Morphology and Magnetic Properties of Platelet \(\gamma\)-Fe\(_2\)O\(_3\) Particles

Mikio Kishimoto\(^1\), Tatsuya Oda\(^2\), Yusuke Ohara\(^2\), Ryoichi Miyamoto\(^2\), Yoshimasa Akashi\(^2\), Hideto Yanagihara\(^1\), Nobuhiro Ohkochi\(^2\) and Eiji Kita\(^1\)

\(^1\)Institute of Applied Physics, University of Tsukuba, Tsukuba 305-0006, Japan
\(^2\)Department of Surgery, Advanced Biomedical Applications, Graduate School of Comprehensive Human Science, University of Tsukuba, Tsukuba 305-0006, Japan

The morphology and magnetic properties of platelet \(\alpha\)-FeOOH and \(\gamma\)-Fe\(_2\)O\(_3\) particles were studied to use hysteresis-loss heating of ferromagnetic particles in magnetic hyperthermia or thermoablation. The platelet \(\alpha\)-FeOOH particles were prepared through the formation of a precipitant followed by the hydrothermal treatment of the precipitant. The shape of the \(\alpha\)-FeOOH particles changed from elongated to platelet-like depending on the quantity of ethanolamine in the precipitant. The size of the platelet \(\alpha\)-FeOOH particles was reduced from 90–120 to 40–60 nm as the precipitant temperature was lowered in the range from 5 to \(-3^\circ\text{C}\). The formation of dimples was observed during the dehydrating process from \(\alpha\)-FeOOH to \(\gamma\)-Fe\(_2\)O\(_3\), and was confirmed from the increase in the BET surface area of the \(\alpha\)-Fe\(_2\)O\(_3\) particles. The particle size and the coercive forces of the platelet \(\gamma\)-Fe\(_2\)O\(_3\) particles were in the range 30–100 nm and 7.6 kA/m (96 Oe) to 13.5 kA/m (169 Oe), respectively.

\[\text{doi:10.2320/matertrans.M2012195}\]

(Received May 23, 2012; Accepted July 2, 2012; Published August 22, 2012)

**Keywords**: nanoparticles, \(\gamma\)-Fe\(_2\)O\(_3\), \(\alpha\)-FeOOH, \(\gamma\)-Fe\(_2\)O\(_3\), coercive force, hydrothermal treatment

1. Introduction

Magnetic hyperthermia or thermoablation using small magnetic particles is a new approach for the non-surgical application of heat to cancerous tumors.\(^{1,2}\) In the relation to this, considerable research has been conducted using magnetic fluids consisting of superparamagnetic iron oxide particles, and these particles show a large specific loss power (SLP) when the drive frequency is well matched with their relaxation condition.\(^3\)

Hysteresis-loss heating using fine ferromagnetic particles is devoid of requirements such as accurate particle size or driving frequency, which are essential in magnetic fluids consisting of superparamagnetic iron oxide particles. To use hysteresis loss, it is essential to apply a high magnetic field equivalent to that applied in superparamagnetic relaxation systems. There are few reports on magnetic hyperthermia or thermoablation using ferromagnetic particles such as hard spinel ferrite CoFe\(_2\)O\(_4\),\(^4\) MgFe\(_2\)O\(_4\) and NiFe\(_2\)O\(_4\) nanoparticles,\(^5\) 14.2 nm FeCo nanoparticles,\(^6\) 16 nm Fe nanocubes,\(^7\) or spinel-structured spherical cobalt-containing iron oxide particles having a particle size of around 20 nm.\(^8-10\)

We have synthesized platelet \(\gamma\)-Fe\(_2\)O\(_3\) particles less than 100 nm in size with dimples on their surface: coercive force of these particles based on their shape anisotropy. We reported that the particles show higher SLP than spherical cobalt-containing iron oxide particles with equivalent coercive force and saturation magnetization, thus indicating that the platelet \(\gamma\)-Fe\(_2\)O\(_3\) particles show a larger minor hysteresis loop.\(^11\)

In this study, we investigated the factors that control the shape and size of the platelet \(\alpha\)-FeOOH particles used as the starting material, and observed a change in the shape of the particles as they changed from \(\alpha\)-FeOOH to \(\gamma\)-Fe\(_2\)O\(_3\) by heating. Further we assessed the magnetic properties of the platelet \(\gamma\)-Fe\(_2\)O\(_3\) particles with different sizes.

2. Experimental Procedure

The platelet \(\alpha\)-FeOOH particles were synthesized by the following process. Ferric chloride (30 g), used as an iron source, was dissolved in 450 g of water. Ethanolamine and sodium hydroxide (45 g), used as an alkaline source, were dissolved in 900 g of water. Ethanolamine was added to control the crystal growth of the \(\alpha\)-FeOOH particles, and the quantity of ethanolamine added was varied in the range 0–90 g. Both solutions were cooled to a temperature below 5°C in a refrigerator while preventing them from freezing. A precipitate was formed by mixing the ferric ion solution with the sodium hydroxide and ethanolamine solution and by stirring at room temperature. The size of the final \(\gamma\)-Fe\(_2\)O\(_3\) particles was remarkably influenced by the precipitant temperature. The precipitant temperature was varied in the range from 5 to \(-3^\circ\text{C}\). After stirring for 30 min, the iron hydroxide precipitant was allowed to stand at room temperature for nearly a day. The precipitant was treated hydrothermally using an autoclave at 180°C for 2 h to grow \(\alpha\)-FeOOH particles.

The \(\alpha\)-FeOOH particles were coated with SiO\(_2\) to prevent sintering during the heating process. The SiO\(_2\) coating was carried out by dissolving a sodium silicate in the dispersant of the \(\alpha\)-FeOOH particles and by neutralizing the dispersant using hydrochloric acid.

The SiO\(_2\)-coated \(\alpha\)-FeOOH particles were first converted to \(\alpha\)-Fe\(_2\)O\(_3\) by heating at 500°C for 1 h in air and were then continuously reduced to Fe\(_3\)O\(_4\) by heating at 380°C for 1 h in H\(_2\) gas. Finally the \(\gamma\)-Fe\(_2\)O\(_3\) particles were obtained by oxidizing Fe\(_3\)O\(_4\) at 250°C for 10 min.

The shapes of the \(\alpha\)-FeOOH, \(\alpha\)-Fe\(_2\)O\(_3\) and \(\gamma\)-Fe\(_2\)O\(_3\) particles were observed using a transmission electron microscope (TEM). The BET surface areas of \(\alpha\)-FeOOH, \(\alpha\)-Fe\(_2\)O\(_3\) and \(\gamma\)-Fe\(_2\)O\(_3\) particles were measured by a nitrogen gas adsorption method.
The magnetization of the dried powder samples was measured. The coercive force and the saturation magnetization were measured using a vibrating sample magnetometer (VSM) under a maximum magnetic field of 1035 kA/m (13000 Oe).

3. Results and Discussion

3.1 Shape control of $\alpha$-FeOOH particles

To examine the effect of ethanolamine on the shape of the $\alpha$-FeOOH particles, three quantities, 0, 45 and 90 g, of ethanolamine were used, and the quantities of ferric chloride, sodium hydroxide, and water were kept constant. The precipitant was formed at 4.8°C, and after it was allowed to stand at room temperature for nearly a day, it was treated hydrothermally at 180°C for 2 h to grow the $\alpha$-FeOOH particles.

Figures 1(a) (G-1), 1(b) (G-2) and 1(c) (G-3) show the TEM photographs of the $\alpha$-FeOOH particles in which the quantities of ethanolamine added were 0, 45 and 90 g, respectively. The shape of the $\alpha$-FeOOH particles G-1 synthesized without adding of ethanolamine was elongated and rod-like. The shape of $\alpha$-FeOOH particles G-2 synthesized by adding 45 g of ethanolamine was platelet-like, and their length/width ratio was approximately 3. When the quantity of ethanolamine was increased, this ratio showed a tendency to decrease. When 90 g of ethanolamine was added, the $\alpha$-FeOOH particles G-3 became platelet-like in shape with a length/width ratio of approximately 2 and had a size of 90–120 nm.

In the subsequent experiments, to obtain the platelet-like particles with a length/width of approximately 2, we fixed the quantity of ethanolamine at 90 g, whereas the quantity of ferric chloride, sodium hydroxide, and water were same as those mentioned in the experimental procedure section.

3.2 Particle size control of $\alpha$-FeOOH particles

Figures 2(a) (G-4), 2(b) (G-5) and 2(c) (G-6) show the TEM photographs of $\alpha$-FeOOH particles synthesized at precipitant temperatures of 1.2, −1.5 and −3.3°C, respectively. The size of $\alpha$-FeOOH particles G-3 synthesized at a precipitant temperature of 4.8°C was 90–120 nm, as shown in Fig. 1(c). When the precipitant temperature was lowered, the size of $\alpha$-FeOOH particles was reduced to 70–100, 50–80 and 40–60 nm at precipitant temperatures of 1.2°C (G-4), −1.5°C (G-5) and −3.3°C (G-6), respectively. Figure 3 shows the relationship between the precipitant temperature and the size of $\alpha$-FeOOH particles.

We examined the effect of the hydrothermal treating temperature and treating time on the size of $\alpha$-FeOOH particles. With a hydrothermal treating temperature and treating time in the range 130–200°C and 1–5 h, respectively, there was no significant change in particle sizes. This showed that the size of the $\alpha$-FeOOH particles was definitely affected by the precipitant temperature.

3.3 Effect of SiO$_2$ coating to shape changes of $\gamma$-Fe$_2$O$_3$ particles

The $\alpha$-FeOOH particles were coated with SiO$_2$ to prevent sintering during heating process. The effect of SiO$_2$ on the shape change of the $\gamma$-Fe$_2$O$_3$ particles was examined by varying the quantity of SiO$_2$ in the range 1–20 mass% of the weight of $\alpha$-FeOOH. As the size of the $\alpha$-FeOOH particles reduced, a larger quantity of SiO$_2$ was needed to prevent sintering.

Figures 4(a) (M-3) and 4(b) (M-4) show the TEM photographs of the $\gamma$-Fe$_2$O$_3$ particles obtained from the $\alpha$-FeOOH particles G-3 (Fig. 1(c)) and G-4 (Fig. 2(a)), respectively, coated with 3 mass% of SiO$_2$. Dimples were clearly observed in the $\gamma$-Fe$_2$O$_3$ particles, although they maintained the external form of the $\alpha$-FeOOH particles. However, the size of $\gamma$-Fe$_2$O$_3$ particles was slightly smaller than that of original $\alpha$-FeOOH particles.
Figures 5(a) (M-5s) and 5(b) (M-5) show the TEM photographs of the $\alpha$-FeOOH particles obtained by coating the $\alpha$-FeOOH particles G-5 (Fig. 2(b)) with 3 and 10 mass% of SiO$_2$, respectively. The outline of the M-5s particles appeared clearer than that of M-5 particles; however the sintering between particles was observed in M-5s. Minor sintering was also confirmed in the M-5 particles because they showed better dispersion than the M-5s particles.

3.4 Change in shape and surface area during heating process

The shape change of particles from $\alpha$-FeOOH to $\gamma$-Fe$_2$O$_3$ during the heating process was examined by TEM observations and the measurements of BET surface areas. Figures 6(a) (H-6) and 6(b) (M-6) show the TEM photographs of the $\alpha$-Fe$_2$O$_3$ and $\gamma$-Fe$_2$O$_3$ particles obtained from the $\alpha$-FeOOH particles G-6 (Fig. 2(c)) coated with 10 mass% of SiO$_2$.

Dimples were clearly observed in the $\alpha$-Fe$_2$O$_3$ particles, although they maintain the external form of the $\alpha$-FeOOH.
particles, thus demonstrating that the dimples were formed during the dehydrating process that converted $\alpha$-FeOOH to $\gamma$-Fe$_2$O$_3$ particles. The dimples were retained in the $\gamma$-Fe$_2$O$_3$ particles; however, the particles shrank and the number of dimples decreased during the reduction process from $\gamma$-Fe$_2$O$_3$ to Fe$_3$O$_4$. A significant change of shape was not observed in the oxidation process from Fe$_3$O$_4$ to $\gamma$-Fe$_2$O$_3$ particles.

The BET surface areas of the $\alpha$-FeOOH particles G-6, $\alpha$-Fe$_2$O$_3$ particles H-6 and $\gamma$-Fe$_2$O$_3$ particles M-6 were 72.0, 90.6 and 75.0 m$^2$/g, respectively. A distinct increase in BET surface area during heating from $\alpha$-FeOOH to $\gamma$-Fe$_2$O$_3$ resulted in the formation of dimples. The decrease in the BET surface area during the reduction process from $\gamma$-Fe$_2$O$_3$ to $\alpha$-Fe$_2$O$_3$ particles resulted in the diminishing of dimples.

3.5 Magnetic properties of $\gamma$-Fe$_2$O$_3$ particles having different sizes

We measured the magnetic properties of M-3, M-4, M-5 and M-6 platelet $\gamma$-Fe$_2$O$_3$ particles having sizes of approximately 70–100, 60–80, 40–70 and 30–50 nm, respectively. The coercive forces of the M-3, M-4, M-5 and M-6 particles were 13.5 kA/m (169 Oe), 11.7 kA/m (152 Oe), 8.7 kA/m (109 Oe) and 7.6 kA/m (96 Oe), respectively. The coercive force of the particles decreased with their size. Saturation magnetization largely depended on the quantity of SiO$_2$, and was 70.5 Am$^2$/kg (70.5 emu/g), 67.1 Am$^2$/kg (67.1 emu/g), 49.1 Am$^2$/kg (49.1 emu/g) and 45.9 Am$^2$/kg (45.9 emu/g) for the M-3, M-4, M-5 and M-6 particles, respectively. Figure 7 shows the relationship between the coercive force and the saturation magnetization of $\gamma$-Fe$_2$O$_3$ particles having different particle sizes. The saturation magnetization of the M-5 and M-6 particles was considerably lower than that of M-3 and M-4 particles because of the existence of many nonmagnetic SiO$_2$ in M-5 and M-6 particles.
4. Conclusions

The morphology and magnetic properties of platelet α-FeOOH and γ-Fe₂O₃ particles were studied to use hysteresis-loss heating of ferromagnetic particles in magnetic hyperthermia or thermoablation. The shape and size of the platelet α-FeOOH particles were controlled by varying the quantity of ethanolamine and the precipitant temperature. The formation of dimples during the dehydrating process of the α-FeOOH to α-Fe₂O₃ particles was confirmed by TEM observations and by the measurement of the BET surface areas. The platelet shape and dimples were retained in the γ-Fe₂O₃ particles; however, particle size and the number of dimples decreased during the reduction process. The size and coercive forces of platelet γ-Fe₂O₃ particles were in the range 30–100 nm and 7.6 kA/m (96 Oe) to 13.5 kA/m (169 Oe), respectively.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research (Grant No. 23300185, 23300362) from the Ministry of Education, Culture, Sports, Science and Technology of Japan, and Innovative Research Support Programs (Pilot Models) in University of Tsukuba.

REFERENCES