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EFFECTS OF DOPING ON THE THERMAL STABILITY OF SPINDLE-SHAPED γ-Fe_2O_3 PARTICLES

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Abstract

Spindle-shaped α-FeOOH particles were synthesized using the chemical coprecipitation method in $Fe(CO_3)_x(OH)_{2(-x)}$ suspensions system by adding metallic ions. The spindle-shaped γ-Fe_2O_3 particles were obtained by dehydration of α-FeOOH, and subsequent reduction and oxidation. Its thermal stability was investigated by differential thermal analysis (DTA). It was found that the transition temperature of γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$ of samples doped with metallic ions is higher than that of the pure γ-Fe_2O_3 and increasing with increase of the size of the metallic ions, and γ-Fe_2O_3 by doping with two or more different metallic ions together has even higher thermal stability. The origin of the improved thermal stability was discussed. Additionally, the magnetic properties of γ-Fe_2O_3 were measured.

Keywords: DTA, γ-Fe_2O_3, thermal stability, spindle-shaped

Introduction

γ-Fe_2O_3 is still the most useful among the oxides employed as particular recording media. It plays an important role today in computer tapes, digital audio recording tapes, and also in flexible and rigid disks [1, 2]. The conventional synthesis processes for γ-Fe_2O_3 usually begin with the nucleation and growth of FeOOH particles, then followed by dehydration to form α-Fe_2O_3, reduction to Fe_3O_4 and then oxidation to form γ-Fe_2O_3 [3, 4]. Magnetic γ-Fe_2O_3 particles can be converted into nonmagnetic α-Fe_2O_3 particles at higher temperatures [5].

As we know, α-Fe_2O_3 phase is a stable phase, and γ-Fe_2O_3 will be definitely converted into α-Fe_2O_3 in the range of 370–650°C. The methods of preparing particles, the size and shape of particles, the perfectness of crystallization, the variety and amount of additives and so on, are responsible for the temperature of phase transformation of γ-Fe_2O_3 into α-Fe_2O_3 [6]. The improved thermal stability has the advantage that the temperature for the oxidation of Fe_3O_4 particles and the phase transition temperature of γ-Fe_2O_3 particles can be considerably increased without the risk of forming nonmagnetic α-Fe_2O_3 particles. It is the object of this research to find the influence of different additives on the thermal

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stability of spindle-shaped γ-Fe_2O_3. In this paper, a series of spindle-shaped γ-Fe_2O_3 particles were obtained by adding different metallic ion respectively to the system of $FeSO_4$–Na_2CO_3 to produce geothite (the concentration, *pH*, temperature, time, air flow rate and the amount of metallic ion were controlled) followed by dehydration, reduction, and oxidation. The thermal stability and magnetic properties of γ-Fe_2O_3 particles were determined by means of DTA and magnetometer respectively. The present procedure of preparing γ-Fe_2O_3 particles benefits for their thermal stability, especially the precursor for γ-Fe_2O_3 contains metallic ions. Furthermore, with increase of the size of metallic ion, the transition temperature of γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$ is increased.

Experimental

Materials

The spindle-shaped α-FeOOH particles were produced by air oxidizing $Fe(CO_3)_x(OH)_{2(1-x)}$ suspension formed in the solution of $FeSO_4$ and Na_2CO_3. The reaction was under the following condition: $[Fe^{2+}]$ 0.2 *M*, $[(CO_3)^{2-}]$ 0.4 *M*, adding Zn^{2+}, Ni^{2+}, Co^{2+}, La^{3+}, Y^{3+} and so on respectively, to the suspensions (*M*/Fe 4 mol%), *pH* 8–10, 50–60°C, 8 h, air flow rate 0.3 –0.5 l/l'min.

The reagents were of analytically pure grade.

The product was washed, filtered, dried and crushed.

α-FeOOH particles were dehydrated to form α-Fe_2O_3 (at 300–450°C for 45 min, α-Fe_2O_3 was reduced to Fe_3O_4 by hydrogen gas at 350–380°C for 30 min, and then Fe_3O_4 was oxidized by air at 180–200°C for 30 min.

X-ray diffraction (XRD)

Powder X-ray diffraction patterns were recorded with a Japanese Rigaku D/max-γA rotation anode X-ray diffractometer, using Cu radiator and Ni filter. The phase identification of the resultant power was characterized by XRD.

Electron microscopy

Electron micrographs were obtained with a Hitachi H-800 transmission electron microscope (TEM). TEM was used to observe the size and shape of the powders.

DTA diagrams

The thermal stability was measured by differential thermal analysis (DTA), which was used as a thermal analytical instrument manufactured by a Rigaku, Japan.

Magnetic properties

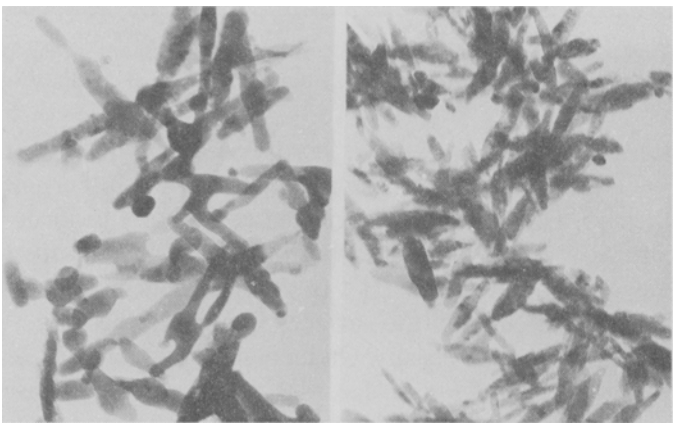
A vibrating sample magnetometer (VSM) was used to measure the magnetic properties, such as saturation magnetization (σ_s) and coercivity (Hc).

Results and discussion

Thermal stability of samples

In Fig. 1, the electron transmission micrographs of Zn-doped and La-doped γ-Fe_2O_3 particles are shown, indicating their shapes.

Figure 2 shows a series of DTA measurements of the resultant powders. Samples were named respectively: (a) undoped, (b) Zn-doped, (c) Ni-doped, (d) Co-doped, (e) La-doped, (f) Y-doped, (g) Sm, Co-doped. DTA curves were recorded under the following conditions: sample weights 8 –10 mg; heating rate 10 deg·min^{-1}; static air atmosphere, temperature from 10 to 800°C.



a (×50000) b (×50000)

Fig. 1 Electron transmission micrographs of Zn-γ-Fe_2O_3 and La-γ-Fe_2O_3 particles; a. Zn-doped γ-Fe_2O_3; b. La-doped γ-Fe_2O_3

On the whole, DTA curves of undoped or metal-ion-doped γ-Fe_2O_3 essentially showed two exothermal effects. The first, a gentle, wide exothermal peak appeared at low temperature. On further increasing temperature (about 650–800°C), there appeared a very sharp, marked exothermal peak. We believe, this is the phase transformation of γ-Fe_2O_3 into α-Fe_2O_3. However, at low temperature, the exothermal peak may be probably attributed to the recrystallization of γ-Fe_2O_3 and the exothermal reaction of $Fe_3O_4 \rightarrow \gamma$-$Fe_2O_3$. In the oxidation process of Fe_3O_4 to γ-Fe_2O_3, Fe_3O_4 particles were probably partially oxidized to form γ-Fe_2O_3, considering that Fe_3O_4 and γ-Fe_2O_3 belong to the

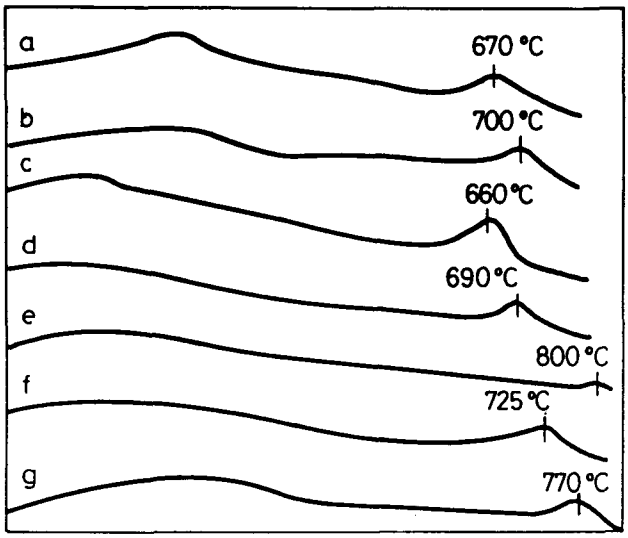


Fig. 2 DTA curves of undoped and metal-ion doped γ-Fe_2O_3 samples; a. undoped; b. Zn-doped; c. Ni-doped; d. Co-doped; e. La-doped; f. Y-doped; g. Sm, Co-doped

spinel structure, so the two phase would easily coexist. Thus, it is reasonable to find that γ-Fe_2O_3 particles contain a small amount of Fe_3O_4 particles. When the sample was heated, Fe_3O_4 would be oxidized continually to form γ-Fe_2O_3 with O_2. Furthermore, some investigators [7] think that the microstructure of γ-Fe_2O_3 contains a fixed amount of 'H'. In the treatment of γ-Fe_2O_3, 'H' would go into the crystal lattice from the surface, stabilizing the γ-Fe_2O_3 phase, and would make $Fe_3O_4 \rightarrow \gamma$-$Fe_2O_3$ easily. On increasing temperature, γ-Fe_2O_3 would be definitely converted to α-Fe_2O_3. In order to ascertain the phase transformation, a series of X-ray diffraction patterns of Zn-doped samples obtained at different heat treatment temperature, were carried out, and they are displayed in Fig. 3.

The XRD patterns of samples unheated to 600°C revealed lines belonging exclusively to γ-Fe_2O_3. The phase of the sample calcined at 680°C for 1 h consisted of α-Fe_2O_3 and γ-Fe_2O_3. When sample was calcined at 700°C for 1 h, the γ-Fe_2O_3 phase disappeared, leaving only the α-Fe_2O_3 phase.

Unfortunately, XRD is unable to solve the problem of phase purity, that is to say, a small amount of Fe_3O_4 or other ferric oxide in γ-Fe_2O_3 samples is very difficult to determine directly from XRD.

So we can obtained the following results from DTA and XRD:

(1) The exothermal peak at lower temperature can not be due to the partial transformation of γ-Fe_2O_3 into α-Fe_2O_3;

(2) It is probable for us to ascribe the exothermal effect at low temperature to the recrystallization of γ-Fe_2O_3 and the oxidation reaction of Fe_3O_4 with O_2;

(3) The temperature of γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$ is in the range of 650–800°C. One can take advantage of this fact in the preparation process. The oxidation temperature of Fe_3O_4 particles can be considerably raised no risk of forming undesirable nonmagnetic α-Fe_2O_3 particles. For this reason, the oxidation time could be greatly reduced.

Therefore, the transition temperature of γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$ of each sample was obtained by DTA curves, with the radius of metallic ion [8] listed in Table 1.

Table 1 Radius of metallic ion and the phase transition temperature of γ-Fe_2O_3 into α-Fe_2O_3 (T_{pt}) of samples

	Δ(Fe)	Zn	Ni	Co	Y	La	Sm, Co
r /pm	75	74	70	72	88	106.1	94.4, 72
T_{pt} /°C	680	700	660	690	725	800	770

The data provide three conclusions: (1) the thermal stability of metal-ion-doped γ-Fe_2O_3 is higher than that of undoped, except the Ni-doped sample; (2) the temperature of phase transformation of γ-Fe_2O_3 into α-Fe_2O_3 is increased with the increase of the radius of metallic ion; (3) γ-Fe_2O_3 doped by two or more different metallic ions also has higher thermal stability.

The lower thermal stability of pure γ-Fe_2O_3 ($Fe_{8/3}\Delta_{1/3}O_4$) is mainly due to cation vacancies, which cause Fe^{3+} to proliferate easily. However, when doped with metallic ion, the metallic ions may occupy the vacancies partially or go into the crystal lattice, restraining the phase transformation of γ-Fe_2O_3, thus the samples have higher thermal stability.

At present, we have no satisfactory explanation for the proportional relationship of temperature of γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$ to the radius of metallic ion. By calculating the lattice parameter from XRD patterns, we could not obtain any further information on this regularity.

Furthermore, γ-Fe_2O_3 doped with two or more metallic ions together has even higher thermal stability. This point is of momentous significance. Practically, we can use different metallic ions together as additives instead of the expensive single metallic ion, with the same effects, possessing economic value.

Magnetic properties of samples

Table 2 shows magnetic properties of samples. Magnetic properties are not as good, mainly due to added mass of additives.

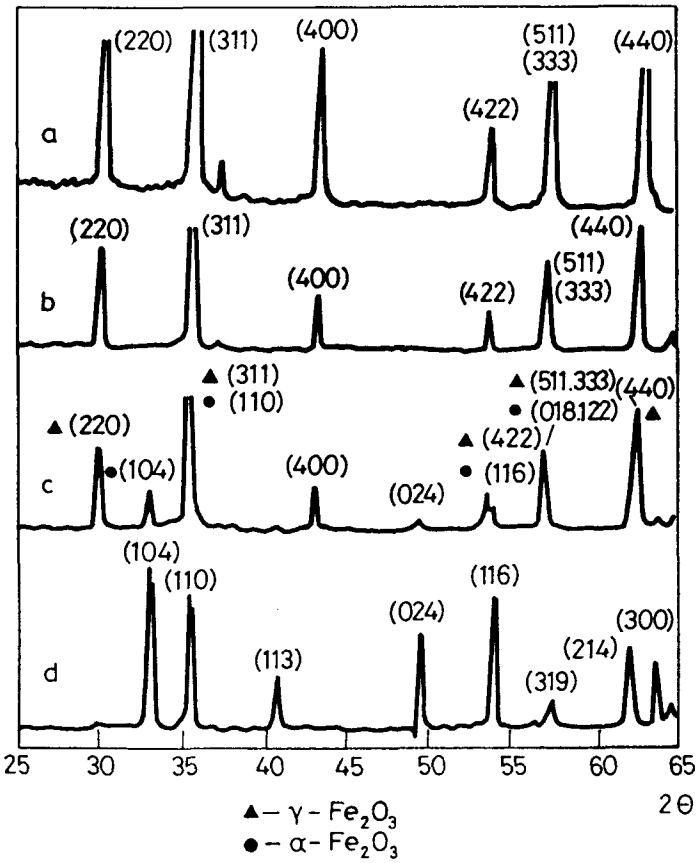


Fig. 3 X-ray powder diffraction patterns of Zn-doped samples; a. unheated; b. 600°C, 1 h; c. 680°C, 1 h; d. 700°C, 1 h

Table 2 Magnetic properties of spindle-shaped doped and undoped γ-Fe_2O_3 particles

Dopings	Δ	Zn	Ni	Co	Y	La	(Sm, Co)
H_c /Oe	308	375	311	576	260	400	469
σ_s /emu·g^{-1}	75.1	70.5	67.0	63.4	65.0	78.4	66.3

Conclusions

The improved thermal stability of spindle-shaped γ-Fe_2O_3 particles has been achieved by doping with metallic ion. By DTA, it was found that the transition temperature of γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$ is increased with the increase of the size of metallic ion. Furthermore, spindle-shaped γ-Fe_2O_3 has higher thermal stability

when doped with different metal ions. The magnetic properties of γ-Fe_2O_3 probably were not much changed with the variety of metallic ion.

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Zusammenfassung — Mittels chemischer Kopräzipitation in $Fe(CO_3)_x(OH)_{2(-x)}$ Suspensionssysteme durch Zusatz von Metallionen wurden spindelförmige α-FeOOH-Partikel hergestellt. Spindelförmige γ-Fe_2O_3-Partikel wurden durch die Dehydratation von α-FeOOH und anschließende Reduktion und Oxidation erhalten. Deren thermische Stabilität wurde mittels DTA untersucht. Man fand, daß die Umwandlungstemperatur von γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$ für Proben, die mit Metallionen versetzt wurden, höher ist als die von reinem γ-Fe_2O_3 und mit anwachsender Größe des Metallions zunimmt und daß γ-Fe_2O_3 durch gleichzeitiges Versetzen mit zwei oder noch mehr unterschiedlichen Metallionen eine höhere thermische Stabilität aufweist. Der Ursprung dieser verbesserten thermischen Stabilität wird diskutiert. Zusätzlich wurden die magnetischen Eigenschaften von γ-Fe_2O_3 gemessen.