FeNi and Fe16N2 Magnets Prepared Using Leaching

Takayuki Kojima1,2,*; Satoshi Kameoka2; Masaki Mizuguchi3,4; Koki Takanashi3,4 and An-Pang Tsai2

1Frontier Research Institute for Interdisciplinary Sciences, Tohoku University, Sendai 980-8578, Japan
2Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan
3Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
4Center for Spintronics Research Network, Tohoku University, Sendai 980-8577, Japan

L10-type FeNi alloys and α′′-Fe16N2 are candidates for permanent magnets without precious metals, but they are difficult to prepare because atomic diffusion is extremely slow below the order-disorder transition temperature of L10-FeNi (320°C) and because α′′-Fe16N2 is a metastable phase. Here, we report trials for preparing them using leaching, which is a method to obtain porous metals with a high surface area. We used such chemically active porous alloys as precursors for preparing L10-FeNi using the driving force of atomic diffusion and for preparing α′′-Fe16N2 using high reactivity with ammonia. No proofs for obtaining the L10-FeNi phase were observed, likely due to an Al impurity of 10 mol% and/or too small of a grain size. An Fe16N2 with α′ phase was obtained. Although the saturation magnetization was smaller than that of Fe, a large coercivity (up to 121 kA m⁻¹) was obtained. [doi:10.2320/matertrans.M20190019]

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1. Introduction

Strong permanent magnets contain rare-earth or noble metal elements, such as Nd–Fe–B and L10-type FePt, because they need large magnetic anisotropy, which is induced by the large orbital magnetic moment of rare-earth elements or large spin–orbit interaction of noble metals.⁴ Due to costs, reserves, and serious environmental pollution from mining,²,³ such precious elements should be altered with ubiquitous elements. L10-type FeNi and α′′-Fe16N2 are alternative material candidates because they have large saturation magnetization (Ms) and large uniaxial magnetic anisotropy energy (Ku), even without precious metals (L10-FeNi: Ms = 1.27 MA m⁻¹; Ku = 1.3 MJ m⁻³; α′′-Fe16N2: Ms = 1.92 MA m⁻¹; Ku = 1.0 MJ m⁻³).⁴⁻⁶

However, synthesis is difficult. For L10-FeNi, atomic diffusions of Fe and Ni are extremely slow below the order–disorder transition temperature (320°C).⁷ Thus, because L10-FeNi exists only in meteorites in nature, artificial syntheses must be conducted using devised techniques such as annealing with neutron irradiation under a magnetic field,⁴,⁵ alternate deposition of Fe and Ni monatomic layers in thin-film form,⁸⁻¹³ crystallization of melt-spun amorphous ribbons,¹⁴ and denitriding of FeNi.¹⁵ The material α′′-Fe16N2 is a metastable phase. Owing to the considerable efforts of many researchers, methods for obtaining high-quality specimens have been established⁶ for thin films using reactive sputtering¹² and for nanoparticle by hydrogen reduction of iron oxides followed by ammonia nitriding.¹⁸

Here, we report trials to obtain L10-FeNi and α′′-Fe16N2 through the method of leaching (dealloying), which is the selective dissolution of less noble metals from a mother alloy using acid or alkaline solutions. Leaching was developed by Raney nearly a century ago for making catalysts because the remaining noble metals often show porous structures with high surface areas.¹⁹⁻²¹ The remaining metals also consist of nano-sized primary particles with poor crystallinity, as indicated by broad X-ray diffraction (XRD) peaks. Therefore, we could obtain L10-FeNi by annealing the FeNi that remains after leaching of M-FeNi (M: metal less noble than FeNi). This is because the high surface area and the nano primary particles would bring fast atomic diffusions at surface and grain boundaries. Furthermore, the poor crystallinity is a driving force for atomic diffusion going into stable states with better crystallinity as well as the crystallization of amorphous states.¹⁴ Actually, the studies using monatomic layer deposition have been built on the advantage of surface diffusion,⁸⁻¹³ and a study using nanometric Fe/Ni multilayer films indicated that the grain boundary diffusion is fast enough, even at 300°C.²² For α′′-Fe16N2, the ammonia nitriding should be done at a temperature below 200°C due to the phase stability. Thus, the Fe that remains after leaching could be suitable for preparing α′′-Fe16N2 under a mild nitriding condition because the high surface area and poor crystallinity would have high reactivity with ammonia. In this study, we sought to prepare L10-FeNi by annealing the leached FeNi and to prepare α′′-Fe16N2 by ammonia nitriding of the leached Fe.

2. Materials and Methods

Al₈₀FeNi and Al₅₀Fe₂ intermetallic compounds were used as mother alloys. An alloy ingot was prepared by arc-melting followed by annealing (Al₈₀FeNi: 600°C, 240 h; Al₅₀Fe₂: 800°C, 48 h) in an Ar atmosphere encapsulated by a quartz tube. The ingot was crushed using a mortar and pestle, and the obtained powder was sieved to a particle size of typically 20–125 μm. XRD (Bragg–Brentano geometry) confirmed that both alloys were single phase. The powder was immersed in an NaOH solution made of distilled water degassed by Ar bubbling. The weight of the NaOH solution was over 20 times greater than that of the powder when using a 20 mass% NaOH solution. Leaching was performed with various NaOH concentrations, temperatures, and time periods. After leaching, the solution was replaced by the same one over 5 times, and then the powder was washed.

*Corresponding author, E-mail: takayuki.kojima.b4@tohoku.ac.jp
with water over 5 times until the pH became neutral. The wet powder was dried in air overnight at room temperature. Alloy compositions, surface area, and microstructures were evaluated by inductively coupled plasma-atomic emission spectrometry, the Brunauer–Emmett–Teller method for N₂ adsorption isotherms at −196°C, and scanning electron microscopy (SEM), respectively.

The leached FeNi powder was loaded into a 4-mm internal diameter quartz tube surrounded by an electric furnace and annealed under hydrogen (purity: 99.99%) flow of 50 cm³ min⁻¹ at 200–400°C for 5 h. The sample atmosphere was shut off from air using valves at both ends of the tube, and then the closed system was transferred into an Ar glove box (O₂ < 20 ppm). The powder (ca. 20 mg) was loaded into a sample holder with epoxy resin in the glove box for a magnetic measurement using a vibrating-sample magnetometer, which was conducted at room temperature. A portion of the powder was carefully extracted with slow oxidation for XRD and SEM.

The leached Fe powder was heated under hydrogen flow at 300–500°C for 1 h in the same tube furnace used for FeNi to reduce oxides formed during drying. After cooling to room temperature, ammonia gas (purity: 99.99%) was introduced at a flow rate of 40 cm³ min⁻¹, and then nitriding was conducted at 100–200°C for 1–24 h. After purging with nitrogen, the sample powder was transferred into the glove box and prepared for each measurement as well as the FeNi.

3. Results and Discussions

3.1 L₁₀-FeNi

Table 1 shows alloy compositions and surface areas after leaching of AlₓFeNi under different conditions. Residual Al decreased with leaching temperature (Samples 1–4). However, dissolution of Fe was observed when leached at 110°C, which was the boiling point of the 20 mass% NaOH solution used, and it was significant when leached using 65 mass% NaOH solution at a boiling point of 178°C. When leached using 5 mass% NaOH solution at a boiling point of 102°C, a smaller Al composition was obtained without Fe dissolution. All samples showed a large surface area. We also tested a KOH solution for leaching (not shown in Table 1), but the results were similar to those using NaOH (surface area was somewhat small when using KOH).

Figure 1 shows XRD patterns after leaching. Peaks around 2θ (diffraction angle) = 44° likely consisted of 111 FeNi and oxide peaks. Peaks around 2θ = 35° likely originated from oxides and increased with the leaching temperature (Samples 1–4). An especially strong oxide peak around 2θ = 35° can be seen for Sample 6 originating from an Fe oxide because bcc-Fe peaks were observed in XRD after the annealing under hydrogen flow. By comparing the aforementioned results, we adopted the conditions of Sample 2 (20 mass% NaOH, 70°C, 2 h) for the next step: preparation of L₁₀-FeNi.

The leached powder was reproduced with the leaching conditions from Sample 2 (20 mass% NaOH, 70°C, 2 h). Its composition was Al₁₀.₄Fe₇.₀Ni₁₂.₆, and the surface area was 91 m² g⁻¹. Although these properties were somewhat different from those of Sample 2 due to reproducibility of the mother alloy preparation and the leaching conditions, a mesoporous structure was obtained, as indicated by around 10 nm grains and pores in an SEM image (Fig. 2(a)) and a hysteresis of adsorption–desorption isotherm (Fig. 2(b)). By annealing under hydrogen flow, the microstructure seemed to become slightly larger at 300°C and certainly larger at 400°C, as shown in Figs. 2(c, d). Figure 3 shows XRD patterns after the annealing. The oxide peak around 2θ = 35° was reduced by the hydrogen annealing, especially at ≥300°C, and 111 and 200 FeNi peaks increased with the annealing temperature, which indicates transformation of the FeNi single phase. Superlattice peaks originating from the L₁₀ structure normally cannot be observed, even if L₁₀-FeNi formed, because they are very weak due to the close atomic scattering factors of Fe and Ni.

The inset of Fig. 4 shows a magnetization curve (M: magnetization; H: magnetic field) for the 300°C annealing. Very similar magnetization curves were obtained for the samples annealed at different temperatures. Figure 4 shows Mₘ and Hₘ (coercivity). The largest Mₘ = 138 A m² kg⁻¹ was obtained when annealed at 300°C. The value is almost the

![Figure 1](image1.png)

**Table 1** Leaching conditions (C NaOH: NaOH concentration; T: temperature; t: time), alloy compositions, and surface area (A) after leaching AlₓFeNi using an NaOH solution.

<table>
<thead>
<tr>
<th>No.</th>
<th>C NaOH (mass%)</th>
<th>T/°C</th>
<th>t/h</th>
<th>Al (mol%)</th>
<th>Fe (mol%)</th>
<th>Ni (mol%)</th>
<th>A /m² g⁻¹</th>
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<tr>
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<td>2</td>
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<td>20</td>
<td>110</td>
<td>2</td>
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<td>49.6</td>
<td>149</td>
</tr>
<tr>
<td>5</td>
<td>65</td>
<td>178</td>
<td>0.5</td>
<td>2.9</td>
<td>20.0</td>
<td>77.1</td>
<td>69</td>
</tr>
<tr>
<td>6</td>
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<td>102</td>
<td>2</td>
<td>6.4</td>
<td>48.6</td>
<td>45.0</td>
<td>111</td>
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</table>
same as that of an L1₀-FeNi powder prepared by denitriding of FeNiN (139 Å m² kg⁻¹), but it is smaller by 10% than that of a bulk (154 Å m² kg⁻¹), likely due to the residual Al. The largest $H_{c}$ was only 12 kA m⁻¹ for the 400°C annealing. Possible reasons for this small $H_{c}$ are a lack of formation of the L1₀-FeNi phase with sufficient ordering and a too small grain size. For the former reason, residual Al (10 mol%) was considered too large for keeping the phase stability of L1₀-FeNi. In addition, an order–disorder transition temperature is known to be reduced in nanoparticles, which might have occurred in the leached samples, the indicated grain size of which was ca. 10 nm by SEM (Fig. 2(c)) and ca. 5 nm by XRD using the Scherrer equation for the 300°C annealing. Such small grain sizes can also make the $H_{c}$ small, even if L1₀-FeNi forms, because a reduction of $D$ (grain size) increases $H_{c}$ if $D > L_{ex}$ (exchange length), but it decreases $H_{c}$ if $D < L_{ex}$. The $L_{ex}$ value of L1₀-FeNi was roughly deduced to be 4 nm if $K_u = 1$ MJ m⁻³ and 12 nm if $K_u = 0.1$ MJ m⁻³ using the average exchange stiffness constants of Fe and Ni. These $L_{ex}$ values are comparable to the actual $D$ values. Thus, an increase in $H_{c}$ with temperature is due to an increase in grain size, as indicated by SEM images (Figs. 2(c, d)) and a shrinking of XRD peak widths (Fig. 3).

3.2 α′′-Fe₁₆N₂
Al₃Fe₂ was leached using a 20 mass% NaOH solution at 70°C for 2h, which was adopted from the conditions in Leoni’s thesis and our pre-experiments. A composition of residual Al was 2.8 mol%. A mesoporous structure was obtained, as indicated by an SEM image (Fig. 5(a)), a hysteresis of adsorption–desorption isotherm (Fig. 5(b)), and
a high surface area of 23 m² g⁻¹, which was consistent with the results by Leoni.²⁵) By hydrogen reduction followed by nitriding, the microstructure became larger as shown in Figs. 5(c, d). Table 2 shows the list of nitrided samples with preparation conditions and properties. Figure 6 shows XRD patterns for the nitrided samples and an as-leached one, together with references in the International Center for Diffraction Data (ICDD) database. The as-leached sample showed bcc-Fe peaks with weak oxide peaks. For samples with hydrogen reduction at 500°C, a tiny 202 Fe₁₆N₂ peak around 2θ = 42.5° was observed in addition to bcc-Fe peaks for nitriding at 100°C, while Fe₁₆N₂ peaks grew with nitriding temperature together with a reduction of Fe peaks (Samples 1–3). However, samples nitrided at 175 and 200°C (Samples 4 and 5) showed no Fe₁₆N₂ peaks but did show other nitride peaks, indicating over-nitriding.

Sample 6, nitrided at 125°C for 24 h, showed only Fe₁₆N₂ peaks, unlike Sample 2 nitrided at 125°C for 5 h, which indicates that both the nitriding time and temperature are important. For samples with hydrogen reduction at 300°C, Sample 7, nitrided at 150°C for 5 h, showed other nitride peaks in addition to the Fe₁₆N₂ peaks, indicating over-nitriding. In contrast, no additional peaks were observed for

<table>
<thead>
<tr>
<th>No.</th>
<th>Tᵣ /°C</th>
<th>Tₓ /°C</th>
<th>tₓ /h</th>
<th>Hₑ /kA m⁻¹</th>
<th>Mₛ /A m² kg⁻¹</th>
<th>Mᵣ /A m² kg⁻¹</th>
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<tr>
<td>1</td>
<td>500</td>
<td>100</td>
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<td>40</td>
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<td>59</td>
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<td>125</td>
<td>5</td>
<td>81</td>
<td>207 ± 5</td>
<td>74</td>
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<tr>
<td>3</td>
<td>500</td>
<td>150</td>
<td>5</td>
<td>88</td>
<td>170 ± 4</td>
<td>59</td>
<td>Fe₁₆N₂</td>
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<tr>
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<td>500</td>
<td>175</td>
<td>5</td>
<td>31</td>
<td>102 ± 2</td>
<td>22</td>
<td>Fe₂N, Fe₁₆N₂</td>
</tr>
<tr>
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<td>500</td>
<td>200</td>
<td>5</td>
<td>35</td>
<td>36 ± 1</td>
<td>8</td>
<td>Fe₂N, Fe₁₆N₂</td>
</tr>
<tr>
<td>6</td>
<td>500</td>
<td>125</td>
<td>24</td>
<td>93</td>
<td>178 ± 5</td>
<td>66</td>
<td>Fe₁₆N₂</td>
</tr>
<tr>
<td>7</td>
<td>300</td>
<td>150</td>
<td>5</td>
<td>71</td>
<td>137 ± 3</td>
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<tr>
<td>8</td>
<td>300</td>
<td>150</td>
<td>1</td>
<td>117</td>
<td>190 ± 5</td>
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<tr>
<td>9</td>
<td>300</td>
<td>125</td>
<td>5</td>
<td>121</td>
<td>186 ± 5</td>
<td>85</td>
<td>Fe₂N, Fe₁₆N₂</td>
</tr>
</tbody>
</table>

Fig. 6 XRD patterns after nitriding. Sample numbers are listed in Table 2. Oxide peaks for as-leached sample were assigned to Fe₂O₃, with space group P4/2/2. Bar patterns are referenced in the ICDD database for α”-Fe₁₆N₂: #078-1865, γ’-Fe₂N: #064-0134, ε-Fe₅N: #049-1662, and ε-Fe₂N: #072-2126. Diffractions by Cu-Kα₁ were subtracted. Relative peak intensities at a higher angle were higher than the references due to insufficient sample amounts (part of the incident X-ray was out of sample at a lower angle).
Samples 8 and 9 nitrided at 150°C for 1 h and 125°C for 5 h, respectively. These results mean that appropriate nitriding conditions for obtaining an Fe16N2 single phase were milder for the samples reduced at 300°C than those at 500°C. This indicates that the 300°C reduced sample was more active for nitriding than the 500°C one. This is also indicated by SEM images, which show that the 300°C reduced sample had a fine microstructure (Fig. 5(d)), while the 500°C sample had a larger microstructure (Fig. 5(c)).

Figure 7 shows XRD patterns measured for a longer time for Samples 3, 6, 8, and 9. These samples showed a 103 Fe16N2 peak that is a fingerprint of the α’ phase and that originates from nitrogen ordering, while that is absent in α phase having no nitrogen ordering. An exact intensity ratio of 103/202 peaks could not be estimated because a 103 peak is very weak and part of the incident X-ray was out of the sample due to an insufficient sample amount. We roughly estimated the 103/202 peak ratio to be around 0.02 in these samples. The ICDD reference (#078-1865) indicates the 103/202 ratio to be 0.047. These values mean that volume fractions of the α’ phase and α phase were 43% and 57%, respectively, if they existed separately.

Figure 8 shows magnetization curves for Samples 3 and 9. They showed a large $H_c$ around 100 kA m$^{-1}$, indicating a high $K_u$. The $H_c$, $M_s$, and $M_r$ (remanent magnetization) values for all samples were estimated from magnetization curves, listed in Table 2. Sample 1, consisting mostly of Fe, had $M_r = 226 \pm 16$ A m$^2$ kg$^{-1}$, which was close to the $M_r$ of bulk Fe (218 A m$^2$ kg$^{-1}$). The somewhat larger $M_s$ originated from a large error in sample weight (13 ± 1 mg). In contrast, Samples 3, 6, 8, and 9, consisting mostly of Fe16N2, had smaller $M_s$ than Fe even though both α’ and α phases had larger $M_s$ than Fe. One possible reason is over-nitriding.

In Fig. 7, the existence of γ’-Fe$_4$N ($M_s = 193$ A m$^2$ kg$^{-1}$) and ε-Fe$_3$N ($M_s = 134$ A m$^2$ kg$^{-1}$) phases was indicated, and this was significant for Sample 3, for which $M_s$ was smaller than in Samples 6, 8, and 9. For Samples 8 and 9 (hydrogen reduced at 300°C), residual Fe oxides likely also decreased the $M_s$ values as indicated by the peaks around 2θ = 35.5° in Fig. 7. In addition, we can speculate that the reduction of Fe magnetic moments due to Al impurities might be larger for Fe16N2 phases than those for Fe phase in these samples. $H_c$ and $M_r$ were larger for Samples 8 and 9 than for Samples 3 and 6. This is due to a difference in grain size between the samples hydrogen reduced at 300°C and 500°C, as shown in Figs. 5(c, d). The $L_{ex}$ value of Fe16N2 was roughly deduced to be 4 nm if $K_u = 1$ MJ m$^{-3}$ and 14 nm if $K_u = 0.1$ MJ m$^{-3}$ using the exchange stiffness constant of Fe. Figures 5(c, d) clearly indicate that $D > L_{ex}$, so the smaller grain size led to the larger $H_c$.

4. Conclusions

We attempted to obtain L1$_0$-FeNi and α’-Fe16N2 magnets using the leaching method. Mesoporous FeNi and Fe with a high surface area were prepared by leaching Al$_x$FeNi and Al$_x$Fe$_2$, respectively. FeNi single phase was obtained after annealing the leached FeNi. The largest $M_s$ was 138 A m$^2$ kg$^{-1}$, which is 90% of the bulk value, and the largest $H_c$ was only 12 kA m$^{-1}$. The 10 mol% residual Al probably reduced the $M_s$ value and might have reduced the phase stability of L1$_0$-FeNi. A too small grain size was another possible reason for the small $H_c$. For the leached Fe, various phases and magnetic properties were obtained after the hydrogen reduction followed by the ammonia nitriding. A high temperature and a long nitriding duration resulted in over-nitriding, forming γ’-Fe$_4$N, ε-Fe$_3$N, and ε-Fe$_2$N. Appropriate conditions of the hydrogen reduction and nitriding almost yielded single phase Fe16N2 with α’ phase. The XRD patterns roughly indicated a volume fraction of the α’ phase around 43%. The largest $M_s$ of the Fe16N2 samples was 190 A m$^2$ kg$^{-1}$, which was smaller than that of Fe. The existences of over-nitriding phases, residual oxides, and Al impurities were possible reasons for the small $M_s$. The $H_c$ values of the Fe16N2 samples were around 100 kA m$^{-1}$, indicating high $K_u$. The largest $H_c$ was 121 kA m$^{-1}$, which was believed to originate from a high $K_u$ and a small grain size.
For obtaining L1₀-FeNi, the residual Al must be reduced by some method, such as changing the mother alloy or the solution and using electrolytic dealloying with potential control. A grain size should also be controlled for to obtain L1₀-FeNi with a large $H_c$. To obtain Fe₁₆N₂ with a much larger fraction of the $\alpha'$ phase and a larger $M_s$, preparation conditions should be further optimized to reduce over-nitriding, residual oxides, and residual Al. Furthermore, the relation between magnetic properties and atomic-level structures should be investigated for samples prepared by this method.

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