Kinetics for Reduction of Aciculate Ultrafine α-Fe$_2$O$_3$ Particles to Fe$_3$O$_4$ Particles[1]

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The reduction kinetics of aciculate ultrafine α-Fe$_2$O$_3$ particles to Fe$_3$O$_4$ in a mixture of H$_2$ and N$_2$ were studied by using the temperature-programmed reduction technique, and the optimum conditions for reduction were investigated for preparation of magnetic powder. The reduction of aciculate ultrafine α-Fe$_2$O$_3$ particles to Fe$_3$O$_4$ was fitted to the nucleation and grain-growth model, and the reduction kinetic equation was written as $d\alpha/dt = 9.00 \times 10^3 \exp(-72.7 \times 10^3/RT)(1-\alpha)\alpha^{0.54}$. There existed a maximum reduction rate at the degree of transformation approximately equal to 0.34, which was considered to be a result of induction effects. The optimum temperature of aciculate ultrafine α-Fe$_2$O$_3$ particle reduction for magnetic powder preparation was 630–670 K. © 1997 Academic Press

Key Words: aciculate ultrafine particles; α-Fe$_2$O$_3$; reduction; kinetics; magnetic; nucleation and grain-growth model

INTRODUCTION

Aciculate ultrafine γ-Fe$_2$O$_3$ powder is widely used as a magnetic material for recording tapes and disks. Production of γ-Fe$_2$O$_3$ usually involves four steps: (1) precipitation of α-FeOOH, (2) dehydration of α-FeOOH, (3) reduction of α-Fe$_2$O$_3$ to Fe$_3$O$_4$, and (4) oxidation of Fe$_3$O$_4$ to γ-Fe$_2$O$_3$. All four steps are critical for the quality of the final product, but an important step in the preparation of γ-Fe$_2$O$_3$ is the reduction of α-Fe$_2$O$_3$, which strongly affects the structure and morphology of the γ-Fe$_2$O$_3$ particle (1). This preparation of γ-Fe$_2$O$_3$ for making magnetic media has been discussed extensively in the literature (2–6). Much of this literature has focused on the structure transition and operation conditions of magnetic powder preparation. Despite the need to know the reduction mechanism and kinetics of α-Fe$_2$O$_3$ powder for determining the operation conditions and designing the reduction reactor, little work has been done on the mechanism and kinetics of the reduction process of aciculate ultrafine α-Fe$_2$O$_3$ particles. Several studies have been executed on the reduction of small spherical and granular Fe$_2$O$_3$ particles (7–10). It must be emphasized, however, that the literature data diverge to a large extent, since different oxides exist (Fe$_2$O$_3$, Fe$_3$O$_4$, FeO) and, moreover, these can contain impurities (in the case of ores, Ca, Mg, Mn, and Si (11)) or dopes (in the case of ammonia synthesis catalysts, Al, Ca, K, Mg, and Si (12)). Furthermore, there are large differences in the literature with respect to, for instance, the selection of reduction temperatures, H$_2$O partial pressure, particle/crystal sizes, and particle structures.

Temperature-programmed reduction (TPR) has been used to gain qualitative information on the reducibility of oxide species, such as metal oxides dispersed on a support (13–17). As an example of the application of this procedure for determining the reduction mechanism, the reduction of small Fe$_2$O$_3$ crystallites has been investigated by Wimmers *et al.* (8). The present study gives the TPR results for aciculate ultrafine α-Fe$_2$O$_3$ particles used for magnetic powder preparation. It will be shown that the reduction rate is a function of the degree of transformation, and the maximum reduction rate is found at a degree of transformation around 0.34.

EXPERIMENTAL

Figure 1 is a schematic of the experimental apparatus. The reactor was a quartz tube with internal diameter 5 mm. Eighty milligrams of aciculate ultrafine α-Fe$_2$O$_3$ powder was held in the center of the reactor, and the temperature of the sample was increased from room temperature to 800 K in a linear temperature program. A mixture of H$_2$ and N$_2$, which was used as the reduction gas, was passed over the oxide sample. H$_2$O, formed by reduction, was trapped in a cold trap and in a 5A molecular sieve column. After the gas mixture had passed through the molecular sieve, its composition was monitored continuously with a thermal conductivity detector. In this study, the gas flow rates of H$_2$ and N$_2$ were 1–5 and 10–25 ml · min^{-1}, respectively. The
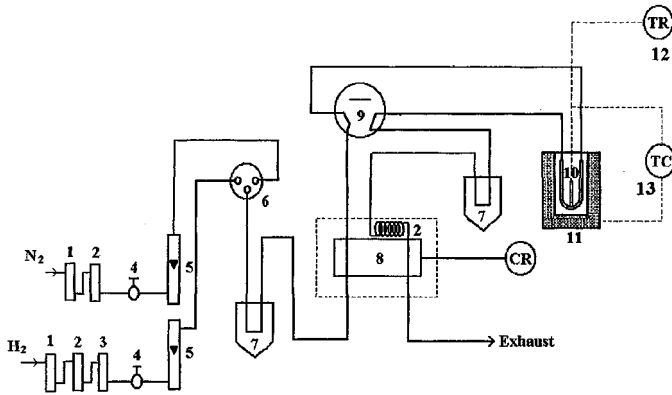
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FIG. 1. Schematic diagram of the experimental setup: (1) silica gel, (2) molecular sieves, (3) Pd/Al₂O₃, (4) valve, (5) flow indicator, (6) three-way injection valve, (7) cold trap, (8) thermal conductivity detector, (9) six-way injection valve, (10) reactor, (11) electric heater, (12) temperature indicator, (13) temperature controller.

heating rate was controlled at 5–45 K/min. α-Fe₂O₃ particles used for this study were prepared by dehydration of α-FeOOH (synthesized according to Gu *et al.* (17)), at 250°C for 30 min and 380°C for 60 min. A transmission electron microscope (JEM, H-300, Japan) was used for observing the particle morphology and size distribution (Fig. 2). The mean particle size of α-Fe₂O₃ was 0.38 μm with an aciculate ratio of 8–10. The specific surface area was determined to be 55 m²/g by means of a BET measurement (ST-300, Beijing, China).

RESULTS AND DISCUSSION

Kinetic Equation

Fine Fe₂O₃ particles and other species of fine oxide particles have such a large specific surface area that induc-
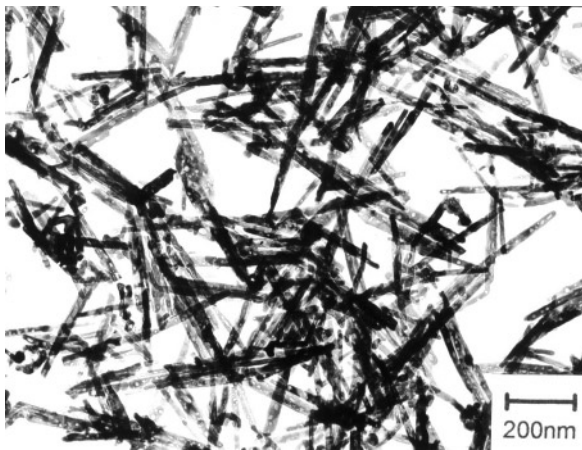

FIG. 2. TEM photograph of aciculate ultrafine α-Fe₂O₃ particles.

tion effects must be considered when the reduction kinetics are investigated (9). The kinetics of nucleation and grain growth for a gas–solid reaction is generally described by an empirical equation of the form (10)

$$\frac{d\alpha}{dt} = k^n t^{n-1}(1-\alpha). \quad [1]$$

α is the degree of transformation, t is the reaction time, and k is a constant independent of α. In Eq. [1] the term t^{n-1} accounts for the increase in reaction rate in the initial stages, whereas the term $(1-\alpha)$ accounts for the gradual decrease in rate as the reaction proceeds beyond the stage when the rate is maximum. The increase in reaction rate may be ascribed to nucleation, i.e., formation of new domains of the product. During later stages, the rate of growth of the new domains decreases because of mutual interference of neighboring domains either through direct impingement or by long-range competition for solute atoms. It should be noted that though k has the dimension t^{n-1}, it is not a true constant because the right-hand side of Eq. [1] contains a t term. It is plausible to assume that a relationship of the following kind would be valid (10):

$$\frac{d\alpha}{dt} = k_m(1-\alpha)\alpha^{(m-1)/m}. \quad [2]$$

k_m is the true reaction rate constant and m is not necessarily equal to n. Considering the process character of TPR, the nucleation and grain-growth kinetic model for aciculate ultrafine α-Fe₂O₃ powder reduction by TPR can be rewritten as

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp\left(\frac{-E_a}{RT}\right)(1-\alpha)\alpha^{(m-1)/m}. \quad [3]$$

$\beta = dT/dt$ is the rate of increase of reaction temperature T, and A is the frequency factor. By use of TPR, α and $d\alpha/dt$ can be obtained at different reaction temperatures and heating rates; then A, E_a, and m can be calculated by numerical methods.

In this study, the reduction of α-Fe₂O₃ to Fe₃O₄ was investigated by TPR at different rates of temperature rise and compositions of the gas mixture. The experimental results at heating rates of 6.5, 8.5, and 14 K · min⁻¹ are listed in Table 1. To use these experimental results to calculate the parameters in the kinetic equation, the form of Eq. [3] must be changed to

$$\ln\left(\frac{d\alpha}{dT}\right) + \ln\beta - \ln(1-\alpha) = \ln A - \frac{E_a}{RT} + \frac{m-1}{m}\ln\alpha. \quad [4]$$

TABLE 1
Experimental TPR Results[a]

β (K·min^{-1})	T (K)	α (%)	$d\alpha/dt$
6.5	591	15.39	0.0057
	597	22.15	0.0085
	609	34.85	0.0163
	623	49.84	0.0197
	633	77.20	0.0156
	643	82.54	0.0126
	648	95.80	0.0073
8.5	597	2.43	0.0032
	608	7.32	0.0047
	616	13.21	0.0072
	628	25.90	0.0102
	642	47.00	0.0158
	663	74.30	0.0163
	668	85.66	0.0122
	679	95.30	0.0070
14.0	597	2.43	0.0032
	608	7.32	0.0047
	616	13.21	0.0072
	628	25.21	0.0102
	642	47.00	0.0158
	663	74.30	0.0163
	668	85.66	0.0122
	679	95.30	0.0070

[a] Mass of α-Fe$_2$O$_3$, 80 mg; H$_2$ flow rate, 3.1 ml·min^{-1}; N$_2$ flow rate, 21.0 ml·min^{-1}.

$\ln(d\alpha/dT) + \ln\beta - \ln(1-\alpha)$, $1/RT$, and $\ln\alpha$ can be easily obtained from these experimental results and then $\ln A$, E_a, and $(m-1)/m$ can be calculated by multielement linear regression. In this study, the authors found that A, E_a, and $(m-1)/m$ were 9.00×10^3, 72.7×10^3 J·mol^{-1}, and 0.54, respectively. The kinetic equation can be written as

$$\frac{d\alpha}{dT} = \frac{9.00 \times 10^3}{\beta} \exp\left(\frac{-72.7 \times 10^3}{RT}\right)(1-\alpha)\alpha^{0.54}. \quad [5]$$

Then the nucleation and grain-growth equation for the reduction of aciculate ultrafine α-Fe$_2$O$_3$ particles to Fe$_3$O$_4$ can be written as

$$\frac{d\alpha}{dt} = 9.00 \times 10^3 \exp\left(\frac{-72.7 \times 10^3}{RT}\right)(1-\alpha)\alpha^{0.54}. \quad [6]$$

Figure 3 gives the relationship between $d\alpha/dt$ and T at different heating rates. From Fig. 3 it can be seen that Eq. [6] fits the experimental results well at 570–720 K.

Sarkar and Ray (10) found that the reduction of Coral Lake pellets by a H$_2$ + H$_2$O mixture at 923–1023 K can be fitted to the Johnson–Mehl equation ($E_a = 100$ kJ·mol^{-1}). Wimmers et al. (8) indicated that the reduction of small Fe$_2$O$_3$ particles (diameter approximately 0.3 μm) to Fe$_3$O$_4$ followed the three-dimensional nucleation model as the rate-determining step ($E_a = 111$ kJ·mol^{-1}). The reduction kinetics of aciculate ultrafine α-Fe$_2$O$_3$ particles to Fe$_3$O$_4$ is different from the mechanics mentioned above because ultrafine Fe$_2$O$_3$ particles have a small particle size and fine pores exist. Small particle size and fine pores made α-Fe$_2$O$_3$ particles acquiring a large reaction activity, lowering the activation energy.

Kinetic Properties

Figure 4 gives the relationships between reaction rate and the degree of transformation at different reduction temperatures. The figure shows that the largest reduction rate of aciculate ultrafine α-Fe$_2$O$_3$ powder is found at α around 0.34. The reduction rate increases with increasing reduction degree of α-Fe$_2$O$_3$ when $\alpha < 0.34$, but decreases with increasing reduction degree of α-Fe$_2$O$_3$ when $\alpha > 0.34$. This maximum rate of reduction is considered to be a result of induction effects, and the slowdown in the rate (after $\alpha = 0.34$) is attributed to the combined effect of the decrease in the reaction rate of each grain and the exhaustion of the smaller particles before the overall reaction is completed. Aciculate ultrafine α-Fe$_2$O$_3$ particles and other species of ultrafine particles have such a large specific surface area that the effects of the surface state must be considered.
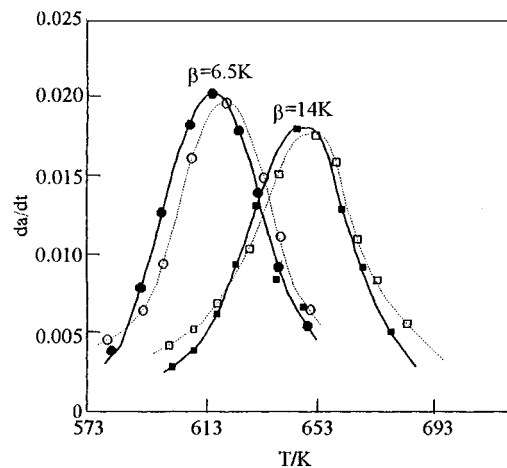

FIG. 3. Reduction rate vs. temperature at two different heating rates. Mass of α-Fe$_2$O$_3$, 80 mg; H$_2$ flow rate, 3.1 ml·min^{-1}; N$_2$ flow rate, 21.0 ml·min^{-1}. (—) calculated from kinetic equation; (···) experimental results.
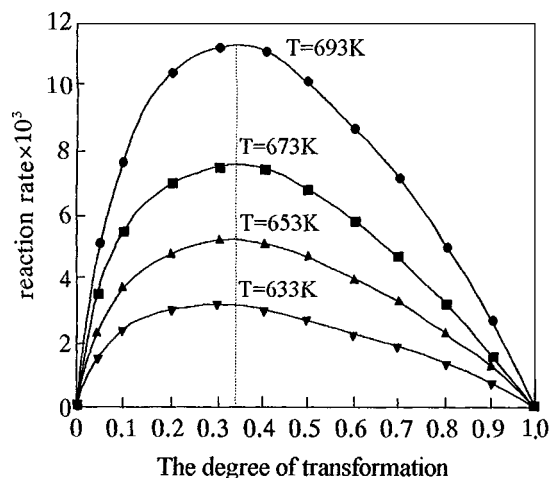
FIG. 4. Relationship between reaction rate and degree of transformation at different reduction temperatures.

FIG. 6. BET specific surface area of Fe$_3$O$_4$ particles at different reduction temperatures. Mass of α-Fe$_2$O$_3$, 80 mg; reduction time, 2.5 h; H$_2$ flow rate, 3.1 ml·min^{-1}; N$_2$ flow rate, 21.0 ml·min^{-1}.

Unal and Bradshaw (9) reduced Coral Lake hematite particles to magnetite at 873 K using a CO + CO$_2$ mixture, and they found that a maximum reduction rate exists when $\alpha \approx 0.15$. The reduction of aciculate ultrafine α-Fe$_2$O$_3$ particles is strongly affected by the particle surface state, because the specific surface area of the aciculate ultrafine α-Fe$_2$O$_3$ particles is much larger than that of Coral Lake hematite particles, which results in the increase in the degree of transformation at which the reduction rate was maximum.

Structure and Magnetic Properties

Temperature is a very important factor in the preparation of γ-Fe$_2$O$_3$ magnetic powder. Figures 5 and 6 give the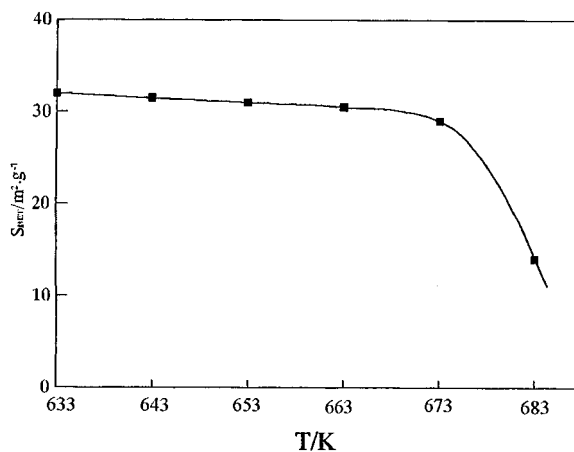 morphology and BET specific surface area at different reduction temperatures. The magnetite particles were not sintered and had fewer fine pores inside the particle than the hematite particles when the reduction temperature was lower than 653 K. The magnetite particles were strongly sintered and were agglutinated when the reduction temperature was greater than 683 K. Figure 6 indicates that the BET specific surface area decreased sharply with temperature when the reduction temperature was greater than 683 K.

The structure and properties of Fe$_3$O$_4$ are very important and must be controlled in the preparation of γ-Fe$_2$O$_3$ magnetic powder. α-Fe$_2$O$_3$ can be reduced completely in an acceptable time when the temperature is greater than 630 K, and this time can be calculated from Eq. [6]. The Fe$_3$O$_4$ particles are not sintered at reaction temperatures lower than 670 K (Fig. 5a). The magnetic properties
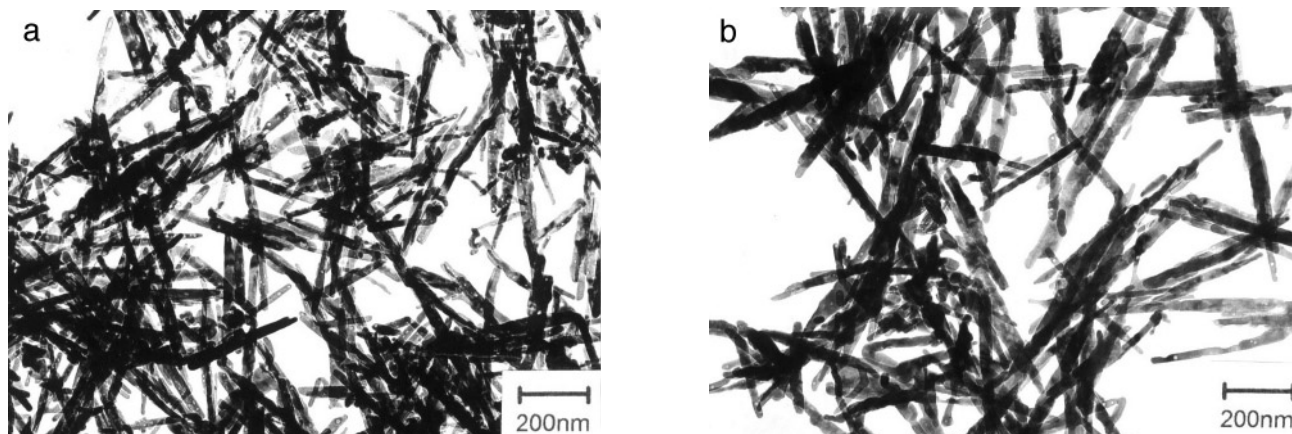

FIG. 5. TEM photograph of Fe$_3$O$_4$ particles at different reduction temperatures: (a) $T = 653$ K; (b) $T = 683$ K. Mass of α-Fe$_2$O$_3$, 80 mg; reduction time, 2.5 h; H$_2$ flow rate, 3.1 ml·min^{-1}; N$_2$ flow rate, 21.0 ml·min^{-1}.

of Fe_3O_4 were investigated by means of a BH instrument (LDJ 7500A, Beijing, China). The coercive force and specific magnetization of Fe_3O_4 powder obtained at 630–670 K were greater than $35.0 \, KA \cdot m^{-1}$ and $85 \, emu \cdot g^{-1}$, respectively.

CONCLUSIONS

(1) Based on an empirical nucleation and grain-growth equation, a kinetic model of nucleation and grain growth for gas–solid reactions was investigated. The reduction of aciculate ultrafine α-Fe_2O_3 particles to Fe_3O_4 was studied by the TPR technique. The kinetic equation can be written as

$$\frac{d\alpha}{dt} = 9.00 \times 10^3 \exp\left(\frac{-72.7 \times 10^3}{RT}\right)(1 - \alpha)\alpha^{0.54}.$$

(2) The reduction rate of the oxide on the outside layer of the particle increases with increasing reduction degree of α-Fe_2O_3. The reduction rate of the oxide inside the particle decreased with increasing reduction degree of α-Fe_2O_3. The reduction temperature of α-Fe_2O_3 for magnetic powder preparation was 630–670 K.

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