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Magnetite/ maghemite mixture prepared in benzyl alcohol for the preparation of  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub>

with  $\alpha$ -Fe

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## Abstract

Fine powder of iron oxide has been required in the preparation of ferromagnetic  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> powder in low temperature nitridation. Its particle size of about 30 nm and less humidity content was crucial in the reproducible  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> preparation in high yield. Magnetite and maghemite mixture with about 40 nm particle size was obtained by the reaction of iron acetylacetonate Fe(acac)<sub>3</sub> of more than 4 g dissolved in 40 mL benzyl alcohol. It was reduced to  $\alpha$ -Fe in hydrogen at 400 °C. Particle size of the  $\alpha$ -Fe was 300 nm in the reduction of iron oxides obtained from 2 g of Fe(acac)<sub>3</sub>. It decreased to 100 nm in the preparation using 8 g of Fe(acac)<sub>3</sub> because smaller iron oxide was easily reduced sintering to larger  $\alpha$ -Fe particle. After the successive nitridation under ammonia flow at 160 °C, the highest yield of  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> in 66 wt% was observed on the nitrated product from the latter  $\alpha$ -Fe because of the smallest  $\alpha$ -Fe particle size after the reduction in the present study. The yield and reproducibility of  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> formation in low temperature nitridation was improved by using the iron oxide prepared in non-aqueous benzyl alcohol compared to the use of magnetite obtained from aqueous solution. Benzyl alcohol was a useful solvent to obtain iron oxide fine powder having less humidity because of its very small water solubility.

Keywords:

Iron oxide; Iron nitride; Magnetic property; Nanoparticle; Non-aqueous synthesis

## Introduction

Large magnetization value has been expected for  $\alpha''\text{-Fe}_{16}\text{N}_2$  thin films<sup>1-3</sup>. Their reported magnetization values were scattered between  $360 \text{ emu}\cdot\text{g}^{-1}$  and the values comparable to  $210 \text{ emu}\cdot\text{g}^{-1}$  of  $\alpha\text{-Fe}$ <sup>1-6</sup>. Its preparation in powder form is necessary to clarify the property but was very difficult for several reasons. Several preparation methods have been reported to obtain the bulk  $\alpha''\text{-Fe}_{16}\text{N}_2$ . Tempering of Fe-N martensite powders and annealing of mechanically alloyed  $\alpha\text{-Fe}$  and  $\varepsilon\text{-Fe}_3\text{N}$  powders at low temperature between 100 and 200 °C have been tried to prepare the single phase of  $\alpha''\text{-Fe}_{16}\text{N}_2$ <sup>7-10</sup>, respectively. However, the  $\alpha''\text{-Fe}_{16}\text{N}_2$  has been prepared in less than 50% purity and was contaminated with impurity phases of  $\alpha\text{-Fe}$  and  $\gamma\text{-Fe-N}^9$  (austenite) or  $\gamma\text{-Fe}_4\text{N}^{10}$ .  $\alpha''\text{-Fe}_{16}\text{N}_2$  is thermally metastable and its very small formation enthalpy value of  $85.2 \pm 46.8 \text{ kJ}\cdot\text{mol}^{-1}$  was expected<sup>11</sup>. It may be a line phase because it has been observed as mixtures either with  $\alpha\text{-Fe}$  or with  $\gamma\text{-Fe}_4\text{N}$ . It is also easily oxidized in air. Single phase of  $\alpha''\text{-Fe}_{16}\text{N}_2$  confirmed by powder x-ray diffraction was prepared by low temperature nitridation at 110 °C for 10 days in ammonia gas of  $\alpha\text{-Fe}$  fine powder obtained from reduction of  $\gamma\text{-Fe}_2\text{O}_3$ <sup>12</sup>. The  $\alpha''\text{-Fe}_{16}\text{N}_2$  showed the saturation magnetization of  $162 \text{ emu}\cdot\text{g}^{-1}$ , which was higher than  $151 \text{ emu}\cdot\text{g}^{-1}$  of  $\alpha\text{-Fe}$  powder before the nitridation, but lower than the previously reported values. The lower value was expected to be due to the effects of non-magnetic surface amorphous oxide and

also  $\text{Al}_2\text{O}_3$  added to improve the durability of in the starting  $\gamma\text{-Fe}_2\text{O}_3$ . We succeeded a preparation of x-ray single phase in a similar low temperature ammonolysis of  $\alpha\text{-Fe}$  fine powder obtained by the reduction of vapor grown  $\gamma\text{-Fe}_2\text{O}_3$  fine powder of about 30 nm in particle size without any additives<sup>13</sup>. The saturation magnetization was  $225 \text{ emu}\cdot\text{g}^{-1}$  at room temperature, but an additional paramagnetic component was observed in the Mössbauer spectrum with an area ratio of 19%. It was found out that the  $\alpha\text{-Fe}$  powder around 100 nm in size obtained by the hydrogen reduction of starting iron oxides was suitable for the successive low temperature nitridation, achieving the higher yield of  $\alpha''\text{-Fe}_{16}\text{N}_2$ <sup>14</sup>. Iron oxides prepared in aqueous solution failed in its preparation even in a similar particle size to the previous studies<sup>15</sup>. Least humidity in the nitridation system was very important in its reproducible preparation with high yield. The use of a smaller-diameter reaction tube less than 25 mm in diameter, high-quality ammonia with a water content of  $\leq 0.05$  ppm, and the starting vapor-grown  $\gamma\text{-Fe}_2\text{O}_3$  fine powder improved the reproducibility of the  $\alpha''\text{-Fe}_{16}\text{N}_2$  yield of the nitridation. However, the starting iron oxide fine powder suitable for the  $\alpha''\text{-Fe}_{16}\text{N}_2$  preparation has been only strictly limited to the vapor-grown  $\gamma\text{-Fe}_2\text{O}_3$  fine powder (C.I. Kasei Co. Ltd.). It can not be commercially available in controlled in particle size and morphology. Fine  $\text{Fe}_3\text{O}_4$  powder (<18 nm) has been prepared by reacting iron acetylacetonate with benzyl alcohol with low water solubility<sup>16</sup>. The size and morphology can be controlled by changing

the reaction conditions, such as a concentration, reaction temperature or duration to improve the phase purity in x-ray diffraction and magnetic measurement. Its small particle size and low water content may be beneficial in the low temperature preparation of  $\alpha$ "-Fe<sub>16</sub>N<sub>2</sub> powder.

In the present study, low temperature nitridation reaction was investigated on the  $\alpha$ -Fe obtained from reduction of iron oxide fine powder prepared in benzyl alcohol changing the amount of iron acetylacetonate, hereafter denoted as Fe(acac)<sub>3</sub>, dissolved as the starting materials.

## Experimental

Various amounts of Fe(acac)<sub>3</sub>, (Kanto Chemical Co. Inc.) 2, 4, 6, 8 g, respectively, were dissolved in 40 mL of benzyl alcohol (>99% Wako Pure Chemical Industries, Ltd.) and then reacted in autoclave at 200 °C for 48 hrs. The precipitates (named as BA2, BA4, BA6 and BA8) were washed twice with ethanol and then with dichloromethane. After drying in ambient, the products were reduced at 400 °C for 10 hrs in hydrogen flow of 30 mL•min<sup>-1</sup>. Hydrogen purity was higher than 99.99% and the diameter of tube furnace was 25 mm as in our previous study<sup>15</sup>. Ammonia, supplied by Sumitomo Seika Chemicals Co. Ltd., with purity of 99.9995% was introduced at 50 mL•min<sup>-1</sup> to the reaction tube without exposing the

reduced powder to air. The ammonolysis was performed at 160 °C for 15 hrs.

The nitrated 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  $\pm 15$  kOe. Other part of the nitrated products was dipped in silicone oil to prevent air exposure and rapid oxidation. Powder x-ray diffraction (PXRD) was performed using monochromatized Cu-K $\alpha$  radiation in a diffractometer (Rigaku, Ultima IV). The yield of  $\alpha'$ -Fe<sub>16</sub>N<sub>2</sub> was estimated by Rietveld fitting of the PXRD data using the program RIETAN-2000<sup>17</sup>. Mössbauer spectroscopy was performed using  $\gamma$  radiation from <sup>57</sup>Co/Rh in equipment supplied by Topologic Systems Co. Ltd. The spectrum was analyzed using the program MossWinn 3.0i.

## Results and discussion

The products obtained after the heating in autoclave at 200 °C for 48 hrs were magnetite with their respective crystallite sizes of 14, 40, 43, 44 nm estimated from the line broadening of the main diffraction peak depending on the amount of Fe(acac)<sub>3</sub> starting materials as shown in Fig. 1. Magnetization at 15 kOe was not saturated on the products

BA2 and BA4 and their values were much smaller than the saturated values on BA6 and BA8 as represented in Fig. 2. Superparamagnetic component in the product was expected to be present because of their smaller particle size than the critical size of about 10 nm as shown in Fig. 3. TEM observation in Fig. 3 showed an agglomeration of irregular particles of about 10 nm on the BA2 product, and rhombohedral particles were clearly observed on the BA6 and BA8 products of particle size in 20 ~ 100 nm.

Their x-ray diffraction patterns have been assumed as pure magnetite because of their structural similarity between  $\text{Fe}_3\text{O}_4$  magnetite and  $\gamma\text{-Fe}_2\text{O}_3$  maghemite<sup>16</sup>. Powder x-ray diffraction pattern of the BA4 was refined as a mixture of  $\text{Fe}_3\text{O}_4$  and  $\gamma\text{-Fe}_2\text{O}_3$  as shown in Fig. 4. The cubic inverse spinel structure (space group:  $\text{Fd-3m}$ ) and the cubic spinel-like structure with cation vacancy ordering ( $\text{P4}_3\text{32}$ ) were used for the structural parameters of  $\text{Fe}_3\text{O}_4$  and  $\gamma\text{-Fe}_2\text{O}_3$ , respectively<sup>18,19</sup>. After the refinement of their lattice constants and peak profile parameters, the observation fit very well with the calculated profile, resulting in  $R_{\text{wp}} = 8.2\%$ ,  $R_e = 6.5\%$  and  $S = 1.3$ . Its phase ratio was 75 wt%  $\text{Fe}_3\text{O}_4$  and 25 wt%  $\gamma\text{-Fe}_2\text{O}_3$ . Their lattice constants were 0.8381(1) nm and 0.8360(2) nm in  $\text{Fe}_3\text{O}_4$  and  $\gamma\text{-Fe}_2\text{O}_3$ , respectively, which were comparable to the reported values of 0.8394 nm and 0.8347 nm<sup>18,19</sup>. Its Mössbauer spectrum supported that the iron oxide was a mixture of magnetite and maghemite<sup>20</sup>. The product was magnetite contaminated with maghemite and an additional

paramagnetic component with  $IS = 0.22 \text{ mm}\cdot\text{s}^{-1}$ ,  $QS = 0.27 \text{ mm}\cdot\text{s}^{-1}$  and its area ratio = 7.4 %.

Relative amount of the paramagnetic component was larger in the heated product suspended on the surface of benzyl alcohol than that settled in the solvent because of its smaller particle size. Carbon contents were less than 0.5 wt% in these oxides in their CHN analysis. The paramagnetic species observed in Mössbauer spectrum was assumed to be the superparamagnetic iron oxides having smaller particle size.

These iron oxide products were reduced to  $\alpha$ -Fe in hydrogen stream at 400 °C for 10 hours instead of the previous reduction temperature at 600 °C because of their smaller particle size than the previous case<sup>13,15</sup>, in order to suppress their grain growth below 100 nm. When the temperature was 600 °C, the reduced  $\alpha$ -Fe grew above 1  $\mu\text{m}$  in grain size, which was too large to be nitrated with high homogeneity<sup>14</sup>. The smaller particle size in iron oxide led to the larger particle size in  $\alpha$ -Fe through their sintering during the hydrogen reduction as depicted in Fig. 5. Sintering was more enhanced between the  $\alpha$ -Fe smaller particles during the hydrogen reduction of the iron oxide with smaller particle size. The nitrated products were mixtures of  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> and  $\alpha$ -Fe as shown in Fig. 6. Their  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> contents increased from 35 wt% on the product prepared from BA2 to 66 wt% on the product from BA8 (see Fig. S1 and Table S1 of supporting information). The yield of  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> was smaller in the ammonia nitrated product of  $\alpha$ -Fe with the larger particle size. In our

previous study,  $\text{Fe}_3\text{O}_4$  nanoparticle with a particle size of 40 nm prepared from aqueous solution was used as a reference of the starting powder in low temperature nitridation. Although the  $\text{Fe}_3\text{O}_4$  had a similar particle size to BA6 and BA8 prepared in this study, the nitrided product was a poorly crystallized mixture of  $\alpha''\text{-Fe}_{16}\text{N}_2$ ,  $\gamma\text{-Fe}_4\text{N}$  and  $\text{Fe}_3\text{O}_4$ , with a small  $\alpha''\text{-Fe}_{16}\text{N}_2$  content<sup>15</sup>. Low humidity contents in the iron oxides prepared in non-aqueous benzyl alcohol solution could improve the reaction yield and crystallinity of the  $\alpha''\text{-Fe}_{16}\text{N}_2$ . The nitrided products showed the larger magnetization of 219 ~ 222  $\text{emu}\cdot\text{g}^{-1}$  than the value of 208  $\text{emu}\cdot\text{g}^{-1}$  for  $\alpha\text{-Fe}$  before nitridation, independent of the starting materials as depicted in Fig. 7. They were soft magnet with magnetic coercivity of less than 0.6 kOe. Their magnetization was not yet saturated at 15 kOe as in our previous reports on  $\alpha''\text{-Fe}_{16}\text{N}_2$  prepared from vapor grown  $\gamma\text{-Fe}_2\text{O}_3$ <sup>13,15</sup>.

## Conclusion

Particle size of iron oxide fine powder was controlled to above 40 nm diameter in its preparation by the hydrolysis of increasing amount of iron acetylacetonate in benzyl alcohol. The iron oxide products were mixtures of magnetite  $\text{Fe}_3\text{O}_4$ , maghemite  $\gamma\text{-Fe}_2\text{O}_3$  and their superparamagnetic component. Ferromagnetic  $\alpha''\text{-Fe}_{16}\text{N}_2$  fine powder could be prepared reproducibly in low temperature nitridation of its reduced  $\alpha\text{-Fe}$  product because of its low

humidity content.

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## References

1. Kim T. K., and Takahashi M., *Appl. Phys. Lett.*, 1972 **20** 492-494.
2. Nakajima K. and Okamoto S., *Appl. Phys. Lett.*, 1990 **56** 92-94.
3. Sugita Y., Takahashi H., and Komuro M., *J. Appl. Phys.*, 1994 **76** 6637-6641.
4. Sakuma A., *J. Magn. Magn. Mater.*, 1991 **102** 127-134.
5. Coey J. M. D., O'Donnell K., Qinian Q., Touchais E., and Jack K. H., *J. Phys.: Condens. Matter*, 1994 **6** 23-28.
6. Takahashi M., Shoji H., Takahashi H., Nashi H., and Wakiyama T., *J. Appl. Phys.*, 1994 **76** 6642-6647.
7. Metzger R. M., Bao X., and Carbucicchio M., *J. Appl. Phys.*, 1994 **76** 6626-6631.
8. Jack K. H., *J. Alloys Compd.*, 1995 **222** 160-166.
9. Huang M. Q., Wallace W. E., Simizu S., Pedziwiatr A. T., Obermyer R. T., and Sankar S. G., *J. Appl. Phys.*, 1994 **75** 6574-6576.
10. Saito T., *J. Appl. Phys.*, 2000 **87** 6514-6516.
11. Tessier F., Navrotsky A., Niewa R., Leineweber A., Jacobs H., Kikkawa S., Takahashi M., Kanamaru F., and DiSalvo F. J., *Solid State Sci.*, 2000 **2** 457-462.
12. Nagatomi A., Kikkawa S., Hinomura T., Nasu S., and Kanamaru F., *J. Jpn. Soc. Powder Powder Metal.*, 1999 **46** 151-155.
13. Kikkawa S., Yamada A., Masubuchi Y., and Takeda T., *Mater. Res. Bull.*, 2008 **43**

3352-3357.

14. Kikkawa S., Kubota K., and Takeda T., *J. Alloys Compd.*, 2008 **449** 7-10.

15. Yamanaka K., Onuma Y., Yamashita S., Masubuchi Y., Takeda T. and Kikkawa S., *J. Solid State Chem.*, 2000 183 2236-2241.

16. Pinna N., Grancharov S., Beato P., Bonville P., Antonietti M., and Niederberger M., *Chem. Mater.*, 2005 **17** 3044-3049.

17. Izumi F., and Ikeda T., *Mater. Sci. Forum*, 2000 **321-324** 198-203.

18. Hill R. J., Craig J. R. and Gibbs G. V., *Phys. Chem. Minerals*, 1979 **4** 317-339.

19. Shmakov A. N., Kryukova G. N., Tsybulya S. V., Chuvilin A. L. and Solovyeva L. P., *J. Appl. Cryst.*, 1995 **28** 141-145.

20. Volenik K., Seberini M., and Neid J., *Czech. J. Phys.*, 1975 **B25** 1063-1071.

## Figure captions

Fig. 1 PXRD of iron oxides prepared from various amounts of  $\text{Fe}(\text{acac})_3$ .

Fig. 2 Magnetization curves of the iron oxides prepared from various amounts of  $\text{Fe}(\text{acac})_3$ .

Thick solid, thin solid, dotted and broken lines represent curves for the products BA2, BA4, BA6 and BA8, respectively.

Fig. 3 TEM of iron oxide particles prepared from various amount of  $\text{Fe}(\text{acac})_3$ .

Fig. 4 Observed (+), calculated (–) and their difference profiles on PXRD for BA4. Vertical bars indicate the the Bragg reflections for  $\text{Fe}_3\text{O}_4$  (upper) and  $\gamma\text{-Fe}_2\text{O}_3$  (lower).

Fig. 5 SEM of BA2 and BA8 iron oxides and their reduced  $\alpha\text{-Fe}$  products BA2' and BA8'.

Fig. 6 PXRD of the nitrated products prepared from the iron oxides BA2 ~ BA8. Stars and circles represent the diffraction lines for  $\alpha\text{-Fe}_{16}\text{N}_2$  and  $\alpha\text{-Fe}$ , respectively.

Fig. 7 Magnetization curves of the nitride products prepared from the precipitate BA2 ~ BA8.

Thick solid, thin solid, dotted and broken lines represent curves for the nitrated products from BA2, BA4, BA6 and BA8, respectively.

Figure 1

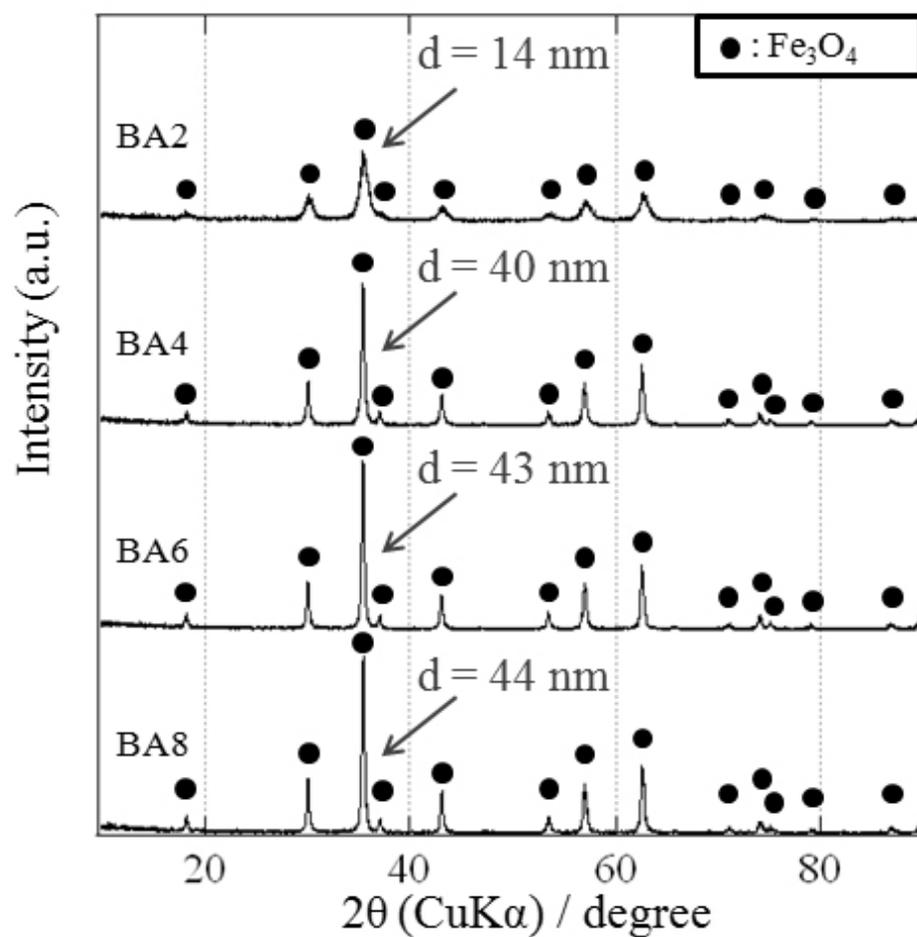


Fig. 1 PXRD of iron oxides prepared from various amounts of  $\text{Fe}(\text{acac})_3$ .

Figure 2

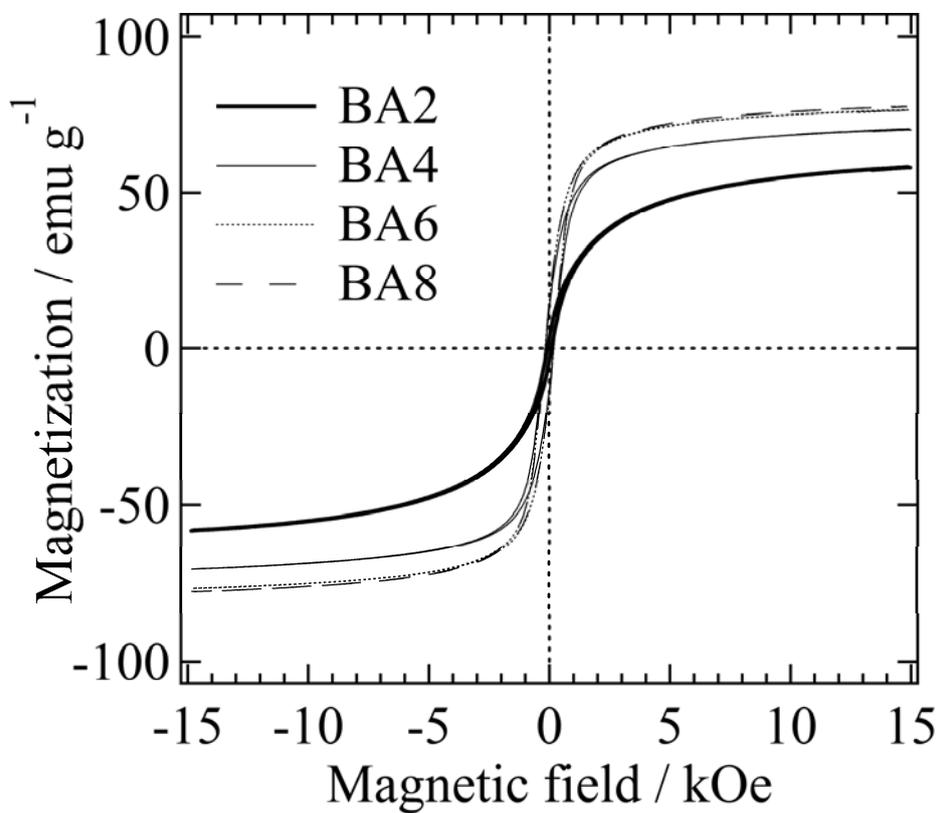


Fig. 2 Magnetization curves of the iron oxides prepared from various amounts of  $\text{Fe}(\text{acac})_3$ .

Thick solid, thin solid, dotted and broken lines represent curves for the products BA2, BA4, BA6 and BA8, respectively.

Figure 3

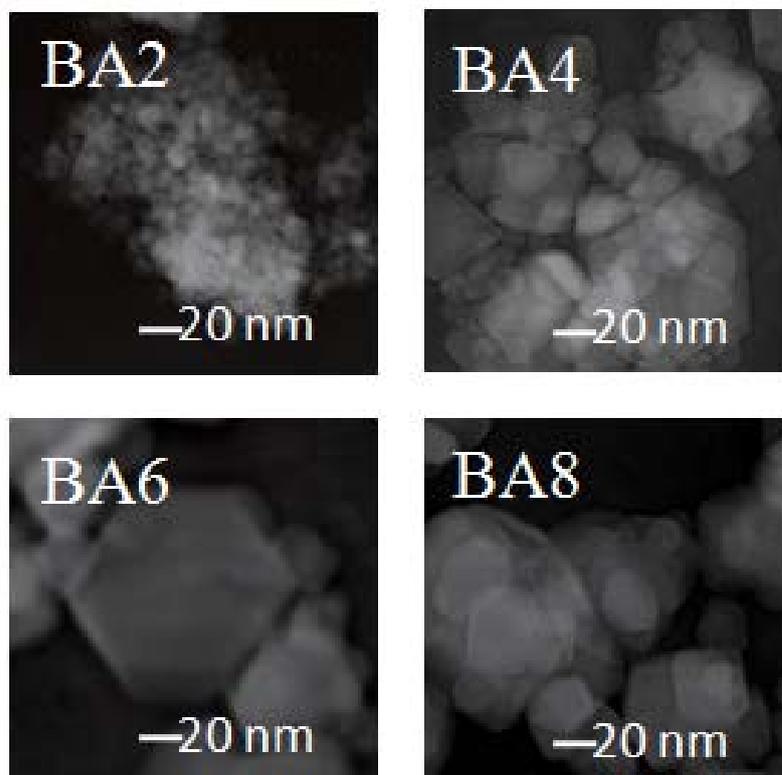


Fig. 3 TEM of iron oxide particles prepared from various amount of  $\text{Fe}(\text{acac})_3$ .

Figure4

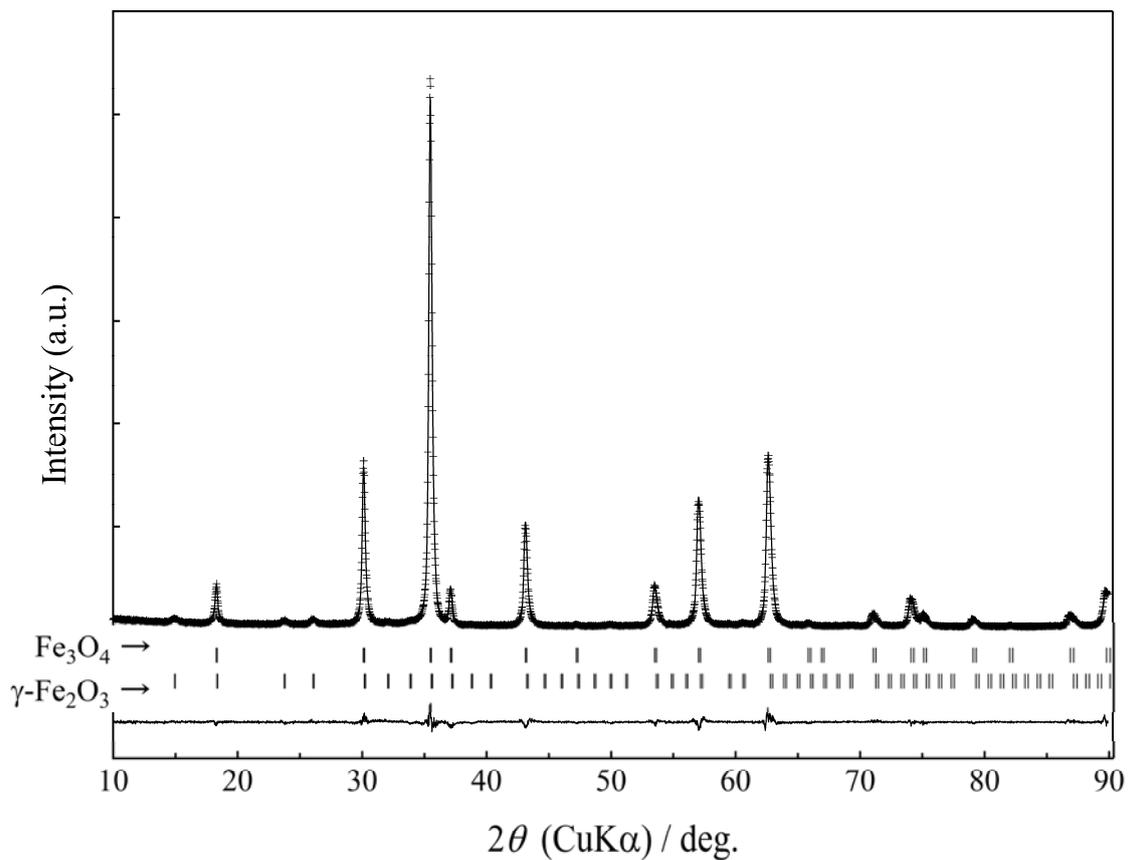


Fig. 4 Observed (+), calculated (-) and their difference profiles on PXRD for BA4. Vertical bars indicate the the Bragg reflections for  $\text{Fe}_3\text{O}_4$  (upper) and  $\gamma\text{-Fe}_2\text{O}_3$  (lower).

Figure 5

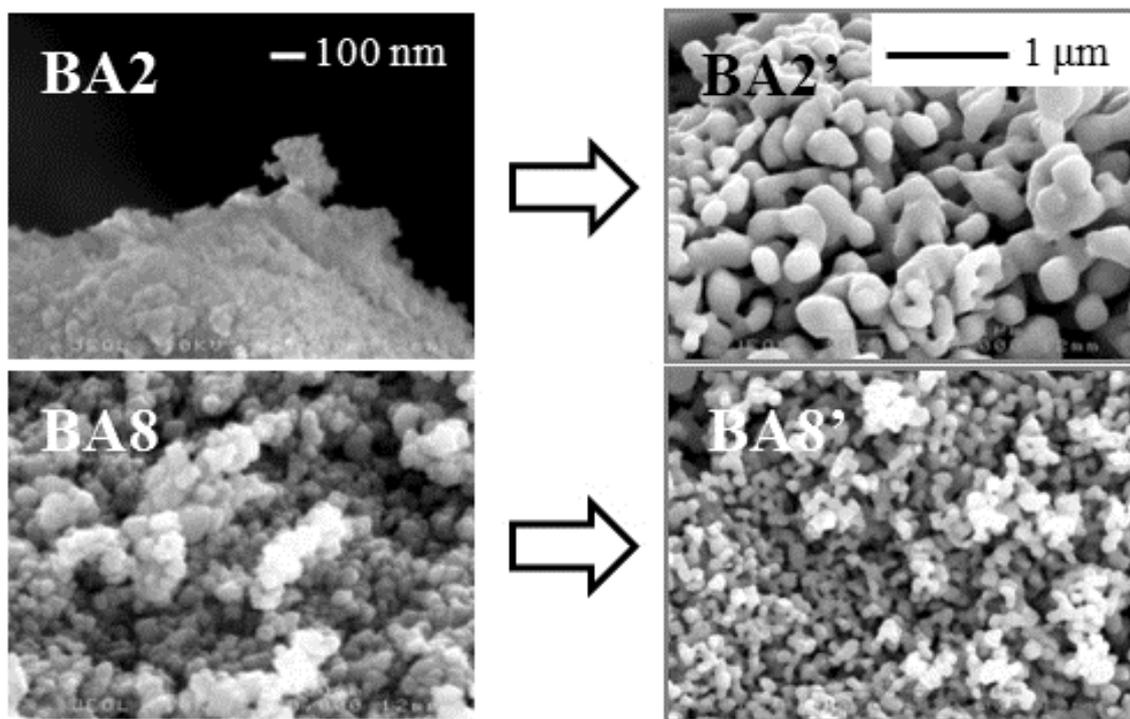


Fig. 5 SEM of BA2 and BA8 iron oxides and their reduced  $\alpha$ -Fe products BA2' and BA8'.

Figure 6

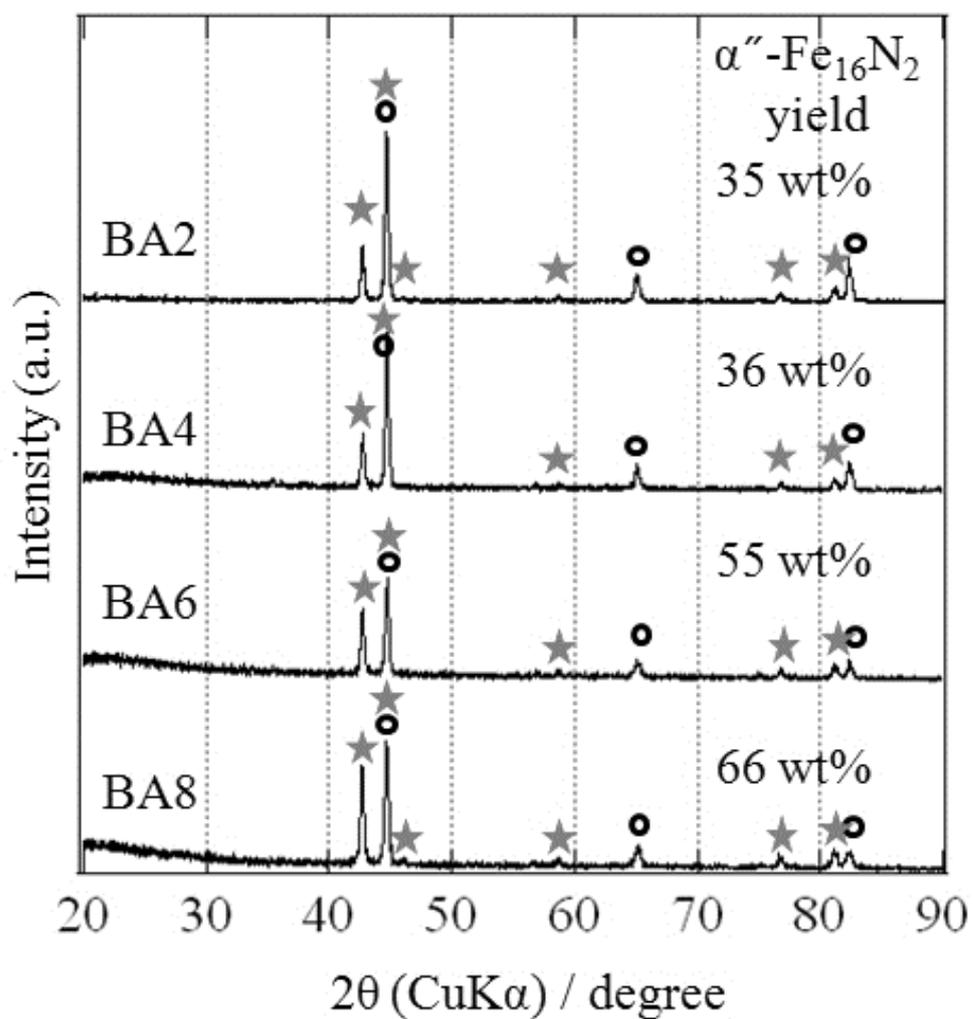


Fig. 6 XRD of the nitrated products prepared from the iron oxides BA2 ~ BA8. Stars and circles represent the diffraction lines for α''-Fe<sub>16</sub>N<sub>2</sub> and α-Fe, respectively.

Figure 7

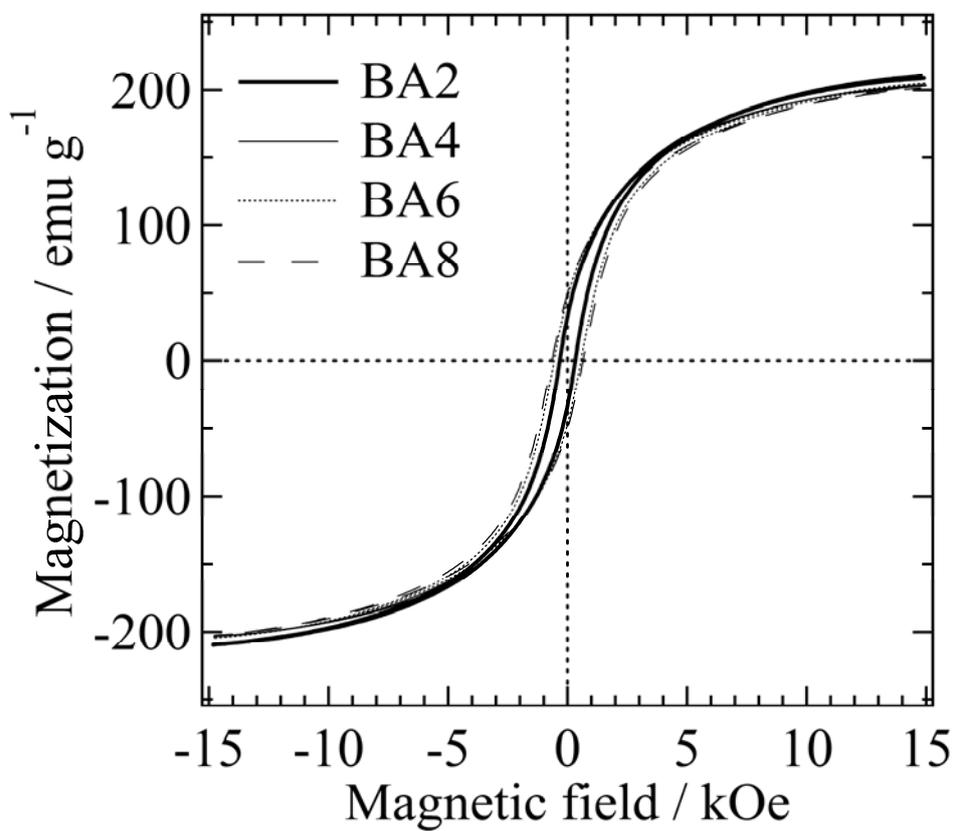


Fig. 7 Magnetization curves of the nitride products prepared from the precipitate BA2 ~ BA8.

Thick solid, thin solid, dotted and broken lines represent curves for the nitrated products

from BA2, BA4, BA6 and BA8, respectively.