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Synthetic route for high-yield α'' -Fe₁₆N₂ submicron-sized powder using CaH₂ drying agent

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The rare-earth-free magnetic material α'' -Fe₁₆N₂ is known to be a high-performance magnetic material. However, a synthetic route for high-yield α'' -Fe₁₆N₂ powder has not yet been established. In this study, a high-yield α'' -Fe₁₆N₂ submicron-sized powder was synthesized from Fe₃O₄ via H₂ reduction, and subsequent nitridation using a CaH₂ 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'' -Fe₁₆N₂ phase of 97 wt% could be obtained. Microstructural observations indicated that α'' -Fe₁₆N₂ submicron-sized powder with primary particles of 20–30 nm diameter could be synthesized. The α'' -Fe₁₆N₂ 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'' -Fe₁₆N₂ 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'' -Fe₁₆N₂ meets the above-mentioned requirements and is expected to be a next-generation ferromagnetic material.⁴

Many studies related to α'' -Fe₁₆N₂ have been reported on thin films^{5–14} and nanoparticles,^{4,15–29} ever since the giant magnetic moment of α'' -Fe₁₆N₂ was discovered by Kim *et al.*⁵ For instance, Sugita *et al.* fabricated single-crystal α'' -Fe₁₆N₂ films by molecular beam epitaxy.⁶ Ogawa *et al.* synthesized single-phase α'' -Fe₁₆N₂ nanoparticles of approximately 100 nm by H₂ reduction and subsequent nitridation.⁴ However, the synthesis of α'' -Fe₁₆N₂ 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 bulk³⁴ forms of α'' -Fe₁₆N₂, 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'' -Fe₁₆N₂ powder for engineering applications.

Owing to the low diffusion rate of N atoms during NH₃ gas nitridation, powdering α'' -Fe₁₆N₂ 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'' -Fe₁₆N₂ nanoparticles by nitridation.¹⁵ Thus, we focused on controlling the crystallite diameter of α -Fe during H₂ reduction of iron oxide powder. In general, the nucleation and growth of nuclei during H₂ 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 CaH₂ into the H₂ reduction system, and the reduction reaction from the Fe₃O₄ powder to α -Fe powder was lowered from 400 to 300 °C.³⁶ Therefore, in this study, synthesis of high-yield α'' -Fe₁₆N₂ submicron-sized powder was attempted *via* H₂ reduction and subsequent nitridation using a CaH₂ drying agent.

2. Materials and methods

A powder mixture sample (0.5 g) of Fe₃O₄ (Kojundo Chemical Lab. Co., 1 μ m pass) and CaH₂ (Sigma-Aldrich Co., LCC) was weighed in a 20:80 weight ratio. The amount of CaH₂ is sufficient to absorb H₂O, which is produced by the reduction

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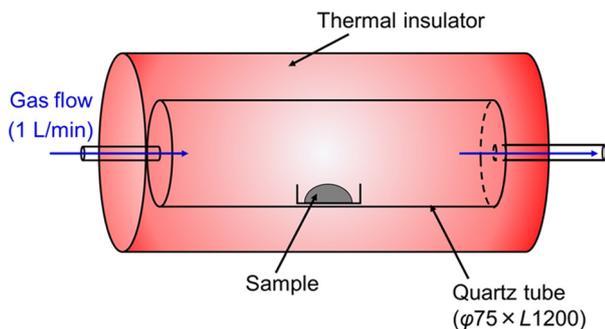


Fig. 1 Schematic diagram of the experimental setting.

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 , $\text{Ca}(\text{OH})_2$, and CaH_2), and subsequently dried in vacuum. Next, a phase analysis of the sample was conducted using X-ray diffraction (XRD) with $\text{Co-K}\alpha$ 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 $\alpha\text{-Fe}$ only, indicating that the reduction was complete as shown in chemical eqn (1). Table 1 shows the $\alpha\text{-Fe}$ 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 $\alpha\text{-Fe}$ with a smaller D_{Fe} could be obtained using CaH_2 than with conventional H_2 reduction (*i.e.*, without a drying agent).

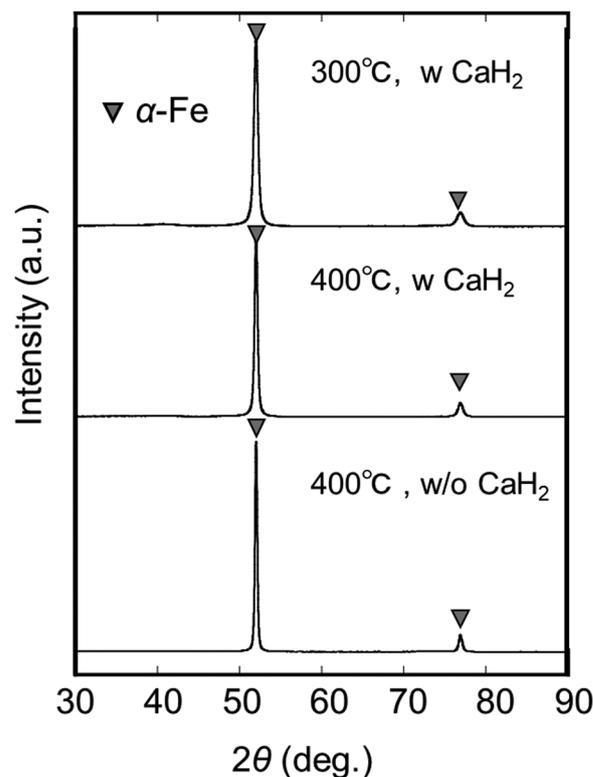
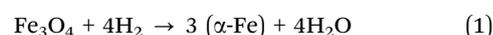


Fig. 2 XRD profiles of samples reduced under H_2 flow at two different temperatures with (w) and without (w/o) CaH_2 .

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 |



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 $\alpha\text{-Fe}$. Therefore, it is understood that a decrease in D_{Fe} in the presence of CaH_2 was owing to the promotion of $\alpha\text{-Fe}$ 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 $\alpha\text{-Fe}$ crystallites. The mechanism described above is considered to be applicable to the reduction reactions of other oxides such as FeO and $\alpha\text{-Fe}_2\text{O}_3$ as well. This will be explored in future work.



3.2. Phase analysis of nitrated samples

Fig. 3(a) shows the XRD patterns of the samples reduced at 400 °C for 4 h and subsequently nitrated at 160–170 °C for 5 h without CaH₂. 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'' -Fe₁₆N₂ referenced from no. 654562, α -Fe from no. 191830, γ' -Fe₄N from No. 79980, and ϵ -Fe₃N from No. 93190. The samples nitrated at 170 °C contained the γ' -Fe₄N phase, whereas those nitrated at 160 °C did not contain the γ' phase. In addition, the samples nitrated at 170 °C contained more α -Fe phase than those nitrated at 160 °C. These results could be attributed to the decomposition of the α'' -Fe₁₆N₂ phase into α -Fe and γ' -Fe₄N phases.³⁷ Consequently, 78 wt% of the maximum yield of the α'' -Fe₁₆N₂ phase was obtained from the nitridation of the samples reduced at 400 °C without CaH₂.

Fig. 4(a) shows the XRD patterns of the samples reduced at 400 °C for 4 h and subsequently nitrated at 120–170 °C for 5 h with CaH₂. Fig. 4(b) shows the production ratio of each phase as calculated by RIR quantification. The sample nitrated at 170 °C contained the γ' phase, as well as the ϵ phase (which is an excessively nitrated phase), whereas that nitrated at 160 °C did not contain the ϵ phase. Additionally, the sample nitrated at 150–170 °C contained the γ' phase, whereas that nitrated 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'' -Fe₁₆N₂ phase was obtained from the nitridation of the samples reduced at 400 °C with CaH₂.

Fig. 5(a) shows the XRD patterns of the samples reduced at 300 °C for 4 h, and subsequently nitrated at 130–170 °C for 5 h with CaH₂. Fig. 5(b) shows the production ratio of each phase,

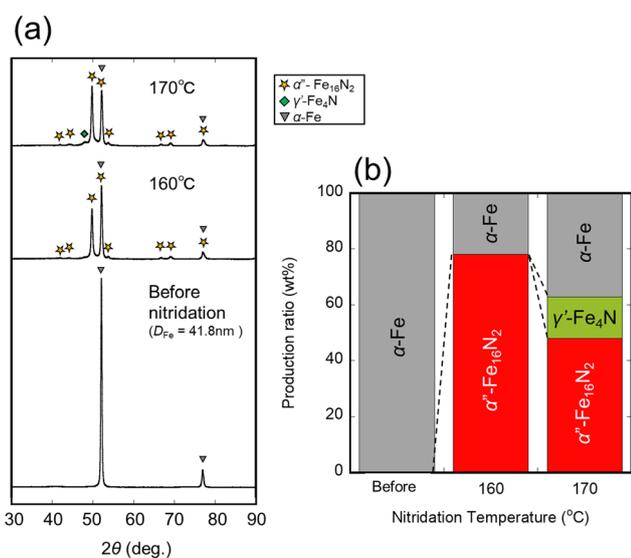


Fig. 3 (a) XRD profiles and (b) production ratio (wt%) of samples synthesized by H₂ reduction at 400 °C, and subsequently nitrated under NH₃ flow at different temperatures without CaH₂.

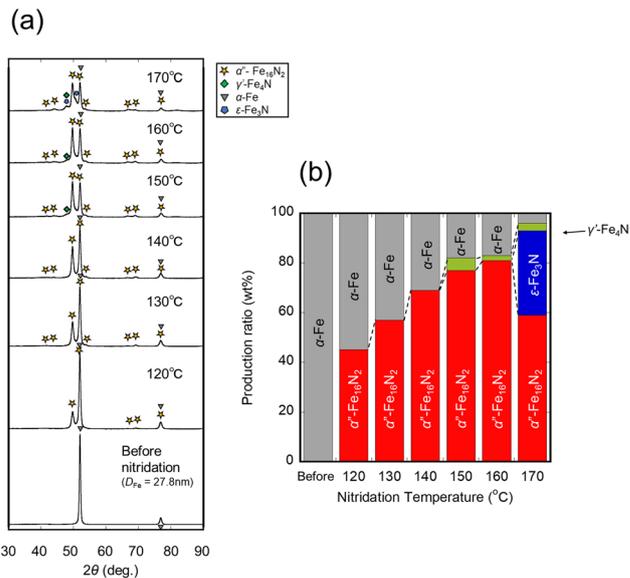


Fig. 4 (a) XRD profiles and (b) production ratio (wt%) of samples synthesized by H₂ reduction at 400 °C, and subsequently nitrated under NH₃ flow at different temperatures with CaH₂.

as calculated by RIR quantification. The sample nitrated at 160–170 °C contained γ' and ϵ phases, whereas that nitrated at 150 °C did not contain any ϵ phase. Additionally, the sample nitrated at 150–160 °C contained the γ' phase, whereas that nitrated 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, 97 wt% of the maximum yield of the α'' -Fe₁₆N₂ phase was obtained from the nitridation of the samples reduced at 300 °C with CaH₂, which is more or less the α'' single phase.

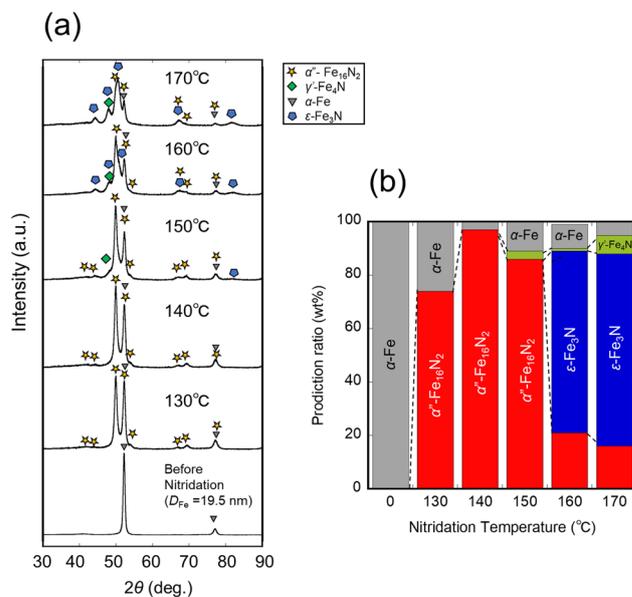


Fig. 5 (a) XRD profiles and (b) production ratio (wt%) of the samples synthesized by H₂ reduction at 300 °C, and subsequently nitrated under NH₃ flow at different temperatures with CaH₂.



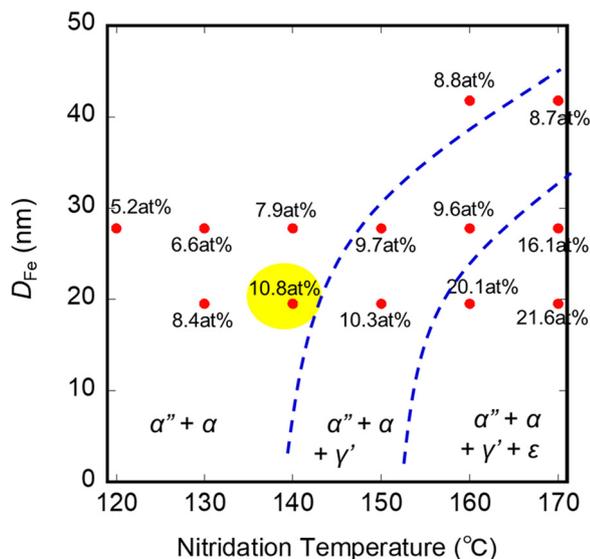
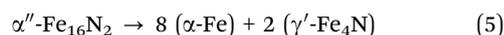
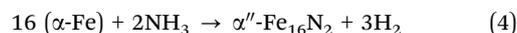
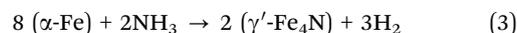
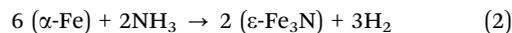


Fig. 6 Nitrogen content and formed phases as a function of nitridation temperature and D_{Fe} .

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.



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 $\alpha''\text{-Fe}_{16}\text{N}_2$ 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 $\alpha''\text{-Fe}_{16}\text{N}_2$

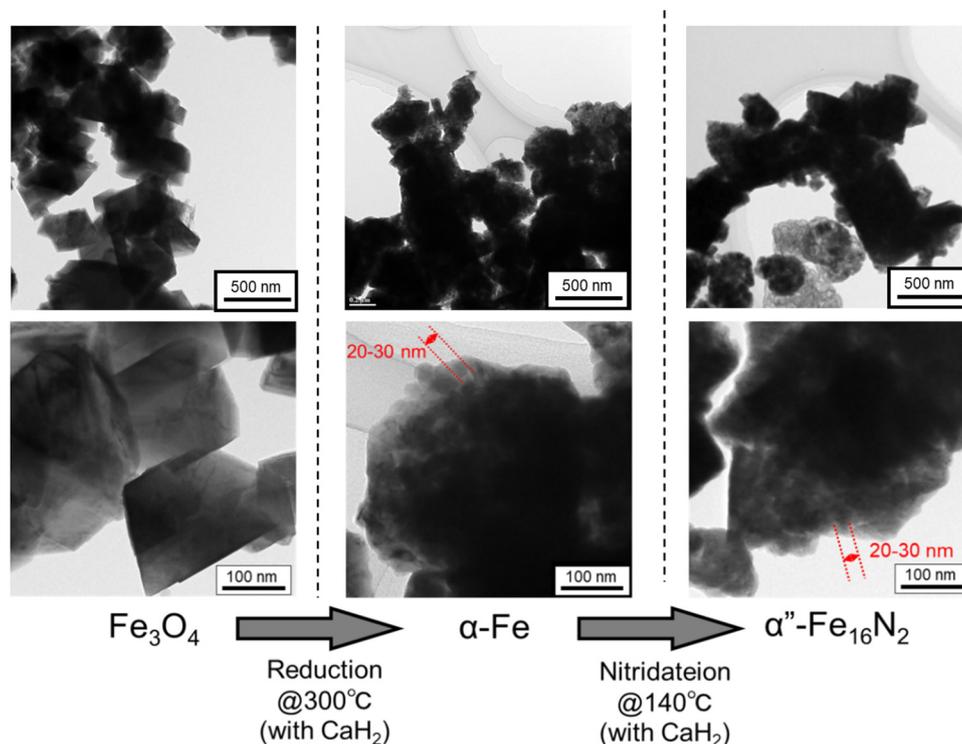


Fig. 7 TEM images of the raw material, reduced sample, and subsequently nitrided sample with CaH_2 drying agent.



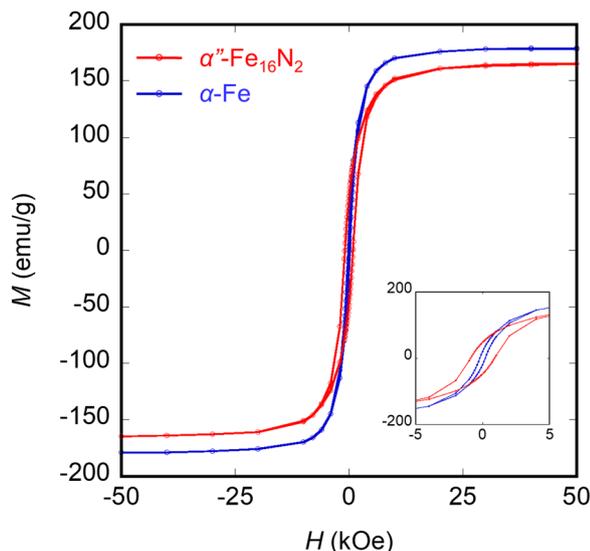


Fig. 8 M - H curve of the sample reduced at 300 °C with CaH_2 drying agent (α -Fe, blue plot), and sample reduced at 300 °C with CaH_2 drying agent and subsequently nitrated at 140 °C (α'' - Fe_{16}N_2 , red plot) measured at 300 K.

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 nitrated 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 $K_u V$ of α'' - Fe_{16}N_2 is strong against thermal fluctuations $k_B T$, 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

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 nitrated 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 |

process. To further improve the magnetization, a process or an implementation that avoids oxidization is required.

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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