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Materials Research Bulletin 40 (2005) 1126–1135



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# Synthesis of fine magnetite powder using reverse coprecipitation method and its heating properties by applying AC magnetic field

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Received 4 November 2004; received in revised form 12 January 2005; accepted 29 March 2005

# Abstract

Nano-sized FeFe<sub>2</sub>O<sub>4</sub> ferrite powder for local thermal coagulation therapy was synthesized by a reverse coprecipitation method. The crystal diameter for the samples from the reverse coprecipitation method was smaller than that from a normal coprecipitation method. The crystal diameter increased with an increase in the synthesized temperature for both methods. The maximum increasing temperature under the AC magnetic field was at around a 12 nm crystal diameter. The FeFe<sub>2</sub>O<sub>4</sub> powder was oxidized to Fe<sub>2</sub>O<sub>3</sub> by calcination at 600 °C in ambient air. The heating ability almost depended on the hysteresis loss value. Although the increased temperature under the AC magnetic field for the fresh FeFe<sub>2</sub>O<sub>4</sub> sample was very close to that for the commercialized MgFe<sub>2</sub>O<sub>4</sub> powder, it was gradually decreased for FeFe<sub>2</sub>O<sub>4</sub> with time in ambient air.

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Keywords: A. Magnetic materials; A. Nanostructures; B. Chemical synthesis; C. X-ray diffraction

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0025-5408/\$ – see front matter © 2005 Elsevier Ltd. All rights reserved. doi:10.1016/j.materresbull.2005.03.014

## 1. Introduction

The thermal coagulation techniques, such as a percutaneous microwave coagulation therapy and a radio frequency interstitial tissue ablation therapy have become important treatments for cancer tissues. In these therapies, tumors have antennas-like needles percutaneously inserted, and then microwaves or a radio frequency is radiated to provide a local coagulation. The same results can be realized by application of an alternating magnetic field from external coils to the tumors with a needle or powdered magnetic material. This therapy makes it not necessary to insert any antenna in the patient. This provides less damage to the patient.

Several magnetic materials as candidates have been reported for the local heating of the cancer tissues in an AC magnetic field [1–4]. Magnetite (FeFe<sub>2</sub>O<sub>4</sub>) has been investigated for this therapy, since nanosized magnetite powder having a good heating property can be easily prepared using a coprecipitation method. In this case, nano-sized FeFe<sub>2</sub>O<sub>4</sub> particle directly forms even below 100 °C in alkaline aqueous solution by following reaction:

$$Fe^{2+} + 2Fe^{3+} + 8OH^{-} \rightarrow FeFe_2O_4 + 4H_2O$$

$$\tag{1}$$

In addition, the heating property in the AC magnetic field is strongly influenced by the particle size [5]. Teraoka et al. [6,7] reported a reverse coprecipitation method, which is very effective for synthesizing a homogeneous fine powder of poly-metallic oxides, such as the perovskite-type materials. For a normal coprecipitation method, the pH value gradually increases, because an alkali solution is dropped into the mixed metal solution. In the case of the reverse coprecipitation method, the mixed metal solution was directly dropped into an alkaline solution. Consequently, it is expected that the magnetite particle does not grow in this reverse method.

On the other hand, we investigated the selection of an appropriate material from many commercialized ferrite powders of (MFe<sub>2</sub>O<sub>4</sub>; M: Mg, Mn, Fe, Co, Ni, Cu, and Sr) having large particle sizes (>1  $\mu$ m) [8,9]. In these ferrites, the MgFe<sub>2</sub>O<sub>4</sub> powder showed the maximum enhancement of the temperature under the AC magnetic field. The reason for this enhancement of the temperature is attributed to the high hysteresis loss of the magnetic properties [9]. However, MgFe<sub>2</sub>O<sub>4</sub> cannot be produced using the coprecipitation method below 100 °C, because the Mg(OH)<sub>2</sub> formed in the alkaline solution decomposes to the oxide at high temperature of around 300 °C [10]. Up to now, the heating properties of MgFe<sub>2</sub>O<sub>4</sub> have not been compared with those of nano-sized FeFe<sub>2</sub>O<sub>4</sub>.

In this study, we examined the heating properties in an AC magnetic field of  $FeFe_2O_4$  nano-sized powders prepared using the reverse coprecipitation method and the normal coprecipitation method. Furthermore, the heating property and stability of the nano-sized  $FeFe_2O_4$  materials were compared with those of commercialized  $MgFe_2O_4$ .

#### 2. Experimental

## 2.1. Preparation of $FeFe_2O_4$ powder

The FeFe<sub>2</sub>O<sub>4</sub> was prepared by two methods, i.e. a normal coprecipitation method and a reverse coprecipitation method. FeCl<sub>2</sub>·4H<sub>2</sub>O (0.10 mol) and FeCl<sub>3</sub>·6H<sub>2</sub>O (0.20 mol) were dissolved in 200 ml of pure water. For the normal coprecipitation method, the mixed solution was placed in a water bath at 35,

50, 70, or 100 °C, and then an NaOH solution (6 mol/l, 140 ml) was added (6 ml/min) with stirring and held at the same temperature for 30 min. For the reverse coprecipitation method, in the opposite direction, the mixed metal solution was dropped into the NaOH (6 mol/l, 140 ml) solution in a water bath at 35, 50, 70, or 100 °C with stirring and then held at the same temperature for 30 min. For the calcined samples, the sample obtained by the reverse coprecipitation method at 100 °C was heated at 400, 600, 800, or 1000 °C for 30 min in ambient air.

## 2.2. Measurements

In order to characterize the materials, their X-ray diffraction (XRD) patterns using Cu K $\alpha$  radiation were recorded using a Rigaku Rint 2000 at a scanning rate of 2°/min at 40 kV and 20 mA. The specific surface area was measured by the one-point BET method. For the calculation of the particle size, the particle shape was assumed to be spherical. Fig. 1 shows the apparatus for the measurement of the temperature in the AC magnetic field. The sample powder (1.0 g) was placed in a glass case (Pyrex: 20 mm Ø, 45 mm). The AC magnetic field was applied to the sample using an external coil. The coil consists of loops of copper pipe (6 Ø) wound around a polypropylene (PP) bobbin (48 mm Ø × 40 mm). The copper pipe was cooled by flowing water to maintain its temperature and impedance. The coil was connected to a power supply (T162-5712B, Thamway Co. Ltd.) through an impedance tuner. The output power of 200 W at 370 kHz corresponds with 4 kA/m at the center of the coil. An infrared thermometer (505 s, Minolta Co. Ltd.) was used for the measurement of sample temperature. The heating property was measured within 5 days after preparation of the sample. Commercial FeFe<sub>2</sub>O<sub>4</sub> and MgFe<sub>2</sub>O<sub>4</sub> powder samples (99.9%, High Purity Chemicals) were also measured to compare the heating properties. The



Fig. 1. Apparatus for measuring temperature in AC magnetic field.

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hysteresis loss was obtained at 500 A/m using a B–H analyzer (HP E5060A, Iwatsu Test Instruments Co. Ltd.). For this measurement, ring-type samples were prepared using a mixture of ferrite powder and epoxy resin adhesive (4:1 weight ratio).

# 3. Results and discussion

## 3.1. Crystal size

Fig. 2 shows the XRD powder diffraction patterns for the products prepared at various temperatures using the reverse coprecipitation method. The XRD patterns showed that the cubic FeFe<sub>2</sub>O<sub>4</sub> ferrite formed at all the examined temperatures. The small peaks of NaCl from the starting materials were detected as an impurity. All the peaks for the magnetite were very broad, which means the crystal size of the magnetite is very small. The FWHM (full width at half height) decreased with the synthesis temperature. For the normal coprecipitation method, similar results were also obtained. Fig. 3 plots the crystal diameter and the particle diameter calculated using Scherrer's law from the XRD peak at  $2\theta = 62.5$  (404 plane) and the surface area from the BET analysis, respectively. All the diameters for the reverse coprecipitation were smaller than those for the normal coprecipitation method. The gradual increase in pH value in the synthesis process would cause the crystal growth for the normal method. The surface area decreased for both methods. The crystal and the particle size estimated from the surface area decreased for both methods. The crystal and the particle diameters approached similar values for the samples made at a high temperature. This difference in the crystal size and particle size is



Fig. 2. XRD results for samples prepared by reverse coprecipitation at various temperatures.



Fig. 3. Diameters of particles and crystals calculated from surface area and XRD peaks, respectively. The samples were prepared by the reverse coprecipitation method and the normal coprecipitation method at various temperatures.



Fig. 4. Temperature of the samples (1.0 g) vs. time under AC magnetic field (370 kHz, 4 kA/m) in ambient air for samples prepared by the reverse coprecipitation.

ascribed to the condensation of the particles and/or polycrystallization in a particle. The condensation would not be progressed for the synthesis at higher temperature. From these results, the reverse coprecipitation method is very effective for producing small crystals and particles of the magnetite powder.

## 3.2. Heating ability in AC magnetic field

Fig. 4 shows the results for the heating properties under an AC magnetic field (370 kHz, 4 kA/m) for the powder samples (1.0 g) prepared by the reverse coprecipitation method. The commercial sample having a large particle size (0.1  $\sim$  5  $\mu$ m from SEM observation) was also measured, but showed a poor heating ability. The temperature increased by applying the AC magnetic field for all the examined samples. The sample temperature almost reached a constant value after 20 min. The heating property in AC magnetic field for the samples of the reverse coprecipitation method improved with the increase in the synthesis temperature, i.e. an increase in the crystal size. The hysteresis loops for the commercial sample and the synthesized sample (reverse coprecipitation method at 100 °C) are compared in Fig. 5. The calculated hysteresis loss (19.5 mW/g) for the synthesized sample having fine particle size was larger than that (4.4 mW/g) for the commercial sample. Fig. 6 plots the relationship between the crystal size and the increased temperature ( $\Delta T$ ) of the AC magnetic field after 20 min. The  $\Delta T$  value showed a maximum at around 12 nm. Table 1 lists the experimental data for the synthesized samples using the two methods. In general, the hysteresis loss increases with a decrease in the crystal size due to the formation of a singledomain magnetic property. In this case, the coercivity (Hc) is proportional to the reciprocal of the crystal diameter (d). When the crystal size is too small, the magnetic property changes to superparamagnetic with an Hc value of theoretically zero. In Fig. 6, the  $\Delta T$  value gradually decreased with the decrease in the



Fig. 5. The hysteresis loops in B–H relationship (370 kHz, 500 A/m) for the commercial sample and the synthesized sample using the reverse coprecipitation method obtained at 100  $^{\circ}$ C.



Fig. 6. Relationship between the crystal size and increased temperature ( $\Delta T$ ) for all the samples prepared by the reverse coprecipitation method and the normal coprecipitation method.

crystal size below 12 nm. This decrease in the  $\Delta T$  value would be due to the fact that the partial crystal changed to superparamagnetic. Ma et al. [5] obtained the maximum heating temperature in the AC magnetic field at around 46 nm, which does not agree with our result. In that paper, the particle diameter was determined by TEM observation, but not the crystal size. The particle size might not agree with the actual crystal size due to polycrystallization in a particle.

# 3.3. Stability of $FeFe_2O_4$

Utilization of a needle-type ferrite material is one of the methods for the coagulation therapy. In this case, the hard material is obtained by sintering in the preparation process. Fig. 7 shows the XRD results of the calcined magnetite at 400, 600, 800, and 1000 °C in ambient air. The magnetite phase is maintained for the sample calcined at 400 °C. The magnetite was easily oxidized to Fe<sub>2</sub>O<sub>3</sub> at 600 °C and above. Table 2 lists the  $\Delta T$  value and hysteresis loss for these samples made by the reverse coprecipitation method. The  $\Delta T$  value and hysteresis loss decreased due to the formation of Fe<sub>2</sub>O<sub>3</sub>. The heating ability in

Table 1

Crystal size determined by XRD peak at  $2\theta = 62.5^{\circ}$ , particle size estimated from surface area (BET method), and  $\Delta T$  values under AC magnetic field (370 kHz, 4 kA/m) for synthesized samples using two methods

Synthesized temperature (°C)	Normal	coprecipitat	tion method	Reverse coprecipitation method				
	35	50	80	100	35	50	80	100
Crystal diameter (nm)	8.5	9.5	14.3	15.6	7.0	8.6	9.6	10.9
Particle diameter (nm)	30.4	24.6	20.4	22.4	23.2	23.6	18.1	13.1
$\Delta T$ (°C)	43.0	47.9	55.4	38.4	44.3	46.4	58.1	69.9



Fig. 7. XRD results for calcined magnetite at various temperatures. The magnetite was prepared by reverse coprecipitation at 100 °C.

the AC magnetic field almost depended on the value of the hysteresis loss. These values are reasonable for the relationship between the  $\Delta T$  and hysteresis values as shown in Table 2. Fig. 8 shows the  $\Delta T$  change with time in ambient air for FeFe<sub>2</sub>O<sub>4</sub> and commercial MgFe<sub>2</sub>O<sub>4</sub>. We found that the commercial MgFe<sub>2</sub>O<sub>4</sub> powder (particle size:  $2 \sim 10 \,\mu$ m) showed a maximum  $\Delta T$  value among the various commercial ferrites of MFe<sub>2</sub>O<sub>4</sub>; M: Mg, Mn, Fe, Co, Ni, Cu, and Sr. The  $\Delta T$  value of fresh FeFe<sub>2</sub>O<sub>4</sub> was almost the same for that of MgFe<sub>2</sub>O<sub>4</sub> [9]. However, the  $\Delta T$  value for the FeFe<sub>2</sub>O<sub>4</sub> gradually decreased with time in ambient air, while that for the MgFe<sub>2</sub>O<sub>4</sub> remained constant. This would be ascribed to the gradual oxidation of the di-valent Fe ion in magnetite. However, we could not confirm the formation of the Fe<sub>2</sub>O<sub>3</sub> phase in the XRD pattern. In Table 2, for the samples synthesized at 100 °C and below, although the  $\Delta T$  value increased with the synthesis temperature, the hysteresis loss remained constant. For the measurement of the hysteresis loss, we did not measure the fresh samples (3 months passed after preparation). These magnetites seem to oxidize on the surface of the particles. As shown in Fig. 3, the particle size by the BET

Table 2

Heating ability ( $\Delta T$ ) (370 kHz, 4 kA/m) and hysteresis loss (370 kHz, 500 A/m) for the FeFe<sub>2</sub>O<sub>4</sub> synthesized by the reverse coprecipitation method at various temperatures and for the samples calcined at various temperatures

Synthesized temperature (°C)	Synthesized				Calcined				Commercial
	35	50	80	100	400	600	800	1000	
$\Delta T$ (°C)	44.3	46.4	58.1	69.9	47.4	39.4	2.6	1.7	8.0
Hysteresis loss (mW/g)	19.0	21.6	19.1	19.5	16.1	5.6	0	0	4.4

Results of commercial FeFe<sub>2</sub>O<sub>4</sub> are also shown in the table.



Fig. 8. Change in heating property ( $\Delta T$ ) with time for the FeFe<sub>2</sub>O<sub>4</sub> prepared by the reverse coprecipitation method at 100 °C, and commercial MgFe<sub>2</sub>O<sub>4</sub> powder.

method decreased with the increased synthesis temperature, which means that the surface area is very high for the samples synthesized at high temperature. The hysteresis loss might decrease to similar values as the synthesized samples due to the rapid deterioration of the hysteresis loss for the samples having a high surface area.

## 4. Conclusions

The reverse coprecipitation method was very effective for synthesizing the fine FeFe<sub>2</sub>O<sub>4</sub> powder with a high heating property in an AC magnetic field. We determined that the best crystal size for FeFe<sub>2</sub>O<sub>4</sub> is 12 nm for the thermal coagulation therapy. The heating property for fine FeFe<sub>2</sub>O<sub>4</sub> powder was very close to that for the commercialized MgFe<sub>2</sub>O<sub>4</sub> powder having a large particle size, but it was attenuated with time in ambient air. One of the most important interests for improving the heating properties is to make a fine MgFe<sub>2</sub>O<sub>4</sub> powder. We are planning to investigate the chemical method to obtain nano-sized MgFe<sub>2</sub>O<sub>4</sub> particles in the future.

## Acknowledgments

The authors thank Mr. Takenaka at the Kyoto Municipal Industrial Research Institute for assistance in the hysteresis loop measurements. The present work was supported by Grants-in-Aid from The Ministry of Education, Science and Culture of Japan (no. 15560610) (H. Aono) and (no. 15700351) (T. Maehara).

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