1. Introduction

Ni–Fe alloys containing 20–65 mass%Fe are especially called permalloys and they are used as magnetic heads in recording, memory, storage devices because of their high magnetic permeabilities and low coercivities.\(^1\)\(^\text{1,2}\) Although permalloys have conventionally been applied for small–scale products, they are recently gaining attention as structural materials and magnetic shields for linear motor trains.\(^3\) Permalloys require both high strength and high ductility in order to achieve the high reliability required for use as a structural material. Therefore, this study focuses on the nanocrystallization of permalloys. In comparison to their course–grained materials, nanostructured materials with an average grain size of less than 100nm have higher tensile strength (following Hall–Petch relationship). Furthermore, Hasnaoui et al.\(^4\) reported that a high volume fraction of grain boundaries enhances grain boundary sliding during plastic deformations, resulting in a high tensile ductility. Grain size refinement also affects the magnetic properties of alloys. According to Herzer et al.\(^5\)\(^\text{,6}\) a decrease in grain size improves the magnetic properties. The substantial changes in coercivity and permeability observed for very small grains can be interpreted in terms of the smoothing part of exchanging interaction averaging out.

There are several synthesis techniques for producing nc metals and alloys such as ball milling,\(^7\)\(^\text{8}\) sputtering,\(^9\) gas–condensation,\(^10\) sol–gel techniques,\(^11\) and electrochemical deposition.\(^12\) Electrodeposition is a technologically and economically viable method to produce bulk nanostructured materials and alloys. Wei et al.\(^13\) fabricated electrodeposited bulk nc Ni–Fe alloys with high strength and good ductility. However, because these alloys exhibited decreased elongation with increasing in Fe content, no electrodeposited bulk nc permalloys with high ductility have been demonstrated.\(^14\)\(^\text{–16}\) Therefore, the aim of this study is to determine optimum deposition conditions for nc permalloys and investigate their mechanical properties.

To improve ductility of electrodeposited nc alloys, Koch et al.\(^19\)\(^\text{,20}\) insisted on obtaining artifact–free bulk samples. The electrodeposition process can induce artifacts such as defects, internal stress, and impurities, depending on the conditions. In previous studies, we developed a new type of sulfamate bath for Ni and Ni alloys.\(^21\)\(^\text{–23}\) Samples produced using this complexing bath contained fewer artifacts, and the mechanical properties were improved. The amount of the artifacts in electrodeposits depends on the grain growth mode during electrodeposition. We assumed that free lateral growth was the most ideal growth mode because the adsorption and release of hydrogen are suppressed.\(^23\)\(^\text{–25}\) As the free lateral growth becomes the dominant growth mode, the X–ray diffraction (XRD) peak intensity of the (200) plane becomes stronger. In the present study, we determined the best electrodeposition conditions for fabricating highly ductile permalloys by investigating the orientation indices of the (200) plane.

2. Materials and Methods

Thin films (with a thickness of approximately 0.2 mm) of Ni–Fe alloys were prepared using an electrodeposition system by varying saccharin content, bath temperatures, and current densities. Details of the bath compositions used for this study are described in Table 1. We used manganese chloride tetrahydrate because it prevents incorporation of sulfur and improves tensile ductility of electrodeposits.\(^26\) The bath temperatures were maintained using a heater with a proportional integral derivative controller. All electrodepositions were performed with a pH of 2.1. The pH value of the solutions was maintained by adding drops of

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Amount (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel sulfamate tetrahydrate</td>
<td>300</td>
</tr>
<tr>
<td>Iron sulfamate heptahydrate</td>
<td>27</td>
</tr>
<tr>
<td>Manganese chloride tetrahydrate</td>
<td>30</td>
</tr>
<tr>
<td>Boric acid</td>
<td>40.0</td>
</tr>
<tr>
<td>Saccharin sodium dihydrate</td>
<td>0–5.0</td>
</tr>
<tr>
<td>Sodium lauryl sulfate</td>
<td>0.3</td>
</tr>
</tbody>
</table>

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100 g/L sulfuric acid. The samples were deposited onto copper substrates of commercial purity (99.9%) using two counter electrodes of titanium baskets with nickel plates (99.8%) and iron plates (99.9%). The Fe content of the electrodeposits was determined by energy-dispersive X-ray spectrometry (EDS) using a scanning electron microscope (HITACHI S-4800). To determine the grain sizes and preferential orientation of the samples, XRD (Rigaku Ultima IV) spectra were measured using Cu–Kα radiation. The formula used to calculate the orientation indices for the (200) plane, \( N_{200} \) is given below.

\[
N_{200} = \frac{I_{200}}{I_{111} + I_{200} + I_{220}}
\]

In the eq. (1), \( I_{hkl} \) is the intensity of the (hkl) diffraction peak of the Ni powder standard from International Center for Diffraction Data database and \( I_{hkl}^{0} \) is the intensity of the (hkl) diffraction peak of the studied Ni–Fe samples. Then, bulk samples (with a thickness of approximately 0.6 mm) were prepared under the optimum deposition conditions. Dog–bone specimens with a gauge length of 12.0 mm and a width of 4.0 mm were prepared for tensile tests by electrical discharge machining from the as deposited plates. Cu substrates were completely removed by grinding before tensile tests. Tensile tests were performed at a strain rate of \( 8.3 \times 10^{-4} \text{s}^{-1} \) at room temperature. The plastic deformation of the tensile specimen after fracture was measured from the change in the gauge length.

3. Results and Discussions

3.1 Fabrication of electrodeposited Ni–Fe alloys

Saccharin sodium is used as an additive agent in electrodeposition baths for depositing several different metals and alloys. It is known that this agent affects the grain size and residual stress of the deposited material.\(^{27}\) In addition, we previously reported that the tensile properties of electrodeposited pure Ni and Ni alloys are influenced by the saccharin sodium content.\(^{22,25}\) To study the optimum amount of saccharin in the complexing bath that enhances the \( N_{200} \) indices, five thin–film samples were electrodeposited with various saccharin contents of 0, 0.5, 1.0, 3.0, and 5.0 g/L. There were some cracks on the thin film surface with a saccharin content of 0 g/L, while there were no cracks with saccharin content of 0.5, 1.0, 3.0, and 5.0 g/L. Figure 1 shows the XRD patterns of the five thin films. The characteristic peaks of the FCC phase were clearly observed. From the width of the (111) diffraction peak, the grain sizes of the electrodeposited samples were estimated to be 15–20 nm using the Scherrer equation.\(^{29}\) The relationship between saccharin content and indices \( N_{200} \) of thin–film Ni–Fe alloys is shown in Fig. 2, where the most preferable saccharin content of the plating bath was determined as 1.0 g/L. Some researchers\(^{29–32}\) previously described the saccharin behavior during electrodeposition experiments. For insufficient saccharin content, the metal ions covered the convex parts of the electrodeposition substrates where electric discharge occurs, the thin–film samples contained numerous defects, and the \( N_{200} \) indices declined. On the other hand, with excessive amount of saccharin, saccharin itself hindered the adsorptions of metallic ions, resulting in a decline the \( N_{200} \) indices. Excessive saccharin also resulted in the adsorptions of sulfur, which segregated at the grain boundaries and led to embrittled materials. All the following depositions in this study were conducted with a saccharin content of 1.0 g/L.

Next, the bath temperatures were investigated. Two thin–film samples were obtained from each bath temperature of (a) 55°C and (b) 60°C. The XRD patterns for these samples are shown in Fig. 3. The \( N_{200} \) indices calculated from eq. (1) were 1.87 and 2.18 for the baths at 55°C and 60°C, respectively. In previous studies,\(^{15,24,25}\) electrodeposited Ni–W alloys, that showed good ductility (elongation to failure \( \varepsilon_f \) = 6.5–13.4%), had \( N_{200} \) indices of 1.80–2.59. Hence, both
temperatures used in this study are considered appropriate for synthesizing ductile Ni–Fe alloys.

Current density is one of the most important parameters in the electrodeposition of alloys because it can affect the cost of process as well as the chemical composition and properties of the coatings. Our previous study in Ni–W alloys has suggested that the adsorption of hydrogen can be affected by current density, resulting in variation of the orientation indices.\textsuperscript{25} A low current density favors adsorption of hydrogen, which disrupts the electrodeposition reaction. A high current density causes the evolution of gaseous hydrogen, resulting in defects in the coating after the gas is released. Hence intermediate current density is required to stimulate only the deposition reactions required to achieve the defect–free samples. Four electrodeposited Ni–Fe alloy samples were prepared at different current densities of 10, 30, 40, and 50 mA/cm\textsuperscript{2}. The relationship between current density and $N_{200}$ indices is shown in Fig. 4. Compared with the high $N_{200}$ indices in previous studies,\textsuperscript{15,24,25} all four samples in this study exhibited enough $N_{200}$ indices (1.80–2.33) for good ductility. Then, we decided to apply two different current densities (10 and 50 mA/cm\textsuperscript{2}) to fabricate electrodeposited bulk Ni–Fe alloys, because peaks were observed at these current density values. From these results, the optimum deposit conditions for fabricating bulk samples were determined.

### 3.2 Mechanical properties of bulk Ni–Fe alloys

A summary of the plating conditions for bulk nc Ni–Fe alloys is shown in Table 2. The first electrodeposition condition used a low current density of 10 mA/cm\textsuperscript{2} (sample LD5). The plating was conducted only at 55°C in order to suppress the evaporation of the deposition solutions during the long plating time (7 consecutive days). The other two bulk Ni–Fe alloys, samples HD5 and HD6, were prepared at a high current density of 50 mA/cm\textsuperscript{2}, with different bath temperatures of 55°C and 60°C respectively for 1.5 days.

After electrodeposition, some warpage of sample LD5 was observed. Compared with high current density deposition, there were fewer discharge sites or nucleation sites of crystal grains on the electrodeposition substrate when a low current density was used. This indicates that the interval between the grains increased, and large internal stresses occurred when several grains coalesced.\textsuperscript{33,34}

Therefore, tensile tests were conducted using samples HD5 and HD6 produced with a high current density. The stress–strain curves of these samples are shown in Fig. 5. Both samples HD5 and HD6 exhibited high ultimate tensile strengths of 1.9 GPa and high plastic elongations of 12.2% and 9.1%, respectively. Table 3 shows the results of various analyses of samples HD5 and HD6. From EDS measurements, the Fe content of these samples was 25–29 mass%, achieving the composition of permalloys. The relationship between Fe content and elongation of electrodeposited pure Ni and Ni–Fe alloys is shown in Fig. 6.\textsuperscript{13–18,22} As Fe content in Ni–Fe alloys increases, elongation seems to decrease in previous work. On the other hand, samples HD5 and HD6 in this study overcome this trade–off relationship.
4. Conclusion

Optimum electrodeposition conditions for fabricating ductile Ni permalloys were investigated by evaluating the N\textsubscript{200} indices of thin-film samples. The results of these analysis suggested that the optimum saccharin content was 1.0 g/L, and the best current density was 10, 50 mA/cm\textsuperscript{2}. Both 55°C and 60°C were considered to be suitable bath temperatures for synthesizing ductile Ni–Fe alloys. Bulk samples produced using the high current density demonstrated an ultimate tensile strength of 1.9 GPa and a high tensile ductility of 9.1–12.2%. These samples had Fe contents of 25–29 mass%; hence we succeeded in fabricating highly ductile permalloys.

Acknowledgments

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