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Synthetic route for high-yield α″-$Fe_{16}N_2$ submicron-sized powder using CaH_2 drying agent

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The rare-earth-free magnetic material α″-$Fe_{16}N_2$ is known to be a high-performance magnetic material. However, a synthetic route for high-yield α″-$Fe_{16}N_2$ powder has not yet been established. In this study, a high-yield α″-$Fe_{16}N_2$ submicron-sized powder was synthesized from Fe_3O_4 *via* H_2 reduction, and subsequent nitridation using a CaH_2 drying agent. Here, controlling the crystallite diameter of α-Fe is crucial to promoting nitridation. α-Fe powder with a crystallite diameter of approximately 20 nm was produced by lowering the reduction temperature and water vapor partial pressure. Thus, a high-yield α″-$Fe_{16}N_2$ phase of 97 wt% could be obtained. Microstructural observations indicated that α″-$Fe_{16}N_2$ submicron-sized powder with primary particles of 20–30 nm diameter could be synthesized. The α″-$Fe_{16}N_2$ powder had much higher coercivity than that of the α-Fe powder. Thus, the process suggested in this study is expected to contribute to the development of applications of α″-$Fe_{16}N_2$ in magnetic materials.

1. Introduction

Ferromagnetic materials have diverse applications, for example, in automotive motors and home appliances.[1,2] Two main ferromagnetic materials used for practical applications include Nd–Fe–B and Ferrite magnets. Of these, the former is known to be the strongest magnet in the world.[1–3] However, it is an expensive material, as it contains the rare-earth element Nd. The latter, *i.e.*, ferrite magnets are inexpensive, as they are rare-earth free; however, their magnetic performance is relatively low.[1,2] Thus, a rare-earth-free magnet with a magnetic performance exceeding that of ferrite is desired. α″-$Fe_{16}N_2$ meets the above-mentioned requirements and is expected to be a next-generation ferromagnetic material.[4]

Many studies related to α″-$Fe_{16}N_2$ have been reported on thin films[5–14] and nanoparticles,[4,15–29] ever since the giant magnetic moment of α″-$Fe_{16}N_2$ was discovered by Kim *et al.*[5] For instance, Sugita *et al.* fabricated single-crystal α″-$Fe_{16}N_2$ films by molecular beam epitaxy.[6] Ogawa *et al.* synthesized single-phase α″-$Fe_{16}N_2$ nanoparticles of approximately 100 nm by H_2 reduction and subsequent nitridation.[4] However, the synthesis of α″-$Fe_{16}N_2$ powder with a high bulk density is necessary for applications in ferromagnetic materials. Although there have been several reports on both powder[30–33] and bulk[34] forms of α″-$Fe_{16}N_2$, it contained some impurities, and its production yield was low, thus hindering its use in any practical applications. Therefore, it has become necessary to establish a synthetic route to high-yield α″-$Fe_{16}N_2$ powder for engineering applications.

Owing to the low diffusion rate of N atoms during NH_3 gas nitridation, powdering α″-$Fe_{16}N_2$ was a challenge that needed to be tackled. One previous study suggested that the smaller the crystallite size of α-Fe nanoparticles, the higher the yield of α″-$Fe_{16}N_2$ nanoparticles by nitridation.[15] Thus, we focused on controlling the crystallite diameter of α-Fe during H_2 reduction of iron oxide powder. In general, the nucleation and growth of nuclei during H_2 reduction depends on the reduction temperature and water vapor partial pressure;[35] therefore, the crystallite diameter of the α-Fe powder can be reduced by controlling these parameters. Our previous study demonstrated that the partial pressure of water vapor was lowered by introducing a drying agent, such as the CaH_2 into the H_2 reduction system, and the reduction reaction from the Fe_3O_4 powder to α-Fe powder was lowered from 400 to 300 °C.[36] Therefore, in this study, synthesis of high-yield α″-$Fe_{16}N_2$ submicron-sized powder was attempted *via* H_2 reduction and subsequent nitridation using a CaH_2 drying agent.

2. Materials and methods

A powder mixture sample (0.5 g) of Fe_3O_4 (Kojundo Chemical Lab. Co., 1 μm pass) and CaH_2 (Sigma–Aldrich Co., LCC) was weighed in a 20 : 80 weight ratio. The amount of CaH_2 is sufficient to absorb H_2O, which is produced by the reduction

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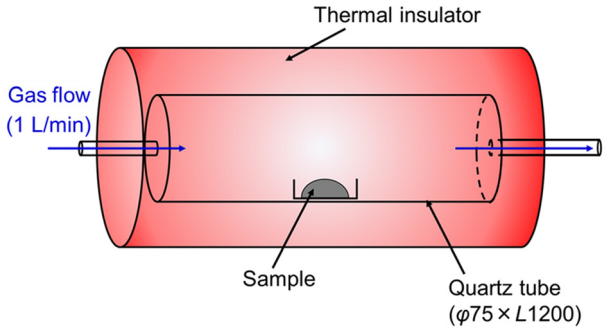

Fig. 1 Schematic diagram of the experimental setting.

reaction of Fe_3O_4. This is effective in lowering the partial pressure of water vapor within the system, thereby promoting the reduction reaction. Both mixed and unmixed samples were investigated. Each of these samples was placed in a tube furnace, as shown in Fig. 1. H_2 reduction was conducted at two temperatures, namely 300 or 400 °C for 4 h under a 1 L min^{-1} H_2 gas flow. Subsequently, using an N_2 gas flow, the sample was cooled to ambient temperature. The sample was subsequently nitrided at a specific temperature in the range of 120–170 °C for 5 h under a 1 L min^{-1} ammonia gas flow. After the nitridation, the sample was cooled to ambient temperature, using the N_2 gas flow. The sample was then slowly oxidized by increasing the oxygen partial pressure in stages to atmospheric concentration before being removed from the tube furnace. The obtained sample was washed several times with a 0.1 M NH_4Cl (FUJIFILM Wako Pure Chemical Corporation) methanol solution and pure methanol to remove the by-products (CaO, $Ca(OH)_2$, and CaH_2), and subsequently dried in vacuum. Next, a phase analysis of the sample was conducted using X-ray diffraction (XRD) with Co-Kα source (Smart Lab, Rigaku); the microstructure of the samples was observed using transmission electron microscopy (TEM; EM-002B, TOPCON); and the magnetic properties of the samples were evaluated using superconducting quantum interference device (SQUID) measurements (MPMS, Quantum Design).

3. Results and discussion

3.1. Phase analysis of reduced samples

Fig. 2 shows the XRD profiles of the samples reduced under different conditions. The diffractions, under all the conditions, were assigned to α-Fe only, indicating that the reduction was complete as shown in chemical eqn (1). Table 1 shows the α-Fe crystallite diameter (D_{Fe}) values, calculated from the XRD profiles using Scherrer equation. First, the samples reduced at 400 °C with and without CaH_2 were compared. D_{Fe} of the sample reduced with CaH_2 was smaller than that of the sample reduced without CaH_2. Next, the samples reduced with CaH_2 were compared. In this case, D_{Fe} of the sample reduced at 300 °C was smaller than that of the sample reduced at 400 °C. From the above it was concluded that α-Fe with a smaller D_{Fe} could be obtained using CaH_2 than with conventional H_2 reduction (*i.e.*, without a drying agent).

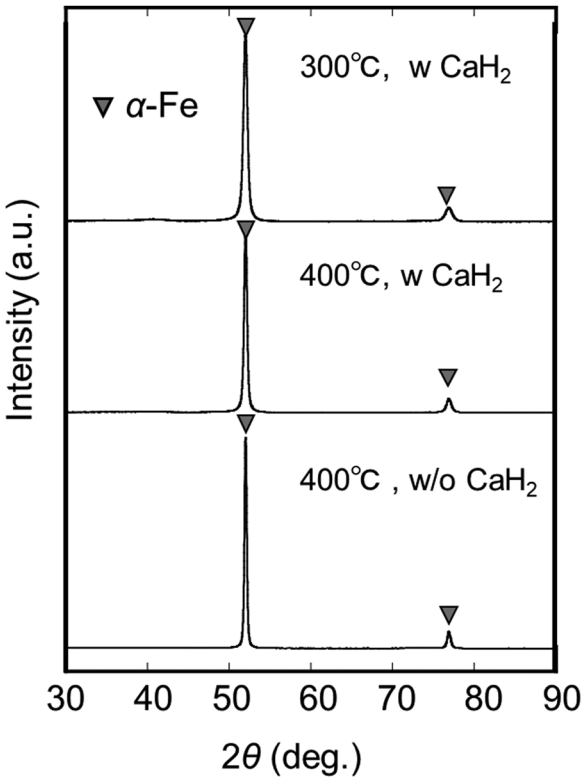

Fig. 2 XRD profiles of samples reduced under H_2 flow at two different temperatures with (w) and without (w/o) CaH_2.

Table 1 D_{Fe} of samples reduced at two different temperatures with and without CaH_2

	400 °C w/o CaH_2	400 °C w CaH_2	300 °C w CaH_2
D_{Fe} (nm)	41.8	27.8	19.5

$$Fe_3O_4 + 4H_2 \rightarrow 3\ (\alpha\text{-Fe}) + 4H_2O \quad (1)$$

Next, the effect of the CaH_2 drying agent and reduction temperature on D_{Fe} will be discussed. For the samples reduced at 400 °C, D_{Fe} decreased in the presence of CaH_2. Our previous study indicated that introducing the CaH_2 drying agent in the H_2 reduction system would lower the local partial pressure of water vapor in the iron oxide powder bed.[36] The decrease in the partial pressure of water vapor, accompanied by an increase in the partial pressure of H_2, would contribute to an increase in the reaction rate and promotion of nucleation of α-Fe. Therefore, it is understood that a decrease in D_{Fe} in the presence of CaH_2 was owing to the promotion of α-Fe nucleation caused by a decrease in the partial pressure of water vapor. As regards the samples reduced with CaH_2, D_{Fe} decreased upon lowering the reduction temperature from 400 to 300 °C. This might have been caused by the suppression of coarsening of the α-Fe crystallites. The mechanism described above is considered to be applicable to the reduction reactions of other oxides such as FeO and α-Fe_2O_3 as well. This will be explored in future work.

3.2. Phase analysis of nitrided samples

Fig. 3(a) shows the XRD patterns of the samples reduced at 400 °C for 4 h and subsequently nitrided at 160–170 °C for 5 h without CaH_2. Fig. 3(b) shows the production ratio of each phase calculated by reference intensity ratio (RIR) quantification. RIR quantification was performed using the software SmartLab Studio II (Rigaku), with PDF data for α″-$Fe_{16}N_2$ referenced from no. 654562, α-Fe from no. 191830, γ′-Fe_4N from No. 79980, and ε-Fe_3N from No. 93190. The samples nitrided at 170 °C contained the γ′-Fe_4N phase, whereas those nitrided at 160 °C did not contain the γ′ phase. In addition, the samples nitrided at 170 °C contained more α-Fe phase than those nitrided at 160 °C. These results could be attributed to the decomposition of the α″-$Fe_{16}N_2$ phase into α-Fe and γ′-Fe_4N phases.[37] Consequently, 78 wt% of the maximum yield of the α″-$Fe_{16}N_2$ phase was obtained from the nitridation of the samples reduced at 400 °C without CaH_2.

Fig. 4(a) shows the XRD patterns of the samples reduced at 400 °C for 4 h and subsequently nitrided at 120–170 °C for 5 h with CaH_2. Fig. 4(b) shows the production ratio of each phase as calculated by RIR quantification. The sample nitrided at 170 °C contained the γ′ phase, as well as the ε phase (which is an excessively nitrided phase), whereas that nitrided at 160 °C did not contain the ε phase. Additionally, the sample nitrided at 150–170 °C contained the γ′ phase, whereas that nitrided at 140 °C did not contain the γ′ phase, but contained α″ and α-Fe phases. The lower the nitridation temperature, the lower the yield of the α″ phase in 120–140 °C range. As a result, 77 wt% of the maximum yield of the α″-$Fe_{16}N_2$ phase was obtained from nitridation of the samples reduced at 400 °C with CaH_2.

Fig. 5(a) shows the XRD patterns of the samples reduced at 300 °C for 4 h, and subsequently nitrided at 130–170 °C for 5 h with CaH_2. Fig. 5(b) shows the production ratio of each phase, as calculated by RIR quantification. The sample nitrided at 160–170 °C contained γ′ and ε phases, whereas that nitrided at 150 °C did not contain any ε phase. Additionally, the sample nitrided at 150–160 °C contained the γ′ phase, whereas that nitrided at 140 °C did not contain the γ′ phase, but contained α″ and α-Fe phases. The lower the nitridation temperature, the lower the yield of the α″ phase in the range of 120–140 °C. As a result, 97wt% of the maximum yield of the α″-$Fe_{16}N_2$ phase was obtained from the nitridation of the samples reduced at 300 °C with CaH_2, which is more or less the α″ single phase.

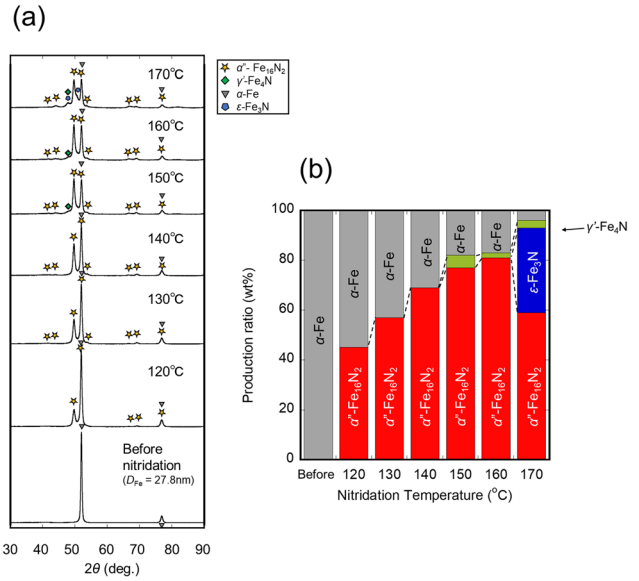

Fig. 4 (a) XRD profiles and (b) production ratio (wt%) of samples synthesize by H_2 reduction at 400 °C, and subsequently nitrided under NH_3 flow at different temperatures with CaH_2.

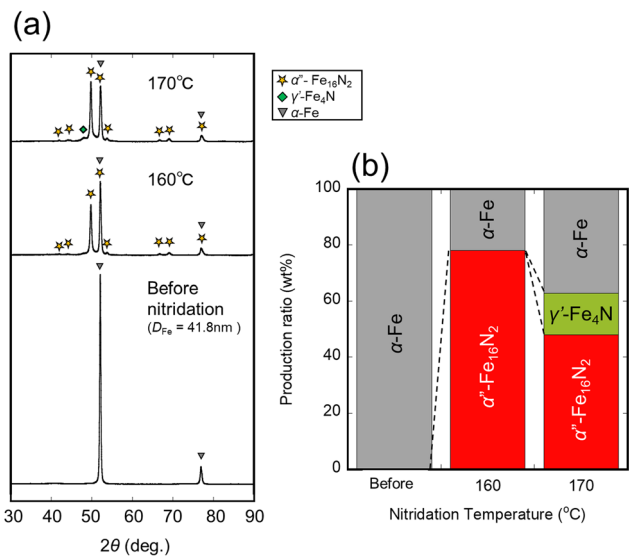

Fig. 3 (a) XRD profiles and (b) production ratio (wt%) of samples synthesized by H_2 reduction at 400 °C, and subsequently nitrided under NH_3 flow at different temperatures without CaH_2.

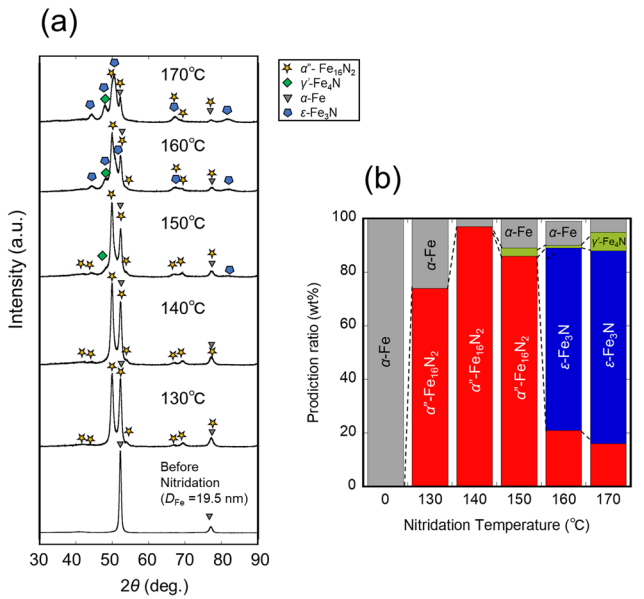

Fig. 5 (a) XRD profiles and (b) production ratio (wt%) of the samples synthesized by H_2 reduction at 300 °C, and subsequently nitrided under NH_3 flow at different temperatures with CaH_2.

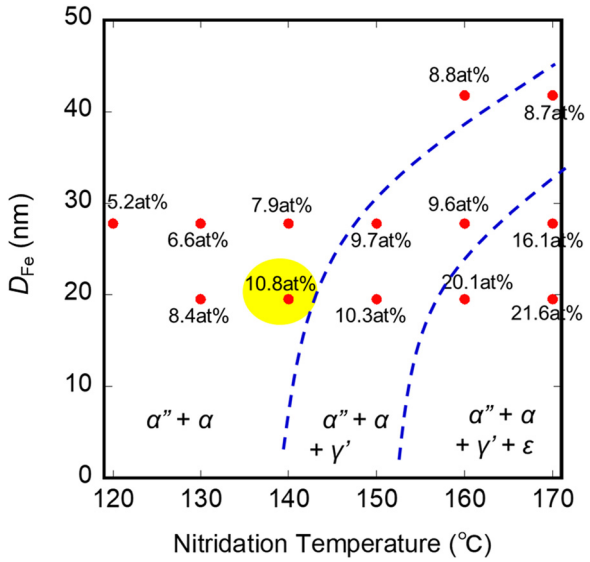

Fig. 6 Nitrogen content and formed phases as a function of nitridation temperature and D_{Fe}.

Fig. 6 shows a plot of the nitrogen content (at%) and the formed phase as a function of nitridation temperature and D_{Fe}, and reveals the effect of D_{Fe} on the phase formation of iron nitrides. It was observed that the nitrogen content increased, and the nitridation temperature at which an excessively nitrided phase was obtained (as shown in chemical eqn (2) and (3)) was lowered with a smaller D_{Fe}. It was inferred that the activation increased with an increase in the crystallite interface, and the diffusion ability of nitrogen improved. As a result, a high-yield α″ phase was obtained by low-temperature nitridation (chemical eqn (4)), in which the decomposition of the α″ phase into α and γ′ (chemical eqn (5)) phases could be prevented.

$$6\ (\alpha\text{-Fe}) + 2NH_3 \rightarrow 2\ (\varepsilon\text{-}Fe_3N) + 3H_2 \quad (2)$$

$$8\ (\alpha\text{-Fe}) + 2NH_3 \rightarrow 2\ (\gamma'\text{-}Fe_4N) + 3H_2 \quad (3)$$

$$16\ (\alpha\text{-Fe}) + 2NH_3 \rightarrow \alpha''\text{-}Fe_{16}N_2 + 3H_2 \quad (4)$$

$$\alpha''\text{-}Fe_{16}N_2 \rightarrow 8\ (\alpha\text{-Fe}) + 2\ (\gamma'\text{-}Fe_4N) \quad (5)$$

3.3. Microstructure

Next, the microstructure of the reduced and nitrided samples was observed to understand the change in microstructure after H_2 reduction and subsequent nitridation. Fig. 7 shows the TEM images of the raw powder; sample reduced at 300 °C for 4 h with CaH_2; and subsequently nitrided at 140 °C for 5 h with CaH_2. The reduced sample was a submicron-sized powder with a nano-cluster structure comprising primary particles of 20–30 nm. The nitrided samples had almost the same structure. This result was consistent with the XRD measurements. Thus, submicron-sized α″-$Fe_{16}N_2$ powder with a nano-cluster structure consisting of primary particles of 20–30 nm was successfully synthesized *via* H_2 reduction and subsequent nitridation using the CaH_2 drying agent.

3.4. Magnetic properties

Two critical magnetic performance properties, namely coercivity (H_c) and saturation magnetization (M_s) of the α″-$Fe_{16}N_2$

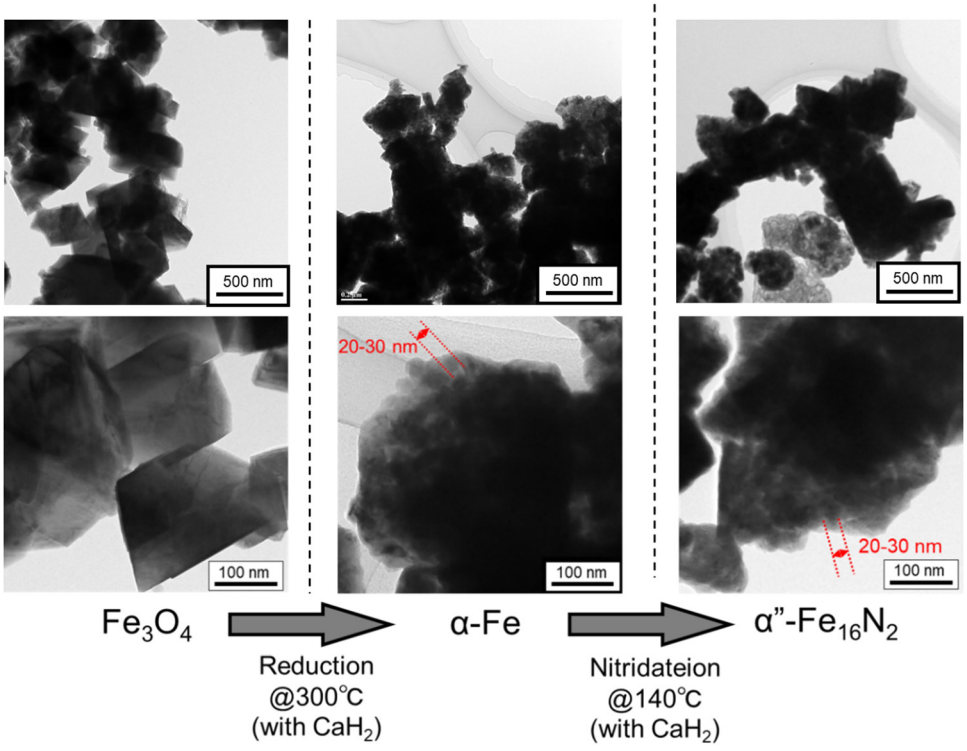

Fig. 7 TEM images of the raw material, reduced sample, and subsequently nitrided sample with CaH_2 drying agent.

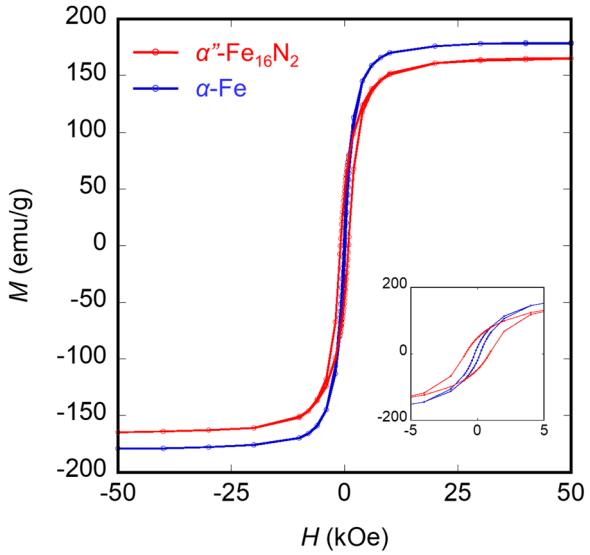

Fig. 8 M–H curve of the sample reduced at 300 °C with CaH_2 drying agent (α-Fe, blue plot), and sample reduced at 300 °C with CaH_2 drying agent and subsequently nitrided at 140 °C (α″-$Fe_{16}N_2$, red plot) measured at 300 K.

powders produced were analyzed. Fig. 8 shows the room temperature M–H curves of the sample reduced at 300 °C with CaH_2 (α-Fe powder), and sample reduced at 300 °C and nitrided at 140 °C with CaH_2 (α″-$Fe_{16}N_2$ powder). Table 2 lists H_c and M_s of each sample. H_c of the α″-$Fe_{16}N_2$ powder was 892 Oe at 300 K which was higher than that of the α-Fe powder (203 Oe). Moreover, the ratio of coercivity at 300 K to 10 K shows a higher value for α″-$Fe_{16}N_2$ powder (∼0.95) than that for α-Fe powder (∼0.71). These suggest that the magnetic anisotropy K_uV of α″-$Fe_{16}N_2$ is strong against thermal fluctuations k_BT, which is considered evidence of the high magnetic anisotropy of α″ phase. Additionally, M_s of the α″-$Fe_{16}N_2$ powder was slightly smaller than that of the α-Fe powder. Thus, α″-$Fe_{16}N_2$ powder with high H_c and M_s could be synthesized *via* H_2 reduction and subsequent nitridation using the CaH_2 drying agent.

On the other hand, M_s of the α-Fe and α″-$Fe_{16}N_2$ powders was much smaller than expected (222 emu g^{-1} for the theoretical value of α-Fe and 234 emu g^{-1} for nanoparticles of α″-$Fe_{16}N_2$).[4,38] In this study, the sample was slowly oxidized and exposed to air. Therefore, it was inferred that the small M_s value was owing to the oxide film formed during the oxidization process. To further improve the magnetization, a process or an implementation that avoids oxidization is required.

Table 2 H_c and M_s of the sample reduced at 300 °C with CaH_2 drying agent (α-Fe), and sample reduced at 300 °C with CaH_2 drying agent and subsequently nitrided at 140 °C (α″-$Fe_{16}N_2$); H_c and M_s were measured at 10 K and 300 K

	H_c (Oe)		M_s (emu g^{-1})	
	@10 K	@300 K	@10 K	@300 K
α″-$Fe_{16}N_2$	937	892	175	165
α-Fe	284	203	182	178

4. Conclusion

In this study, a high-yield α″-$Fe_{16}N_2$ submicron-sized powder, which is known to be a high-performance magnetic material, was synthesized *via* H_2 reduction and subsequent nitridation using CaH_2 as a drying agent. α-Fe powder with a small D_{Fe} of 19.5 nm was produced *via* H_2 reduction at 300 °C for 4 h in the presence of CaH_2 drying agent. α″-$Fe_{16}N_2$ powder with a high yield of 97 wt% was successfully synthesized by nitridation of the α-Fe powder obtained as explained earlier at 140 °C for 5 h. From the microstructure observation, the α″-$Fe_{16}N_2$ powder had a nano-cluster structure consisting of primary particles of 20–30 nm diameter. Magnetic property measurements indicated that the synthesized α″-$Fe_{16}N_2$ powder had a high H_c of 892 Oe and M_s of 165 emu g^{-1}. The results of this study are significant for the application of α″-$Fe_{16}N_2$ as a magnetic material and contribute to the development of the automotive and home appliance industries. Experimental validation as a permanent magnet is necessary and will be addressed in future work.

Data availability

All the data presented in this article are present in the form of figures and tables in the manuscript itself.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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