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Full length article

Magnetite/maghemite mixture prepared in benzyl alcohol for the preparation of α''-$Fe_{16}N_2$ with α-Fe

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Abstract

Fine powder of iron oxide has been required in the preparation of ferromagnetic α''-$Fe_{16}N_2$ powder in low temperature nitridation. Magnetite and maghemite mixture was obtained by the reaction of iron acetylacetonate $Fe(acac)_3$ in benzyl alcohol. It was reduced to α-Fe in hydrogen at 400 °C. Particle size of the α-Fe was 300 nm in the reduction of iron oxides obtained from 2 g of $Fe(acac)_3$. It decreased to 100 nm in the preparation using 8 g of $Fe(acac)_3$. After the successive nitridation under ammonia flow at 160 °C, the highest yield of α''-$Fe_{16}N_2$ in 66 wt.% was observed on the nitrided product from the latter α-Fe, because of the smallest α-Fe particle size after the reduction in the present study. The yield and reproducibility of α''-$Fe_{16}N_2$ formation in low temperature nitridation was improved using the iron oxide prepared in non-aqueous benzyl alcohol compared to the use of magnetite obtained from aqueous solution.

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1. Introduction

Large magnetization value has been expected for α''-$Fe_{16}N_2$ thin films.[1–3] Their reported magnetization values were scattered between 360 emu g^{-1} and the values comparable to 210 emu g^{-1} of α-Fe.[1–6] 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 α''-$Fe_{16}N_2$. Tempering of Fe–N martensite powders and annealing of mechanically alloyed α-Fe and ε-Fe_3N powders at low temperature between 100 and 200 °C have been tried to prepare the single phase of α''-$Fe_{16}N_2$,[7–10] respectively. However, the α''-$Fe_{16}N_2$ has been prepared in less than 50% purity and was contaminated with impurity phases of α-Fe and γ-Fe–N[9] (austenite) or γ-Fe_4N.[10] α''-$Fe_{16}N_2$ is thermally metastable and its very small formation enthalpy value of 85.2 ± 46.8 kJ mol^{-1} was expected.[11] It may be a line phase because it has been observed as mixtures either with α-Fe or with γ-Fe_4N. It is also easily oxidized in air. Single phase of α''-$Fe_{16}N_2$ confirmed by powder X-ray diffraction was prepared by low temperature nitridation at 110 °C for 10 days in ammonia gas of α-Fe fine powder obtained from reduction of γ-Fe_2O_3.[12] The α''-$Fe_{16}N_2$ showed the saturation magnetization of 162 emu g^{-1}, which was higher than 151 emu g^{-1} of α-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 Al_2O_3 added to improve the durability of the starting γ-Fe_2O_3. We succeeded a preparation of X-ray single phase in a similar low temperature ammonolysis of α-Fe fine powder obtained by the reduction of vapor grown γ-Fe_2O_3 fine powder of about 30 nm in particle size without any additives.[13] The saturation magnetization was 225 emu 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 α-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 α''-$Fe_{16}N_2$.[14] Iron oxides prepared in aqueous solution failed in its preparation even in a similar particle size to the previous studies.[15] 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$0.05 ppm, and the starting vapor-grown γ-Fe_2O_3 fine powder improved the reproducibility of the α''-$Fe_{16}N_2$ yield of the nitridation. However, the starting iron oxide fine powder suitable

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for the α''-$Fe_{16}N_2$ preparation has been only strictly limited to the vapor-grown γ-Fe_2O_3 fine powder (C.I. Kasei Co. Ltd.). It cannot be commercially available in controlled particle size and morphology. Fine Fe_3O_4 powder (<18 nm) has been prepared by reacting iron acetylacetone with benzyl alcohol with low water solubility.[16] 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 α''-$Fe_{16}N_2$ powder.

In the present study, low temperature nitridation reaction was investigated on the α-Fe obtained from reduction of iron oxide fine powder prepared in benzyl alcohol changing the amount of iron acetylacetonate, hereafter denoted as $Fe(acac)_3$, dissolved as the starting materials.

2. Experimental

Various amounts of $Fe(acac)_3$, (Kanto Chemical Co. Inc.) 2, 4, 6 and 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 h. 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 h in hydrogen flow of 30 mL min^{-1}. Hydrogen purity was higher than 99.99% and the diameter of tube furnace was 25 mm as in our previous study.[15] Ammonia, supplied by Sumitomo Seika Chemicals Co. Ltd., with purity of 99.9995% was introduced at 50 mL min^{-1} to the reaction tube without exposing the reduced powder to air. The ammonolysis was performed at 160 °C for 15 h.

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 ±15 kOe. Other part of the nitrided products was dipped in silicone oil to prevent air exposure and rapid oxidation. Powder X-ray diffraction (PXRD) was performed using monochromatized Cu-Kα radiation in a diffractometer (Rigaku, Ultima IV). The yield of α''-$Fe_{16}N_2$ was estimated by Rietveld fitting of the PXRD data using the program RIETAN-2000.[17] Mössbauer spectroscopy was performed using γ radiation from $^{57}Co/Rh$ in equipment supplied by Topologic Systems Co. Ltd. The spectrum was analyzed using the program MossWinn 3.0i.

3. Results and discussion

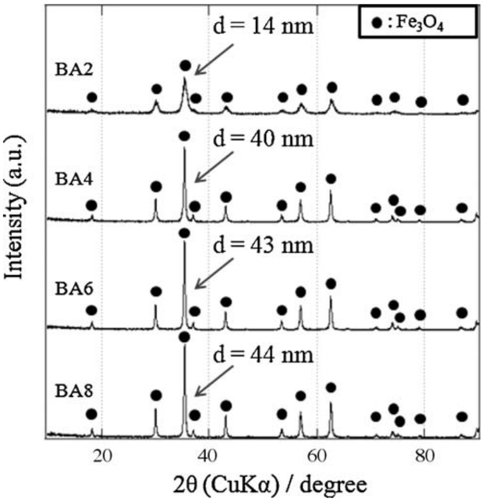

Fig. 1. PXRD of iron oxides prepared from various amounts of $Fe(acac)_3$.

The products obtained after the heating in autoclave at 200 °C for 48 h were magnetite with their respective crystallite sizes of 14, 40, 43 and 44 nm estimated from the line broadening of the main diffraction peak depending on the amount of $Fe(acac)_3$ 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 shows 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 Fe_3O_4 magnetite and γ-Fe_2O_3 maghemite.[16] Powder X-ray diffraction pattern of the BA4 was refined as a mixture of Fe_3O_4 and γ-Fe_2O_3 as shown in Fig. 4. The cubic inverse spinel structure (space group: Fd-3m) and the cubic spinel-like structure with cation vacancy ordering ($P4_332$) were used for the structural parameters of Fe_3O_4 and γ-Fe_2O_3, respectively.[18,19] After the refinement of their lattice constants and peak profile parameters, the observation fit very well with the calculated profile, resulting in $R_{wp} = 8.2\%$, $R_e = 6.5\%$ and $S = 1.3$. Its phase ratio was 75 wt.% Fe_3O_4 and 25 wt.% γ-Fe_2O_3. Their lattice constants were 0.8381(1) nm and 0.8360(2) nm in Fe_3O_4 and γ-Fe_2O_3, respectively, which were comparable to the reported values of 0.8394 nm and 0.8347 nm.[18,19] Its Mössbauer spectrum sup-

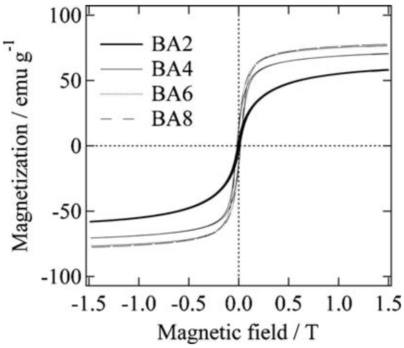

Fig. 2. Magnetization curves of the iron oxides prepared from various amounts of $Fe(acac)_3$. Thick solid, thin solid, dotted and broken lines represent curves for the products BA2, BA4, BA6 and BA8, respectively.

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