

Preparation of cobalt-modified magnetite and its magnetic properties^①

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Abstract: Magnetite was modified by reaction with alkaline solution containing Co^{2+} and Fe^{2+} to obtain a cobalt ferrite layer on the surface of particles. The influences of modification conditions on the properties were investigated. The as-prepared particles were characterized by X-ray diffraction (XRD) and transmission electron microscope (TEM). The results show that pH value influences the particles composition directly, the desirable CoFe_2O_4 is obtained as pH value is 12. The coercivity of particles increases with the increase of cobalt content, and the cobalt efficiency reaches a maximum value at cobalt content of 2.71% (mass fraction). With cobalt modification, the magnetite particles have the similar lattice constant and structure to that without cobalt modification, and the squareness ratio is almost 0.5. The increase of the coercivity is attributed to the uniaxial magnetic anisotropy and magnetocrystalline anisotropy of cobalt-ferrite itself.

Key words: magnetite; cobalt; magnetic property

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1 INTRODUCTION

Acicular magnetite has a number of novel properties and performances, its high magnetic and thermal properties, good electric conduction and black color make it a new type of materials promising in magnetic recording field^[1,4]. With the development of high recording density application such as video and audio tape, instrumentatic tapes and flexible disks, it is needed to increase the coercivity of magnetite particles further. For this purpose, an effective method is to deposit at or near the surface of magnetite particles^[5]. Doping with cobalt on the surface is thought to form an epitaxial layer of cobalt-ferrite, CoFe_2O_4 , on the surface of oxide particles, which results in increase in the coercivity and magnetocrystalline anisotropy and these in turn greatly improve the recording density^[6-8]. This technique is widely used to produce cobalt modified $\gamma\text{-Fe}_2\text{O}_3$ particles^[9-11]. However, most of cobalt-modified magnetite is still dependent on importation. Some reports^[1, 12] about cobalt-doped magnetite only gave a simple process, which lacked completely satisfactory explanation of the origin of coercivity of cobalt surface-modified iron oxide and this is one of the most intriguing of the unsolved problems in the field of recording materials, so there exists theoretical and practical significance on study and exploitation of cobalt-modified magne-

tite. In this paper, the influences of process variables such as pH, cobalt content, reaction time in the precipitation reaction have been investigated in detail, the reason of enhancement of coercivity is clarified.

2 EXPERIMENTAL

In this study, Fe_3O_4 was used as the precursor, whose average specific surface area is $25.06 \text{ m}^2/\text{g}$, coercivity (H_c) and saturation magnetization (σ_s) are 28.48 kA/m and $75 \text{ A} \cdot \text{m}^2/\text{kg}$, respectively. $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were used as sources of Co^{2+} and Fe^{2+} ions in the aqueous solution, and the concentration of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was 5 g/L . NaOH was used as precipitant. The Fe_3O_4 particles were suspended in the metal ions solution for 20 min with nitrogen blowing in. To convert the sulfates into hydroxides of cobalt and iron, NaOH solution was added drop likewise so as to get the pH value of 9, 10, 11 and 12. Then the suspension was heated at $90 \text{ }^\circ\text{C}$ for 2, 4, 6 h, respectively. The resultant particles were filtered, washed with water and dried. The phase composition and lattice constant of the particles were characterized by XRD. The morphologies were observed by TEM. The magnetic properties

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were measured by a vibrating sample magnetometer under a magnetic field of 400 kA/m. The difference between the coercivity of the core particles and final product (ΔH_c) was determined. Specific surface area (SSA) was determined by BET method. Cobalt content in the particles was measured by means of chemical analysis.

3 RESULTS AND DISCUSSION

3.1 Effect of pH value

The XRD patterns of the Fe_3O_4 precursor and products at different pH values are given in Fig. 1 and Fig. 2, respectively. At pH value of 9, the product yields undesired impurity in addition to desired $CoFe_2O_4$ and precursor. When the pH value is 12, all Co is precipitated, resulting in the formation of pure $CoFe_2O_4$. These changes are reflected in the magnetic properties and cobalt content of the product as shown in Table 1. With the increase of pH value from 9 to 12, the cobalt content varies by about 0.8%, the coercivity of the product increases from 30.8 to 37.04 kA/m, and Q_s increases from 62.4 to 88.5 $A \cdot m^2/kg$. This may be attributed to the increase of $CoFe_2O_4$ content in the product.

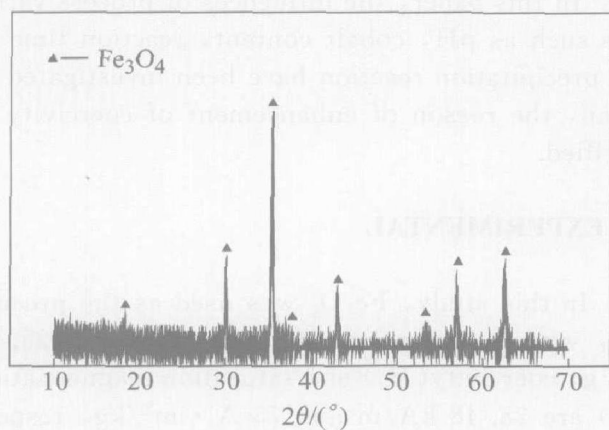


Fig. 1 XRD pattern of precursor of Fe_3O_4

3.2 Effect of cobalt content

At pH value of 12, different amounts of cobalt were added into the solution. The effects of cobalt content on the magnetic properties of the product

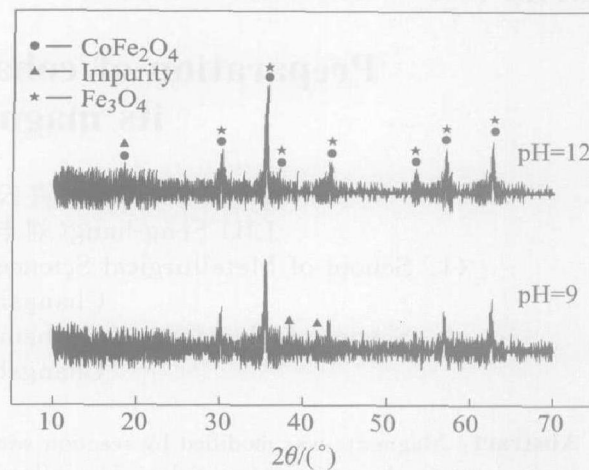


Fig. 2 XRD patterns of Co-modified Fe_3O_4

Table 1 Effects of pH on properties of product

pH	$w(Co)/\%$	$H_c / (kA \cdot m^{-1})$	$\Delta H_c / (kA \cdot m^{-1})$	$Q_s / (A \cdot m^2 \cdot kg^{-1})$
9	1.1	30.80	2.16	62.4
10	1.23	31.44	2.96	74.4
11	1.81	34.48	6.00	74.5
12	1.83	37.04	8.56	93.5

are shown in Table 2. The formation of cobalt ferrite on the surface of Fe_3O_4 results in the increase of coercivity. The incorporation of 2.71% (mass fraction) Co results in the increase of coercivity by 56% over than that of the precursor. Further increasing cobalt content to 5.03% (mass fraction), the coercivity shows no obvious increase.

Fig. 3 shows the correlation between cobalt efficiency (H_c divided by the mass fraction of cobalt in the particles) and cobalt content. The cobalt efficiency reaches the peak at cobalt content of 2.71%, and then decreases to level of about 3.22. The result can be explained by the following reasons. One is that nonferromagnetic materials such as $Co_2O_3 \cdot nH_2O$ are expected to be present, although XRD shows only $CoFe_2O_4$. The second is that the product becomes loosely, which is verified with the larger SSA shown in Table 2. The results

Table 2 Effects of cobalt content on properties of product

$w(Co)/\%$	$H_c / (kA \cdot m^{-1})$	$\Delta H_c / (kA \cdot m^{-1})$	$Q_s / (A \cdot m^2 \cdot kg^{-1})$	Squareness ratio	SSA / ($m^2 \cdot g^{-1}$)
0	28.48	0	75.0	0.42	25.06
0.48	29.2	0.8	75.8	0.43	-
1.28	32.32	3.84	75.8	0.41	-
1.83	37.04	8.56	88.5	0.42	-
2.71	44.48	16.00	86.3	0.41	24.99
5.03	44.72	16.24	65.7	0.43	30.1

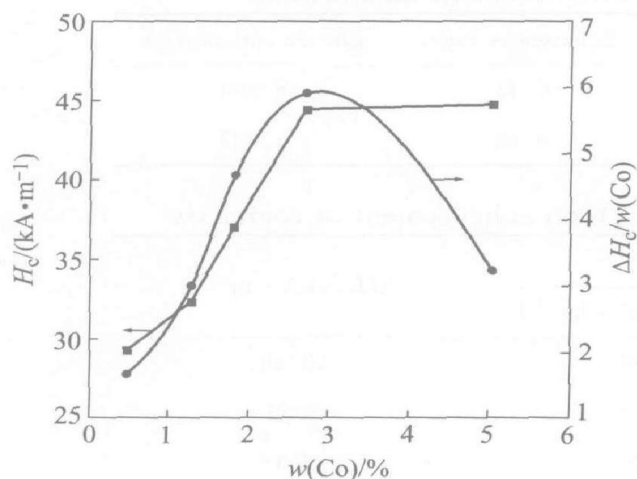


Fig. 3 Influence of Co content on cobalt efficiency

agree well with the results in the Ref. [13]. The third is that demagnetization field of inner core Fe₃O₄ decreases with increasing cobalt content, which will be discussed in later section.

3.3 Effect of reaction time

The effect of reaction time on the product is shown in Table 3. The coercivity increases with increasing reaction time, because the crystalline is more regular and integrated with the time increasing. However, the saturation magnetization decreases when the reaction time is 6 h. It is probable that Co²⁺ is unstable and oxidized to Co³⁺. XPS can detect the presence of Co₂O₃ · nH₂O in CoFe₂O₄ [14].

Table 3 Effects of reaction time on product

Time/h	H _c / (kA · m ⁻¹)	σ _s / (A · m ² · kg ⁻¹)
2.5	36.4	65.2
4	37.04	88.5
6	37.28	79.8

3.4 Effect of axial ratio of Fe₃O₄

The effects of axial ratio of Fe₃O₄ on the product are shown in Table 4. High axial ratio favors uniform distribution of cobalt and results in the increase of coercivity and saturation magnetization.

Table 4 Effects of axial ratio of Fe₃O₄ on product

Axial ratio	H _c / (kA · m ⁻¹)	σ _s / (A · m ² · kg ⁻¹)	Squareness ratio
6: 1	37.04	88.5	0.42
8: 1	45.6	92.8	0.43

3.5 Post-treatment of product

Magnetite is unstable in chemical composition due to the oxidation of Fe²⁺, these in turn affect the stability of magnetic properties. As a result,

the magnetic recording media may suffer from magnetic accommodation and print-through effects. Therefore, it is necessary to improve the stability of cobalt-modified magnetite. Coating an SiO₂ layer is an effective method to increase the stability of oxide^[15]. In order to confirm the behavior of SiO₂, the particles with and without SiO₂-treatment are exposed to air for 20 days at 50 °C. The results are shown in Table 5. The particles with SiO₂-treatment is more stable than that without treatment, which shows similar stability to CoFe₂O₄ & Fe₂O₃.

Table 5 Stability of different magnetic powders

Magnetic powders	Δw (FeO) / %	ΔH _c / (kA · m ⁻¹)	Δσ _s / (A · m ² · kg ⁻¹)
Fe ₃ O ₄	- 4	- 1.60	- 15
Co-Fe ₃ O ₄	- 1.5	- 0.80	- 8
SiO ₂ -Co-Fe ₃ O ₄	- 0.8	- 0.40	- 5
Co & Fe ₂ O ₃	- 0.7	- 0.48	- 6

3.6 Analysis of effect of cobalt modification on magnetic properties of magnetite

The major aim of cobalt modification is to increase the coercivity of the powder. There are some interpretations on the origin of enhancement of coercivity, which mainly comes from the following three aspects^[7, 10, 16]: 1) magnetocrystalline anisotropy of cobalt-ferrite, 2) shape anisotropy, 3) magnetic induced anisotropy.

Table 2 shows that the coercivity increases with increasing cobalt content. This indicates that the magnetocrystalline anisotropy of cobalt-ferrite plays an important role in the enhancement of coercivity.

Fig. 4 and Fig. 5 show the TEM photographs of Fe₃O₄ and cobalt-modified Fe₃O₄ particles, respectively. It is clear that the photographs are almost the same except for the larger short axis in Fig. 5. So the shape anisotropy of these particles would not be different. The lattice constants of the two particles shown in Table 6 are also the same. These results mean that the shape anisotropy has little effect on the increase of coercivity.

The larger the saturation magnetization of inner core Fe₃O₄, the greater the demagnetization field^[7]. Different saturation magnetization can be obtained by controlling the content of FeO in Fe₃O₄^[17]. The effect of magnetic properties of inner core Fe₃O₄ on the coercivity enhancement is shown in Table 7. It is seen that the coercivity enhancement is dependent on the value of saturation magnetization. The squareness ratio of the particles before and after modification shown in Table 6 is about 0.5. This indicates that the particles ap

Table 6 Properties of Fe₃O₄ with and without cobalt modification

Powder	$H_c / (\text{kA} \cdot \text{m}^{-1})$	$\alpha_s / (\text{A} \cdot \text{m}^2 \cdot \text{kg}^{-1})$	Squareness ratio	Lattice constant/ Å
Fe ₃ O ₄	28.48	75	0.42	8.396
Co-Fe ₃ O ₄	45.60	92	0.43	8.397

Table 7 Effect of magnetic properties of Fe₃O₄ on enhancement of coercivity

$w(\text{FeO}) / \%$	Fe ₃ O ₄ before modification		$\Delta H_c / (\text{kA} \cdot \text{m}^{-1})$
	$H_c / (\text{kA} \cdot \text{m}^{-1})$	$\alpha_s / (\text{A} \cdot \text{m}^2 \cdot \text{kg}^{-1})$	
31.3	29.12	86	10.40
29.5	28.48	75	8.56
26.6	28.00	66	6.4
22.8	28.08	61	5.12

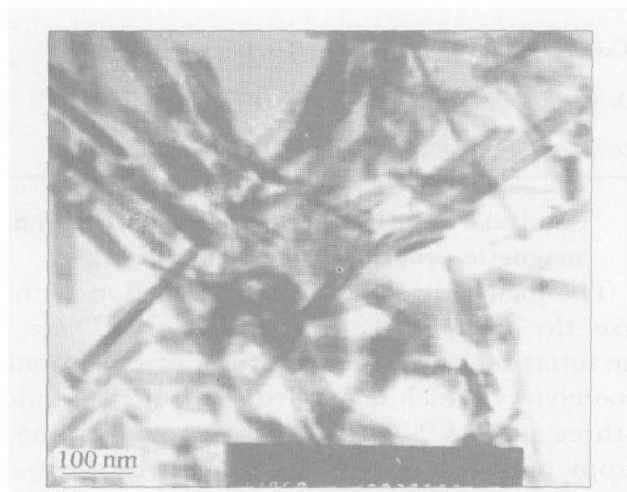


Fig. 4 TEM photograph of Fe₃O₄

and the demagnetization field decreases with the thickness very sharply. That is to say, the demagnetization field decreases with increasing cobalt content. As a result, demagnetization field is equal to zero and can't induce uniaxial magnetic anisotropy while cobalt content gets to some amount. Thus we can explain why there exists a maximum value of cobalt efficiency in Fig. 3.

4 CONCLUSIONS

1) Cobalt-modified magnetite is prepared by reaction with alkaline solution containing Co²⁺ and Fe²⁺ at 90 °C, the optimum conditions are reaction time of 4 h, cobalt content of 2.71% and pH value of 12.

2) The pH value influences the composition of the product directly, the desired CoFe₂O₄ is obtained at pH 12. The formation of CoFe₂O₄ on the surface of magnetite results in the increase of coercivity. The coercivity increases with increasing cobalt content, and the cobalt efficiency reaches a maximum value at cobalt content of 2.71%. The increase of the coercivity is attributed to the uniaxial magnetic anisotropy induced by inner core Fe₃O₄ and magnetocrystalline anisotropy of cobalt-ferrite itself.

3) The chemical and magnetic stability are improved by coating with a layer SiO₂.

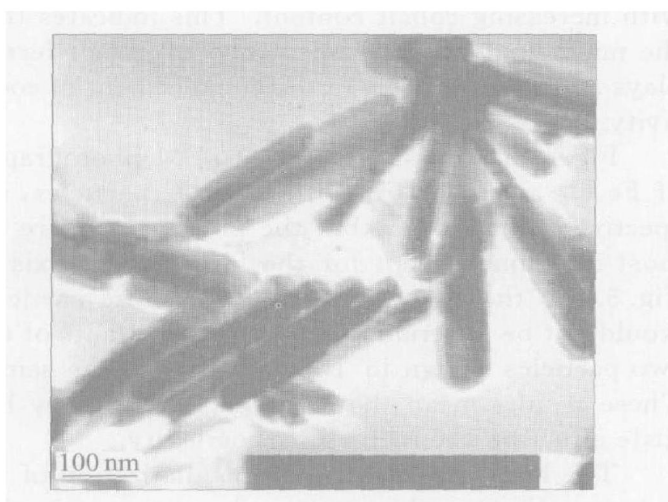


Fig. 5 TEM photograph of cobalt-modified Fe₃O₄

pear to have uniaxial magnetic anisotropy, which results from migration of Co²⁺ ions to the preferred sites alignment with the direction of magnetic field of the core Fe₃O₄. So the uniaxial magnetic anisotropy induced by inner core Fe₃O₄ leads to the enhancement of coercivity. The cobalt-ferrite layer thickness increases with increasing cobalt content,

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