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Humidity effects in Fe₁₆N₂ fine powder preparation by low-temperature nitridation

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ABSTRACT

Low-temperature nitridation has been reported to produce ferromagnetic α'' -Fe₁₆N₂ by ammonia nitridation of α -Fe fine powder, which was obtained from the reduction of vapor-grown γ -Fe₂O₃. The effects of humidity during this preparation were investigated in the present study. α'' -Fe₁₆N₂ was inconsistently obtained, and at low yield, from Fe₃O₄ fine powder (MT-40) prepared from aqueous solution. Reducing the adsorbed water content in the iron oxide starting powder resulted in improved reproducibility of the α'' -Fe₁₆N₂ yield of the nitridation. The use of a smaller-diameter reaction tube, less than 25 mm in diameter, enabled more reproducible preparation from vapor-grown γ -Fe₂O₃ powder (CI-30). The reaction yield was further improved by using high-quality ammonia with a water content of ≤ 0.05 ppm. Minimizing the humidity made it possible to obtain a fine powder with a high α'' -Fe₁₆N₂ content. Enhancement of the magnetization to 210 emu g⁻¹ at room temperature was observed from a nitrided mixture of α'' -Fe₁₆N₂ with residual α -Fe, compared to 199 emu g⁻¹ for an α -Fe fine powder reduced from γ -Fe₂O₃. However, excess nitrogen and residual oxygen in the nitrided products reduced the magnetization below the value of α -Fe powder after nitridation. The magnetization was enhanced in nitrided products with a nitrogen content slightly below the stoichiometric amount for α'' -Fe₁₆N₂.

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1. Introduction

Iron nitride, α'' -Fe₁₆N₂, was first reported by Jack as a mixture with α -Fe and austenite from α -Fe nitrided at 750 °C. An α'' -Fe₁₆N₂ content of about 50% was attained after annealing austenite, which had been nitrogen-quenched to room temperature, at 120 °C for 19 days [1]. He reported the crystal structure to adopt space group *I4/mmm* with $a=0.572$ nm and $c=0.629$ nm. One-sixteenth of the interstitial sites on all the edge centers are occupied in an ordered way by nitrogen atoms in the α -Fe body-centered cubic lattice. The unit cell is a $2 \times 2 \times 2$ superlattice of α -Fe, expands by about 10% along the c -axis by the incorporation of interstitial nitrogen atoms.

The magnetic properties of α'' -Fe₁₆N₂ have attracted attention because initial experimental results suggested the possibility of achieving a large magnetic moment above 3 μ_B in thin films [2–4]. Several theoretical calculations of the electronic structure were performed, and an average magnetic moment of 2.4–2.6 μ_B was obtained [5–8]. The previously reported large magnetization was not reproducible in products prepared by different preparation

methods, either as thin films or bulk powders prepared at high temperature [9–14]. The reported magnetic moments for α'' -Fe₁₆N₂ were scattered, ranging from values comparable to that of α -Fe to much higher values, and most of the products were mixtures, with impurities such as α' -martensite, austenite, α -Fe, or γ' -Fe₄N.

Low-temperature preparation of α'' -Fe₁₆N₂ is required because of its thermal metastability. Tessier et al. [15] estimated that the standard enthalpy of formation was 85.2 ± 46.8 kJ mol⁻¹ for α'' -Fe₁₆N₂ by extrapolating the values obtained from solution calorimetry for several kinds of iron nitrides such as γ' -Fe₄N and ϵ -Fe₂N. Pure α'' -Fe₁₆N₂, according to powder X-ray diffraction (XRD), was obtained by low-temperature ammonolysis at 110 °C for 10 days of α -Fe fine powder obtained from the reduction of a γ -Fe₂O₃ needle, 200 nm long and 20 nm in diameter, at 500 °C for 4 h in hydrogen [16]. The saturation magnetization was 162 emu g⁻¹, which was higher than the 151 emu g⁻¹ of the initial fine α -Fe powder, but lower than the previously reported values. The lower value was due to the presence of a surface oxide and additives such as Al₂O₃ in the γ -Fe₂O₃, which were added to improve its durability. A similar low-temperature ammonolysis was performed after the reduction of commercially available γ -Fe₂O₃ fine powder (C.I. Kasei Co. Ltd.). Saturation magnetization values of about 200 and 218 emu g⁻¹ were reported by two different research groups [17,18]. These values were not reproducible, for unidentified reasons [19].

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A high-density recording media was recently developed using a similar ammonolysis of spherical magnetite particles coated with Y, Al, and Si compounds to prevent Fe oxidation [20]. Its coercivity, which was as high as 0.34 T, was thought to be caused by an exchange bias at the core–shell interface [21–23]. High-density recording capability was expected, because the spherical shape of the particles should lead to a high packing density. The saturation magnetization was 85.5 emu g^{-1} , which is comparable to that of conventional magnetic oxides [20]. The magnetic properties of $\alpha''\text{-Fe}_{16}\text{N}_2$ itself remains an open question.

To properly investigate the magnetic properties of $\alpha''\text{-Fe}_{16}\text{N}_2$, there were two requirements: a method for the reproducible preparation of pure $\alpha''\text{-Fe}_{16}\text{N}_2$ powder, and saturation magnetization values for iron nitrides with nitrogen contents comparable to $\alpha''\text{-Fe}_{16}\text{N}_2$. The preparation and the resulting magnetic properties were found to be highly sensitive to humidity in the low-temperature nitridation of $\alpha\text{-Fe}$ fine powder. The control of nitrogen content is also important to obtain pure $\alpha''\text{-Fe}_{16}\text{N}_2$, because its saturation magnetization values may depend on its nitrogen content. The present study examined the effects of humidity on both the preparation and magnetic properties of low-temperature nitrided $\alpha''\text{-Fe}_{16}\text{N}_2$ fine powders. The magnetic properties of products with slightly higher or lower than stoichiometric nitrogen content were also investigated.

2. Experimental

Two different iron oxide fine powders were investigated as starting materials. One was a very porous and spongy $\gamma\text{-Fe}_2\text{O}_3$ powder, with an average particle size of 30 nm, prepared by the oxidation of iron vapor in a vacuum chamber. This powder had a density of 0.22 g cm^{-3} , a specific surface area of $45 \text{ m}^2 \text{ g}^{-1}$, was purchased from C.I. Kasei Co. Ltd., and is hereafter called CI-30. Its water content was a very low 1.4 at%. The other powder was more densely packed Fe_3O_4 powder, prepared by Toda Kogyo Co. Ltd. from aqueous solution with a spherical particle shape and a particle size of 40 nm, and is hereafter called MT-40.

The powders were reduced in a hydrogen stream in Pyrex glass tubes 500 mm long with diameters of 50, 25, and 18 mm. The hydrogen gas was supplied by Air Water Inc., with $\geq 99.99\%$ purity and was used at a flow rate of 30 mL min^{-1} . The tube furnace temperature was raised normally to 500°C at 5°C min^{-1} , and then held for 12 h to perform the reduction. After cooling to ambient conditions, the hydrogen gas in the reaction tube was purged with Ar gas (Air Water. Inc. $\geq 99.99\%$ purity) at a flow rate of 100 mL min^{-1} for 30 min. Then, ammonia gas was introduced at 50 mL min^{-1} to the reaction tube, without exposure of the reduced powder to air. Three kinds of ammonia, supplied by Sumitomo Seika Chemicals Co. Ltd., were used for the ammonolysis, with purities of 99.9995%, 99.999%, and 99.9%, respectively. Hereafter, these are called ammonias A, B, and C. The nitridation temperature was raised to $120\text{--}180^\circ\text{C}$ at 1°C min^{-1} and held for 10–100 h. Then, the temperature was reduced to 100°C at $10^\circ\text{C min}^{-1}$, and finally to room temperature by ambient exposure.

The nitrided products in the reaction tube were introduced to a glove box with a dew point below -110°C and an oxygen concentration of 0.01 ppm (Miwa MFG Co. Ltd., NM3-P60S). Magnetization at ambient temperature was measured with the products sealed in acrylic resin capsules, using a vibrating sample magnetometer (Riken Denshi Co. Ltd., BHV-50) in a magnetic field of $\pm 1.5 \text{ T}$. The measurements were calibrated with a nickel foil, and the estimated error was less than $\pm 1\%$. The oxygen and nitrogen contents were measured using an oxygen/nitrogen combustion analyzer (Horiba, EMGA-620W). Other part of the nitrided products was dipped in silicone oil to prevent air

exposure and rapid oxidation. Powder XRD was performed using monochromatized $\text{CuK}\alpha$ radiation in a diffractometer (PANalytical, X'Pert-MPD). The yield $Y\%$ of $\alpha''\text{-Fe}_{16}\text{N}_2$ was estimated from the relative XRD intensities as follows:

$$Y = \{I(202, \alpha'') + I(220, \alpha'')\} / \{I(110, \alpha) + I(202, \alpha'') + I(220, \alpha'')\} \times 100$$

here α'' and α represent the diffraction lines for $\alpha''\text{-Fe}_{16}\text{N}_2$ and $\alpha\text{-Fe}$, respectively. $\alpha\text{-Fe}(110)$ and $\alpha''\text{-Fe}_{16}\text{N}_2(220)$ peaks were deconvoluted by assuming the peak intensity for the latter was half that of the $\alpha''\text{-Fe}_{16}\text{N}_2(202)$ peak intensity due to its tetragonal lattice. Mössbauer spectroscopy was performed using γ radiation from $^{57}\text{Co/Rh}$ in equipment supplied by Topologic Systems Co. Ltd. The spectrum was analyzed using the program MossWinn 3.0i. The magnetic properties at ambient temperature were also measured using a strong magnet, 18T-SM in the High Field Laboratory for Superconducting Materials, Tohoku University, with approval no. 2008-1475.

3. Results and discussion

3.1. Preparation temperature of $\alpha''\text{-Fe}_{16}\text{N}_2$

Iron oxide powders were reduced in a hydrogen flow at several temperatures between 350 and 650°C . Using MT-40, particle size of the reduced $\alpha\text{-Fe}$ product grew larger in its simultaneous sintering with the reduction, from 22 to 31 nm, with increasing reduction temperature. For CI-30 samples, the particle size was relatively constant, from 33 to 35 nm, and temperature independent. This was probably because the primary iron grains obtained in the reduction were much more separated from each other in the latter spongy iron oxide powder, preventing sintering during the reduction. SEM observation revealed that CI-30 reduced at 500°C produced homogeneous, spherical particles, several tens of nm in diameter, as shown in Fig. 1. The product reduced at 650°C showed a slight growth of the primary particles, with extensive sintering to form secondary agglomerates larger than $1 \mu\text{m}$.

MT-40, after reduction at 400°C , was nitrided in a flow of ammonia A in a reaction tube 50 mm in diameter for 100 h at temperatures from 130 to 180°C . The product nitrided at 180°C was a poorly crystallized mixture of $\alpha''\text{-Fe}_{16}\text{N}_2$, $\gamma'\text{-Fe}_4\text{N}$, and Fe_3O_4 . A very small amount of $\alpha''\text{-Fe}_{16}\text{N}_2$ appeared as a mixture with $\alpha\text{-Fe}$ and Fe_3O_4 after nitridation at 170 or 150°C , but not in products nitrided at lower temperatures or for shorter nitridation times.

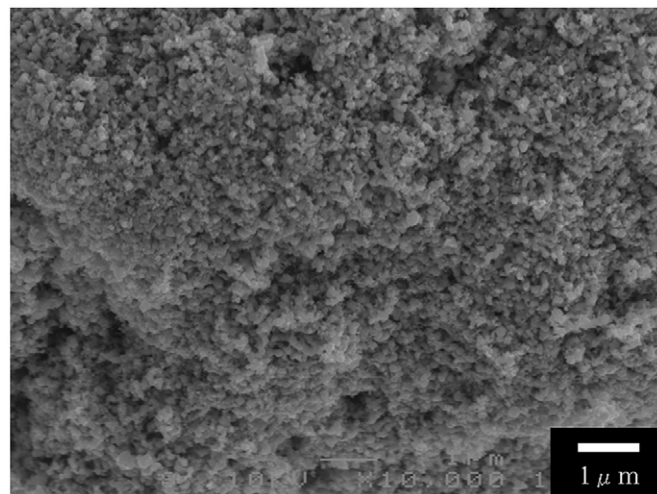


Fig. 1. SEM micrograph of CI-30 after reduction at 500°C for 12 h.

CI-30, after reduction at 500 °C, was nitrified in an ammonia flow for 50 h at temperatures of 120–200 °C. The nitrified product was much more crystalline than the MT-40 products, and was composed of ϵ -Fe₂₋₃N at 200 °C, and a mixture of ϵ -Fe₂₋₃N and γ' -Fe₄N at 180 °C. α'' -Fe₁₆N₂ appeared, mixed with α -Fe and a small amount of γ' -Fe₄N at 160 °C. More α'' -Fe₁₆N₂ was observed than in the nitrified MT-40 products, probably because of the less-sintered α -Fe intermediate. At 140 °C, the γ' -Fe₄N disappeared, and the product was again a mixture of α'' -Fe₁₆N₂ and α -Fe. After nitridation at 120 °C, only α -Fe was observed. The magnetic properties were studied at room temperature. The magnetization at ± 1.5 T was small for products nitrified at 200 or 180 °C, due to the formation of ϵ -Fe₂₋₃N. With the formation of α'' -Fe₁₆N₂, the magnetization increased to relatively high values of 186.0 and 181.3 emu g⁻¹, with magnetic coercivities of 0.44 and 0.55 T, in products nitrified at 160 and 140 °C, respectively, as shown in Fig. 2. The magnetization values were comparable to that of α -Fe fine powder before nitridation, and the coercivity was almost twice the pre-nitridation value. The magnetization was not saturated at ± 1.5 T, but did at 5 T, as described in the following section. α'' -Fe₁₆N₂ was obtained at temperatures between 140 and 160 °C, but the yield was not reproducible, and varied drastically because of the humidity effects described in the next section.

3.2. Humidity effects on the preparation

Reduced α -Fe fine powder should be immediately nitrified in ammonia flow, because it is very easily oxidized in air. However, to improve the reproducibility of the α'' -Fe₁₆N₂ yield, it is very important to first remove any water vapor formed during the reduction, before performing nitridation. Unfortunately, water vapor that formed in the 50-mm-diameter reaction tube during the hydrogen reduction of iron oxide could not be fully removed, even under an Ar flow at 100 mL min⁻¹ for 30 min. Therefore, the 50-mm-diameter reaction tube was unsuitable for reproducible, high-yield α'' -Fe₁₆N₂ production under the present reaction conditions.

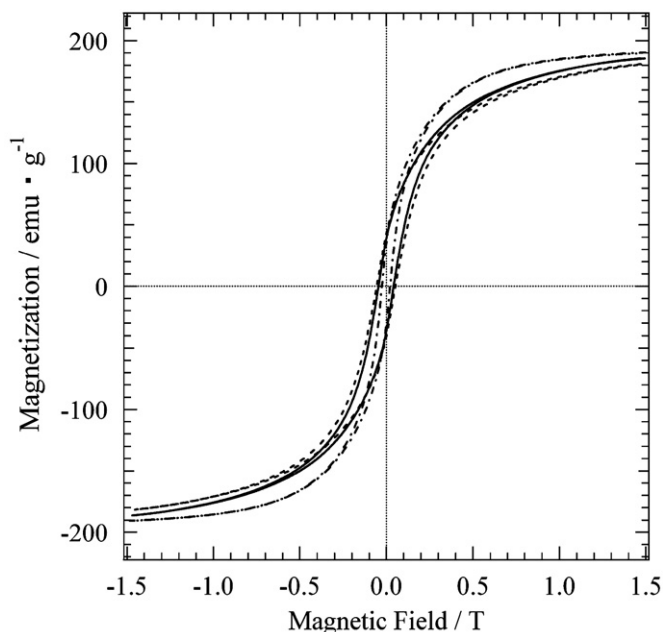


Fig. 2. Magnetic hysteresis curves for nitrified products 50 h after the reduction of CI-30. The solid, broken, and dotted lines correspond to hysteresis of products nitrified at 160 and 140 °C and of the as-reduced product, respectively.

The reaction tube diameter was reduced from 50 to 25 or 18 mm, to better remove any humidity formed during the hydrogen reduction process. About 0.5 g of CI-30 powder was nitrified on a stainless steel boat at 160 °C for 50 h in an ammonia flow of 50 mL min⁻¹ after reduction at 500 °C for 12 h. The nitrified product in the 50-mm-diameter tube was mainly α -Fe, as shown in Fig. 3(a). The {110} diffraction peak of cubic α -Fe split into {220} and {202} diffraction peaks of tetragonal α'' -Fe₁₆N₂. Moreover, the {202} peak was the most intense (highest multiplicity), with a 2:1 relative intensity ratio. The yield of α'' -Fe₁₆N₂ was 50%. The formation of α'' -Fe₁₆N₂ was enhanced in product prepared in a 25-mm-diameter reaction tube, as shown in Fig. 3(b). The yield was estimated to be 86%, and a small amount of γ' -Fe₄N also appeared. The 18-mm-diameter tube produced a similar product, except for a slightly increased amount of γ' -Fe₄N impurity. The humidity formed in the reduction process was easier to remove from smaller-diameter reaction tubes, which greatly improved the yield and reproducibility of α'' -Fe₁₆N₂ formation.

The effect of ammonia purity on α'' -Fe₁₆N₂ formation was investigated using three types of ammonia: A, B, and C. Their reported water contents were less than 0.5 ppm for A, and 1 ppm for B. Since ammonia C was prepared under the least stringent conditions, without significant control of the humidity, it almost certainly had a much higher water content than ammonias A and B. Ammonolysis was performed on reduced CI-30 powder in a 25-mm-diameter reaction tube at 140 °C for 24 h. The nitrified

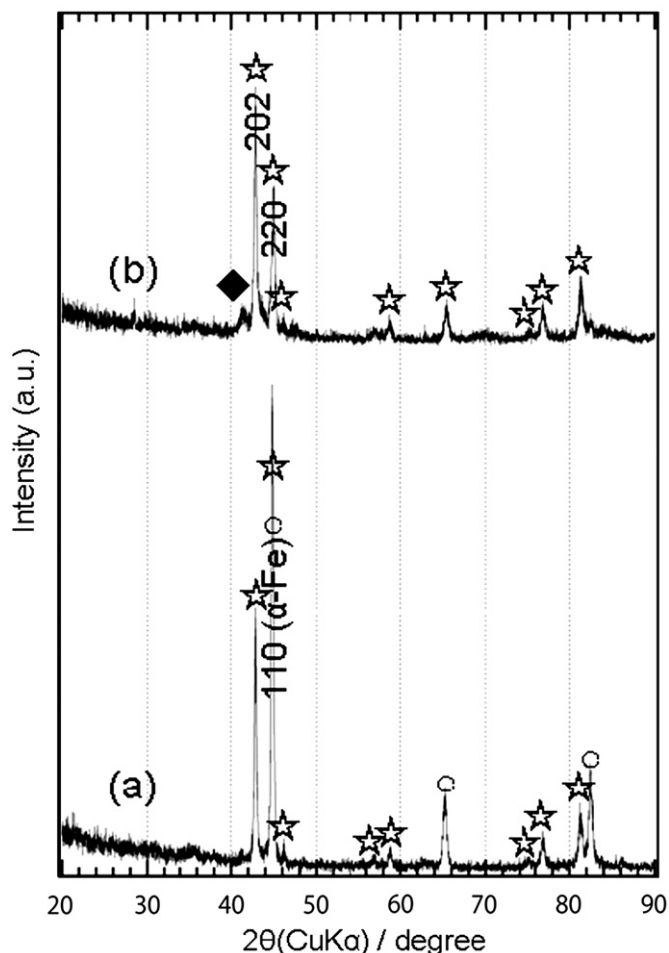


Fig. 3. XRD of products nitrified at 160 °C for 50 h in reaction tubes with diameters of (a) 50 mm and (b) 25 mm. Diffraction peaks marked with open stars, circles, and filled diamond correspond to α'' -Fe₁₆N₂, α -Fe, and γ' -Fe₄N, respectively.

products were a mixture of $\alpha''\text{-Fe}_{16}\text{N}_2$ and $\alpha\text{-Fe}$. The yields of $\alpha''\text{-Fe}_{16}\text{N}_2$ were 84%, 33%, and 18% in products prepared from ammonias A, B, and C, respectively. Clearly, a lower humidity was more favorable to the formation of $\alpha''\text{-Fe}_{16}\text{N}_2$. The yield increased to 88% for the product nitrated at 160 °C. However, the magnetization in 1.5 T decreased from 185.3 emu g^{-1} for the product at 140 °C to 154.9 emu g^{-1} for the product 160 °C after 50 h of nitridation, due to the appearance of $\gamma'\text{-Fe}_4\text{N}$ impurity. The former value is comparable to or slightly below the value of 190.5 emu g^{-1} for $\alpha\text{-Fe}$ before nitridation. The nitrated product after 5 h at 140 °C had a magnetization of 194.4 emu g^{-1} . This product was a mixture of $\alpha''\text{-Fe}_{16}\text{N}_2$ and $\alpha\text{-Fe}$, with a yield of 53%.

3.3. Magnetic property dependence on nitrogen and oxygen content

Nitrogen content was analyzed in nitrated mixtures with high yields of $\alpha''\text{-Fe}_{16}\text{N}_2$ to determine the phase relationships around Fe_{16}N_2 . Oxygen content was also measured together because the $\alpha''\text{-Fe}_{16}\text{N}_2$ product was highly reactive against oxidation. The nitrogen content was 17–18 at% in products nitrated at 160 °C, and 7–16 at% in products nitrated at 140 °C, as shown in Fig. 4. The magnetization in 1.5 T was larger than 200 emu g^{-1} in products containing less than 11.1 at% nitrogen, which is the stoichiometric value for $\alpha''\text{-Fe}_{16}\text{N}_2$. The products were mixtures of $\alpha''\text{-Fe}_{16}\text{N}_2$ and $\alpha\text{-Fe}$ in this compositional range. The magnetization decreased to about 190 emu g^{-1} in products with slightly higher than stoichiometric nitrogen content. These products were $\alpha''\text{-Fe}_{16}\text{N}_2$, according to XRD, and had reduced crystallinity. They were also slightly contaminated with amorphous $\gamma'\text{-Fe}_4\text{N}$. The

magnetization decreased further in products with more than 16.6 at% nitrogen, which were contaminated with crystalline $\gamma'\text{-Fe}_4\text{N}$ impurity. All of them were also slightly contaminated with amorphous iron oxide observed in XRD. The enhancement of the magnetization was remarkable in products with nitrogen contents slightly below stoichiometric. Their magnetic coercivity values were as low as 0.26–0.40 T, approaching that of $\alpha\text{-Fe}$ before nitridation (0.25 T). The magnetization was not saturated, even in a magnetic field of 1.5 T. $\alpha''\text{-Fe}_{16}\text{N}_2$ products contaminated with amorphous $\gamma'\text{-Fe}_4\text{N}$ had relatively large magnetic coercivities of about 1 T, probably because of the lower symmetry of the crystal structure. The magnetization was not saturated at 1.5 T, and maintained a constant value of 217 emu g^{-1} when measured in a magnetic field above 5 T in a strong magnetic field.

The nitrated products had about 10 at% oxygen content as amorphous iron oxide impurity. As-reduced $\alpha\text{-Fe}$ products from CI-30 iron oxide had about 12 at% oxygen content. Reducing the residual oxygen should enhance the nitridation reaction, and improve the magnetic properties. The reaction tube was evacuated by a rotary pump for 10 min of every hour during the reduction, which reduced the residual oxygen content to 7.6(1) at% in $\alpha\text{-Fe}$. Mössbauer spectra were measured for products nitrated at 140 °C for 50 h. The products were $\alpha''\text{-Fe}_{16}\text{N}_2$, according to XRD, with a yield of about 90%, but may have been contaminated with amorphous $\gamma'\text{-Fe}_4\text{N}$ and iron oxide impurities. The oxygen and nitrogen contents were 6.9(1) and 13.6(2) at%, respectively, for the nitride products with pumping, and 10.5(2) and 10.9(2) at%, respectively, for those without pumping. The Mössbauer spectra in Figs. 5 and 6 could be fit by three kinds of magnetic sextets for the crystallographic sites, Fe(4e), Fe(8h), and

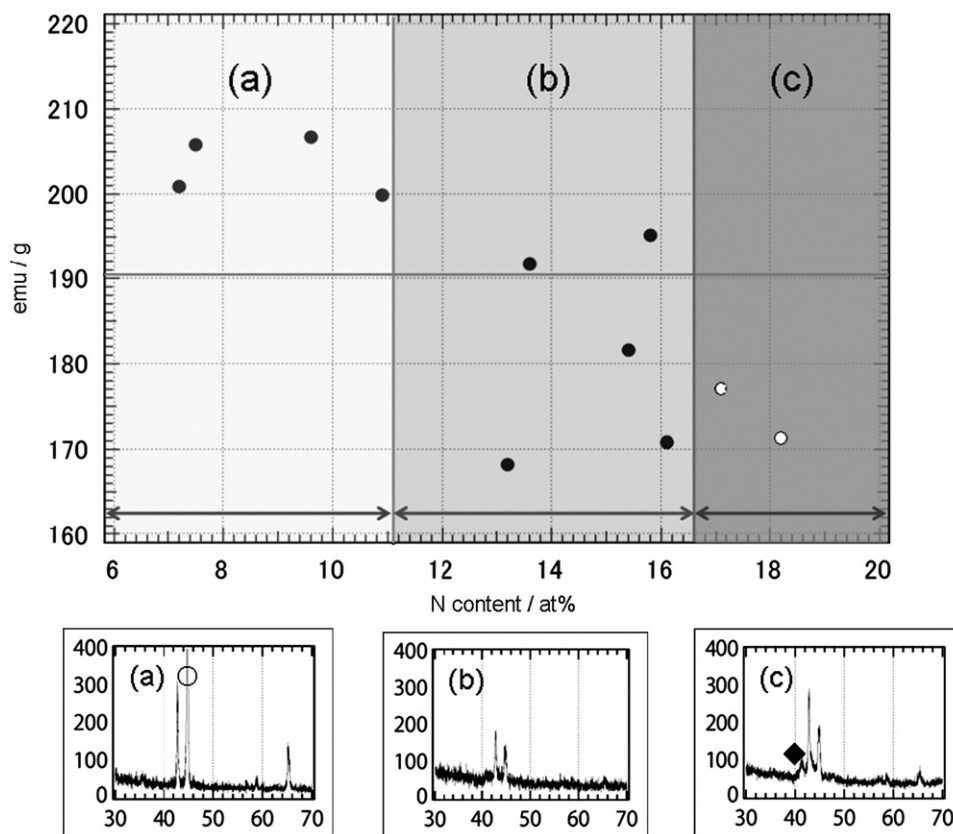


Fig. 4. Magnetization in 1.5 T, represented by open and filled circles for products nitrated at 160 and 140 °C, respectively, vs. nitrogen content. The magnetization of the as-reduced product was 190.5 emu g^{-1} before nitridation. The nitrogen content of stoichiometric $\alpha''\text{-Fe}_{16}\text{N}_2$ is 11.1 at%. XRD patterns are for products with different nitrogen contents. The Fe_{16}N_2 product was contaminated with $\alpha\text{-Fe}$ (○) in the compositional range of (a), and with $\gamma'\text{-Fe}_4\text{N}$ (◆) in the range of (c). Its crystallinity was reduced in the (b) region.

Fe(4d) in α'' -Fe₁₆N₂ with a paramagnetic doublet having an isomer shifts $\delta \approx -0.2(2)$ and $-0.3(2)$ mm s⁻¹ and quadrupole splitting QS $\approx 0.36(1)$ and $0.39(2)$ mm s⁻¹, respectively. Similar spectra were reported in our previous manuscript [18]. The

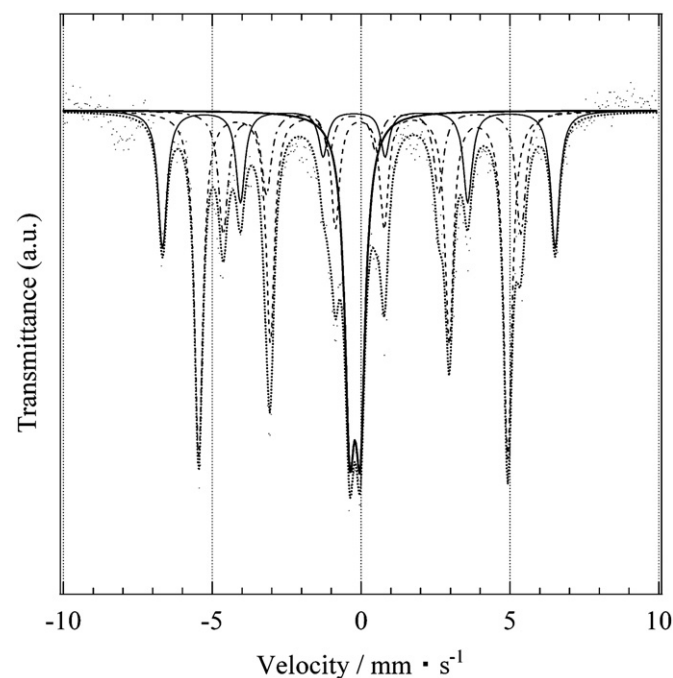


Fig. 5. Mössbauer spectrum of α'' -Fe₁₆N₂ prepared using Cl-30, which was reduced without pumping. It had 10.5 at% oxygen and 10.9 at% nitrogen. The spectrum observed was fitted with the sum (thick dotted line) of four kinds of spectra: 4e (thin dotted line), 8h (thin broken line), 4d (thin solid line) for Fe in α'' -Fe₁₆N₂, and an additional paramagnetic impurity (thick solid line).

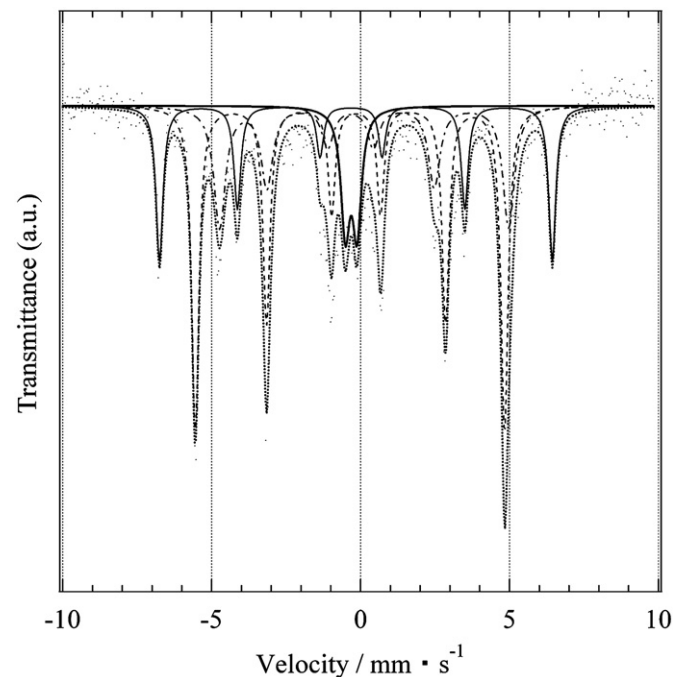


Fig. 6. Mössbauer spectrum of α'' -Fe₁₆N₂ prepared using Cl-30, which was reduced with pumping. It had 6.9 at% oxygen and 13.6 at% nitrogen. The spectrum observed was fitted with the sum (thick dotted line) of four kinds of spectra: 4e (thin dotted line), 8h (thin broken line), 4d (thin solid line) for Fe in α'' -Fe₁₆N₂, and an additional paramagnetic impurity (thick solid line).

spectrum area ratio was about Fe(4e):Fe(8h):Fe(4d)=1:2:1, which corresponds to the ratio of crystallographic sites in α'' -Fe₁₆N₂. Their respective percentage values were 17.4(3)%, 43.0(5)%, and 18.0(3)% for nitrated product without pumping, and 26.4(4)%, 43.7(5)%, and 19.8(3)% with pumping. The hyperfine field H_f values were 30.1(3), 32.2(3), and 40.9(4) T for both nitrated products. The residual percentage of the paramagnetic component decreased from 21.6(4)% to 9.9(2)% with decreasing oxygen content in these two samples. The paramagnetism may have been induced by the amorphous iron oxide. The average magnetic moment for the present α'' -Fe₁₆N₂ products was estimated using the H_f values and the population of Fe(4e), Fe(8h), and Fe(4d) sites and the formula $H_f = A\mu_{Fe}$, where $A(4e) = A(8h) = 13.15$ and $A(4d) = 13.5$ [24]. The calculated value increased from 2.0 ± 0.05 to $2.3 \pm 0.1 \mu_B$ with decreasing oxygen content. The change is not really significant but the latter is slightly larger than the value for α -Fe of $2.1 \mu_B$.

4. Conclusion

The removal of humidity from the reaction system was very important to obtaining α'' -Fe₁₆N₂ from low-temperature nitridation of fine iron oxide powder. The iron oxide powder should also be very porous and spongy, to separate the grains and limit agglomeration of the reduced α -Fe fine powder. Water vapor formed during hydrogen reduction of the fine iron oxide powder must be removed as quickly and completely as possible to maintain the reproducibility of α'' -Fe₁₆N₂ fine powder formation with high yield. Water impurity in the ammonia must also be minimized. Enhancement of the saturation magnetization was clearly observed in α'' -Fe₁₆N₂ ammonolysis products with lower than stoichiometric nitrogen content. It was difficult to prepare α'' -Fe₁₆N₂ having its corresponding exact nitrogen content, probably because it is a line phase. The magnetization gradually decreased with increasing nitrogen content above the stoichiometric composition, reducing the crystallinity of α'' -Fe₁₆N₂ and causing the subsequent formation of γ' -Fe₄N. Moreover, it is likely that any α -Fe remaining after nitridation contains a higher nitrogen content than pure α -Fe. Its magnetic properties may therefore be slightly different from those of pure α -Fe. Surface amorphous iron oxide should be removed because it reduces magnetization.

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References

- [1] K.H. Jack, Proc. R. Soc. A208 (1951) 216–224.
- [2] T.K. Kim, M. Takahashi, Appl. Phys. Lett. 20 (1972) 492–494.
- [3] K. Nakajima, S. Okamoto, Appl. Phys. Lett. 56 (1990) 92–94.
- [4] Y. Sugita, H. Takahashi, M. Komuro, J. Appl. Phys. 76 (1994) 6637–6641.
- [5] A. Sakuma, J. Magn. Magn. Mater. 102 (1991) 127–134.
- [6] J.M.D. Coey, K. O'Donnell, Q. Qinian, E. Touchais, K.H. Jack, J. Phys.: Condens. Matter 6 (1994) 23–28.

- [7] S. Mater, P. Mohn, G. Demazeau, B. Siberchicot, *J. Phys.* 48 (1998) 1761.
- [8] R. Coehoorn, G.H.O. Daalderop, *Phys. Rev. B* 48 (1993) 3830–3834.
- [9] M. Takahashi, H. Shoji, H. Takahashi, H. Nashi, T. Wakiyama, *J. Appl. Phys.* 76 (1994) 6642–6647.
- [10] R.M. Metzger, X. Bao, *J. Appl. Phys.* 76 (1994) 6626–6631.
- [11] M. Takahashi, H. Shoji, *J. Magn. Magn. Mater.* 208 (2000) 145–157.
- [12] K.H. Jack, *J. Alloys Compd.* 222 (1995) 160–166.
- [13] M.Q. Huang, W.E. Wallace, S. Shimizu, A.T. Pedziwiatr, R.T. Obermyer, S.G. Sankar, *J. Appl. Phys.* 75 (1994) 6574–6576.
- [14] T. Saito, *J. Appl. Phys.* 87 (2000) 6514–6516.
- [15] F. Tessier, A. Navrotsky, R. Niewa, A. Leineweber, H. Jacobs, S. Kikkawa, M. Takahashi, F. Kanamaru, F.J. DiSalvo, *Solid State Sci.* 2 (2000) 457–462.
- [16] A. Nagatomi, S. Kikkawa, T. Hinomura, S. Nasu, F. Kanamaru, *J. Jpn. Soc. Powder & Powder Metal.* 46 (1999) 151–155.
- [17] T. Hattori, N. Kamiya, Y. Kato, *J. Magn. Soc. Jpn.* 25 (2001) 927–930.
- [18] S. Kikkawa, A. Yamada, Y. Masubuchi, T. Takeda, *Mater. Res. Bull.* 43 (2008) 3352–3357.
- [19] S. Kikkawa, K. Kubota, T. Takeda, *J. Alloys Compd.* 449 (2008) 7–10.
- [20] Y. Sasaki, N. Usuki, K. Matsuo, M. Kishimoto, *IEEE Trans. Magn.* 41 (10) (2005) 3241–3243.
- [21] T. Oku, T. Kikuchi, T. Shinohara, J. Suzuki, Y. Ishii, M. Takeda, K. Kakurai, Y. Sasaki, M. Kishimoto, M. Yokoyama, Y. Nishihara, *Physica B* 404 (2009) 2575–2577.
- [22] E. Kita, K. Shibata, H. Yanagihara, Y. Sasaki, M. Kishimoto, *J. Magn. Magn. Mater.* 310 (2007) 2411–2413.
- [23] S. Uchida, T. Kawakatsu, A. Sekine, T. Ukai, *J. Magn. Magn. Mater.* 310 (2007) 1796–1798.
- [24] J.M.D. Coey, *J. Appl. Phys.* 76 (1994) 6632–6636.