Effect of particle growth on heat generation ability in AC magnetic field for nano-sized magnetic $\text{Y}_3\text{Fe}_5\text{O}_{12}$ powder prepared by bead milling

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A superparamagnetic magnetic $\text{Y}_3\text{Fe}_5\text{O}_{12}$ ferrite of 20.5 nm in particle size was prepared by bead milling using 0.05 mm ϕ beads for 10 h. The heat generation ability in an AC magnetic field (370 kHz, 1.77 kA·m^{−1}) was 0.34 W·g^{−1} for the bead-milled sample and was improved by calcination at low temperature. The main reason for this heat generation property of the milled samples was ascribed to a Néel relaxation of the superparamagnetic material. The maximum ability of 0.46 W·g^{−1} in an AC magnetic field (370 kHz, 1.77 kA·m^{−1}) was obtained for the sample (36.8 nm in particle size) calcined at 700°C. The heat generation ability was decreased with particle growth when the calcination temperature was higher than 700°C. For the sample calcined at 600°C, the heat generation ability (W·g^{−1}) was proportional to the square of the magnetic field (H/kA·m^{−1}). In the case of the calcination at 700°C, the heat generation ability (W·g^{−1}) depended on the cube of the magnetic field. The heat generation mechanism would change from superparamagnetic to ferrimagnetic due to the particle growth at 700°C.

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1. Introduction

Magnetic materials having a high heat generation ability in an AC magnetic field have been investigated for application to thermal coagulation therapy of cancer tumors.^{1)–5)} For a nano-sized superparamagnetic material, the FeFe_2O_4 (magnetite) nanoparticle has been mainly investigated for use in thermal coagulation therapy, because the preparation of the nano-sized FeFe_2O_4 particles is possible in solution at low temperature by a conventional coprecipitation method.⁶⁾

In our previous studies, the heat generation ability was studied for ferrimagnetic materials such as $\text{Mg}_{1-x}\text{Ca}_x\text{Fe}_2\text{O}_4$ ferrite.^{7)–13)} Furthermore, we found that the $\text{Y}_3\text{Fe}_5\text{O}_{12}$ -based materials prepared by a reverse coprecipitation method showed the highest heat generation ability among the reported materials.¹⁴⁾ The reason for the heat generation is attributed to the hysteresis loss in the B–H curve for ferromagnetic and ferrimagnetic materials.¹⁵⁾ This hysteresis loss is due to the magnetic moment rotation within the magnetic domains in the AC magnetic field.

As demonstrated in our previous studies, the nano-sized superparamagnetic materials with high heat generation ability can be prepared by bead milling method.^{16),17)} Nano-sized $\text{Y}_3\text{Fe}_5\text{O}_{12}$ ferrite prepared using the bead milling also showed a high heat generation ability.^{18),19)} For the bead-milled $\text{Y}_3\text{Fe}_5\text{O}_{12}$, the highest heat ability in an AC magnetic field was obtained for a fine ferrite powder (26.3 nm in particle size) milled for 4 h using 0.1 mm ϕ beads. For a superparamagnetic material having a smaller particle size, Néel relaxation and Brownian relaxation become a calorogenic cause.^{20)–25)} For the Néel relaxation and the Brownian relaxation, the energy loss is due to the magnetic moment rotation

within the crystal and particle rotation in the dispersed solvent, respectively.

In this study, we prepared a thoroughly bead-milled $\text{Y}_3\text{Fe}_5\text{O}_{12}$ powder using 0.05 mm ϕ beads for 10 h. The particle size of this powder is smaller than that of the sample having the highest heat ability milled for 4 h using 0.1 mm ϕ beads.^{18),19)} The Néel relaxation would be reduced by the bead-milling for 10 h using small beads. The effect of particle growth on the heat generation ability was studied for the calcined samples at low temperature.

2. Experimental

2.1 Preparation of samples

A bead mill (DMS65, Ashizawa Finetech, Ltd.) was utilized to prepare the fine ferrite powders of various particle sizes. The apparatus consisted of a zirconia (0.14 L) vessel and beads. A commercial $\text{Y}_3\text{Fe}_5\text{O}_{12}$ (99.9%, Kojyundo Chemical Lab.) powder was used as the milling samples. Ethanol was used as the solvent during the milling. The final bead-milled sample was obtained using 0.05 mm ϕ beads for 10 h after pre-milling using 0.3 mm ϕ beads for 2 h and then 0.1 mm ϕ beads for 2 h. After the bead milling, the solvent was evaporated at 100°C.

2.2 Characterization

The samples were characterized by the X-ray diffraction peaks (XRD, Model Rint 2000, Rigaku Co., using Cu-K α radiation). The specific surface area was measured by the one-point BET method, and then the particle size was calculated by assuming a spherical particle size.

2.3 Measurement of heat generation ability

Figure 1 shows the apparatus for measuring the heat generation ability of the ferrite powder in the AC magnetic field. The powder sample (2.0 g) in 10 ml water was placed in a glass case

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Fig. 1. (Color online) The apparatus for measuring the heat generation ability.

(Pyrex: 20 mm ϕ , 45 mm), and an AC magnetic field (370 kHz, 1.77 kA $\cdot$ m $^{-1}$) was applied to the sample using an external coil. The coil consisted of eight loops of copper pipe (6 ϕ) wound around a polypropylene (PP) bobbin (48 mm ϕ $\times$ 40 mm). The copper pipe was cooled by flowing water in order to maintain its temperature and impedance. The coil was connected to a power supply (T162-5712B, Thamway Co., Ltd.) through an impedance tuner. The temperature of the surface on the dispersed water was measured using a radiation thermometer (505s, Minolta Co., Ltd.). The temperature measurement was started after maintaining the temperature at 25°C in ambient air for several hours. The air bubbling in water is necessary for the same temperature distribution and the homogeneous $\text{Y}_3\text{Fe}_5\text{O}_{12}$ particle dispersion for both of surface and bottom in the sample.

The heat generation ability ($\text{W}\cdot\text{g}^{-1}$) was calculated using the temperature enhancement ratio ($dT/dt = \text{K}\cdot\text{s}^{-1}$) for the initial 5 min of the ΔT measurement using the following equation:

$$\text{Heat generation ability} = C \cdot (dT/dt)/M \quad (1)$$

where M and C are the sample weight (g), and the estimated total heat capacity ($\text{J}\cdot\text{K}^{-1}$) of 10 ml of water and the glass case (contacted area to water), respectively.

3. Results and discussion

3.1 Particle size of calcined samples

The average particle diameter of the commercial sample was 2.9 μm , which was estimated using the BET method. The average particle size of the bead-milled powder using 0.05 mm ϕ beads was estimated to be 20.5 nm. **Figure 2** shows the XRD results for the calcined $\text{Y}_3\text{Fe}_5\text{O}_{12}$ powder. Peaks of a cubic $\text{Y}_3\text{Fe}_5\text{O}_{12}$ phase were obtained for all the samples examined. The XRD peaks of a commercial sample were very sharp due to the large crystallite size. Although the peaks of the milled sample (Non-calcined sample) were very broad due to the decrease in the crystallite diameter, they became sharp with an increase in calcination temperature.

Figure 3 plots the crystallite and particle diameters for the calcined bead-milled $\text{Y}_3\text{Fe}_5\text{O}_{12}$ samples at various temperatures. The crystallite and particle diameters were calculated using the Scherrer equation from the XRD peak at $2\theta = 55.5^\circ$ (642) and the BET surface area, respectively. The crystallite diameter and particle diameter increased with the increase in calcination temperature. The particle size was greater than the crystallite size for the samples calcined at higher temperature. The cohesion of the small crystallites would result in larger particles with the calcination.

3.2 Heat generation ability in AC magnetic field

Figure 4 shows a comparison of the heat generation ability of the non-calcined sample and calcined sample at 700°C. The

Fig. 2. XRD results for the calcined $\text{Y}_3\text{Fe}_5\text{O}_{12}$ powder prepared by bead milling at various temperatures.

Fig. 3. Crystallite diameter and particle diameter of bead-milled $\text{Y}_3\text{Fe}_5\text{O}_{12}$ samples calculated using the Scherrer equation from the XRD peak and the BET method.

temperature increased with time for these samples. The heat generation rate was improved by the calcination at 700°C. **Table 1** lists particle diameter and the heat generation ability. The maximum heat generation ability was obtained for the powder materials calcined at 700°C. The heat generation was strongly reduced for the samples sintered at higher temperatures. **Figure 5** plots the relationship between the particle diameter and heat generation ability. The maximum heat generation ability in the AC magnetic field was obtained for the sample having ca. 30-nm particle size.

3.3 Mechanism of the heat generation

Figure 6 shows the relationship between the magnetic field (370 kHz) and the heat generation ability for the samples calcined at 600 and 700°C. The energy losses were proportional to the square and cube of the magnetic field for the samples calcined at 600 and 700°C, respectively. It was confirmed that the heat

Fig. 4. Comparison of temperature enhancement (ΔT) from room temperature in an AC magnetic field (370 kHz, $1.77 \text{ kA} \cdot \text{m}^{-1}$) for the sample of $\text{Y}_3\text{Fe}_5\text{O}_{12}$ powder (2.0 g) in 10 ml water. Non-calcined sample and calcined sample at 600°C are utilized as the $\text{Y}_3\text{Fe}_5\text{O}_{12}$ powder.

Table 1. The particle size and heat generation ability of the calcined $\text{Y}_3\text{Fe}_5\text{O}_{12}$ powder at various temperatures

Calcining temperature ($^\circ\text{C}$)	Particle size (nm)	Heat generation ability ($\text{W} \cdot \text{g}^{-1}$)
0	20.5	0.34
200	17.8	0.33
300	18.0	0.32
400	18.9	0.37
500	25.0	0.38
600	27.4	0.41
700	36.8	0.46
800	51.9	0.37
900	87.1	0.088
1000	180	0.029
1100	511	0.029
1150	1020	0.036
1200	4250	0.046
1300	8460	0.030

generation ability for all the samples was proportional to the frequency of the AC magnetic field. The energy losses (heat generation ability) of magnetite nanoparticles due to the Néel relaxation and Brownian relaxation are proportional to the square of the magnetic field (H^2) and its frequency (f).^{18)–25)} The equation for the sample calcined at 600°C is expressed as:

$$\text{Heat generation ability } (\text{W} \cdot \text{g}^{-1}) = 3.19 \times 10^{-4} \cdot f \cdot H^2 \quad (2)$$

where f and H are the frequency (kHz) and the magnetic field ($\text{kA} \cdot \text{m}^{-1}$), respectively. The heat generation ability of the sample calcined at 500°C and lower temperature was also proportional to the square of the magnetic field (H^2). For these calcined superparamagnetic materials, the Néel relaxation would be the main calorogenic cause, because the Brownian relaxation can be ignored due to the cohesion of the small crystallites. On the other hand, we have briefly reported that the heat generation ability of the samples was proportional to the cube of the magnetic field (H^3) for a ferrimagnetic sample (Rayleigh law).¹⁴⁾ For the sample calcined at 700°C , the heat generation ability is expressed by the equation:

Fig. 5. Relationship between the particle size and heat generation ability for calcined $\text{Y}_3\text{Fe}_5\text{O}_{12}$ powders at various temperatures.

Fig. 6. Relationship between the magnetic field (370 kHz) and heat generation ability of two types of calcined $\text{Y}_3\text{Fe}_5\text{O}_{12}$ powder at 600 and 700°C .

$$\text{Heat generation ability } (\text{W} \cdot \text{g}^{-1}) = 1.91 \times 10^{-4} \cdot f \cdot H^3 \quad (3)$$

The heat generation mechanism in the AC magnetic field would change due to the calcination at 700°C from superparamagnetism to ferrimagnetism. The heat generation ability of the sample calcined at 800°C was also proportional to the cube of the magnetic field (H^3). Higher heat generation ability was obtained for the $\text{Y}_3\text{Fe}_5\text{O}_{12}$ sample calcined at 700°C for the ferrimagnetic materials above $1.6 \text{ kA} \cdot \text{m}^{-1}$, because the heat generation ability depended on the cube of the magnetic field (H^3).

4. Conclusions

Using the bead-milling method, a nano-sized $\text{Y}_3\text{Fe}_5\text{O}_{12}$ powder was physically prepared from a commercial powder. The calcination temperature influenced to the heat generation ability. The heat generation ability ($\text{W} \cdot \text{g}^{-1}$) of the samples calcined at 600 and 700°C was proportional to the square (H^2) and cube (H^3) of the magnetic field, respectively. This calcination temperature is the boundary between the superparamagnetic and the ferromagnetic properties.

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References

- 1) A. Jordan, R. Scholz, K. Maier-Hauff, M. Johannsen, P. Wust, J. Nadobny, H. Schirra, H. Schmidt, S. Deger, S. Loening, W. Lanksch and R. Felix, *J. Magn. Magn. Mater.*, **225**, 118–126 (2001).
- 2) P. Moroz, S. K. Jones and B. N. Gray, *Int. J. Hyperthermia*, **18**, 267–284 (2002).
- 3) M. Johannsen, U. Gneveckow, B. Thiesen, K. Taymoorian, C. H. Cho, N. Waldöfner, R. Scholz, A. Jordan, S. A. Loening and P. Wust, *Eur. Urol.*, **52**, 1653–1662 (2007).
- 4) A. Jordan, R. Scholz, K. Maier-Hauff, F. K. H. Landeghem, N. Waldöfner, U. Teichgraber, J. Pinkernelle, H. Bruhn, F. Neumann, B. Thiesen, A. Deimling and R. Felix, *J. Neuro-Oncol.*, **78**, 7–14 (2006).
- 5) K. Maier-Hauff, R. Rothe, R. Scholz, U. Gneveckow, P. Wust, B. Thiesen, A. Feussner, A. Deimling, N. Waldöfner, R. Felix and A. Jordan, *J. Neuro-Oncol.*, **81**, 53–60 (2007).
- 6) H. Aono, H. Hirazawa, T. Naohara, T. Maehara, H. Kikkawa and Y. Watanabe, *Mater. Res. Bull.*, **40**, 1126–1135 (2005).
- 7) T. Maehara, K. Konishi, T. Kamimori, H. Aono, T. Naohara, H. Kikkawa, Y. Watanabe and K. Kawach, *Jpn. J. Appl. Phys.*, **41**, 1620–1621 (2002).
- 8) T. Maehara, K. Konishi, T. Kamimori, H. Hirazawa, H. Aono, T. Naohara, S. Nomura, H. Kikkawa, Y. Watanabe and K. Kawachi, *J. Mater. Sci.*, **40**, 135–138 (2005).
- 9) S. Yukumi, Y. Watanabe, A. Horiuchi, T. Doi, K. Sato, M. Yoshida, T. Maehara, H. Aono, T. Naohara and K. Kawachi, *Anticancer Res.*, **28**, 69–74 (2008).
- 10) S. Yukumi, Y. Watanabe, A. Horiuchi, T. Doi, K. Sato, M. Yoshida, Y. Yamamoto, T. Maehara, H. Aono, T. Naohara and K. Kawachi, *Int. J. Hyperthermia*, **25**, 416–421 (2009).
- 11) Y. Watanabe, K. Sato, S. Yukumi, M. Yoshida, Y. Yamamoto, T. Doi, H. Sugishita, T. Naohara, T. Maehara, H. Aono and K. Kawachi, *Biomed. Mater. Eng.*, **19**, 101–110 (2009).
- 12) H. Aono, H. Hirazawa, T. Ochi, T. Naohara, K. Mori, Y. Hattori, T. Maehara, H. Kikkawa and Y. Watanabe, *Chem. Lett.*, **34**, 482–483 (2005).
- 13) H. Hirazawa, S. Kusamoto, H. Aono, T. Naohara, K. Mori, Y. Hattori, T. Maehara and Y. Watanabe, *J. Alloys Compd.*, **461**, 467–473 (2008).
- 14) H. Aono, K. Moritani, T. Naohara, T. Maehara, H. Hirazawa and Y. Watanabe, *Mater. Lett.*, **65**, 1454–1456 (2011).
- 15) M. Ma, Y. Wu, J. Zhou, Y. Sun, Y. Zhang and N. Gu, *J. Magn. Magn. Mater.*, **268**, 33–39 (2004).
- 16) H. Hirazawa, H. Aono, T. Naohara, T. Maehara and Y. Watanabe, *J. Magn. Magn. Mater.*, **323**, 675–680 (2011).
- 17) H. Aono, Y. Watanabe, T. Naohara, T. Maehara, H. Hirazawa and Y. Watanabe, *Mater. Chem. Phys.*, **129**, 1081–1088 (2011).
- 18) H. Aono, H. Ebara, R. Senba, T. Naohara, T. Maehara, H. Hirazawa and Y. Watanabe, *J. Am. Ceram. Soc.*, **94**, 4116–4119 (2011).
- 19) H. Aono, H. Ebara, R. Senba, T. Naohara, T. Maehara, H. Hirazawa and Y. Watanabe, *J. Magn. Magn. Mater.*, **324**, 1985–1991 (2012).
- 20) A. Jordan, P. Wust, H. Föhling, W. John, A. Hinz and R. Felix, *Int. J. Hyperthermia*, **9**, 51–68 (1993).
- 21) R. Hergt, W. Andrä, C. G. D'Ambly, I. Hilger, W. A. Kaiser, U. Richter and H. Schmidt, *IEEE Trans. Magn.*, **34**, 3745–3754 (1998).
- 22) R. E. Rosensweig, *J. Magn. Magn. Mater.*, **252**, 370–374 (2002).
- 23) J. Fortin, C. Wilhelm, J. Servais, C. Ménager, J. Bacri and F. Gazeau, *J. Am. Chem. Soc.*, **129**, 2628–2635 (2007).
- 24) T. Atsumi, B. Jeyadevan, Y. Sato and K. Tohji, *J. Magn. Magn. Mater.*, **310**, 2841–2843 (2007).
- 25) B. Jeyadevan, *J. Ceram. Soc. Japan*, **118**, 391–401 (2010).