

# Improved thermal stability of Mo-modified $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> particles

J. H. Hsu

Physics Department, National Taiwan University, Taipei, Taiwan, Republic of China

P. C. Kuo and C. W. Hsu

The Graduate Institute of Materials Engineering, National Taiwan University, Taipei, Taiwan, Republic of China

Acicular  $\alpha$ -(FeO)OH particles were synthesized using the chemical coprecipitation method with the reaction system of Fe<sub>2</sub>Cl<sub>2</sub>-NaOH. The Mo-modified  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> particles are obtained by adding the proper amount of sodium molybdate to the solution of goethite, followed by the processes of dehydration, reduction, and oxidation. The thermal stability was investigated by thermal differential analysis. It was found that the transition temperature of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>  $\rightarrow$   $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> increases from 544 °C for the unmodified particles to 720 °C for particles containing 4% by weight of molybdenum. The improved thermal stability has the advantage that the temperature for the oxidation of Fe<sub>3</sub>O<sub>4</sub> particles can be considerably increased without the risk of forming nonmagnetic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles. The magnetization ( $\sigma_s$ ) and coercivity ( $H_c$ ) of the magnetic acicular  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> have been determined from room temperature to 200 °C with a vibrating sample magnetometer. The results indicate that both  $\sigma_s$  and  $H_c$  at room temperature decrease with increasing Mo content. The dependence of  $H_c$  can be approximately described by the linear equation  $H_c = H_{c0}(1 - AT)$  over that temperature range. The temperature coefficient  $A$  decreases with Mo content until the Mo content reaches 4 wt. %. The origin of improved thermal stability is discussed.

## I. INTRODUCTION

Acicular magnetic  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> particles have long been used as the major material for recording medium.<sup>1</sup> Even with the advent of many new materials, ferric oxide still dominates the applications today. The manufacturing process comprises several steps of heat treatments which will cause the breaking of particles or the change of particle shape.<sup>2</sup> Thus, the particle may lose its acicularity and consequently it does not possess adequate coercivity for recording utilization.<sup>3</sup> Magnetic  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> particles can be converted into nonmagnetic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles at high temperatures.<sup>4</sup> Thus, it is the object of this research to find a new method of coating the particles with some good thermally stable material so that the modified particles do not suffer in magnetic performance. The element molybdenum has been well known as a refractory material. Therefore, it can be considered as a good candidate to study.

## II. EXPERIMENT

The preparation of acicular Mo- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> particles begins with the growth of acicular  $\alpha$ -(FeO)OH particles. In this process the chemical coprecipitation method is used with the FeCl<sub>2</sub>-NaOH reaction system. While the particle is grown, the pH value of the solution mixture is around 13–14. The Mo adsorption is carried out on the stage right after the growth of acicular  $\alpha$ -(FeO)OH particles. According to our experiments, before slowly adding the proper amount of Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O and FeCl<sub>2</sub>·4H<sub>2</sub>O into the solution, the pH value of the above solution must be reduced to about 6. Otherwise, Mo and Fe ions cannot be adsorbed on the  $\alpha$ -(FeO)OH particles. For this purpose, CH<sub>3</sub>COOH is added to the above solution before coating. The adsorbed compounds are believed to be Fe(OH)<sub>2</sub> and Mo(OH)<sub>2</sub>.<sup>5</sup> The

formed adsorbed (Fe)OH is then dehydrated followed by reduction as well as oxidation. The produced acicular  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> particles are approximately 0.3  $\mu$ m long with uniform size distribution.

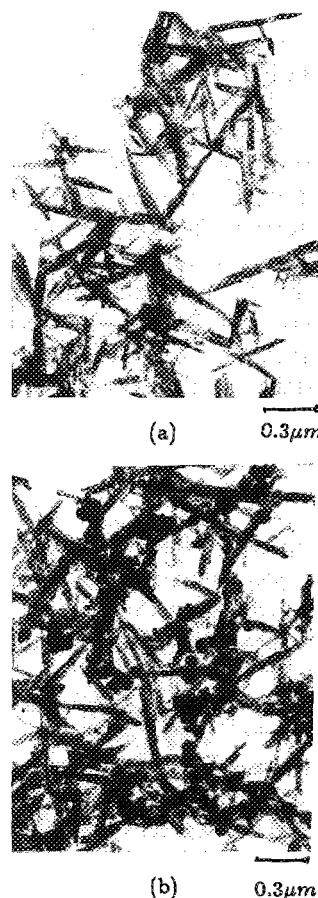


FIG. 1. Electron transmission micrographs of Mo- $\alpha$ -(FeO)OH particles (a) in weak acid solution and (b) in the strong base solution.

The Mo content of the particles is determined from analysis of atomic absorption spectrum. The thermal stability against transformation from  $\gamma\text{-Fe}_2\text{O}_3$  into  $\alpha\text{-Fe}_2\text{O}_3$  was investigated by means of differential thermal analysis. During the phase transformation, a number of calories are released. The measurements of magnetic properties were performed on a vibrating sample magnetometer between room temperature and 200 °C.

### III. RESULTS AND DISCUSSION

In Fig. 1, the electron transmission micrographs of Mo- $\alpha\text{-(FeO)OH}$  particles are shown. It has been found that the coating must be done in a weak acid solution. If a strong alkaline solution is used, new granular particles will be pro-

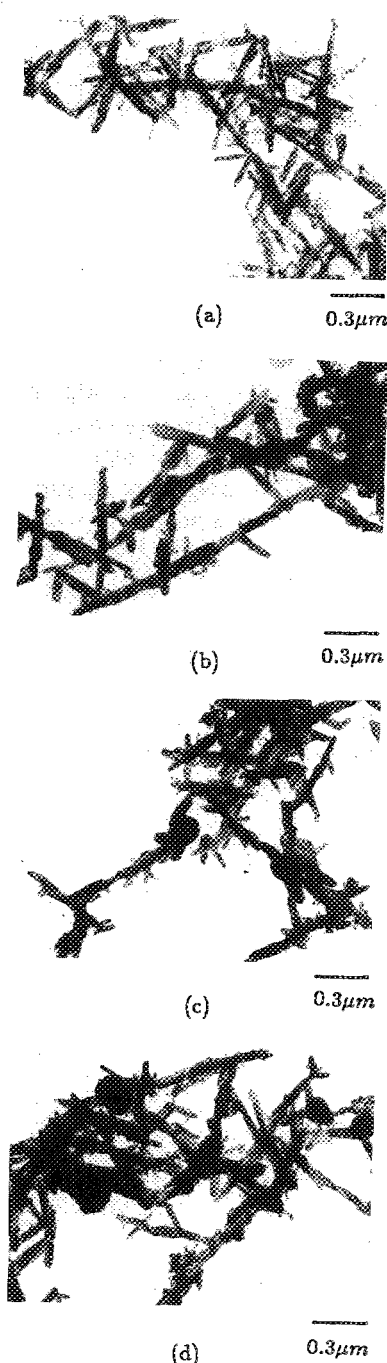


FIG. 2. Electron transmission micrographs of Mo- $\alpha\text{-(FeO)OH}$  particles with Mo content equal to (a) 5 wt. %, (b) 10 wt. %, (c) 15 wt. %.



FIG. 3. Electron transmission micrographs of Mo- $\gamma\text{-Fe}_2\text{O}_3$  particles.

duced instead. Furthermore, the particles become larger with increasing amounts of Mo. Once the Mo content exceeds 15 wt. %, the final particles will lose their acicularity as shown in Fig. 2.

The dehydration step will create many micropores inside the particles, especially near the surface of the particles. Therefore, later heat treatments will produce a rough surface due to the collapse of pores which are near the surface. It has been found that with the Mo adsorption, the particles show a smooth surface (see Fig. 3), which may be due to the formation of a hard layer of Mo oxide on the particle surface. Unfortunately, the structure of the Mo oxide is very difficult to determine directly from x-ray diffraction patterns due to the small amount of Mo. The precise determination of Mo compounds by ESCA is underway.

The dependence of the phase transformation temperature  $T_{\text{phase}}$  of  $\gamma\text{-Fe}_2\text{O}_3$  into  $\alpha\text{-Fe}_2\text{O}_3$  on Mo content is plotted in Fig. 4. It indicates that  $T_{\text{phase}}$  increases rapidly with

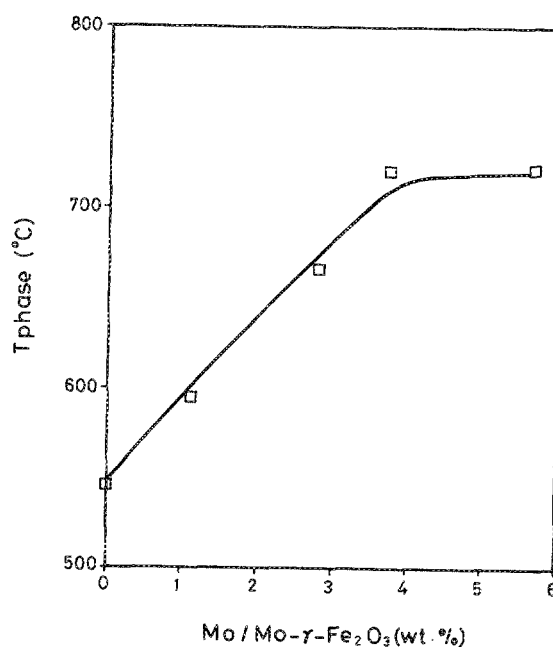


FIG. 4. Dependence of phase transformation temperature  $T_{\text{phase}}$  of  $\gamma\text{-Fe}_2\text{O}_3$  into  $\alpha\text{-Fe}_2\text{O}_3$  on Mo content.

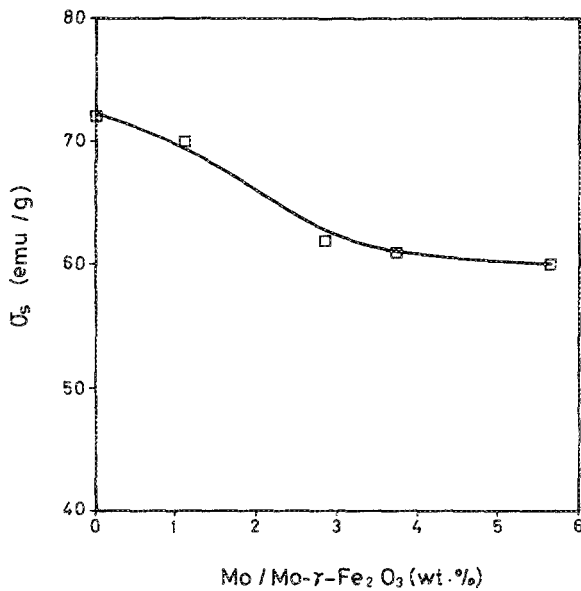


FIG. 5. Specific magnetization  $\sigma_s$  of Mo- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> particles as a function of Mo content.

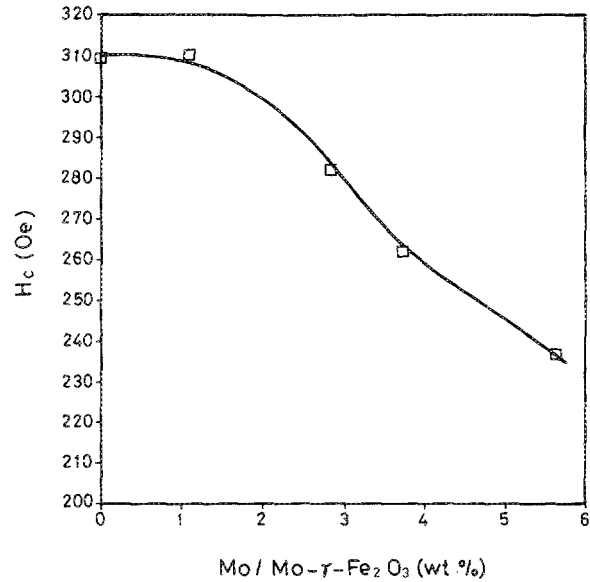


FIG. 6. Coercivity,  $H_c$  of Mo- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> particles as a function of Mo content.

Mo content until it reaches about 4% by weight of molybdenum. One can take advantage of this fact in the preparation process. The oxidation temperature of Fe<sub>3</sub>O<sub>4</sub> particles can be considerably raised without the risk of forming non-magnetic undesirable  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles. For this reason, the oxidation time could be greatly reduced.

The specific magnetization as a function of Mo content is shown in Fig. 5. It first decreases with increasing Mo content because of the nonmagnetic Mo ferrite layer. However, the decrease becomes smaller as the Mo content exceeds about 3 wt. %. On the contrary, as shown in Fig. 6,  $H_c$  is about 310 Oe for nonmodified particles and does not change with small Mo content. It starts to drop if the Mo content is greater than about 1%. The reduction of  $H_c$  becomes more

significant with increasing Mo content. This is because the heat treatments become less effective with increasing Mo content so that the particles still contain many micropores which are the source of self-demagnetizing field.

The thermal stability of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> particles was also studied by measuring the coercivity between room temperature and 200 °C. The normalized coercivity is plotted as a function of temperature in Fig. 7. It is noted that  $H_c$  can be approximately described by a linear equation:

$$H_c = H_{c,0} (1 - AT), \quad (1)$$

over that temperature range where the temperature coefficient  $A$  is a function of Mo content. It is also indicated in Fig. 7 that  $A$  decreases until the Mo content reaches 4 wt. %. The coercivity of magnetic ferric oxide particles mainly originates from shape anisotropy.<sup>6</sup> It is, however, not quite clear yet why  $A$  decreases with increasing Mo content.

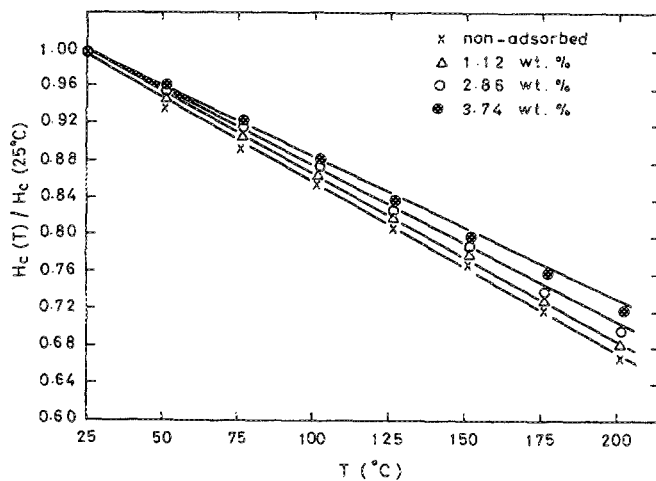


FIG. 7. Normalized coercivity of Mo- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> particles as a function of temperature.

#### IV. CONCLUSION

The improved thermal stability of acicular  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> particles has been achieved with the adsorption of 1 wt. % Mo on the particle and the Mo modified particles preserve the magnetic properties of unmodified particles.

<sup>1</sup> E. P. Wohlfarth, ed., *Ferromagnetic Materials* (North-Holland, Amsterdam, 1980), Vol. 2, Chap. 7.

<sup>2</sup> A. R. Corradi and E. Mello Ceresa, *IEEE Trans. Magn.* **MAG-15**, 1068 (1979).

<sup>3</sup> J. H. Hsu, C. R. Chang, P. C. Kuo, and J. H. Huang, *J. Magn. Mater.* (to be published).

<sup>4</sup> C. Gustard and W. J. Schuele, *J. Appl. Phys.* **37**, 1168 (1966).

<sup>5</sup> G. Bate, *Proc. IEEE* **74**, 1513 (1986).

<sup>6</sup> P. E. Eagle and J. C. Mallinson, *J. Appl. Phys.* **38**, 995 (1976).