Synthesis and Characterization of L1₀-FeNi Powders

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FeNi powders were synthesized by reductive reaction of iron nickel chloride below 320 °C. Calcium hydride (CaH₂) was used as a reductant. The coercivity of synthesized powders depends on the amount of CaH₂, and the largest coercivity of 54 kA/m was obtained. The (001) diffraction line due to the L1₀ superstructure was observed by anomalous synchrotron X-ray diffraction using synchrotron radiation, indicating the formation of L1₀-FeNi.

Key words: L1₀-FeNi, low-temperature-reduction, CaH₂, coercivity, powder, anomalous X-ray diffraction

1. Introduction

L1₀ type Fe-Ni alloy (L1₀-FeNi) is one of candidates for rare-earth-free magnets. It is found in a meteorite and has a superstructure of iron monolayer and nickel monolayer. It shows an order-disorder transition temperature at 320 °C¹. The interdiffusion coefficient below the temperature is very small. Therefore, it is hard to be synthesized by conventional heat treatments. Various syntheses such as neutron irradiation², mechanical alloying³, reduction of nanocrystalline NiFe₂O₄⁴ and alternate monoatomic layer deposition^{5,6} have been investigated. However, the synthesis to balance mass productivity with performance has not been developed.

In this paper, we propose a new synthesis process. FeNi powders were synthesized by reduction of iron-nickel chlorides with calcium hydride (CaH₂) as a reductant below 320 °C.

2. Experiments

Iron (II) chloride tetrahydrate and nickel chloride hexahydrate were dissolved in the distilled water. Concentrations of iron and nickel were fixed as 0.2 M in total and the ratio of iron to nickel were varied from 9:1 to 1:4. The water solution was dried at 125 °C for 12 hours in vacuum condition. Dried powders which were called “precursor” were mixed with CaH₂ (varied from 25 to 150% in weight) and heated at 270 to 310 °C for 12 hours in a furnace controlled Ar atmosphere. The heated samples were rinsed for 10 minutes with 0.1 M HCl and continuously with distilled water a few times. Finally, powders were condensed under magnetic field and dried at 125 °C for 2 hours.

Magnetic properties of samples were investigated by the Vibrating Sample Magnetometer (Quantum Design: VersaLab/VSM). Energy Dispersive X-ray Spectroscopy (EDX) analysis was performed using SHIMAZU EDX 800HS spectrometer. Crystal structures were investigated by an anomalous X-ray diffraction using synchrotron X-ray radiation at SPring-8.

3. Results and Discussions

We assumed a reaction as follows.

Here (Fe,Ni)Cl₂ · 2H₂O is a precursor. The stoichiometric molar ratio of CaH₂ to precursor is 2:1. Molecular weights of precursor and CaH₂ are 164.17 and 42.09, respectively. Therefore the stoichiometric ratio of CaH₂ to precursor is 51% in weight.

Figure 1 shows the coercivity as a function of the amount of CaH₂ (in weight ratio to precursor). The reduction temperature was 300 °C. The maximum coercivity was obtained when 63% of CaH₂ was employed.

According to the XRD analysis, it was revealed that iron oxides tended to be generated when the CaH₂ ratio was small. This might be because nickel chloride might be preferentially reduced and iron chloride might be

Fig. 1 Coercivities as a function of the weight ratio of CaH₂ to precursor.

hydrolyzed. When the CaH_2 ratio was large, the amount of iron oxides was extremely small and that of FeNi alloy was large. A possible reason for the low coercivity is the formation of disordered alloy because the reduction rate is too large to form the ordered alloy.

Figure 2 shows the coercivity as a function of reduction temperature for samples with the ratio of 50% and 50% for iron and nickel, respectively. The molar ratio of iron in the precursor was 50%, and CaH_2 ratio to precursor was 63%. The coercivity did not change significantly even if the temperature of reduction was varied from 270 to 310 °C.

Figure 3 shows the coercivity and saturation magnetization as a function of the ratio of iron in precursor. Here the CaH_2 was 63% in weight to precursor, and the reduction temperature was 290 °C.

The maximum coercivity was over 50 kA/m at 75% and much larger than that of previously reported FeNi

Fig. 2 Coercivity as a function of reduction temperature.

Fig. 3 Coercivity and saturation magnetization as a function of the iron ratio in precursor.

Table 1 Compositional change during the synthesis process.

Process Composition	As reduced	Rinsed with distilled water	Rinsed with hydrochloric acid
Fe (at%)	51.6	51.7	34.8
Ni (at%)	48.4	48.3	65.2

powder⁷). The magnetization was maximized at 66%.

Table 1 shows the compositional change during the synthesis process. Compositions are normalized molar ratios so that the total of Fe and Ni may become 100. The compositional change occurred when it was rinsed with acid. Fe was preferentially dissolved into acid than Ni. Therefore coercivity would be maximized at the iron-rich ratio of precursor as shown in Fig. 3.

Figure 4 shows a magnetization curve for the sample when the CaH_2 ratio to precursor, the iron ratio in precursor and the reduction temperature were 63%, 66 %, and 290 °C, respectively. It is worth to note that the primary particle size was about 5 nm. Also the recoil curves are shown in the figure. The sweep-rate was 8 kA/m/sec. The recoil curves were almost linear and inclined greatly, suggesting that it was contained considerable amount of soft magnetic materials as secondary phase. A possible reason why the saturation magnetization is less than a theoretical value of 1130 kA/m is a nickel-rich composition of the alloy.

Figure 5 shows a distribution of coercivities that was estimated simply by using the following equations.

$$P(H_r \leq H_c < H_r + dH_r) \propto dM_r(H_r) / 2M_s \quad (2)$$

Here $P(H_r \leq H_c < H_r + dH_r)$ is a probability of finding a value of coercivity in a range between H_r and $H_r + dH_r$, $dM_r(H_r)$ is the reduction of remanent magnetization

Fig. 4 Magnetization curve for a sample with the CaH_2 ratio to precursor.

Fig. 5 Probability of finding a value of coercivity. The solid line is a guide for eyes.

after applying the reverse magnetic field H_r , dH_r is change of H_r , H_c is a coercivity, and M_s is a saturation magnetization. Probability had a peak at the coercivity of around 80 kA/m, and a maximum coercivity was 220 kA/m proved by a peak fitting curve.

Because of the small difference of scattering factors of iron and nickel, it is expected that superlattice peaks are very weak. Therefore, we adopted the anomalous scattering technique. Since the absorption edge of iron is 7.11 keV, we performed XRD measurements around the energy of 7.11 keV. Figure 6 shows XRD patterns for the sample ($H_c=54$ kA/m) taken with different energies. Diffraction patterns were indexed based on the body centered tetragonal (bct) structure. When the structure was disordered, FeNi (100) (around 2.53 Å) and FeNi

Fig. 6 X-ray diffractions with various energies for the sample with $H_c=54$ kA/m.

Fig. 7 Comparison of XRD patterns for the samples with $H_c=54$ and 16 kA/m.

(001) (around 3.58 Å) diffractions were not observed because of an extinction rule. On the other hand, when the superlattice peaks were observed, we could confirm that it contained $L1_0$ -FeNi phase. (100) and (001) diffractions were successfully observed at the energy of 7.11 keV. Figure 7 shows a comparison of XRD patterns for the samples with $H_c=54$ kA/m and 16 kA/m. The diffractions of (100) were observed in both case, however, the diffraction of (001) was observed only for the $H_c=54$ kA/m sample. The position of the (100) diffraction of $L1_0$ -FeNi is 2.53 Å and close to that of the (311) diffraction of nickel ferrite ($Ni_xFe_{3-x}O_4$: $x=0$ to 1) and they are indistinguishable, but the position of the (001) diffraction is 3.58 Å and unique to $L1_0$ -FeNi. Therefore, we consider that $L1_0$ -FeNi is contained only in the sample with $H_c=54$ kA/m in which the (001) diffraction was observed.

4. Conclusions

We synthesized FeNi powders by the low-temperature-reduction of iron-nickel chlorides. The FeNi powders of the coercivity that exceeded 50 kA/m by optimizing the synthesis condition were obtained. By means of anomalous X-ray diffraction, we confirmed the formation of $L1_0$ -FeNi phase.

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