MAGNETIC PROPERTIES OF AEROSOL SYNTHESIZED IRON OXIDE PARTICLES

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Fine iron oxide particles have been prepared by an aerosol technique. The particles are spherical with a mean size of 0.1 μm. Heat treatment in air or nitrogen at various temperatures for various times leads to a variety of phase mixtures of α-Fe$_2$O$_3$, γ-Fe$_2$O$_3$ and Fe$_3$O$_4$. The magnetic properties of these various samples are presented.

1. Introduction

A considerable amount of interest has developed in the last decade in the magnetic properties of small magnetic particles. The reason for this interest is two-fold: magnetic properties as a function of size and morphology yield information regarding the fundamental sources of magnetism, and small particles have unique properties of technological importance. Thus, methods for preparation of small particles are important. In this paper we describe the preparation of small iron oxide particles using an aerosol technique. Aerosol synthesis techniques have the potential to create particles of unique composition and magnetic behavior. This paper demonstrates the facility of this technique in the creation of iron oxide particles with various magnetic properties.

Iron oxides are widely used in magnetic storage media [1]. Bate has reviewed those iron oxide reactions which are relevant to the preparation of particles for recording media [2]. Most of these reactions involve aqueous phase precipitation and subsequent oxidation–reduction processes. On the other hand, an aerosol technique has been used to generate iron oxide particles [3], but their magnetic properties have not been studied.

2. Experimental methods

Fine iron oxide particles have been prepared by an aerosol technique similar to that described by

Ramamurthi and Leong [3]. Fig. 1 is a schematic diagram of the aerosol generation system used in this study. Ferric sulfate was dissolved in distilled, deionized water and nebulized to form a liquid drop aerosol of this solution. The ferric salt was used rather than the ferrous salt because the latter slowly decomposes to Fe$_2$O$_3$ in aqueous solution. To a first approximation the mean iron oxide particle size is linearly dependent on the cube root of the initial Fe$_2$(SO$_4$)$_3$ concentration. We used concentrations in the range of 15 to 20 g/ℓ. The solution was nebulized at a rate of about 5 mℓ/h using a constant output atomizer (Model 3075, TSI, St. Paul, MN) at a pressure of 35 psig producing a mass flow of roughly 80 mg/h of Fe$_2$(SO$_4$)$_3$ and a gas flow (N$_2$) of 2.6 ℓ/min. The liquid drop aerosol stream passed through a diffusion dryer (a 60 cm long, 2 cm ID wire screen surrounded by the desiccant CaSO$_4$) to remove the water. The dried ferric sulfate particles then passed through a tube furnace. This furnace con-
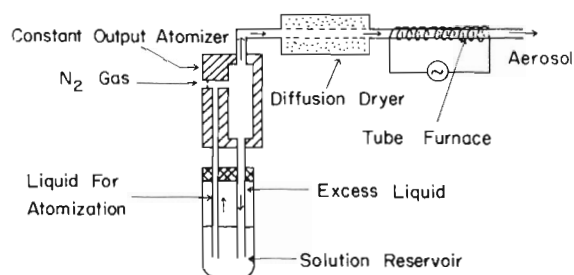

Fig. 1. Schematic diagram of the aerosol particle generator.

sisted of a 1 cm ID quartz tube which was held at 800°C. The residence time of the particles in the tube could be varied by changing the length of the heated section of the tube furnace. It was in this tube furnace that initial decomposition of the ferric sulfate to form the iron oxides occured.

After the tube furnace, the aerosol particles were collected on cover glasses by thermophoresis. Our thermophoretic precipitator consisted of two 6 cm by 12 cm metal plates placed 1 mm apart. A thermal gradient was established by maintaining room temperature on one plate and 500°C on the other plate. The particles deposited on the cover glasses which were held on the cold plate. Thermophoretic sampling has the advantage that all sizes of particles are collected with equal efficiency and it makes use of the already hot aerosol gas coming out of the tube furnace. Powder samples were obtained by scraping the particles off the cover glasses.

Once the particles were obtained, further heat treatments, beyond the few seconds of residence time in the tube furnace, were made in an oven. These treatments were made in both nitrogen and air environments at different temperatures and for different times.

A number of physical observations were made to characterize the particles produced in the above manner. The microstructure of the fine particles was studied by scanning electron microscopy (SEM), and electron and X-ray diffraction. A SQUID magnetometer was used to measure the magnetic properties of the particles.

3. Results and discussion

3.1. As-received samples

By varying the residence time (t_R) of the aerosol in the tube furnace, two samples "as received" were made from the aerosol generator: $t_R = 0.7$ and $t_R = 1.4$ s. X-ray diffraction studies showed a mixture of crystallized phases of α-Fe$_2$O$_3$ and γ-Fe$_2$O$_3$ in both samples. Magnetization data confirmed these mixture phases because both samples had saturation magnetization values between those of α-Fe$_2$O$_3$ (0.6 emu/g) and γ-Fe$_2$O$_3$ (76 emu/g) bulk materials.

Table 1
Phases and magnetic properties of the as-received samples at 300 K

T_R (s)	Phases	σ_s (emu/g)	H_c (Oe)
0.7	α-Fe$_2$O$_3$, γ-Fe$_2$O$_3$	24.4	0
1.4	α-Fe$_2$O$_3$, γ-Fe$_2$O$_3$	13.3	28

Table 1 gives the data for the as-received samples. The saturation magnetization, σ_s, decreases with the increase of residence time which indicates a transformation of γ-Fe$_2$O$_3$ to α-Fe$_2$O$_3$. This is consistent with qualitative changes in the X-ray peaks due to each phase in the samples and with our earlier report on iron oxide particles produced from ferrous sulfate [4].

Scanning electron microscopy was used to size the aerosol particles and to determine the morphology. All particles were spherical in shape. Fig. 2 displays a log-probability plot of the particle size distribution for an as-received sample. The nearly linear dependence seen in fig. 2 indicates the size distribution is log-normal. From fig. 2 we obtained a count median diameter of 0.1 μm with a geometric standard deviation of 2.0. This geometric standard deviation is the same as measured on a NaCl aerosol produced by the same atomizer [5].
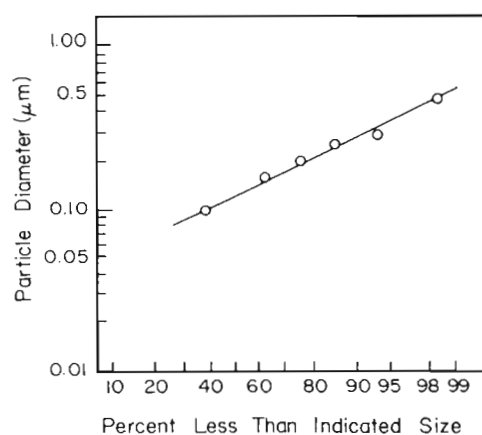

Fig. 2. Log-probability plot of the particle size distribution for an as-received sample. Particles were spherical. Straight line indicates a log-normal distribution.

Table 2
Phases and magnetic properties of the 4 h (14 400 s) heat-treated samples at 300 K

Treatment	$500\,^\circ$C in air	$800\,^\circ$C in air	$500\,^\circ$C in N_2	$800\,^\circ$C in N_2
σ_s (emu/g)	1.8	1.0	12.5	78.1
Phases	α-Fe_2O_3	α-Fe_2O_3	α-Fe_2O_3 γ-Fe_2O_3	α-Fe_2O_3 Fe_3O_4

3.2. Heat-treated samples

The as-received samples have indicated a transformation of γ-Fe_2O_3 to α-Fe_2O_3 with time at high temperature. The second or so of the residence time available to the aerosol in the tube furnace, however, is simply not long enough to complete this transformation. Thus we have heat-treated the as-received samples at 500 and $800\,^\circ$C in both air and N_2 gas for 4 h. The phases, as determined by X-ray diffraction, and magnetization results are shown in table 2.

Many authors have studied the transformation of γ-Fe_2O_3 to α-Fe_2O_3. Imaoka [6] found that for non-acicular particles this transformation took place at $250-400\,^\circ$C whereas $400-500\,^\circ$C was reported by Bando et al. [7].

Table 2 shows that a nearly complete $\gamma \rightarrow \alpha$ transformation can be reached by heat-treating samples in air at 500 and $800\,^\circ$C. Magnetization values of 1.8 and 1.0 emu/g for these two samples are very close to that in α-Fe_2O_3 bulk (0.6 emu/g) but suggest the possibility of some small remnant of γ-Fe_2O_3. Thus these results confirm previous work [6,7]. Heat-treating in nitrogen environment, however, is different. The $500\,^\circ$C heat-treatment temperature only decreased the magnetization by 6% relative to the $t_R = 1.4$ s sample (from 13.3 to 12.5 emu/g) and the mixture of α-Fe_2O_3 and γ-Fe_2O_3 still remained.

When heat-treated at $800\,^\circ$C in nitrogen gas, the sample experienced an obvious change both in magnetization and phases. Magnetization became 4.9 times that at $t_R = 1.4$ s. The original α-Fe_2O_3 and γ-Fe_2O_3 mixture of phases in the as-received samples became a mixture of α-Fe_2O_3 and Fe_3O_4.

Transformation from α and γ ferric oxides to magnetite in N_2 gas is described by the following reaction

$$6Fe_2O_3 \rightarrow 4Fe_3O_4 + O_2.$$
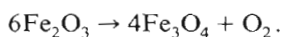
In oxygen-rich environments (e.g. air) ferric oxide cannot lose oxygen atoms to become magnetite due to the finite partial pressure of O_2. When heated in air, γ-Fe_2O_3 transforms to the most stable form of ferric oxide, α-Fe_2O_3.

It seems that when we heat-treat the sample in a nitrogen environment at $800\,^\circ$C, gradual evolution through three phases (γ-Fe_2O_3, α-Fe_2O_3 and Fe_3O_4) is involved. Therefore, we heat-treated our samples under these conditions for different times. This heat-treatment time has the same meaning as the residence time and is added to the original residence time. Table 3 shows the evolution of phases and magnetic properties with this residence time. Magnetization and coercivity are also shown in figs. 3 and 4.

While heat treatment caused a monotomic increase of magnetization, coercivity responded differently. The spherical morphology of the particles and low magnetocrystalline anisotropy of iron oxides contributed to the relatively low coercivity (below 265 Oe). The higher coercivity found at the intermediate residence time may be attributed to the coexistence of two strong magnetic phases

Table 3
Evolution of phases and magnetic properties as a function of time when heat treated at $800\,^\circ$C in a N_2 environment

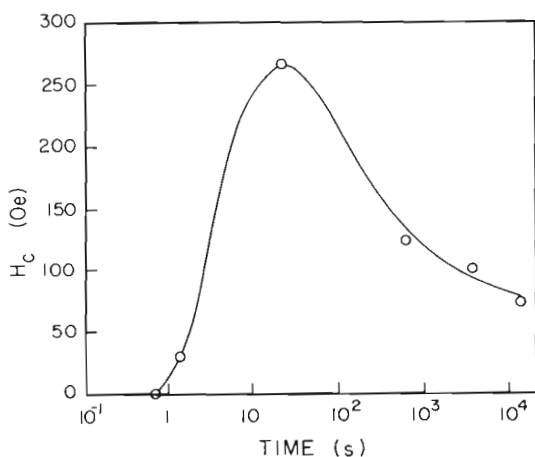| Sample	T_R (s)	Phases	α_s (emu/g)	H_c (Oe)
1	0.7	α-Fe_2O_3 γ-Fe_2O_3	24.4	0
2	1.4	α-Fe_2O_3 γ-Fe_2O_3	13.3	28
3	21.4	α-Fe_2O_3 γ-Fe_2O_3 Fe_3O_4	20.2	265
4	600	α-Fe_2O_3 γ-Fe_2O_3 Fe_3O_4	39.2	125
5	3600	α-Fe_2O_3 Fe_3O_4	68.0	100
6	14 400	α-Fe_2O_3 Fe_3O_4	78.1	75

Fig. 3. Saturation magnetization as a function of heat-treatment time at 800°C in a N_2 atmosphere.

Fig. 5. Phase behavior as a function of heat-treatment time at 800°C in a N_2 atmosphere.

(γ-Fe_2O_3 and Fe_3O_4) which changed the magneto-crystalline anisotropy. When the γ-Fe_2O_3 disappeared, the coercivity dropped.

An estimate of the fractions of each phase in the samples was obtained by considering the total magnetization value of the samples and the known values of σ_s for the bulk α-Fe_2O_3 (0.6 emu/g at 300 K), γ-Fe_2O_3 (76 emu/g at 300 K) and Fe_3O_4 (92 emu/g at 300 K). For samples 1, 2, 5 and 6, this estimate was straightforward because only

Fig. 4. Coercivity as a function of heat-treatment time at 800°C in a N_2 atmosphere.
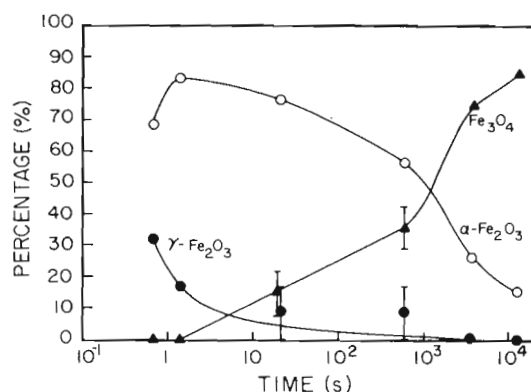
two phases were observed. For samples 3 and 4 X-ray diffraction indicated the existence of three phases. Therefore we made estimates by assuming that the fraction of γ-Fe_2O_3 decreased linearly and has a range of 16.8% (corresponding to $t_R = 1.4$ s) to 0% (corresponding to $t_R = 3600$ s). Error bars were given to these two points. All estimates are illustrated in fig. 5.

The evolution for the three phases with time can be easily seen in fig. 5. α-Fe_2O_3 existed in the whole process and decreased with time except for a narrow region at small time. γ-Fe_2O_3 decreased monotonically and disappeared around 1000 s. Fe_3O_4 started to appear around 10 s and grew at the expense of the other ferric oxides. Fig. 5 suggests that a high fraction of Fe_3O_4 can be obtained by long heat-treatment time in an oxygen-free environment.

4. Conclusions

We find that aerosol synthesis of small, magnetic iron oxide particles is a facile and useful method. Small spherical particles of iron oxide were readily obtained. The phase composition of these particles could be varied among various mixtures of α-Fe_2O_3, γ-Fe_2O_3 and Fe_3O_4. The magnetic properties of the particles directly followed from the phases present and their bulk properties.

Acknowledgment

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