Depression of particle growth with calcination at low temperature and their heat generation property in AC magnetic field for the nano-sized magnetic $Y_3Fe_5O_{12-n}SmFeO_3$ powders prepared by bead-milling

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Nano-sized $Y_3Fe_5O_{12-n}SmFeO_3$ mixed powder (ca. 20 nm in particle size) was prepared by bead-milling using 0.05 mmφ beads for 10 h. For the SmFeO₃-free sample ($n=0$), 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 it was increased by a calcination at low temperature. 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 $Y_3Fe_5O_{12}$ ($n=0$) sample (36.8 nm in particle size) calcined at 700°C. The heat generation mechanism changed from superparamagnetic to ferrimagnetic due to particle growth at 700°C for the $n=0$ sample, because the heat generation ability (W·g⁻¹) depended on the cube of the magnetic field. A mixed SmFeO₃ phase acted as an impurity for depression of the particle growth for the $Y_3Fe_5O_{12}$ particles. The heat generation ability was slightly improved by the addition of SmFeO₃ and the maximum value was 0.48 W·g⁻¹ in an AC magnetic field (370 kHz, 1.77 kA·m⁻¹) for $n=0.2$ and 0.4 samples. The maximum heat generation ability was decreased for the excessive SmFeO₃ mixed sample ($n=0.6$). The calcination temperature for the formation of the ferrimagnetic material was increased by the SmFeO₃ addition due to the depression of particle growth.

Key-words : $Y_3Fe_5O_{12}$, Thermal coagulation therapy, AC magnetic field, Nano particle, Bead milling, Particle growth

1. Introduction

Powdered magnetic materials having a high heat generation ability in an AC magnetic field have been investigated for utilization in new thermal coagulation therapy of cancerous tumors.1–6 This therapy using an AC magnetic field produces less damage to the human body. Nano-sized $FeFe_2O_4$ synthesized by a chemical method has been mainly studied for this therapy.7,8 In our previous study, we have reported the MgFe₂O₄ and the Mg₁₋ₓCaₓFe₂O₄ systems as materials having high heat generation ability in an AC magnetic field.9–13 Furthermore, we found that $Y_3Fe_5O_{12}$ has the most superior heat ability among the reported materials.14–16 For the ferrimagnetic materials, the $Y_3Fe_5O_{12}$ was prepared by a reverse coprecipitation method.14,15 In the case of nano-sized superparamagnetic materials, a bead milling was very effective for obtaining the high heat ability.16–19 Furthermore, we found that the heat generation mechanism was changed by calcination at lower temperature for the bead-milled $Y_3Fe_5O_{12}$ from superparamagnetic to ferrimagnetic due to particle growth.15 The addition of stable materials such as perovskite type $RFeO_3$ ($R$ = Rare earth) might control the magnetic property due to the depression of particle growth.

In this study, we prepared mixed materials of nano-sized $Y_3Fe_5O_{12-n}SmFeO_3$ powders using the bead-milling (0.05 mmφ beads for 10 h). The effect on the heat generation ability was studied for the calcined samples at low temperature when SmFeO₃ was added for the depression of the growth in $Y_3Fe_5O_{12}$ particles.

2. Experimental

2.1 Preparation of samples

Commercial $Y_3Fe_5O_{12}$ powder (99.9%, Kojyundo Chemical Lab.) was utilized as the starting material in the bead-milling. In the case of SmFeO₃ powder, the starting material was synthesized by a reverse coprecipitation method. For the preparation of the precursor, stoichiometric materials of Sm(NO₃)₃·6H₂O and Fe(NO₃)₃·9H₂O as SmFeO₃ (0.03 mol) were dissolved in pure water (50 mL) to prepare the mixed solution. The NaOH solution (6 mol/L, 40 mL) was placed in a hot water bath at 100°C. The mixed solution was then directly added at the rate of 1.5 ml/min to the NaOH solution with stirring and held at 90–100°C for 1 h. The precipitate was filtered and washed with deionized water until the pH of the washed water dropped below 9. The dried powder (precursor) was then calcined at 1200°C (heating rate: 2°C/min) to obtain SmFeO₃ powder.

The fine mixed ferrite powder was prepared by the bead-mill (DMS65, Ashizawa Finetech, Ltd.), which consisted of a zirconia (0.14 L) vessel and beads. The mixture of commercial $Y_3Fe_5O_{12}$ powder and the synthesized SmFeO₃ was used for the milling samples as the $Y_3Fe_5O_{12-n}SmFeO_3$ ($n=0, 0.2, 0.4, 0.6$) system. Ethanol was used as the solvent during the milling. The final bead-milled samples were obtained using the 0.05 mmφ beads for 10 h after pre-milling using the 0.3 mmφ beads for 2 h and then...
0.1 mmφ beads for 2 h. Finally, the suspension after the bead-milling was quickly dried using a spray drier (ADL311S, Yamato Co.).

2.2 Characterization
The samples were characterized by the peaks of X-ray diffraction (XRD, Model Rint 2000, Rigaku Co., using Cu-Kα radiation). The particle morphology was observed by a field emission scanning electron microscope (FE-SEM, S-5500, Hitachi, Ltd.). The specific surface area was measured by the one-point BET method (FlowSorb II 2300, Shimadzu Co.), and then the particle size was calculated by assuming a spherical particle.

2.3 Measurement of heat generation ability

**Figure 1** shows the apparatus for measuring the heat generation ability (W·g⁻¹) of the ferrite powder in the AC magnetic field. The powder sample (2.0 g) with 10 mL of pure water was placed in a glass case (Pyrex: 20 mmφ, 45 mm), and an AC magnetic field (370 kHz, 1.77 kA·m⁻¹) was applied to the sample using an external coil consisting of eight loops of copper pipe (6φ). The copper pipe was cooled by flowing water in order to maintain its temperature and impedance. A power supply (T162-5712B, Thamway Co., Ltd.) was connected with the coil through an impedance tuner. The temperature of the powder samples was measured using a radiation thermometer (TP-L0225EN, Chino Co.). Air was bubbled into the glass case for stirring the water and the homogeneous sample particle dispersion.

The heat generation ability was calculated using the temperature enhancement ratio (dT/dt = K·s⁻¹) of the samples for the initial 5 min using the following equation:

\[
\text{Heat generation ability} = C \cdot \left(\frac{dT}{dt}\right) \cdot M^{-1}
\]

where M and C are the sample weight (g) and the estimated total heat capacity (J·K⁻¹) of the 10 mL pure water and glass case, respectively. The average value for the measurement of three samples or more was used for this calculation. The heat capacity of the part of the non-contacted glass to water and environmental air was not included in this calculation of the heat generation ability, because their heat capacities with thermal conduction from water are negligibly small.

3. Results and discussion

3.1 Particle size of calcined samples after bead-milling
The estimated particle diameters of the commercial Y₃Fe₅O₁₂ and the prepared SmFeO₃ before the bead-milling were 2.9 and 1.3 μm, respectively. The average particle of the bead-milled powder using 0.05 mmφ beads for the Y₃Fe₅O₁₂–nSmFeO₃ system was estimated to be ca. 20 nm. **Figure 2** shows the XRD results for the calcined Y₃Fe₅O₁₂–0.6SmFeO₃ powder after bead-milling. Peaks of a cubic Y₃Fe₅O₁₂ phase were obtained for all the samples examined. An orthorhombic SmFeO₃ phase was detected for the samples calcined at low temperature. However, their peaks disappeared for the samples calcined at high temperature. The broad peaks of the milled sample (Non-calcined sample) for the Y₃Fe₅O₁₂ phase became sharp with an increase in the calcination temperature due to the particle growth.

**Figure 3** shows relationship between the calcination temperature and the lattice constant for the Y₃Fe₅O₁₂–0.6SmFeO₃. The lattice constant for the samples calcined at 1300°C for the Y₃Fe₅O₁₂–nSmFeO₃ samples is also plotted as an inside figure in Fig. 3. The lattice constant for the samples calcined at 1300°C agreed with the estimated linear line using that of Y₃Fe₅O₁₂ and Sm₃FeO₅ (see the inside figure). The reaction between the Y₃Fe₅O₁₂ phase and SmFeO₃ phase occurred completely and the Sm₃+ was partially substituted to form a Y₃₋ₙSmₙFe₅O₁₂ phase for the samples calcined at 1300°C. The lattice constant for n = 0.6 increased with the increase in the calcination temperature and showed a constant value for the samples calcined above 900°C. This result agreed that the XRD peaks of the SmFeO₃ phase were disappeared at around 900°C by the reaction of the two phases as shown in the XRD results (Fig. 2). Although the single cubic phase was detected for the samples calcined at higher temperature, a small amount of impurity phases such as the perovskite type SmFeO₃ and Fe₂O₃ would remain at the grain boundary.

**Figure 4** plots the particle diameters for the calcined samples at various temperatures. The particle diameter increased with an increase in the calcination temperature for all the samples. The particle growth for the Y₃Fe₅O₁₂ cubic phase was depressed by the SmFeO₃ addition, i.e., the Sm³⁺ partial substitution into the cubic phase and the existence as an impurity at the grain boundary.

**Figure 5** shows SEM photos of the samples calcined at 1000°C. The particle sizes were clearly decreased by the SmFeO₃ addition. The particle sizes of 200 nm for n = 0 and 50–100 nm for n = 0.2–0.6 agreed with the values in Fig. 4.

3.2 Heat generation ability in AC magnetic field
**Figure 6** shows a comparison of the heat generation in the AC magnetic field for the typical samples of the non-calcined...
Y₃Fe₅O₁₂ (n = 0) sample, calcined Y₃Fe₅O₁₂ sample at 700°C, and calcined n = 0.2 sample at 800°C. The temperature increased with time for these samples. The heat generation rate of Y₃Fe₅O₁₂ was improved by the sample calcination. A higher heat generation ability was obtained for the n = 0.2 sample calcined at 800°C.

Figure 7 plots the relationship between the particle diameter and the heat generation ability for the samples calcined at various temperatures. The maximum heat generation ability in the AC magnetic field was obtained for the samples of ca. 40 nm in particle size. The maximum ability of 0.46 W·g⁻¹ was obtained for the n = 0 sample calcined at 700°C (36.8 nm in particle size). Further particle growth decreased the heat generation ability for these samples. The heat generation of these samples was strongly reduced for the samples sintered at higher temperatures. The heat generation ability for n = 0.2 and 0.4 samples was slightly higher than that for the non-SmFeO₃-added sample (n = 0). The maximum heat generation ability for n = 0.2 and 0.4 samples was slightly higher than that for the non-SmFeO₃-added sample (n = 0). The maximum heat generation ability for n = 0.2 and 0.4 samples was slightly higher than that for the non-SmFeO₃-added sample (n = 0).
Calcined at 800°C. The heat generation value for the Y₃Fe₅O₁₂ phase and the depression of the particle growth might for the SmFeO₃-containing samples. However, the SmFeO₃ samples prepared by the chemical method having a variety of particle sizes hardly generated heat energy in the AC magnetic field. The energy loss (heat generation ability) of magnetic nanoparticles due to the Néel relaxation and Brownian relaxation are proportional to the square of the magnetic field (H²) and its frequency (f). The equation for the superparamagnetic Y₃Fe₅O₁₂–SmFeO₃ samples [e.g., Y₃Fe₅O₁₂ (n = 0) calcined at 600°C] is expressed as:

\[
\text{Heat generation ability (W·g}^{-1}) = k_1 \cdot f \cdot H^2
\]  

(2)

where f, H and k₁ are frequency (kHz), magnetic field (kA·m⁻¹) and a constant for superparamagnetic material, respectively. The heat generation ability for the sample calcined at 500°C and lower temperature was also proportional to the square of the magnetic field (H²). The k₁ = 3.19 × 10⁻⁴ for the Y₃Fe₅O₁₂ sample calcined at 600°C in Fig. 8 was about 2.5 times higher than k₁ = 1.29 × 10⁻⁴ for the nano-sized magnetite (Fe₃O₄) powder prepared by the chemical method. On the other hand, we have reported that the heat generation ability for the samples was proportional to the cube of the magnetic field (H³) for a ferrimagnetic sample. Hysteresis loss for ferrimagnetics was proportional to the square of the magnetic field (H²) in low amplitude of AC magnetic field. In the case of magentite fine particle, heat generation mechanism changed at ca. 20 nm in particle diameter from superparamagnetism to ferrimagnetism. For the ferrimagnetic Y₃Fe₅O₁₂–SmFeO₃ samples [e.g., Y₃Fe₅O₁₂ (n = 0) calcined at 700°C and the n = 0.2 sample calcined at 800°C], the heat generation abilities are expressed as:

\[
\text{Heat generation ability (W·g}^{-1}) = k_2 \cdot f \cdot H^3
\]  

(3)

where k₂ is a constant for ferrimagnetic material. In the case of Y₃Fe₅O₁₂ (n = 0) samples, 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 for the ferrimagnetic sample calcined at 700°C was higher compared with that for the superparamagnetic sample calcined (n = 0) samples calcined at 600°C were proportional to the square of the magnetic field. For the Y₃Fe₅O₁₂ (n = 0) samples calcined at 700°C and the n = 0.2 sample calcined at 800°C, the heat generation ability was proportional to the cube of the magnetic field. It was also confirmed that the energy losses for all the samples were proportional to the frequency of the AC magnetic field.

Table 1. Properties of the Y₃Fe₅O₁₂–nSmFeO₃ with calcination temperature

| Sample     | Calcination temperature (°C) | Particle size (nm) | Heat generation ability (370kHz, 1.77 kA·m⁻¹) (W·g⁻¹) | Equation for heat generation ability | Magnetism |
|------------|-----------------------------|-------------------|------------------------------------------------------|------------------------------------|-----------|
|            |                             |                   |                                                       |                                    | F: Ferri |
| Non-calcination |                             |                   |                                                       |                                    | S: Superpara |
| n = 0      | 600                         | 27.4              | 0.41                                                 | $3.19 \times 10^{-4}F_{H^2}$       | S         |
|            | 700                         | 36.8              | 0.46                                                 | $1.91 \times 10^{-4}F_{H^3}$       | F         |
| n = 0.2    | 800                         | 51.9              | 0.37                                                 | $1.55 \times 10^{-4}F_{H^4}$       | F         |
|            |                             |                   |                                                       |                                    |           |
| Non-calcination |                             |                   |                                                       |                                    |           |
| n = 0      | 700                         | 34.9              | 0.47                                                 | $4.09 \times 10^{-4}F_{H^2}$       | S         |
| n = 0.2    | 800                         | 46.2              | 0.48                                                 | $2.26 \times 10^{-4}F_{H^3}$       | F         |
| n = 0.2    | 900                         | 62.1              | 0.32                                                 | $1.71 \times 10^{-4}F_{H^4}$       | F         |
|            |                             |                   |                                                       |                                    |           |
| Non-calcination |                             |                   |                                                       |                                    |           |
| n = 0      | 700                         | 32.9              | 0.48                                                 |                                    |           |
| n = 0.4    | 800                         | 40.4              | 0.47                                                 | $3.99 \times 10^{-4}F_{H^2}$       | S         |
| n = 0.4    | 900                         | 53.0              | 0.31                                                 | $1.70 \times 10^{-4}F_{H^3}$       | F         |
|            |                             |                   |                                                       |                                    |           |
| Non-calcination |                             |                   |                                                       |                                    |           |
| n = 0.6    | 700                         | 37.0              | 0.38                                                 | $3.77 \times 10^{-4}F_{H^2}$       | S         |
| n = 0.6    | 800                         | 45.6              | 0.38                                                 | $3.90 \times 10^{-4}F_{H^3}$       | S         |
| n = 0.6    | 900                         | 56.0              | 0.39                                                 | $3.65 \times 10^{-4}F_{H^2}$       | S         |
| 1000       | 70.6                        | 0.34               | $1.74 \times 10^{-4}F_{H^3}$                       | F         |

Fig. 8. Relationship between the magnetic field (370kHz) and heat generation ability for three types of calcined samples.
at 600°C above 1.6 kA·m⁻¹, because the heat generation ability depended on the cube of the magnetic field (H³). For the n = 0.2 sample calcined at 800°C, the heat ability was slightly higher than that of the n = 0 sample. The particle size and heat generation ability for various samples are listed in Table 1. The boundary between the superparamagnetic and the ferrimagnetic materials was ca. 30–35 nm in the particle size for Y₂Fe₅O₁₂ (n = 0). This diameter agreed with the upper limit (35 nm) of superparamagnetic behavior of the Y₂Fe₅O₁₂ prepared by a sol–gel method.24 The calcination temperature for the change in the mechanism was increased to 800°C for the n = 0.2 sample. The SmFeO₃ addition caused an increase in the calcination temperature for the formation of the ferrimagnetic material due to the depression of particle growth. The calcination temperature for the ferrimagnetic material was increased to 900 and 1000°C for n = 0.4 and n = 0.6, respectively. The particle size for the ferrimagnetic material was increased by the SmFeO₃ addition, i.e., 36.8 nm (n = 0), 46.2 nm (n = 0.2), 53.0 nm (n = 0.4), and 56.6 nm (n = 0.6). The Sm³⁺ substitution would also affect the particle size for the formation of the ferrimagnetic property.

4. Conclusions

Nano-sized Y₂Fe₅O₁₂–nSmFeO₃ mixtures were prepared by the bead-milling method. The heat generation mechanism was changed by the calcination at low temperature from the superparamagnetism to the ferrimagnetism. The calcination temperature for the ferrimagnetic material was increased by the addition of SmFeO₃ because of depression of the particle growth and the Sm³⁺ substitution in the cubic Y₂Fe₅O₁₂ phase. The particle size of the boundary between both mechanisms was increased with the amount of the added SmFeO₃.

References

1) M. Johannsen, B. Thiesen, A. Jordan, K. Taymoorian, U. Gneveckow, N. Waldöfner, R. Scholz, M. Koch, M. Lein, K. Jung and S. A. Loening, Prostate, 64, 283–292 (2005).
2) H. Pardoe, P. R. Clark, T. G. St. Pierre, P. Moroz and S. K. Jones, Magn. Reson. Imaging, 21, 483–488 (2003).
3) B. Ankamwar, T. C. Lai, J. H. Huang, R. S. Liu, M. Hsiao, C. H. Chen and Y. K. Hwu, Nanotechnology, 21, 075102 (2010).
4) E. Duguet, S. Vasseur, S. Mornet, G. Goglio, A. Demourgues, J. Portier, F. Grasset, P. Veverka and E. Pollert, Bull. Mater. Sci., 29, 581–586 (2006).
5) T. Sadhu kha, T. S. Wiedmann and J. Panyam, Biomaterials, 34, 5163–5171 (2013).
6) R. Hertg, R. Hiergeist, I. Hilger and W. Kaiser, Recent Res. Devel. Mat. Sci., 3, 723–742 (2002).
7) H. Aono, H. Hirazawa, T. Naohara, T. Maehara, H. Kikkawa and Y. Watanabe, Mater. Res. Bull., 40, 1126–1135 (2005).
8) M. Suto, Y. Hirota, H. Mamiya, R. Kasuya, A. Fujita, K. Tohji and B. Jeyadevan, J. Magn. Soc. Japan, 33, 391–395 (2009).
9) T. Maehara, K. Konishi, T. Kamimori, H. Aono, T. Naohara, H. Kikkawa, Y. Watanabe and K. Kawachi, Jpn. J. Appl. Phys., 41, 1620–1621 (2002).
10) H. Aono, T. Naohara, T. Maehara, H. Hirazawa and Y. Watanabe, J. Ceram. Soc. Japan, 118, 1207–1211 (2010).
11) 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).
12) 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).
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) T. Nishimori, T. Naohara, T. Maehara, H. Hirazawa and H. Aono, J. Iron Steel Res. Int., 19(Suppl. 1), 600–603 (2012).
16) H. Aono, H. Ebara, R. Senba, T. Naohara, T. Maehara, H. Hirazawa and Y. Watanabe, J. Am. Ceram. Soc., 94, 4116–4119 (2011).
17) H. Aono, H. Ebara, R. Senba, T. Naohara, T. Maehara, H. Hirazawa and Y. Watanabe, J. Magn. Magn. Mater., 324, 1985–1991 (2012).
18) T. Nishimori, Y. Akiyama, T. Naohara, T. Maehara, H. Hirazawa and H. Aono, J. Ceram. Soc. Japan, 121, 13–16 (2013).
19) H. Aono, R. Senba, T. Nishimori and T. Naohara, J. Am. Ceram. Soc., 96, 3483–3488 (2013).
20) H. Hirazawa, S. Kusamoto, H. Aono, T. Naohara, K. Mori, Y. Hattori, T. Maehara and Y. Watanabe, J. Alloys Compd., 461, 467–473 (2008).
21) L. Rayleigh, Philos. Mag., 23, 225–248 (1887).
22) R. Hiergeist, W. Andra, N. Buske, R. Hertg, I. Hilger, U. Richter and W. Kaiser, J. Magn. Magn. Mater., 201, 420–422 (1999).
23) R. Herzig, W. Andrä, C. G. D’Ambly, I. Hilger, W. A. Kaiser, U. Richter and H. G. Schmidt, IEEE Trans. Magn., 34, 3745–3754 (1998).
24) R. D. Sánchez, J. Rivas, P. Vaqueiro, M. A. López-Quintela and D. Caeiro, J. Magn. Magn. Mater., 247, 92–98 (2002).