Characterization of Ultrafine $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ Particles Synthesized by Co-Precipitation: Size Regulation and Magnetic Properties

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Ultrafine Ni(II)-bearing ferrites (UNFs) with 14–100% Ni(II)-substitution of x in $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ for Fe^{2+} in magnetite were synthesized by hydrolysis of Ni^{2+} , Fe^{2+} , and Fe^{3+} ions at 60°C, followed by aging of the co-precipitates at 60°C and heating to 300°C. The aged precipitates were the precursors of the UNFs, into which they were transformed by heating at 300°C. The Ni(II)-substitution of the UNF was corroborated by a decrease in the lattice constant with an increase in the Ni(II) content of the product. The ferrite particles were nearly spherical and uniform. The average crystallite sizes ranged from 8 to 17 nm, which decreased with an increase in the Ni(II) content of the ferrite. In the average size range from 14 to 17 nm, the UNFs with various Ni(II)-substitutions could be synthesized by changing the aging conditions. A transition of the UNF ($x=1.0$) from superparamagnetic to ferrimagnetic particles at room temperature occurred in the crystallite size range from 8 to 14 nm. The UNFs gave a room-temperature saturation magnetization (M_s) much lower than the theoretical M_s .

Key words: ultrafine ferrite, $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ ($x=0.14\text{--}1.0$), co-precipitation, magnetic properties

1. Introduction

Magnetite Fe_3O_4 has the spinel structure in which ferrous ions occupy the octahedral (B) and ferric ions occupy both the tetrahedral (A) and the octahedral sites.¹⁾ The ferrous ions can be progressively replaced by bivalent metal ions, which gives M(II)-bearing ferrite solid solutions of $\text{M}_x\text{Fe}_{3-x}\text{O}_4$ system (M =bivalent transition metals, Zn, Co, Mn, *etc.*) The magnetic properties of the M(II)-bearing ferrite vary depending on the level of M(II)-substitution in magnetite and on the microstructural features such as morphology and crystallite size. Especially, it is of great academic interest that ultrafine powder of the ferrite gives magnetic behavior different from that of the same material in the coarse crystalline form.

The conventional solid state reactions for preparation of Ni(II)-bearing ferrite $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ ($0.0 < x \leq 1.0$) at

high temperatures give rise to the formation of polycrystalline compound of the ferrite with a large crystallite size, which lose their fine particle nature. Many kinds of ferrites smaller than 50 nm in size can be prepared by several wet methods which include 1) co-precipitation, 2) hydrothermal, 3) spray drying, and 4) freeze-drying methods. Synthesis of ultrafine Fe_3O_4 or NiFe_2O_4 particles has been studied in the wet methods by many investigators. However, there have been no reports on the synthesis of ultrafine ferrite solid solutions between Fe_3O_4 and NiFe_2O_4 .

This paper will describe the synthesis of ultrafine $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ crystallite under the regulation of size by co-precipitation method. The magnetic properties of the ultrafine Ni(II)-bearing ferrites were also studied.

2. Experimental

2.1 Synthesis of ultrafine Ni(II)-bearing ferrite

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (12.16 g) was dissolved in distilled water (0.15 dm³) degassed by passing nitrogen gas. Appropriate proportions of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were dissolved at 60°C in the FeCl_3 solution: the Ni(II)/ Fe_{total} molar ratio in the solution, $r=0.05\text{--}0.50$. An appropriate amount of NaOH (7.20 g) for neutralization of the metals was dissolved in 0.15 dm³ of distilled water degassed and the solution was kept at 60°C. The mixed metal chloride solution was added to the NaOH solution at 60°C with vigorous stirring for coprecipitation. The co-precipitate obtained was aged in the mother solution at a desired temperature for 1–64 h. The aged co-precipitate (ACP) was collected by centrifuging at 14000 rpm. After washing with distilled water, and successively with acetone, it was dried *in vacuo* at 60°C for a day. The ACP was then heated in an N_2 gas stream at 300°C for 1.0–1.5 h to remove any incorporated H_2O and OH group.

2.2 Characterization of products

The products were identified by X-ray diffractometry with Fe-K_α radiation (Rigaku RAD 2A diffractometer). The lattice constants of the spinel compounds were estimated from the X-ray diffraction (XRD) peak posi-

Table 1 Chemical compositions, lattice parameters, and crystallite sizes of ultrafine Ni(II)-bearing ferrites (UNFs)

Sample	r^{*1}	R^{*2}	Chemical composition	a_o (nm)	Crystallite size (nm)	
					D	d
a	0.05	0.049	$Ni^{2+}_{0.14}Fe^{2+}_{0.66}Fe^{3+}_{2.20}O_{4.10}$	0.8388	17	15
b	0.10	0.096	$Ni^{2+}_{0.26}Fe^{2+}_{0.62}Fe^{3+}_{2.12}O_{4.06}$	0.8384	17	16
c	0.15	0.136	$Ni^{2+}_{0.36}Fe^{2+}_{0.45}Fe^{3+}_{2.19}O_{4.10}$	0.8376	16	16
d	0.20	0.176	$Ni^{2+}_{0.45}Fe^{2+}_{0.45}Fe^{3+}_{2.10}O_{4.05}$	0.8372	15	13
e	0.30	0.299	$Ni^{2+}_{0.69}Fe^{2+}_{0.19}Fe^{3+}_{2.12}O_{4.05}$	0.8357	14	12
f	0.40	0.395	$Ni^{2+}_{0.85}Fe^{2+}_{0.13}Fe^{3+}_{2.02}O_{4.01}$	0.8354	12	8
g	0.50	0.514	$Ni^{2+}_{1.02}Fe^{2+}_{0.13}Fe^{3+}_{1.98}O_{3.99}$	0.8350	8	6
f ^{*3}	0.40	0.360	$Ni^{2+}_{0.79}Fe^{2+}_{0.21}Fe^{3+}_{2.00}O_{4.00}$	0.8356	15	13
g ^{*3}	0.50	0.485	$Ni^{2+}_{0.98}Fe^{2+}_{0.21}Fe^{3+}_{2.02}O_{4.01}$	0.8348	14	12

*1 Ni(II)/Fe_{total} mole ratio in the starting solution.

*2 Ni(II)/Fe_{total} mole ratio in the products obtained by heating the ACPs at 300°C in an N₂ gas stream.

3 These samples were prepared at a different aging temperature (90°C) and for different periods (24 h for sample f^{} and 64 h for sample g^{*}, respectively).

Fig. 1 XRD patterns of the UNF samples prepared at various Ni(II)/Fe_{total} molar ratios (r) in starting solutions of (a), 0.15, (b) 0.30, (c) 0.40, and (d) 0.50.

tions of the (220), (311), (400), (511), and (440) planes of the spinel structure by extrapolation ($\theta \rightarrow 90^\circ$) of the linear Nelson–Riley function *vs.* lattice constant plot. The infrared (IR) spectra were recorded by the KBr disc technique (Shimadzu, model FTIR-8500). The thermal analysis was carried out by using thermogravimeter-mass spectrometer (TG-MS) (Mac Science, model TG DTA 200 and VG Anatech, model QUADRUPOLES 560) at a heating rate of 20°C min⁻¹. The Mössbauer spectra were recorded at room temperature with a ⁵⁷Co source. The chemical compositions were determined both by inductively coupled plasma (ICP) spectroscopy

Fig. 2 XRD patterns of aged co-precipitates (ACPs) prepared at various Ni(II)/Fe_{total} molar ratios (r) in starting solutions. Samples correspond to those of Fig. 1.

(Seiko Instruments SPS7000) and by colorimetry with a HITACHI model U-1100 spectrophotometer using 2,2'-dipyridyl²⁾ after dissolving the samples in an HCl solution. The particle size and morphology of the products were examined by transmission electron microscopy (TEM). The average crystallite size D was obtained using the Scherrer's equation from the line width of the 311 XRD peak of the spinel structure. The magnetic measurement was carried out using vibrating sample magnetometer (VSM).

Fig. 3 TEM micrographs of the UNF samples (a) c, (b) f, (c) g, (d) f', and (e) g'.

3. Results and Discussions

The chemical compositions, lattice parameters and average crystallite sizes of the ultrafine Ni(II)-bearing ferrites (UNFs) were listed in Table 1; the samples were obtained by co-precipitation at 60°C, followed by aging of the co-precipitates at 60°C for 1 h and heating to 300°C. The UNF samples gave only peaks of spinel structure in the XRD patterns (Fig. 1). The Ni(II)/Fe_{total} molar ratios (R) of the samples were nearly the same as those (r) of the starting solutions for preparation, indicating that most of Ni(II), Fe(II), and Fe(III) ions were incorporated in the products of the samples. The chemical compositions of the samples were estimated from chemical analysis assuming that the products were ferrite solid solutions of NiFe_2O_4 - Fe_3O_4 - γ - Fe_2O_3 . The chemical compositions of the samples a-e showed that the ferrites of the samples were nonstoichiometric with respect to the oxygen composition and contained some amount of γ - Fe_2O_3 component. Ni(II)-substitution in $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ system can be evidenced by the decrease in the lattice constant with an increase in the x . The lattice constant of the UNF decreased with increasing x , indicating that the Ni(II) ions in the samples were incorporated into the lattice points of the spinel structure.

The XRD patterns of the aged co-precipitates (ACPs) before heating to 300°C are shown in Fig. 2. Only the peaks attributed to spinel structure appeared in the XRD patterns. However, the lattice constants of the ACPs did not decrease with an increase in the Ni(II) content x ; they varied randomly with x in the a_0 range from 0.8371–0.8383 nm. TG-analysis showed that the weight of the ACP decreased in an N_2 gas stream at the temperature range from 40 to 400°C. The significant weight loss of 6.0 wt% was observed. The effluent gases of H_2O and CO_2 were detected by mass spectrom-

eter. Most of the weight loss of 6.0 wt% corresponded to the amount of H_2O evolved (5.5 wt%) and the rest to that of CO_2 evolved (0.5 wt%). In the IR spectra of the ACPs, the absorption bands at 3400 and 1620 cm^{-1} were observed, which can be assigned as the stretching vibrations and the deformation, respectively, of H_2O . The ACP will contain some quantity of coordinated water and/or OH group in the lattice, which is expected to influence the lattice constant. Thus, the ACPs were not identified as the UNFs although they gave the XRD peaks of spinel structure. They were regarded as the precursors of the UNFs in the present preparation process. Such water and OH^- in the ACPs are considered to be released by heating to 300°C for 1–1.5 h; in the IR spectra of the samples after the heat treatment, the absorption bands at 3400 and 1620 cm^{-1} disappeared. The precursors of the ACPs could be transformed to the UNFs by the heat treatment at 300°C.

The ACPs obtained at $r=0.05$ – 0.30 showed nearly the same diffraction patterns giving the relatively sharp spinel peaks (Fig. 2a and b). The spinel peaks were broadened as the value of r increased above 0.40 (Fig. 2c and d). The UNFs with almost the same average crystallite size D , ranging from 14 to 17 nm, could be obtained by the heat treatment of the precursor ACPs obtained at $r=0.05$ – 0.30 (Table 1; samples a–e). At $r \geq 0.4$, however, the D value of the UNF obtained by the heat treatment significantly decreased with increasing r (samples f and g). The TEM micrographs of the samples a–e showed the nearly spherical ultrafine particles of the size ranging from 10 to 20 nm (Fig. 3a). On the other hand, the samples f and g showed the larger distribution in size, ranging from 4 to 20 nm, and the portion of the particles smaller than 10 nm increased with r (Fig. 3b and c). The crystallite size (d) was also estimated from the TEM observation: the number of

Fig. 4 Mössbauer spectra of samples (a) g and (b) g' at 300 K.

Table 2 Saturation magnetization (M_s) of the samples at 300 K

Sample	M_s (G cm ³ g ⁻¹)	Theo. M_s^* (G cm ³ g ⁻¹)
b	62.0	82
d	59.2	74
e	54.4	63

* The theoretical saturation magnetizations at 0 K were estimated by assuming that the Ni(II) ions, Fe(II) ions, and cation vacancies are distributed in B sites, and the Fe(III) ions in both A and B sites.¹⁾

particles counted for the size determination was *ca.* 30–50. The d values were in good agreement with D values (Table 1). The size distribution was also estimated from TEM micrograph for sample c: the counted number was 200. 90% of the particle sizes distributed in the narrow range from 12 to 19 nm.

The co-precipitates obtained at $r=0.4$ and 0.5 were aged at 90°C for 24 and 64 h, respectively, followed by heating to 300°C. The D values of the samples f and g increased to 15 and 14 nm, respectively (Table 1; samples f' and g'). The nearly spherical ultrafine particles in the size range 10–20 nm were observed in the TEM micrographs of the samples f' and g' (Fig. 3d and e). Therefore, we have obtained here the ultrafine

Ni_xFe_{3-x}O₄ ($x=0.14$ – 1.0) having nearly the same crystallite size in the D range 14–17 nm.

The Mössbauer spectra of the samples g and g' at 300 K are shown in Fig. 4 as an indication of aging effect. The sample g with $D=8$ nm gave a large absorption of a doublet with very small magnetically split patterns (Fig. 4a). The sample g' with $D=14$ nm showed only the magnetically split patterns of the sextets (Fig. 4b), which are characteristic of the ferrospinels.³⁾

Usually, the theoretical saturation magnetizations at 0 K (theo. M_s) given in Table 2 nearly agrees with the M_s of the bulk ferrite observed at 300 K. The UNFs prepared exhibited much lower values of M_s than the theoretical values. The superparamagnetic fraction in these UNF samples makes the M_s somewhat lower at 300 K. In the usual collinear-structure model, the magnetization of tetrahedral (A) sublattice is antiparallel to that of octahedral (B) sub-lattice. However, Haneda *et al.*⁴⁾ have found by Mössbauer spectroscopy that ultrafine NiFe₂O₄ and γ -Fe₂O₄ both have non-collinear magnetic structure in the surface layer, which decreases their M_s values. The presence of the non-collinear magnetic structure in the surface layer of the UNF samples may result in lower M_s values. Besides these effects, there is also possibility that the UNFs have incomplete crystal structure of spinel or cation distribution different from that of the bulk ferrite, which is expected to influence the M_s value.

4. Conclusion

We could synthesize the nearly spherical and uniform UNFs with various Ni(II)-substitutions ($x=0.14$ – 1.0) having almost the same crystallite size in the D range from 14 to 17 nm by changing the aging conditions. A transition of the UNF ($x=1.0$) from superparamagnetic to ferromagnetic particles at 300 K occurred in the crystallite size range from 8 to 14 nm. The UNFs gave M_s values much lower than the theoretical M_s at 300 K.

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