PREPARATION AND MAGNETIC PROPERTIES OF (Co,Zn)-DOPED γ-Fe₂O₃ PARTICLES

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Abstract—Oxidation temperatures and times of Fe_3O_4 to produce (Co,Zn)-doped γ-Fe₂O₃ particles were examined in this study to relate these two parameters to void, particle size, saturation magnetization, coercivity, and squareness. The effect of Zn/Co ratio on magnetization and coercivity of the particles was also studied.

The partial substitution of Zn for Co in Co-γ-Fe₂O₃ increased the σ value and environmental stability, but decreased the $_iH_c$ and the squareness of γ-Fe₂O₃.

INTRODUCTION

Co-γ-Fe₂O₃ particles, which find extensive application in high desity recording media, are produced by the dehydration, reduction, and oxidation of wet-chemically prepared α-FeOOH. The addition of Zn, which was produced by absorbing Co and Zn ions on the surface of γ-Fe₂O₃[1-2], has been found to be capable of increasing the stability of Co-γ-Fe₂O₃ particles. A preliminary study[3], in which Co and Zn ions were initially absorbed on the surface of α-FeOOH instead of γ-Fe₂O₃ and then through the dehydration, reduction, and oxidation processes, has shown that (Co,Zn)-γ-Fe₂O₃ particles have some interesting magnetic properties. In this article a further study is undertaken on the preparation of (Co,Zn)-doped γ-Fe₂O₃ particles by the oxidation of (Co,Zn)-Fe₃O₄ and their magnetic properties.

EXPERIMENTAL

Acicular (Co,Zn)-doped Fe₃O₄ particles containing 5 and 8 wt% of of Co and Zn ions in total (Co+Zn+Fe) and having various Zn/Co ratios were produced by first wet-chemically synthesizing α-FeOOH particles. This was next followed by adding Co and Zn ions onto the surface of the α-FeOOH particles, dehydrating α-FeOOH to form α-Fe₂O₃, and reducing α-Fe₂O₃ to form Fe₃O₄ by hydrogen. The details of the preparative procedures are reported elsewhere[3].

Various temperatures and times were used to oxidize (Co, Zn)-Fe₃O₄ particles. Because DTA analysis indicated that the complete oxidation temperature of γ-Fe₃O₄ is 252°C, oxidation temperatures ranging from 320 to 420°C were selected.

After the preparations of the particles, XRD, TEM, and VSM were used to examine the particles.

RESULTS AND DISCUSSION

The σ value (saturation magnetization) of γ-Fe₂O₃ indicated in Figure 1 and 2 was found to decrease with increases of both the oxidation temperature ranging from 310°C to 420°C for 1.5 hrs and oxidation time ranging from 1 to 53 hrs at 350°C. XRD analysis indicates that this phenomena occurred because some of the γ-Fe₂O₃ was transformed into α-Fe₂O₃.
The σ value of γ-Fe₂O₃ illustrated in Figure 3 was found to increase with the Zn/Co ratio ranging from 0 to 0.7 since cobalt zinc ferrite has higher magnetic moments than pure cobalt ferrite. The σ value of lowest curve in Figure 1 and Figure 2, which contained no zinc ion, decreased more rapiely than other (Co,Zn)-γ-Fe₂O₃ at high temperature region. This would imply the effect of zinc is to increase the high temperature stability of Co-γ-Fe₂O₃, i.e., the resistance of γ-Fe₂O₃ to α-Fe₂O₃ transformation. The σ values of (Co,Zn)-γ-Fe₂O₃(8wt%) given in Figure 3 were always slightly smaller than those of (Co,Zn)-doped γ-Fe₂O₃(5wt%). This phenomena is difficult to explain since the σ values of pure CoO·Fe₂O₃(80 emu/g) is larger than that of pure γ-Fe₂O₃(76 emu/g)[4]. It may be due to some nonmagnetic phase, which can not be detected by XRD analysis, existing in the (Co,Zn)-doped γ-Fe₂O₃.

The $_iH_c$(coercivity) of (Co,Zn)-doped γ-Fe₂O₃ (Figure 4 and Figure 5) increased with a higher oxidation temperature or longer oxidation time of Fe₃O₄ because more Co diffuses inside γ-Fe₂O₃ and forms more cobalt ferrite which has higher coercivity than pure γ-Fe₂O₃. A trace amount of α-Fe₂O₃, which was produced either at a higher oxidation temperature or a longer oxidation period, might introduce a stress field in the sample and subsequently increase the $_iH_c$ value of γ-Fe₂O₃. The removal of pores (Figuire 6) at a higher oxidation temperature removes the demagnetizing field and, subsequently, also increases the coercivity of γ-Fe₂O₃. The $_iH_c$ of the sample was found to increase with an increasing (Co+Zn) content. However, it would decrease with an increasing Zn/Co ratio because of a large anisotropy constant of cobalt ferrite and the addition of zinc ion decreases its anisotropic constant(K_1).

The squareness of (Co,Zn)-doped γ-Fe₂O₃ (Figure 8 and 9) was found to have the same properties as $_iH_c$, which increases with either a higher oxidation temperature or longer oxidation time of Fe₃O₄.

DTA analysis in Figure 10 shows that the partial substitution of Zn for Co in Co-doped γ-Fe₂O₃ particles stabilized γ-Fe₂O₃ because the transformation temperature from γ-Fe₂O₃ to α-Fe₂O₃ increased with Zn/Co ratio. The $_iH_c$ of the (Co, Zn)-doped γ-Fe₂O₃ (Figure 11) increased with the aging time at 60°C in air within 90 days because of γ-Fe₂O₃ oxidation.

Although a different method was used to produce (Co,Zn)-doped Fe₂O₃ in this study, the magnetic properties were found to be similar to those of previous works[1-2].

CONCLUSIONS

The σ value of (Co,Zn)-γ-Fe₂O₃ decreased with increased of both the oxidation temperature and oxidation time of Fe₃O₄. The σ value of γ-Fe₂O₃ increased with the Zn/Co ratio but decreased with the (Co+Zn) content. The partial substitution of Zn for Co in Co-γ-Fe₂O₃ increased the resistance of γ-Fe₂O₃ to α-Fe₂O₃ transformation.

The $_iH_c$ and squareness of (Co,Zn)-doped γ-Fe₂O₃ increased

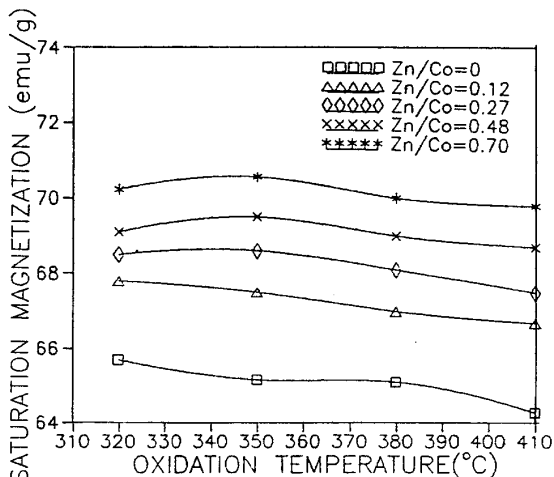Figure 1 σ value of (Co,Zn)-γ-Fe₂O₃ related to various oxidation temperatures of γ-Fe₂O₃ (oxidation time = 1 hr, (Co+Zn)/(Fe+Co+Zn) = 8 wt%)
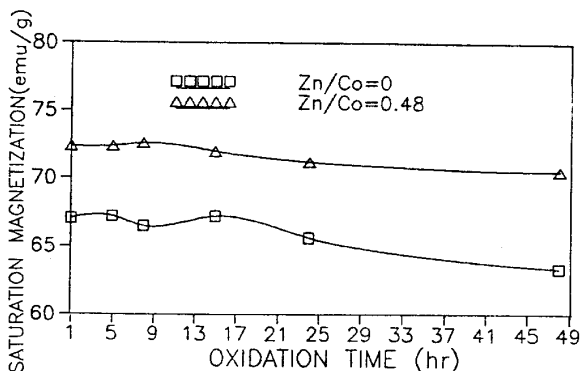

Figure 2 σ value of (Co,Zn)-γ-Fe₂O₃ related to various oxidation times of γ-Fe₂O₃ (oxidation temperature = 350°C, (Co+Zn)/(Fe+Co+Zn) = 8 wt%)
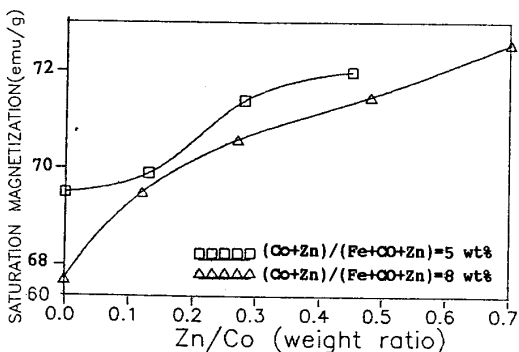

Figure 3 σ value of (Co,Zn)-γ-Fe₂O₃ related to various Zn/Co ratios (T=350°C, t=1.5 hrs)

with a higher oxidation temperature or longer oxidation time of Fe₃O₄ because of the formation of more cobalt ferrite, the stress field of α-Fe₂O₃, and the removal of pores. The ₁Hc of γ-Fe₂O₃ was increase with an increasing (Co+Zn) content, decreased with an increasing Zn/Co ratio because of smaller K₁ value of zinc ferrite.

The partial substitution of Zn for Co in Co-γ-Fe₂O₃ increased the σ value and environmental stability, but decreased the ₁Hc and squareness of γ-Fe₂O₃.

REFERENCES

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[2] A. Rousset, C. Bonino, M. Gougeon and P. Mollard, ibid. MAG-23, pp.77, 1987.

[3] P.C. Kuo and J.A. Chen, J. Matl. Sci., pp.817, 1993.

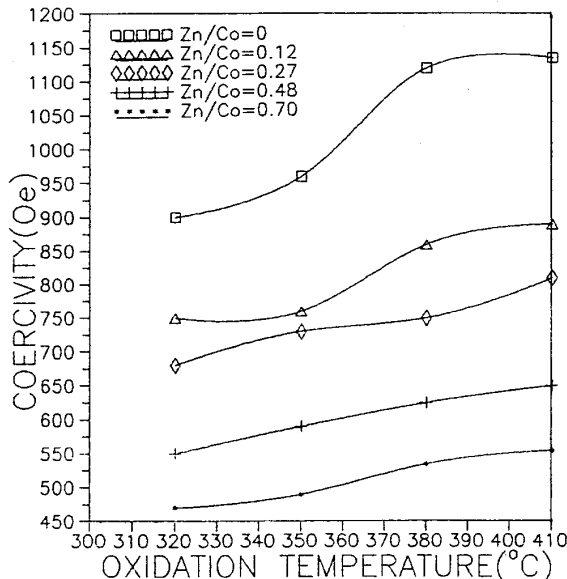[4] B.D. Cullity, Introduction to Magnetic Materials, 1972, pp.190-201

Figure 4 ₁Hc value of (Co,Zn)-γ-Fe₂O₃ related to various oxidation temperatures of γ-Fe₂O₃ (oxidation time = 1.5 hrs, (Co+Zn)/(Fe+Co+Zn) = 8 wt%)
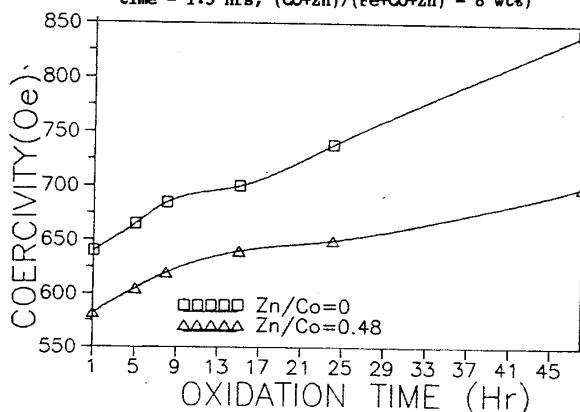

Figure 5 ₁Hc value of (Co,Zn)-γ-Fe₂O₃ related to various oxidation times of γ-Fe₂O₃ (oxidation temperature = 350°C, (Co+Zn)/(Fe+Co+Zn) = 8 wt%)
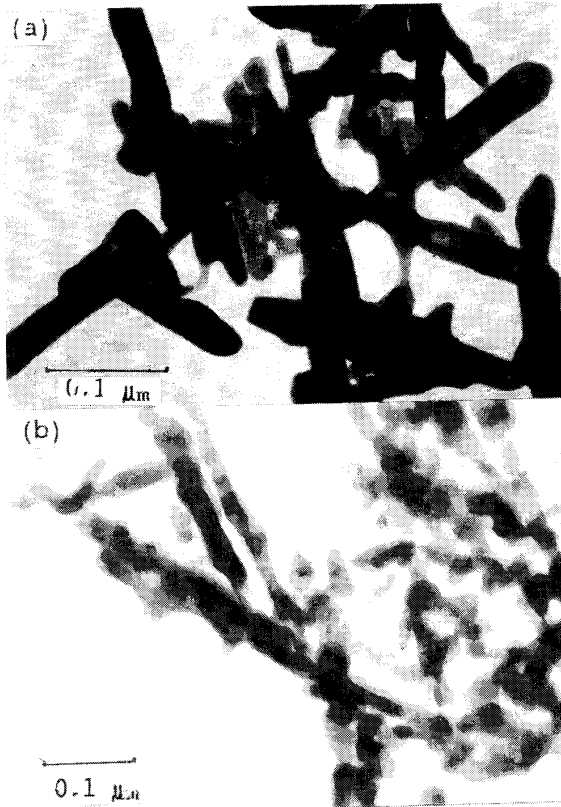
(a)

0.1 μm

(b)

0.1 μm

Figure 6   Electron Micrographs of (Co,Zn)-γ-Fe₂O₃
t=1.5 hrs, (a) T=320°C, (b) T=410°C
(Co+Zn)/(Fe+Co+Zn) = 8 wt%, Zn/Co=0.27

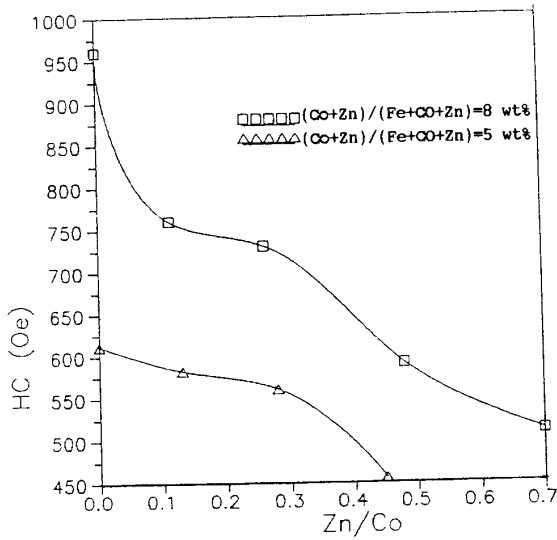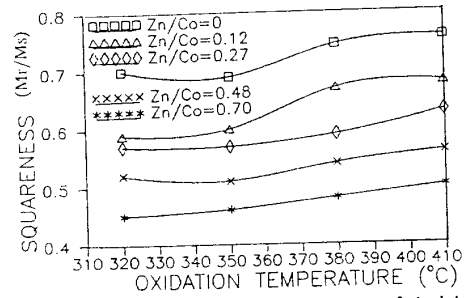Figure 8   Squareness of (Co,Zn)-γ-Fe₂O₃ related to various
oxidation temperatures of γ-Fe₂O₃ (oxidation
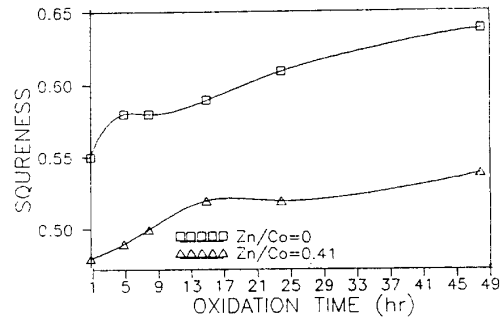time = 1.5 hrs, (Co+Zn)/(Fe+Co+Zn) = 8 wt%)

Figure 9   Squareness of (Co,Zn)-γ-Fe₂O₃ related to various
oxidation times of γ-Fe₂O₃ (oxidation temper-
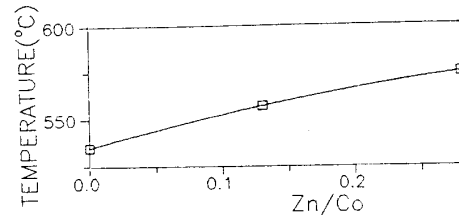ature = 350°C, (Co+Zn)/(Fe+Co+Zn) = 8 wt%)

Figure 10   Transformation temperature of (Co,Zn)-γ-Fe₂O₃
to α-Fe₂O₃ (Co+Zn)/(Fe+Co+Zn) = 5 wt%)

Figure 7   ᵢHc value of (Co,Zn)-γ-Fe₂O₃ at various Zn/Co
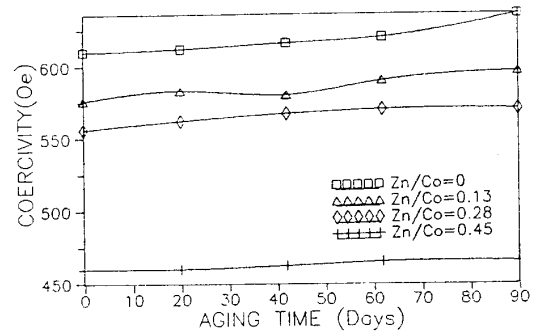ratios (T=350°C, t=1.5 hrs)

Figure 11   Environmental stability of ᵢHc in open air
at 60°C, (Co+Zn)/(Fe+Co+Zn) = 5 wt%)