Characterization of Spinel-Structured Iron Oxide Particles Synthesized by Heating α -Fe₂O₃ Platelets in Tetra-Ethylene Glycol

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Platelet particles of α -Fe₂O₃ 30–50 nm in size were heated in tetra-ethylene glycol to obtain spinel-structured iron oxide particles, which were confirmed by X-ray diffraction. With heating, 100 nm platelets were formed, and the proportion of the 100 nm platelets increased in comparison to 30–50 nm platelets with increasing duration of heating. In all the samples, irrespective of the heating time used during synthesis, the coercive force, which was considered to be dependent on the shape anisotropy of the platelet particles, remained nearly constant at 12.7–13.5 kA/m (160–170 Oe). The saturation magnetization initially increased and then decreased with the heating time and the maximum value observed was 80.5 Am²/kg (80.5 emu/g). The reduction and oxidation were considered to occur simultaneously during the synthesis.

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1. Introduction

Iron oxide particles have been widely studied on account of their magnetic properties that can be harnessed in biomedical applications, ferrofluids, high-density magnetic recording media, etc. Magnetic hyperthermia or thermoablation therapies using highly specific loss power from ferromagnetic or ferrimagnetic nanoparticles has attracted considerable attention as a promising anti-cancer treatment.^{1–4)} Spinel-structured iron oxide particles are specially suitable in such applications because of their chemical stability. Many methods like co-precipitation,^{5–7)} sol–gel method^{8–10)} and hydrothermal treatment^{11,12)} have been used for the preparation of iron oxide particles. We previously synthesized γ -Fe₂O₃ platelets from α -FeOOH platelets using hydrogen gas as a reduction agent for application in magnetic hyperthermia and thermoablation therapies by hysteresis-loss heating.^{13,14)} In the study, SiO₂ coated α -FeOOH was dehydrated to α -Fe₂O₃ and the α -Fe₂O₃ was reduced by hydrogen to form Fe₃O₄. The hence obtained Fe₃O₄ was oxidized to obtain γ -Fe₂O₃ platelets. The protocol is known well to produce magnetic particles for particulate recording media.¹⁵⁾ The typical size, coercive force and saturation magnetization of the γ -Fe₂O₃ platelets were about 30–100 nm, 8.0–15.9 kA/m (100–200 Oe) and 40–80 Am²/kg (40–80 emu/g), respectively. In the process, SiO₂ coating on α -FeOOH platelets is essential to prevent sintering of particles. However the SiO₂ decreases the saturation magnetization of γ -Fe₂O₃ and Fe₃O₄ platelets.

Iron¹⁶⁾ and iron-based alloy^{17,18)} particles have been synthesized by reducing precursor metal salt solutions with a polyhydric alcohol. The particles assumed spherical or cubical shapes. In this study, we attempted to synthesize spinel-structured iron oxide particles from α -Fe₂O₃ platelets without SiO₂ coating by a similar liquid-phase reduction process using a polyhydric alcohol as the reducing agent. Further, we examined the variation in magnetic properties, crystal structure, and particle shapes of structures obtained by heating the α -Fe₂O₃ platelets for different times in the polyhydric alcohol.

2. Experimental Procedure

α -Fe₂O₃ platelets which were used as the precursor material were prepared by a previously reported processes.¹⁴⁾ First, an aqueous solution of ferric chloride and a solution of sodium hydroxide and ethanolamine were mixed to obtain a precipitate. The precipitate was then stirred at room temperature, during which the temperature of the precipitate was adjusted to –3°C. After stirring for 30 min, the precipitate was allowed to stand for about 1 day at room temperature. Subsequently, the precipitate was treated hydrothermally in an autoclave at 130°C for 2 h to grow α -FeOOH platelets. The α -FeOOH platelets were then converted to α -Fe₂O₃ by heating at 250°C for 10 min in air.

To synthesize spinel-structured iron oxide particles, tetra-ethylene glycol was used as the polyhydric alcohol. The α -Fe₂O₃ platelets (0.4 g) obtained by the protocol described above were dispersed in 100 g of tetra-ethylene glycol using a sonicator. The dispersion of α -Fe₂O₃ platelets was sealed in a stainless steel receptacle and was heated at 290°C for 2 to 32 h in air.

The variation of the crystal structures of the particles with heating time was examined by X-ray diffraction (XRD). The magnetic properties 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 observation

Figure 1(a) shows the transmission electron microscopy (TEM) image of the α -Fe₂O₃ platelets. Particle sizes of about 30–50 nm and dimples formed by the dehydration were clearly observed in the platelets.

Figures 1(b)–1(f) show the TEM images of the particles obtained by heating precursor α -Fe₂O₃ platelets in tetra-ethylene glycol for 2–32 h. The particles obtained by heating for 2 h nearly showed similar platelet shapes with sizes in the range 30–50 nm and contained dimples like the precursor α -Fe₂O₃ platelets, although the external shape contracted

Fig. 1 (a)–(g) TEM images of the precursor α -Fe₂O₃ platelets (a) and particles obtained by heating the precursor in tetra-ethylene glycol for 2 h (b), 4 h (c), 8 h (d), 16 h (e) and 32 h (f). The SEM image of the particles obtained by heating the precursor in tetra-ethylene glycol for 32 h (g) is also furnished.

slightly and became rounded, as shown in Fig. 1(b). Circular 100 nm platelet particles formed by crystal growth in the direction of the platelet plane appeared by heating the

Fig. 2 X-ray diffraction patterns of the precursor α -Fe₂O₃ platelets and the particles obtained by heating the precursor in tetra-ethylene glycol for 2–32 h.

precursor particles for 4 h. The proportion of the circular platelet particles increased with increasing heating time (Figs. 1(c)–1(f)), while maintaining the platelet shapes.

Figure 1(g) shows the scanning electron microscopy (SEM) image of the particles obtained by heating the precursor α -Fe₂O₃ platelets for 32 h, which indicates the stacking of 30–100 nm platelets to form several layers.

3.2 Structure analyses

Figure 2 shows the XRD patterns of the precursor α -Fe₂O₃ platelets and that of the particles obtained by heating α -Fe₂O₃ for various durations in the range 2–32 h. The peaks shown by the particles obtained by heating the precursor α -Fe₂O₃ in tetra-ethylene glycol for 2 h corresponded to the presence of spinel-structured materials mostly composed of Fe₃O₄ or γ -Fe₂O₃ and with α -Fe₂O₃, to a minor extent. The intensity of the diffraction peaks corresponding to α -Fe₂O₃ increased with increase in the heating time to 8 h. However, the peak originating from α -Fe₂O₃ became faint in XRD patterns acquired from samples obtained by heating for 16 h and gained intensity in XRD patterns of samples prepared by heating for 32 h.

3.3 Magnetic properties

Figures 3 and 4 show the variation of the coercive force and saturation magnetization with heating time. The coercive force showed a nearly constant value of 12.7–13.5 kA/m (160–170 Oe) irrespective of the heating. However, the samples obtained by heating the dispersion for 2 h showed a saturation magnetization of 58.8 Am²/kg (58.8 emu/g) and the value decreased with increasing heating time and the saturation magnetization of samples obtained after heating for 8 h was 45.4 Am²/kg (45.4 emu/g). For samples heated for durations longer than 8 h, the saturation magnetization increased and the maximum value of 80.5 Am²/kg (80.5 emu/g) was obtained for samples prepared by heating for 16 h. Prolonged heating (for 32 h) was observed to result in a slight decrease in the saturation magnetization.

Fig. 3 Relationship between coercive force and heating time.

Fig. 4 Relationship between saturation magnetization and heating time.

The variation of the saturation magnetization with heating time matched with the variation in the proportion of the spinel-structured iron oxides and α -Fe₂O₃ present exhibited by the various samples, as shown in Fig. 2.

The reduction and oxidation of the precursor is considered to occur simultaneously during the synthesis and the variation in the magnetic properties is explained below. By heating for 2 h, the α -Fe₂O₃ platelets were reduced to Fe₃O₄, which exhibited a saturation magnetization of about 60 Am²/kg (60 emu/g). With increasing heating time to until about 8 h, the oxidation in the dispersion preceded the reduction and the previously reduced Fe₃O₄ particles were reverted α -Fe₂O₃ resulting in the gradual decrease in saturation magnetization. When heating was carried out for about 16 h, the reduction dominated the oxidation after all the oxygen was nearly used and the saturation magnetization attained the maximum value (>80 Am²/kg (80 emu/g)). In samples obtained by heating for prolonged times, the saturation magnetization slightly decreased owing to the presence of residual oxygen. However, the coercive force was nearly constant at 12.7–13.5 kA/m (160–170 Oe) for all the samples in contrast to the remarkable variation in saturation magnetization in samples obtained by varying the heating times. By heating, the particles grew from 30–50 nm to about 100 nm. While the particles retained the platelet shapes, the proportion of particles 100 nm in size increased with increasing heating time. The coercive force being dependent on the shape anisotropy of the platelets shows a nearly constant value.

4. Conclusions

Spinel-structured iron oxide particles were synthesized by heating α -Fe₂O₃ platelet particles in tetra-ethylene glycol. Particles showed an increase in size from 30–50 nm to about 100 nm with increasing heating times, although the platelet shapes were maintained. The coercive force showed a nearly constant value of 12.7–13.5 kA/m (160–170 Oe) and was considered to be dependent on the shape anisotropy of the platelets. The saturation magnetization first increased and then decreased with the heating time and a maximum value of 80.5 Am²/kg (80.5 emu/g) was observed. The reduction and oxidation were thought to occur simultaneously in the synthesis.

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