

## Synthesis of $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> powders from ferric nitrate solution

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### 1. Introduction

It is well-known that there are three kinds of iron oxide, *i.e.*, FeO, Fe<sub>2</sub>O<sub>3</sub>(hematite) and Fe<sub>3</sub>O<sub>4</sub>. In addition, Fe<sub>2</sub>O<sub>3</sub> has two different polymorphism of an  $\alpha$ -phase and a  $\gamma$ -phase[1].

Of these two different phases, the  $\gamma$ -form has ferrimagnetic properties and is therefore used widely as a magnetic recording medium. It is generally obtained by oxidizing Fe<sub>3</sub>O<sub>4</sub> or dehydrating  $\gamma$ -FeOOH[2]. It has a spinel-type crystal structure with a lattice parameter of 8.34Å and transforms to anti-ferromagnetic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> at a certain temperature. The high temperature phase of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> has a corundum-type rhombohedral crystal structure[3].

Recently,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> powders and films are studied for gas-sensing materials because of good sensitivity to reducing gases due to the surface conductivity changes[4-7].

$\alpha$ -Fe<sub>2</sub>O<sub>3</sub> powders have been produced by various techniques such as precipitation[2], sol-gel[8], pyrolysis[9], hydrothermal[10] and spray drying process[11], etc. From the view of the cost and mass production possibility for commercial applications, the precipitation and the pyrolysis process are appropriate for the synthesis of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> powders.

The purpose of this research was to prepare  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> powders from ferric nitrate solution using pyrolysis and precipitation process, respectively.

### 2. Experimental Procedures

The procedure for synthesizing  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> powders by pyrolysis from ferric nitrate solution is schematically illustrated in Fig. 1(a). The mixed solution of ferric nitrate(Fe(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O) and ethylene glycol(HOCH<sub>2</sub>CH<sub>2</sub>OH) was stirred at the constant rate for 5 hours and then it was dried at 100°C for 4~5 days. All

the experiments were performed at same conditions mentioned above, with the exceptions of reaction temperature and the concentration of ferric nitrate. The synthesized iron complexes were heated at 250~450°C in order to obtain Fe<sub>2</sub>O<sub>3</sub> powders.

The experimental procedure for preparing  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> powders by precipitation is shown in Fig. 1(b). The mixed solution of ferric nitrate and ethanol(CH<sub>2</sub>CH<sub>3</sub>OH) was stirred at 150 rpm and 80°C for 4 hours, with the molar ratio of ferric nitrate to ethanol being 1 : 15, 1 : 20 and 1 : 25, respectively. The iron hydroxides powders were collected by centrifuging at 1000 rpm for 20 minutes. The precipitated iron hydroxides powders were dried at 100°C for 10 hours and then heated at 250, 500°C in order to obtain Fe<sub>2</sub>O<sub>3</sub> powders.

The pH value was measured to study the hydrolysis reaction and the variation of viscosity to observe the polymerization effect of the mixed solution of ferric nitrate and ethylene glycol. The decomposition temperature of the synthesized gel complexes and precipitates was investigated using X-ray diffractometer. SEM and TEM were performed to characterize the effects of the experimental conditions such as reaction temperature and precursor composition on the size and shape of the particles.

### **3. Results and Discussion**

#### **3. 1. Synthesis of $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> powders by pyrolysis process**

During stirring the solution of ferric nitrate dissolved in ethylene glycol at 80°C, the viscosity of the solution increased as shown in Fig. 2. This suggests that iron complexes were formed because of the polymerization effect between Fe<sup>3+</sup> ions and ethylene glycol[12].

X-ray diffraction patterns of Fe<sub>2</sub>O<sub>3</sub> powders calcined at 250, 350 and 450°C are given in Fig. 3. The transformation of  $\gamma$ -phase to  $\alpha$ -phase occurred at about 350°C.

Fig. 4 and Fig. 5 show the effects of the composition and reaction temperature on the size and shape of the particles. As shown in Fig. 4 and Fig. 5, large and round-shaped primary particles of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> powders were synthesized at higher reaction temperature and ferric nitrate concentration.

#### **3. 2. Synthesis of $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> powders by precipitation process**

During stirring the solution of ferric nitrate dissolved in ethanol at 80°C, the

pH value of the solution decreased with the reaction time, as shown in Fig. 6. It is expected that the increase of H<sup>+</sup> ions is due to the hydrolysis of ferric nitrate solution[13].

Fig. 7 shows X-ray diffraction patterns of Fe<sub>2</sub>O<sub>3</sub> powders dried at 100°C and calcined at 250, 500°C. As shown in Fig. 7, the amorphous phase was observed in case of dried powders and the crystallization of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> did occur at over 250°C.

The effect of the concentration of ferric nitrate on the particle size is shown in Fig. 8. It was observed that the primary particle size decreased with the concentration of ferric nitrate.

#### 4. Conclusion

The nanometer size of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles was obtained by the pyrolysis and the precipitation processes. The average size of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles was 20~100 nm and the round-shaped particles was achieved. The size of the primary particles was considerably affected by the concentration of the ferric nitrate and the reaction temperature.

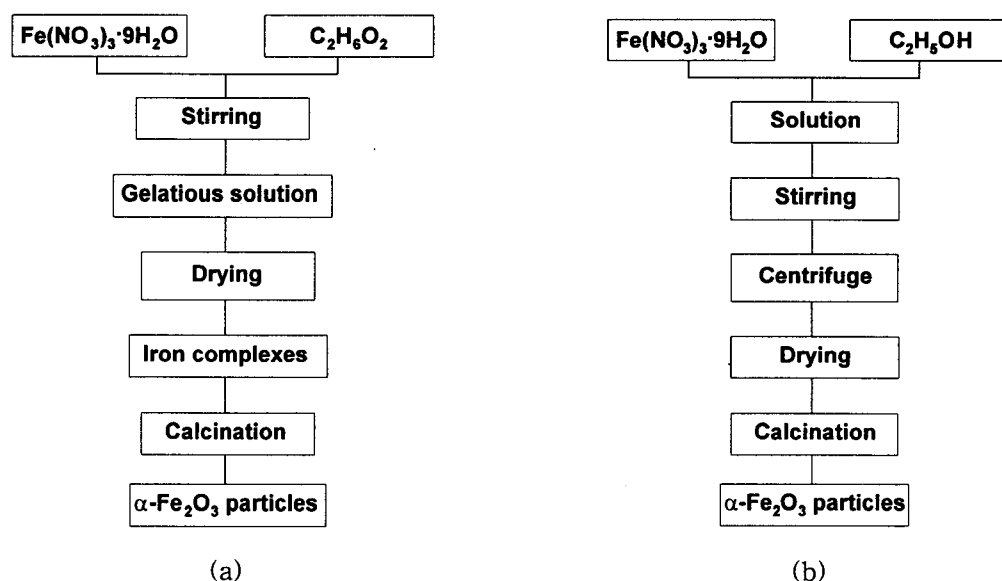


Fig. 1 Experimental procedure for the synthesis of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> powders by (a) pyrolysis and (b) precipitation process

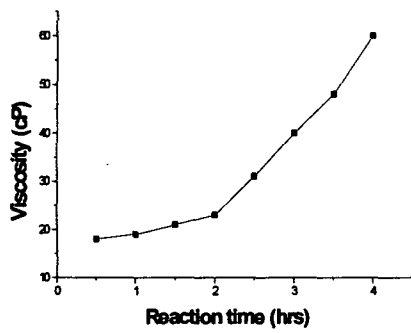


Fig. 2 Variation of the viscosity of ferric nitrate solution with reaction time.

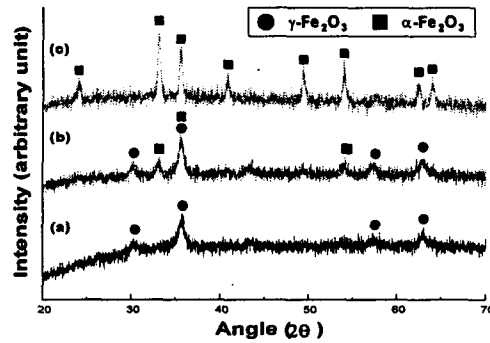


Fig. 3 X-ray diffraction patterns of Fe<sub>2</sub>O<sub>3</sub> powders calcined at (a) 250 (b) 350 and (c) 450°C. (ferric nitrate content: 15 wt%, reaction temperature: 80°C)

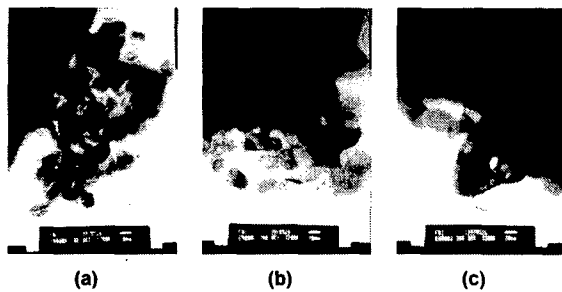


Fig. 4 Transmission electron micrographs of  $\alpha$ -hematite powders synthesized with the compositions of ferric nitrate and ethylene glycol; (a) 15:85, (b) 30:70 and (c) 50:50 wt% (reaction temperature: 80°C, calcined temperature: 450°C)

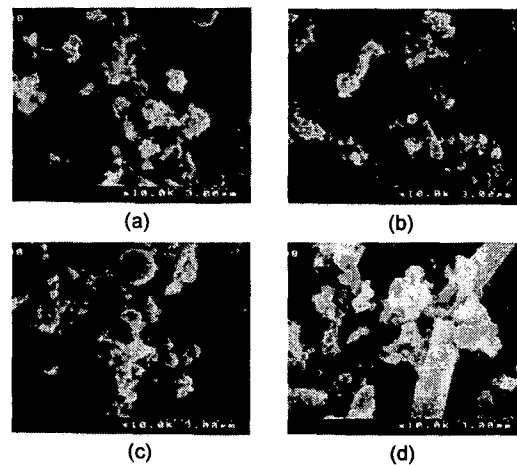


Fig. 5 Scanning electron micrographs of  $\alpha$ -hematite powders synthesized at the reaction temperatures; (a) 60, (b) 80, (c) 100 and (d) 120°C (ferric nitrate content: 15wt%, calcined temperature: 450°C)

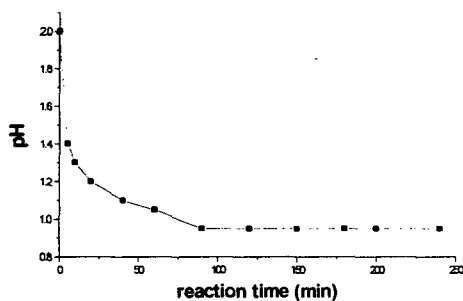


Fig. 6 Variation of pH value with a reaction time.

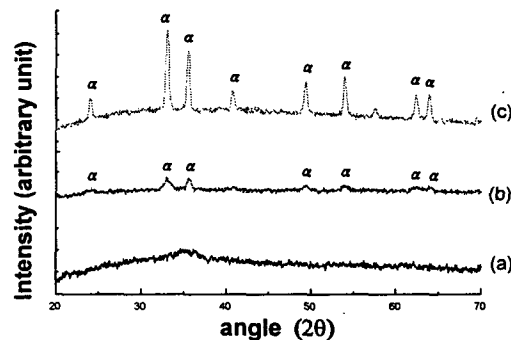


Fig. 7 XRD patterns of powders; (a) dried at 100°C for 10 hours, (b) calcined at 250°C for 3 hours, and (c) calcined at 500°C for 3 hours.

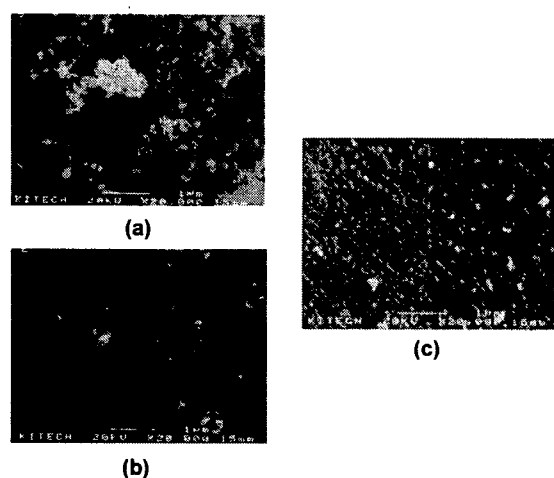


Fig. 8 SEM micrographs of  $\alpha$ -hematite powders reacted at 80°C for 2 hours and calcined at 500°C for 3 hours. The molar ratios of ferric nitrate to ethanol were (a) 1:15, (b) 1:20 and (c) 1:25.

## 5. Reference

- [1] Y. Nakatani and M. Matsuoka, Japanese Journal of Applied Physics 22 (1983) 233
- [2] S. V. S Parsad and V. Rao, Journal of Materials Science 19 (1984) 3266
- [3] R. C. Evans, An Introduction to Crystal Chemistry 2nd ed.(Cambridge University, UK, 1966) 165
- [4] J. Peng and C. C. Chai, Sensors and Actuators B 13-14 (1993) 591
- [5] C. Cantalini, M. Faccio, G. Ferri and M. Pelino, Sensors and Actuators B 15-16 (1993) 293
- [6] C. C. Chai, J. Peng and B. P. Yan, Journal of Electronic Materials 24 (1995) 799
- [7] W. Y. Chung and D. D. Lee, Thin Solid Films 200 (1991) 329
- [8] Y. Azuma, K. Nogami and N. Ohshima, Journal of the Ceramic Society of Japan 100 (1992) 646
- [9] K. Suresh and K. C. Patil, Journal of Materials Science Letters 12 (1993) 572
- [10] T. B. Byeon and J. G. Sohn, Journal of the Korean Ceramic Society 31 (1993) 117
- [11] G. L. Messing and W. T. Minehan, Journal of the Ceramic Society of Japan 99 (1991) 1036
- [12] N. Takahashi, N. Kakuta, A. Ueno, K. Yamaguchi, T. Fujji, T. Mizushima and Y. Udagawa, Journal of Materials Science 26 (1991) 497
- [13] E. Matijevic and P. Scheiner, Journal of Colloid and Interface Science, 63 (1978) 509