Heat generation ability of nanosized $\text{Mg}_{1-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ ferrite in an AC magnetic field

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$\text{Mg}_{0.4}\text{Cu}_{0.6}\text{Fe}_2\text{O}_4$ ferrite with the highest heat generation ability in AC magnetic field for the $\text{Mg}_{1-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ ($X=0-1.0$) series was prepared by the solid reaction method, and then bead milled to examine the effect of particle size on the heat generation ability. Nanosized $\text{Mg}_{0.4}\text{Cu}_{0.6}\text{Fe}_2\text{O}_4$ was obtained by bead milling using 0.3 mm and 0.1 mm diameter ZrO_2 beads. The heat generation ability increased with decreasing particle diameter to ca. 16.1 nm. However, the heat generation ability decreased with decreasing particle diameter below 14.6 nm.

Key words: $\text{Mg}_{1-x}\text{Cu}_x\text{Fe}_2\text{O}_4$, AC magnetic field, Nanoparticle, Bead milling, Heat generation ability

1. Introduction

Powdered magnetic materials capable of high heat generation in an AC magnetic field have been investigated for application in the thermal coagulation therapy of cancer tumors¹⁻³. To date, magnetite (FeFe_2O_4) has been investigated as a candidate material⁴, but was found to have insufficient heat generation ability. Moreover, the mechanism for heat generation in nanosized ferrite powders in an AC magnetic field has not yet been sufficiently clarified.

In our previous study, MgFe_2O_4 was found to exhibit the highest heat generation among various commercial ferrites³. Moreover, the heat generation ability in an AC magnetic field was improved by Cu^{2+} ion doping of the MgFe_2O_4 (Fig. 1). The reason for the high heat generation in $\text{Mg}_{1-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ ($X=0.6$) was an increase in the hysteresis loss due to the phase separation of cubic MgFe_2O_4 and tetragonal CuFe_2O_4 from the cubic single

phase, and the crystal distortion caused by Cu^{2+} substitution.

In this study, $\text{Mg}_{0.4}\text{Cu}_{0.6}\text{Fe}_2\text{O}_4$ ferrite with the highest heat generation ability in the $\text{Mg}_{1-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ ($X=0-1.0$) series was prepared by solid state reaction method, and then bead milled to examine the effect of particle size on the heat generation ability in an AC magnetic field.

2. Experimental

2.1. Preparation of nanosized ferrite

$\text{Mg}_{0.4}\text{Cu}_{0.6}\text{Fe}_2\text{O}_4$ was prepared using the solid state reaction method. A bead mill (DMS65, Ashizawa Finetech Ltd.) apparatus was utilized to prepare fine ferrite powders with various particle sizes. A zirconia vessel (0.14 L) and zirconia beads were used. Ethanol was used as the solvent for milling. The milling time and bead size (0.3 and 0.1 mm diameter) were varied to obtain different particle sizes. The sample prepared using the 0.1 mm diameter beads was first milled using the 0.3 mm diameter beads for 2 h.

2.2. Characterization

Phase identification of the milled samples was conducted using X-ray diffraction (XRD; Rigaku Rint 2000) with $\text{Cu K}\alpha$ radiation.

The specific surface area was measured using the one-point Brunauer-Emmet-Teller (BET) method. Particle sizes were calculated assuming that the particles were spherical. The grain size distribution and morphology of the milled samples sputter coated with carbon were investigated using field emission scanning electron microscopy (FE-SEM). The hysteresis loss value in an AC magnetic field was obtained at 500 A/m using a B-H analyzer (HP E5060A, Hewlett-Packard, Co., Ltd). Ring-type samples were prepared for this measurement using a mixture of ferrite powder

Fig. 1 Temperature enhancement for $\text{Mg}_{1-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ ($X=0, 0.6, 1.0$) and FeFe_2O_4 powder (1.0 g) in an AC magnetic field (370 kHz, 1.77 kA).

Fig. 2 Schematic diagram of the apparatus used to measure the sample temperature in an AC magnetic field.

and epoxy resin adhesive (4:3 w/w).

2.3. Measurement of heat generation ability

Fig. 2 shows the apparatus used for measurement of the heat generation ability of $\text{Mg}_{0.4}\text{Cu}_{0.6}\text{Fe}_2\text{O}_4$ in an AC magnetic field. A powder sample (1.0 g) was placed in a glass vessel (Pyrex: 20 mm diameter, 45 mm long), and an AC magnetic field (370 kHz, 1.77 kA/m) was applied to the sample for 20 min using an external coil connected to a power supply (T162-5712B, Thamway Co., Ltd). The coil consisted of eight loops of copper pipe (6.0 mm diameter) wound around a polypropylene (PP) bobbin (48 mm diameter, 40 mm long). The copper pipe was cooled by water flow to maintain the temperature and impedance. The temperature of the sample was measured using a radiation thermometer (TP-L0225EN, Chino, Ltd.).

3. Results and discussion

3.1 Characterization

Fig. 3 shows XRD patterns of bead-milled $\text{Mg}_{0.4}\text{Cu}_{0.6}\text{Fe}_2\text{O}_4$ samples. All milled samples were single phase with a cubic ferrite structure and no impurity peaks were detected. No peak shifts were identified for any the milled samples, which indicates that no crystal distortion was caused by bead milling. The cubic $\text{Mg}_{0.4}\text{Cu}_{0.6}\text{Fe}_2\text{O}_4$ peaks became broader with increasing milling time, which suggests that the crystal size is reduced. Smaller crystallite sizes, as evidenced by broader peaks, were obtained by milling with the 0.1 mm diameter beads.

Fig. 4 shows the particle diameter calculated from the measured BET specific surface area. The particle diameter decreased with increasing milling time. Smaller particles were obtained by milling with the 0.1 mm diameter beads than with the 0.3 mm diameter beads. The smallest particle size of ca. 13.1 nm was obtained by milling for 10 h with the 0.1 mm diameter beads.

Fig. 5 show a FE-SEM micrograph of the powder

Fig. 3 XRD patterns for $\text{Mg}_{0.4}\text{Cu}_{0.6}\text{Fe}_2\text{O}_4$ milled using (a) 0.3 and (b) 0.1 mm diameter ZrO_2 beads for various milling times.

Fig. 4 Relationship between milling time and particle diameter for $\text{Mg}_{0.4}\text{Cu}_{0.6}\text{Fe}_2\text{O}_4$.

Fig. 5 FE-SEM image of $\text{Mg}_{0.4}\text{Cu}_{0.6}\text{Fe}_2\text{O}_4$ prepared by bead milling (0.1 mm diameter beads, 6 h).

milled with 0.1 mm diameter beads for 6 h. It is approximate that the gain size of small particles exist in this photograph. The particle size is similar to the average particle diameter of the $\text{Mg}_{0.4}\text{Cu}_{0.6}\text{Fe}_2\text{O}_4$ sample milled for 6 h with the 0.1 mm diameter beads, which was estimated using the BET method. However, large particles are also evident in this micrograph, which suggests the agglomeration of small particles.

3.2 Heat generation ability for nanosized $\text{Mg}_{0.4}\text{Cu}_{0.6}\text{Fe}_2\text{O}_4$

Fig. 6 shows the relationship between the $\text{Mg}_{0.4}\text{Cu}_{0.6}\text{Fe}_2\text{O}_4$ particle diameter and temperature enhancement from room temperature (ΔT) after 20 min in an AC magnetic field. The heat generation ability increased with decreasing particle diameter to approximately 16.1 nm; the highest ΔT of 34 °C was obtained for the 16.1 nm particles. However, heat generation decreased as the particle size was further decreased below 16.1 nm.

The heat generation ability in an AC magnetic field is generally affected by hysteresis loss. **Fig. 7** shows the relationship between the particle diameter and hysteresis loss for all the milled samples. A similar tendency to the temperature enhancement was obtained for the hysteresis loss; the hysteresis loss increased with decreasing particle size. The ΔT value and hysteresis loss were different for samples milled with 0.3 or 0.1 mm diameter beads, but with the same particle size of ca. 25 nm. It is considered that the fine powder prepared using the 0.1 mm diameter beads has a large amount of single magnetic domains; however, uniform powders without single magnetic domains were obtained by long time milling with the 0.3 mm diameter beads. Although the hysteresis loss was high, the heat generation ability decreased for long time milling to produce particle sizes less than 16.1 nm. The reason for this difference may be that the hysteresis loss was measured at room temperature, so that a small amount of single magnetic domain particles with almost the same volumes, such as superparamagnetic particles, influenced the heat fluctuation by increasing the ΔT value in the AC magnetic field. Excessive milling would produce a large amount of superparamagnetic nanoparticles.

Fig. 8 shows the effect of frequency on the temperature enhancement for the sample milled for 6 h using 0.1 mm diameter beads. The ΔT value increased proportionally with frequency under 350 kHz; however, the ΔT value increased significantly at 370 kHz. The heat generation of ferrite powder in an AC magnetic field by hysteresis loss generally increases in proportion to the frequency. Moreover, it has been reported that the energy loss (heat generation ability) of magnetic nanoparticles due to Néel relaxation is proportional to the square of the magnetic field and its frequency⁵⁾. Therefore, the high heat generation at 370 kHz may be caused by Néel relaxation in addition to hysteresis loss.

Fig. 6 Relationship between the particle diameter and ΔT for $\text{Mg}_{0.4}\text{Cu}_{0.6}\text{Fe}_2\text{O}_4$ powder in an AC magnetic field.

Fig. 7 Relationship between the particle diameter and hysteresis loss value for $\text{Mg}_{0.4}\text{Cu}_{0.6}\text{Fe}_2\text{O}_4$ powder.

Fig. 8 Relationship between the temperature enhancement and frequency of the AC magnetic field for $\text{Mg}_{0.4}\text{Cu}_{0.6}\text{Fe}_2\text{O}_4$ milled with 0.1 mm diameter beads for 6 h.

4. Conclusions

Nanosized $\text{Mg}_{0.4}\text{Cu}_{0.6}\text{Fe}_2\text{O}_4$ prepared by bead-milling was investigated as a heat generation material. The heat generation ability of the ferrite increased with decreasing particle diameter to ca. 16.1 nm, and the highest heat generation ($\Delta T=34\text{ }^\circ\text{C}$) was obtained at 370 kHz. The high heat generation may be caused by both hysteresis loss and Néel relaxation. However, the high heat generation ability decreased with decreasing particle diameter to less than 14.6 nm. Excessive milling would produce a large amount of superparamagnetic nanoparticles. It was concluded that control of the ferrite particle size is very important for improvement of the heat generation ability.

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