Effect of zinc on the magnetic properties of acicular cobalt-modified γ-Fe$_2$O$_3$ particles

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Acicular α-FeOOH particles with a particle length of about 0.35 μm and an axial ratio of about 7 were synthesized by the coprecipitation method using the reaction of FeCl$_2$-NaOH. The (Co, Zn)-modified γ-F$_2$O$_3$ particles were produced by absorbing Co^{2+} and Zn^{2+} ions on the surfaces of α-FeOOH particles followed by dehydration, reduction and oxidation. The saturation magnetization and thermal stability of the coercivity of (Co, Zn)-γ-Fe$_2$O$_3$ particles were all higher than those of Co-γ-F$_2$O$_3$ particles. For the same (Co + Zn) content, the saturation magnetization of (Co, Zn)-γ-Fe$_2$O$_3$ particles increased with increasing zinc content but the coercivity decreased.

1. Introduction

Acicular cobalt-modified γ-Fe$_2$O$_3$ particles (Co-γ-Fe$_2$O$_3$ particles) are widely used in high-density recording applications. Usually, Co-γ-Fe$_2$O$_3$ particles are made by growing CoFe$_2$O$_4$ crystals on the surface of acicular γ-Fe$_2$O$_3$ particles using a hydrothermal treatment [1-3]. However, CoFe$_2$O$_4$ crystals cannot be grown on the surface of α-Fe$_2$O$_3$ or α-FeOOH particles because they do not have the spinel crystal structure [4]. In a previous study [5], we found that Co^{2+} ions can be absorbed on the surfaces of acicular α-FeOOH particles by dripping CoSO$_4$ solution into a strong alkaline solution which contained α-FeOOH particles. After dehydration, reduction and oxidation, these Co-α-FeOOH particles can be transformed into Co-γ-Fe$_2$O$_3$ particles.

Although the coercivity of Co-γ-Fe$_2$O$_3$ particles is much higher than that of γ-Fe$_2$O$_3$ particles, the thermal stability of the magnetic properties of Co-γ-Fe$_2$O$_3$ particles is lower than that of γ-Fe$_2$O$_3$ particles. It has been found that the substitution of Fe^{3+} ions and vacancies of the partially reduced γ-Fe$_2$O$_3$ particles with Zn^{2+} and Co^{2+} ions simultaneously, will increase the saturation magnetization and the thermal stability of the magnetic properties of Co-γ-Fe$_2$O$_3$ particles [6, 7]. The particles were obtained by absorbing cobalt and zinc on γ-Fe$_2$O$_3$ and then reducing them with hydrogen to an Fe^{2+} content of 14.5-19.5 wt % [6].
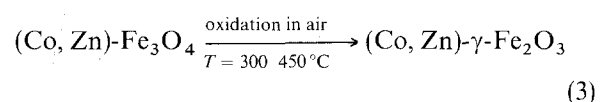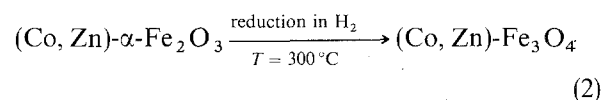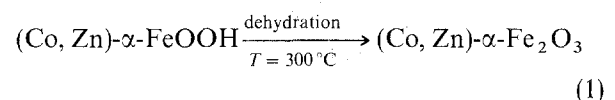
In this paper, we describe the use of acicular α-FeOOH particles as nuclei for simultaneously absorbing Co^{2+} and Zn^{2+} ions on the particle surfaces. After suitable heat treatment, these (Co, Zn)-absorbed α-FeOOH particles ((Co, Zn)-α-FeOOH particles) can be transformed into (Co, Zn)-modified γ-Fe$_2$O$_3$ particles ((Co, Zn)-γ-Fe$_2$O$_3$ particles). We find this kind of particle also has good magnetic properties and thermal stability.

Particles with various (Co + Zn) and zinc contents were prepared. The effects of heat-treatment condition and zinc content on the magnetic properties of the particles and the concentration profile of cobalt in the particles were studied.

2. Experimental procedure

Acicular α-FeOOH particles were prepared by the reaction system of FeCl$_2$-NaOH [5]. Equal amounts of FeCl$_2$ solution and NaOH solution were mixed together by stirring. The concentrations of the FeCl$_2$ and NaOH solutions before mixing were 0.5 M and 2.5 M, respectively. Air was bubbled uniformly into the mixed solution to precipitate acicular α-FeOOH particles. The reaction temperature was maintained at 30 °C. When this reaction was finished, the pH value of the mixed solution was about 13.5. These α-FeOOH particles were then coated with cobalt and zinc. The CoSO$_4$ and ZnSO$_4$ solutions were mixed together by stirring and then dripped slowly into the mixed solution in which α-FeOOH particles were precipitated. After coating, the (Co, Zn)-α-FeOOH particles were washed and filtered, then dried at 60 °C.

(Co, Zn)-α-FeOOH particles were transformed into (Co, Zn)-γ-Fe$_2$O$_3$ particles by the following heat treatments

$$\text{(Co, Zn)-}\alpha\text{-FeOOH} \xrightarrow[T = 300\,°C]{\text{dehydration}} \text{(Co, Zn)-}\alpha\text{-Fe}_2\text{O}_3 \quad (1)$$

$$\text{(Co, Zn)-}\alpha\text{-Fe}_2\text{O}_3 \xrightarrow[T = 300\,°C]{\text{reduction in H}_2} \text{(Co, Zn)-Fe}_3\text{O}_4 \quad (2)$$

$$\text{(Co, Zn)-Fe}_3\text{O}_4 \xrightarrow[T = 300\,450\,°C]{\text{oxidation in air}} \text{(Co, Zn)-}\gamma\text{-Fe}_2\text{O}_3 \quad (3)$$

The reduction time is 10 min and the oxidation time 90 min. The phase transformation temperature was determined by differential thermal analysis (DTA). Magnetic properties of the particles were measured by a vibrating sample magnetometer (VSM) with a maximum applied field of 10 kOe. The crystal structure of the particles was investigated by X-ray diffraction (XRD), and the particle size and morphology by transmission electron microscopy (TEM). The cobalt and zinc contents of the particles were determined by atomic absorption analysis. The concentration profiles of cobalt and zinc in the particles were determined by the dissolution method [5].

3. Results and discussion

Fig. 1 shows the acicular α-FeOOH particles which were used to prepare (Co, Zn)-α-FeOOH particles. The average particle length is about 0.35 μm and the axial ratio (length/width) is about 7. After absorbing Co^{2+} and Zn^{2+} ions, the shape of (Co, Zn)-α-FeOOH particles is the same as that of the α-FeOOH particles, as shown in Fig. 2. On comparing Fig. 2 with Fig. 1, no coating layer, could be distinguished.

After the (Co, Zn)-α-FeOOH particles were washed, filtered and dried, we found that the (Co, Zn)-α-FeOOH particles were nonmagnetic. The materials which absorbed on the α-FeOOH particles are believed to be $Co(OH)_2$ and $Zn(OH)_2$ or $Co(OH)_2$ $Zn(OH)_2$, CoO and ZnO [8].

After dehydration and reduction, the (Co, Zn)-α-FeOOH particles were transformed into (Co, Zn)-

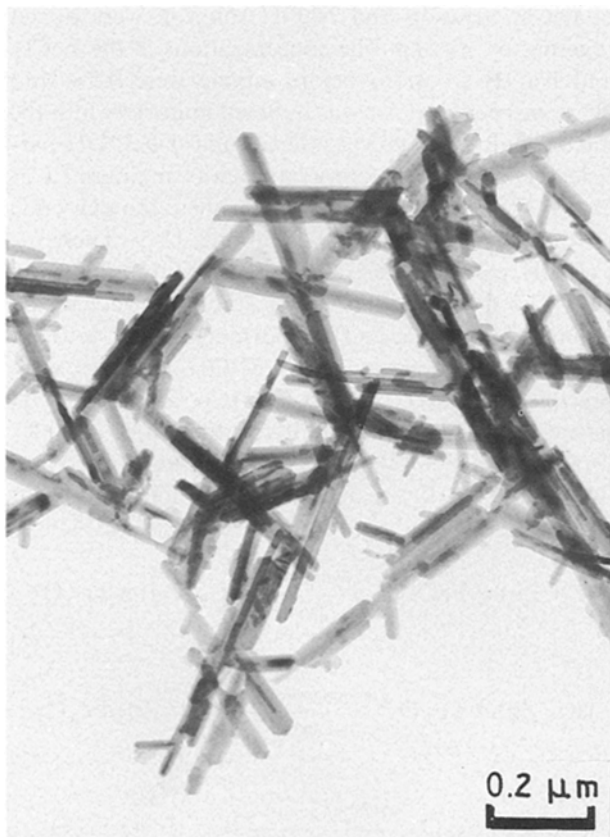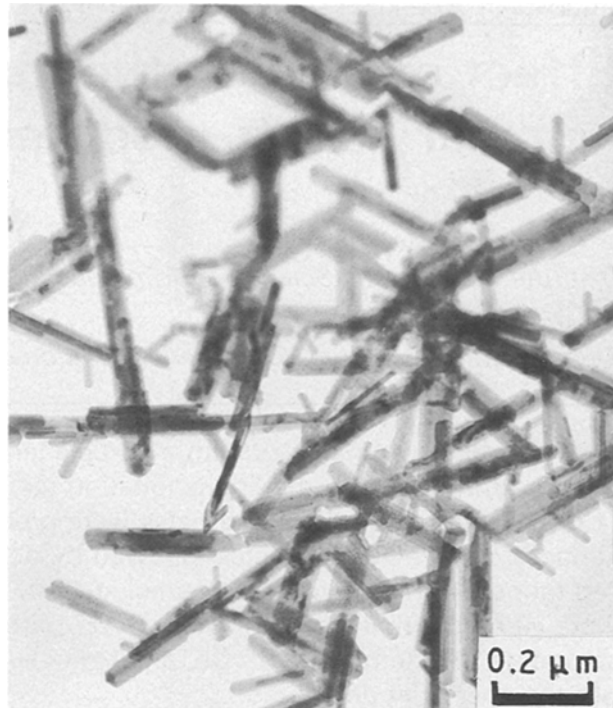Figure 2 Electron micrograph of the (Co, Zn)-α-FeOOH particles for which the (Co + Zn) content is [(Co + Zn)/total Fe] = 9 wt % and the weight ratio of zinc to cobalt is Zn/Co = 0.067.

Fe_3O_4; the core particles were transformed into Fe_3O_4, and the Co^{2+} and Zn^{2+} ions on the surface layer would diffuse into the particles. During reduction, the presence of Fe^{2+} ions would facilitate the migration of Co^{2+} ions into the particle [9] (Fe^{2+}/total Fe = 33% for pure Fe_3O_4). After the (Co, Zn)-Fe_3O_4 particles were oxidized in air for 90 min, the core phase was transformed into γ-Fe_2O_3 and the compounds formed in the surface layer were $CoFe_2O_4$ and $ZnFe_2O_4$ [7, 10] as determined by XRD. The relations between the coercivities of various (Co, Zn)-γ-Fe_2O_3 particles and oxidation temperature are shown in Figs 3 and 4. From the determination of DTA, the transformation temperatures of (Co, Zn)-γ-Fe_2O_3 → (Co, Zn)-α-Fe_2O_3 are all higher than 470 °C for these particles. For the particles with the same (Co + Zn) content, this transformation temperature is increased with increasing zinc content. The (Co + Zn) contents of the particles of Figs 3 and 4 are [(Co + Zn)/total Fe] = 6 wt % and [(Co + Zn)/total Fe] = 9 wt %, respectively. However, the Zn/Co weight ratios of various particles are different. Because the Co^{2+} ions will diffuse more deeply into the particles at higher oxidation temperature, the coercivity of particles is increased with increasing oxidation temperature. For the particles with [(Co + Zn)/total Fe] = 6 wt %, the coercivity cannot be raised further as the oxidation temperature is higher than 400 °C, as shown in Fig. 3. This may be because the Co^{2+} and Zn^{2+} ions in the particles are all $CoFe_2O_4$ and $ZnFe_2O_4$ which have been formed. Although the Co^{2+} and Zn^{2+} ions can diffuse more deeply into the particles, when the oxidation temperature is higher than 400 °C, the amount of $CoFe_2O_4$ and $ZnFe_2O_4$
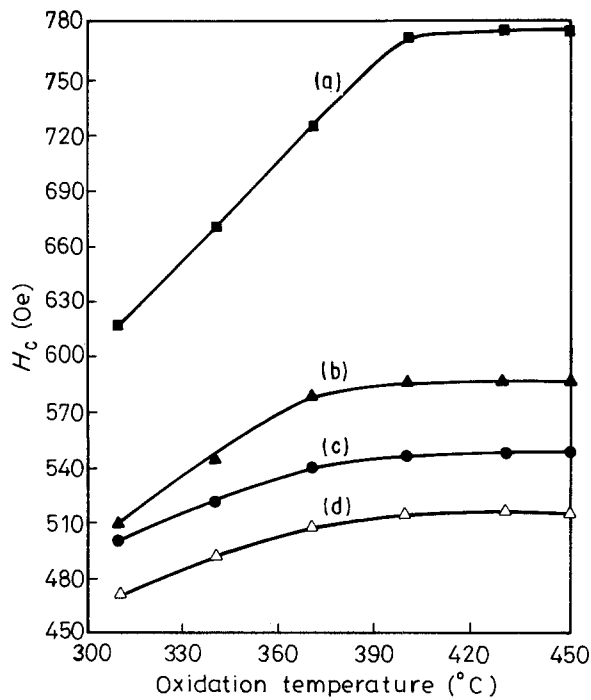

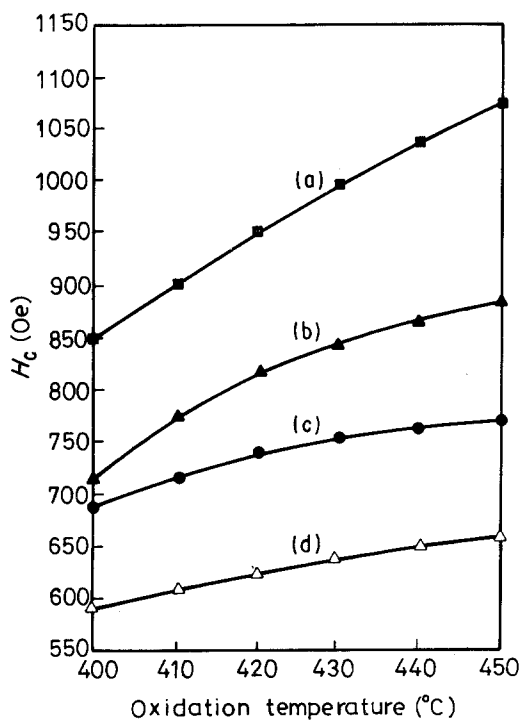Figure 1 Electron micrographs of the α-FeOOH particles.

Figure 3 Variations of coercivities with oxidation temperature of various (Co, Zn)-γ-Fe_2O_3 particles. The $(Co + Zn)$ content of these particles is $[(Co + Zn)/\text{total Fe}] = 6$ wt%. Zn/Co: (a) 0, (b) 0.095, (c) 0.140, (d) 0.214.

Figure 4 Variations of coercivities with oxidation temperature of various (Co, Zn)-γ-Fe_2O_3 particles. The $(Co + Zn)$ content of these particles is $[(Co + Zn)/\text{total Fe}] = 9$ wt %. Zn/Co: (a) 0, (b) 0.067, (c) 0.168, (d) 0.291.

cannot be increased again. The coercivity of pure Co-γ-Fe_2O_3 particles is about 610 Oe for the oxidation temperature of 310 °C and saturated to about 770 Oe if the oxidation temperature is higher than 400 °C. However, the coercivity will drop to about 460–590 Oe when a small number of Co^{2+} ions is substituted by Zn^{2+} ions. This may be caused by the formation of

$ZnFe_2O_4$ in the outer layer of the particles instead of $CoFe_2O_4$. Although the shape anisotropies of these particles are the same, the magnetocrystalline anistropy of the particles is decreased with increasing zinc content [11]. For the particles with $[(Co + Zn)/\text{total Fe}] = 9$ wt%, the coercivity of pure Co-γ-Fe_2O_3 particles is increased from 850 Oe to 1075 Oe when the oxidation temperature is raised from 400 °C to 450°C, as shown in Fig. 4. When a small amount of cobalt was substituted by zinc, the coercivity of the particles decreases, but their coercivities were all higher than 600 Oe when the Zn/Co weight ratio was less then 0.29. No saturation of the coercivity of these particles can be seen for the oxidation time of 90 min. But the saturation phenomenon appeared for longer oxidation times, when the Co^{2+} on the surface all diffused into the particles and formed $CoFe_2O_4$.

In the oxidation temperature range 300–450 °C, we found the change in σ_s of the (Co, Zn)-γ-Fe_2O_3 particles with oxidation temperature was very small and could be neglected. Fig. 5 shows the variation of σ_s of the (Co, Zn)-γ-Fe_2O_3 particles with Zn/Co weight ratio. It is obvious that the σ_s increases with increasing zinc content. This is due to the substitution of Fe^{3+} ions and vacancies by Zn^{2+} ions in the γ-Fe_2O_3 lattice [10]. The Zn^{2+} ions are located at tetrahedral A sites and force the Fe^{3+} ions from A sites to octahedral B sites, so the magnetic moment of the spinel lattice is increased [7]. For the $[(Co + Zn)/\text{total Fe}] = 6$ wt % particles, σ_s increased from 67.1 e.m.u. g^{-1} to 71 e.m.u. g^{-1} as the Zn/Co weight ratio of the particles increased from 0.0 to 0.214, as shown in the upper curve.

During heat treatment, the Co^{2+} and Zn^{2+} ions which absorbed on the surfaces of α-$FeOOH$ particles will diffuse into the particles. By the dissolution method [5], the relations between residual cobalt content and dissolved ratio of various cobalt-modified particles are shown in Fig. 6a for the Co-α-$FeOOH$ particles after drying at 60 °C and Fig. 6b for the
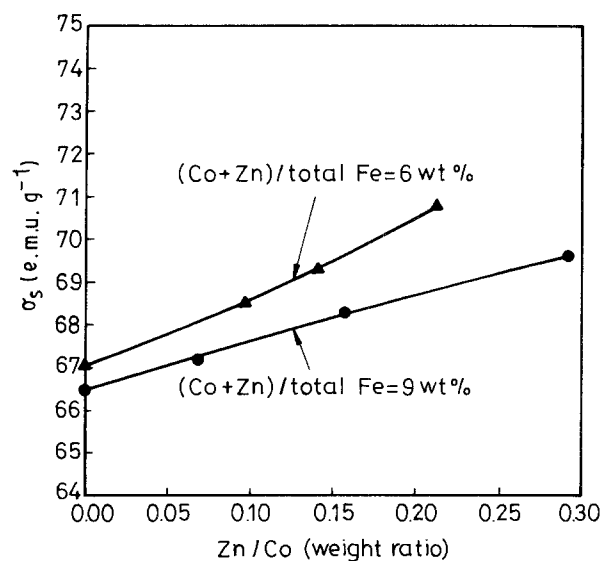

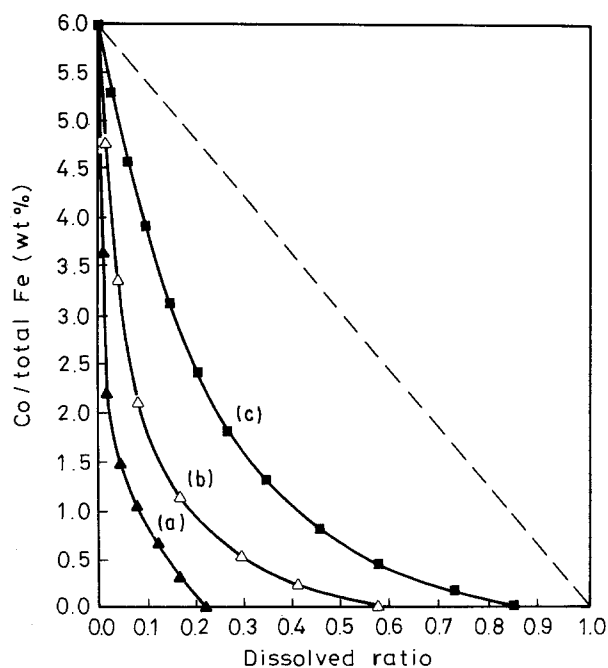*Figure 5* Relationship between σ_s and Zn/Co weight ratio of various (Co, Zn)-γ-Fe_3O_4 particles.

Figure 6 Variation of the cobalt content within the particles with dissolved ratio of various kinds of particles: (a) Co-α-FeOOH, (b) Co-Fe$_3$O$_4$, and (c) Co-γ-Fe$_2$O$_3$.

Figure 7 Variation of cobalt content within the particle with dissolved ratio of (a) Co-γ-Fe$_2$O$_3$ particles and (b) (Co, Zn)-γ-Fe$_2$O$_3$ particles (Zn/Co = 0.14). The oxidation temperature is 400 °C.

Co–Fe$_3$O$_4$ particles which were dehydrated and reduced from Sample a. Fig. 6c shows curve for Co-γ-Fe$_2$O$_3$ particles which were oxidized from Sample b at 400 °C. The particles are completely dissolved when the dissolved ratio was equal to 1.0. The ordinate shows the cobalt content retained in the particle during dissolving; this is equal to the total cobalt content minus the amount of cobalt which dissolved in the HCl solution. The dotted line indicates that the Co^{2+} ions within the particles are homogeneously distributed. From Fig. 6c we can see that for the dissolved ratio of 0.5, the corresponding cobalt content is (Co/ total Fe) = 0.7 wt %. This means that after half the volume of the Co-γ-Fe$_2$O$_3$ particles is dissolved, the cobalt content in the inner half of the particles is (Co/total Fe) = 0.7 wt %. From Fig. 6 we can see that the total cobalt content of these particles is (Co/total Fe) = 6 wt %, and the amount of cobalt is decreased rapidly from the particle surface to the inner part. During heat treatment, the Co^{2+} ions will diffuse into the particles gradually. For the same oxidation temperature, we find that the distribution of Co^{2+} ions in the Co-γ-Fe$_2$O$_3$ particles is deeper than that of the Co^{2+} and Zn^{2+} ions in the (Co, Zn)-γ-Fe$_2$O$_3$ particles; Fig. 7 shows a representative case. This indicates that the addition of Zn^{2+} ions will inhibit the diffusion of Co^{2+} ions into the particle due to the formation of stable ZnFe$_2$O$_4$ which reduces the migration of Co^{2+} ions in the crystal. According to Fig. 7, Co^{2+} ions only exist in two-thirds of the outer layer of the (Co, Zn)-γ-Fe$_2$O$_3$ particle, but Co^{2+} ions can diffuse into four-fifths of the Co-γ-Fe$_2$O$_3$ particle for the same oxidation temperature. Fig. 8 shows a micrograph of (Co, Zn)-γ-Fe$_2$O$_3$ particles with [(Co + Zn)/total Fe] = 6 wt %.

Kishimoto et al. [12] found that the squareness of randomly oriented Co-γ-Fe$_2$O$_3$ particles is 0.51, if the
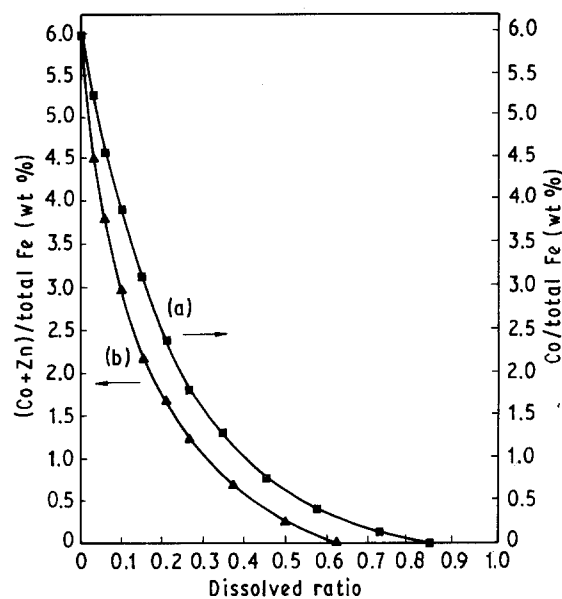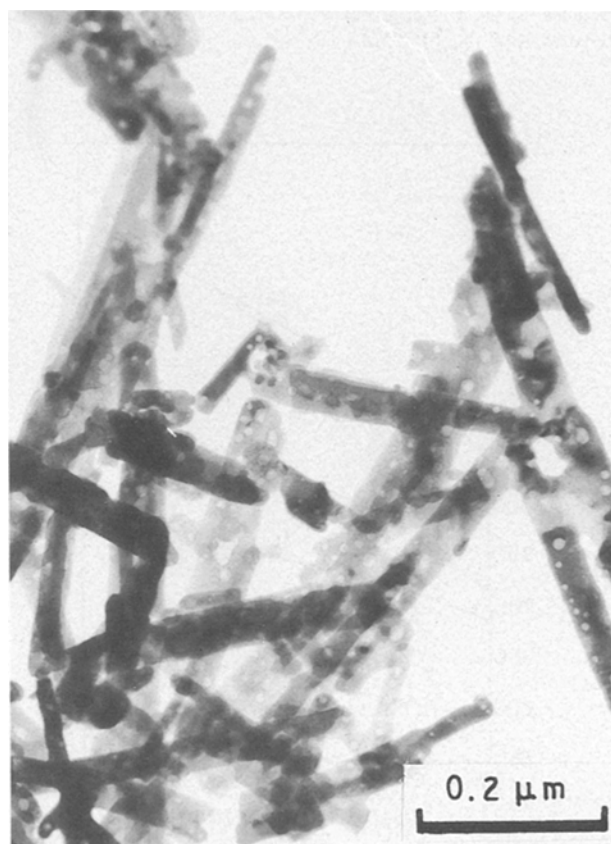

Figure 8 Electron micrograph of the (Co, Zn)-γ-Fe$_2$O$_3$ particles ([(Co + Zn)/total Fe] = 6 wt %, Zn/Co = 0.14).

CoFe$_2$O$_4$ is epitaxially grown on the surface of acicular γ-Fe$_2$O$_3$ particles. This is due to the migration of Co^{2+} ions to the preferred sites whose symmetry axis is most aligned with the direction of the magnetic field which is along the long axis of the acicular core γ-Fe$_2$O$_3$ particle [13]. Magnetic anisotropy of the particle is consequently along the elongated direction.

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For the body-doped Co-γ-Fe$_2$O$_3$ particles, Köster [14] has shown that squareness was increased with increasing cobalt content at room temperature. The squareness is about 0.78 for the particles with 4 wt % Co [14]. For our particles, the relation between squareness, M_r/M_s, and oxidation temperature is shown in Fig. 9. The squareness of randomly oriented pure Co-γ-Fe$_2$O$_3$ particles is increased with oxidation temperature. For the oxidation temperature of 310 °C, the squareness is about 0.515 and it rises to about 0.63 for the oxidation temperature of 430 °C. According to Wohlfarth and Tonge [15, 16], the squareness of the particles with shape + cubic magnetocrystalline anisotropies is 0.5, and the squareness is 0.83 for six easy directions (e.g. CoFe$_2$O$_4$). Because the squareness and H_c of our Co-γ-Fe$_2$O$_3$ particles are all increased with oxidation temperature, we conjecture this is due to the Co^{2+} ions on the particle surfaces diffusing deeper into the particles and forming more CoFe$_2$O$_4$ when the oxidation temperature is increased. When a small number of Co^{2+} ions is substituted by Zn^{2+} ions, the squareness of the particles drops to about 0.45–0.52, as shown in Fig. 9. The reason is still not understood.

Fig. 10 shows the temperature dependence of the coercivity of various (Co, Zn)-γ-Fe$_2$O$_3$ particles for which the (Co + Zn) content is [(Co + Zn)/total Fe] = 6 wt %. It is obvious that the thermal stability of the coercivity is increased with increasing zinc content. For the particles of Zn/Co = 0, the coercivity at 125 °C is about 52% of the coercivity at 25 °C, as shown in Fig. 10a. This coercivity ratio is raised to about 67% for the particles with a zinc content of Zn/Co = 0.214, as shown in Fig. 10d. This is due to the decreasing contribution of magnetocrystalline anisotropy to the particles coercivity as the Zn/Co
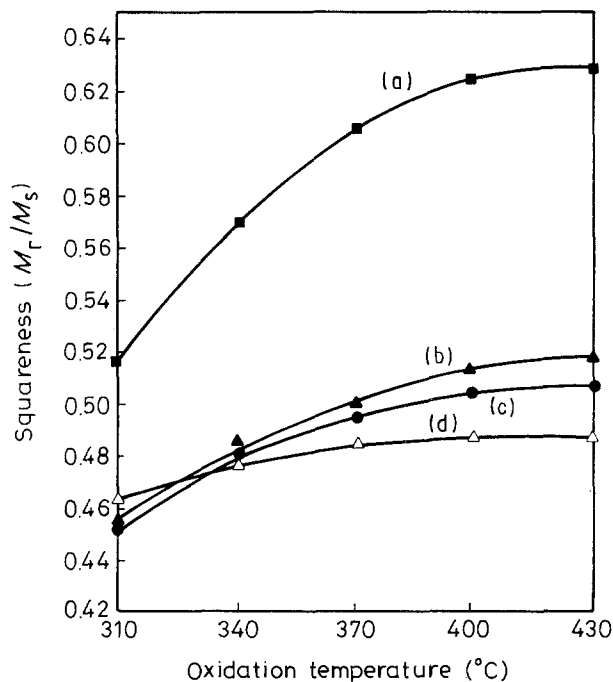

Figure 10 Relationship between the coercivity ratio $H_c(T)/H_c$ (25 °C) with temperature of various (Co, Zn)-γ-Fe$_2$O$_3$ particles for which the [(Co + Zn)/total Fe] weight ratio is 6 wt %. Zn/Co: (a) 0, (b) 0.095, (c) 0.140, (d) 0.214.
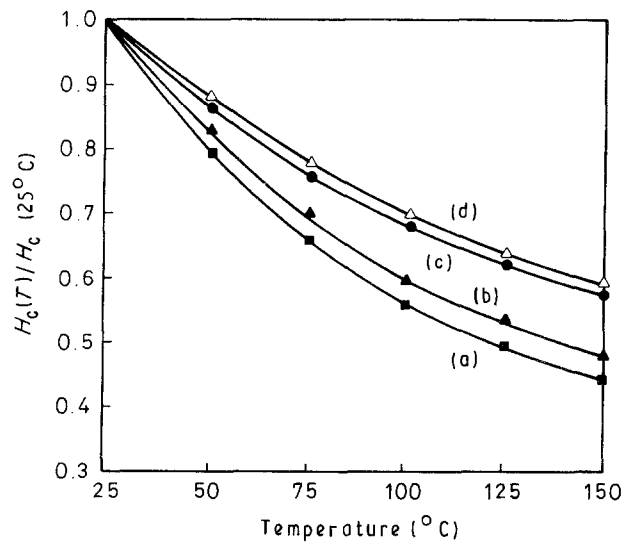
ratio is increased. The shape anisotropy of the particle is independent of temperature. Because K_1 of the particle is decreased as the Zn/Co ratio is increased [11], the contribution of shape anisotropy to the coercivity is increased with Zn/Co ratio, and the decrease of H_c with increasing temperature becomes smaller.

4. Conclusion

New acicular (Co, Zn)-γ-Fe$_2$O$_3$ particles were synthesized by coating cobalt and zinc on the acicular α-FeOOH particles followed by dehydration, reduction and oxidation.

The saturation magnetization of the (Co, Zn)-γ-Fe$_2$O$_3$ particles increased with increasing zinc content when the (Co + Zn) content of the particles was kept constant. However, the coercivity of the particles decreased. During heat treatment, the Zn^{2+} ions in the particle inhibited the migration of Co^{2+} ions into the particle. The squareness of randomly oriented acicular (Co, Zn)-γ-Fe$_2$O$_3$ particles was lower than that of the Co-γ-Fe$_2$O$_3$ particles.

The thermal stability of the coercivity of (Co, Zn)-γ-Fe$_2$O$_3$ particles was higher than that of Co-γ-Fe$_2$O$_3$ particles.

Figure 9 Variations of squareness with oxidation temperature of various (Co, Zn)-γ-Fe$_2$O$_3$ particles for which the [(Co + Zn)/total Fe] weight ratio is 6wt %. Zn/Co: (a) 0, (b) 0.095, (c) 0.140, (d) 0.214.

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