEMS)¹³⁾ and magnetic shields.⁸⁾ Furthermore, by combining photolithography techniques, forming with near net shapes has been also expected.¹⁴⁾

However, although electrodeposited bulk nanocrystalline alloys are not primarily to a true lack of resistance to damage, they do suffer from a processing defect.¹⁵⁾ For instant, adsorbed hydrogen or gaseous hydrogen hamper the deposition reaction¹⁶⁾ and then generate defects and high internal stress,¹⁷⁾ during electrodeposition. To produce the electrodeposits free from artifacts, minimization of the inhibitor is important.¹⁸⁾ In the case of electrodeposition for Ni and Ni alloys, the desired growth mode, which can ignore the presence of inhibitors, resulted in a strong (200) texture on electrodeposits.^{16,18)} Also, even in using the same bath, growth mode can be either free mode or inhibited mode,

depending on the electrodeposition conditions such as current density and bath temperature.¹⁹⁾ Connecting the electrodeposition conditions to a resulted orientation of electrodeposits is required to minimize the processing defects. In addition to this, current is biased according to the shape, which is well known as an edge effect. Thus, in fabrication of electrodeposited member with three-dimensional shape, an electrodeposition process that can obtain free mode in a wide current density range is needed. On the other hand, in electrodeposition of Ni-Fe alloys, the effect of current density on the resulted microstructure, mechanical properties, or soft magnetic properties has not been discussed.

Therefore, the aim of this study was to clarify the range of the current density at which the desired growth mode can be obtained in electrodeposition for bulk nanocrystalline Ni-Fe alloys. Electrodeposition was run at a wide current density range, and then their microstructure, mechanical properties, and soft magnetic properties were examined.

2. Experimental Procedure

Ten bulk samples of nanocrystalline Ni-Fe alloys were electrodeposited. The deposition bath that primarily consisted of nickel sulfamate and iron chloride were prepared, and the details of bath composition are given in Table 1. All samples were deposited onto copper substrates of commercial purity by using two counter-electrodes of nickel plates (99.98%) and iron rods (99.5%). Electrodeposition was performed using 1-L deposition systems, and the details of deposition systems are described in previous paper.²⁰⁾ The bath temperature and pH were maintained at 55°C and 2.2,

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Table 1 Bath composition for Ni-Fe alloys. $\text{Ni}^{2+}/\text{Fe}^{2+}$ ion ratio of the bath is 7.0.

Chemicals	g/L
Nickel sulfamate tetrahydrate	300.0
Iron chloride tetrahydrate	26.4
Boric acid	40.0
Malonic acid	2.0
Saccharin sodium dihydrate	1.0
Sodium lauryl sulfate	0.5

respectively. The pH values of the solutions during electrodeposition were maintained by addition drops of 1.0 mol/L sulfamic acid or 5.0 mol/L sodium hydroxide. The current density ranged from 10 to 150 mA/cm². The target electrodeposits thickness was typically 1 mm for mechanical testing,¹⁰⁾ which requires approximately 12–144 h of deposition run time to achieve.

After electrodeposition, we performed the following analysis. The current efficiency of deposition bath CE was calculated using the Fe content of electrodeposits x_{Fe} and following equation.

$$CE = \frac{wnF}{It} \left/ \left((1 - x_{\text{Fe}})A_{\text{Ni}} + x_{\text{Fe}}A_{\text{Fe}} \right) \right. \quad (1)$$

where w is the mass change of cathode before and after electrodeposition, n is the valence electron number, F is the Faraday constant, I is the applied current value, t is the deposition time, and A_{Ni} and A_{Fe} are the atomic weight of Ni and Fe, respectively. The Fe contents of the electrodeposited samples were determined by using energy-dispersive X-ray spectroscopy (EDX, Shimadzu EDX-8000). The C and S contents were quantified by infrared absorption after combustion in a high frequency induction furnace (LECO CS-LS600). The grain sizes were estimated by X-ray diffraction (XRD, Rigaku MiniFlex600) using Cu K α radiation. This estimation was done by the fundamental parameter method, with the Rigaku software package PDXL2.²¹⁾ To evaluate the hardness of the electrodeposits, micro-Vickers hardness tests were conducted on bulk samples using a load of 500 g for 10 s. Each reported data point represents the average value for at least 12 indentations. Dog-bone specimens with a gauge length of 12 mm, width of 3.0 mm, and thickness of approximately 1.0 mm were machined by electrical discharge machining (EDM) for tensile tests. Note that the surface grinder removed the copper substrate and the layer affected by EDM. Three specimens were cut from each bulk plate of electrodeposited Ni-Fe alloys. The tensile tests were carried out at room temperature and a strain rate of $1 \times 10^{-3} \text{ s}^{-1}$ using universal testing machine (Shimadzu AUTOGRAPH AG-X plus). Each reported data point represented the average of three measurements. After tensile tests, we cut out strip-shaped test pieces, with a length of 15 mm, width of 3 mm, and thickness of approximately 1.0 mm, from the grip section, and the soft magnetic properties were measured by a micro-single sheet tester.

Fig. 1 Current efficiency of deposition baths as a function of current densities of 10–150 mA/cm².

Fig. 2 Fe content of electrodeposits as a function of current densities of 10–150 mA/cm².

3. Results and Discussion

We prepared bulk samples of Ni-Fe alloys by electrodeposition with current density of 10–150 mA/cm². Note that green precipitation of nickel hydroxide was confirmed as applying a current density of 200 mA/cm². Thus, no further increases in the current density were attempted. The current efficiencies of the deposition bath with current density of 10–150 mA/cm² are shown in Fig. 1. Applying current density of 10–20 mA/cm² showed the lower current efficiency around 80%. The current efficiencies increased with increasing the current density to 150 mA/cm²: the deposition bath at current density of 150 mA/cm² showed the highest efficiency of 93%.

The Fe content for bulk samples is plotted against the current density in Fig. 2. This shows the trend that the Fe content gently decreased from 23 to 17 at% with increasing the current density. In previous study,⁵⁾ Ni/Fe ratio of 7.0, which is same ratio as this study, produced Ni-Fe alloys with Fe content of 16–23 at%. This agreement indicated that Fe content was mainly tied to the Ni/Fe molar ratio in the deposition bath. Furthermore, the Fe content could be by finely adjusted by the current density.

Electrodeposited Ni and Ni alloys are generally contaminated with impurities such as C and S, which come from additives.^{6,22)} We also measured the C and S contents of each Ni-Fe alloys and these alloys had C and S contents of 30–40 and 290–360 ppm, respectively. These results indicated that the current density did not greatly change the C and S contents of electrodeposited Ni-Fe alloys. Also, these values

Fig. 3 XRD patterns of Ni-Fe alloys electrodeposited with different current densities. The results of analysis on these patterns are given in Table 2.

Table 2 Summary of XRD analysis results for electrodeposited Ni-Fe alloys.

Current density (mA/cm ²)	Grain size (nm)	N_{111}	N_{200}
10	17 ± 8	0.92	1.70
15	17 ± 8	0.85	1.86
20	17 ± 9	0.74	2.13
25	17 ± 9	0.71	2.20
30	18 ± 9	0.64	2.36
40	17 ± 8	0.65	2.34
50	17 ± 8	0.74	2.11
70	18 ± 9	0.56	2.55
100	17 ± 9	0.68	2.27
150	19 ± 10	0.58	2.51

are comparable to those in electrodeposited Ni and Ni alloys in previous works.^{18,22,23)}

Figure 3 shows representative XRD patterns for the electrodeposited samples. All XRD patterns showed a single face-centered cubic structure and exhibited strong (111) (200) fiber texture as shown in Fig. 3. Similar textures were often confirmed in electrodeposited Ni and Ni alloys.^{24,25)} To compare the preferential orientation of samples, we calculated orientation indices for the (111) and (200) planes and results are listed in Table 2. The trend similar to the current efficiency as shown in Fig. 1 can be observed on the relationship between orientation index for the (200) plane and current density. Some studies^{16,26,27)} have reported that the orientation of electrodeposits reflects the growth mode: uninhibited growth produce a dominant (200) texture, while growth inhibited by hydrogen gas introduce a dominant (111) texture. Increase in the current density resulted in the higher current efficiency as shown in Fig. 1. This improvement of current efficiency could decrease the generation of hydrogen gas by side reaction during the electrodeposition. As a result, the higher current density resulted in the stronger (200) texture on the electrodeposited Ni-Fe alloys.

We also estimated grain size of electrodeposited alloys from XRD patterns, and the results are given in Table 2.

Fig. 4 Hardness as a function of current densities of 10–150 mA/cm². Solid line stands for the average value.

All Ni-Fe alloys had a grain size of 17–19 nm and narrow distribution. These sizes were independent of current density. The grain size of electrodeposited Ni and Ni alloys was mainly tied to their impurity and solute contents.^{5,22,28,29)} Giallonardo,³⁰⁾ on the electrodeposited Ni-Fe alloys, pointed to that alloying of Fe up to 15 mass% dramatically decreased grain size, while that greater than 15 mass% had a lesser effect on decreasing the grains size. For this study, the Fe content of alloys ranged 17–23 at% where the grain refinement effect by Fe alloying is saturated. In addition to this, there is almost no difference in impurity contents among the Ni-Fe alloys, as mention above. These resulted in similar grain size and distribution on each sample.

Figure 4 shows the hardness values of the nanocrystalline Ni-Fe alloys as a function of current density. Each alloy exhibited a hardness of 5.0–5.1 GPa and the standard deviation was less than 0.04 GPa which was a uniform value. These hardness values were also independent of current density. Representative stress-strain curves of bulk nanocrystalline Ni-Fe alloys are presented in Fig. 5(a), and the details of the results are summarized in Fig. 5(b). Bulk nanocrystalline Ni-Fe alloys exhibited a similar elongation of approximately 10%, except for current density of 10 mA/cm². The elongation of electrodeposited nanocrystalline Ni alloys was related to the orientation index for the (200) plane.^{19,20)} At current density of 10 mA/cm², orientation index (200) plane was 1.7, which is the lower value compared to other current densities (15–150 mA/cm²). This difference pointed to that inhibited growth, which reduces elongation of electrodeposits, occurred more actively, as applying current density of 10 mA/cm².

Unlike the results of hardness or elongation, the tensile strength decreased from 1.92 to 1.77 GPa with increase in the current density. The Fe-Ni alloys for this study had almost no difference in grain size, and Fe hardly causes solid solution strengthening with respect to Ni.²²⁾ Based on these results, it seemed that there was no difference in strength as well as results of hardness. On the other hand, recently it have been reported that grain boundary stability has an effect on the strength, especially in nanocrystalline metals and alloys.³¹⁾ At the present stage, this stability are only qualitatively evaluated by comparison of hardness values before and after thermal treatment.^{32–34)} For deep understanding the strength behavior, it is necessary to further understand the quantification of the grain boundary stability and its effects.

Fig. 5 (a) Representative stress-strain curve of electrodeposited bulk nanocrystalline Ni-Fe alloys. (b) Tensile strength and total elongation as a function of current densities of 10–150 mA/cm².

Table 3 Magnetic properties for electrodeposited nanocrystalline Ni-Fe alloys obtained from literatures and determined in this study.

Samples	Current density (mA/cm ²)	Saturation magnetic flux density (T)	Coercivity (A/m)
Ni-17at% Fe	70	1.27	67.1
Ni-19at% Fe	40	1.17	72.0
Ni-21at% Fe	25	1.30	73.7

The Ni-Fe alloys is often applicable to a soft magnetic material as is known as a Permalloy alloy. We examined the soft magnetic properties for bulk nanocrystalline Ni-Fe alloys electrodeposited at current densities of 25, 40, and 70 mA/cm². The saturation magnetic flux density and coercivity are 1.2–1.3 T and 67–74 A/m, respectively (Table 3). Table 3 indicates that the both properties were independent of current density. The saturation magnetic flux density of electrodeposited ferromagnetic materials is only dependent on the composition: Fe content determine the magnetic saturation for electrodeposited Ni-Fe alloys.³⁵⁾ In fact, the values of saturation magnetization for this study well agreed with the past report.³⁵⁾ The coercive force is proportional to sixth power of grain size in grain size range less than around 50 nm.³⁶⁾ The coercivity for this study was also a value in accordance with this theorem developed by Herzer.³⁶⁾ The soft magnetic properties of the Ni-Fe alloys follow the theorem. In this study, the current density did not greatly affect the Fe content and grain size of alloys, respectively, so that there was no significant change of soft magnetic properties.

4. Conclusions

We conducted electrodeposition of Ni-Fe alloys, varying the current density of 10–150 mA/cm² to clarify the effects of current density. The current efficiency was affected by the current density: at a current density of 25–150 mA/cm², the high current efficiency around 90% was observed. These baths that showed high efficiency produced the Ni-Fe alloys with Fe content of 17–20 at%. The Fe content showed a tendency to decrease with increasing current density, while

there was no change in the contents of impurity such as C and S. XRD analysis showed that the all Ni-Fe alloys had a strong (111) (200) fiber texture and grain size of 17–19 nm for all current densities. At current density of 10 mA/cm², orientation index (200) plane was less than 1.9, indicating that inhibited growth preferentially occurs. As for the hardness values, no effect of the current density was confirmed. Also, there was no effect on elongation, except for the current density of 10 mA/cm². Although there was tendency to decrease with increasing current density, the alloys exhibited a high tensile strength of 1.8–1.9 GPa at all current densities. Furthermore, there was no clear effect by the current density on the saturation magnetization and coercive force. The results of this study showed that developed deposition bath could produce bulk nanocrystalline Ni-Fe alloys with constant characteristics at a wide current density.

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