Magnetic studies of fine iron and iron-oxide particles

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The magnetic and structural properties of fine iron and iron-oxide particles have been studied. The samples of iron oxide were prepared by the aerosol method and those of pure iron were prepared by the vapor deposition technique. Electron micrographs showed the size of aerosol particles to be 200 nm and that of vapor deposition particles to be 10–20 nm. The maximum coercivity at 10 K obtained for aerosol particles was approximately 700 Oe, and for vapor deposited particles it was 1540 Oe.

I. INTRODUCTION

Fine magnetic particles show unique magnetic properties which are interesting both scientifically and technologically. The properties may be different from their bulk. For Fe and Co the saturation magnetization is reported to be 20%–90% of that of the bulk metals, depending on the fineness of the particles.[1] Ultrafine magnetic particles of these samples show high coercivities exceeding 1000 Oe. A giant coercivity of 2500 Oe has recently been reported[2] in granular Fe-(SiO_2) solids at 2 K.

Our research effort is aimed at creating fine particles with interesting and unique magnetic properties. We intend to explore a variety of preparation techniques which may lead to a variety of composition, phases, and particulate morphologies. This variety of techniques will also give us greater facility in the materials we can process into fine particles. In this paper we report our initial efforts in the use of two techniques, aerosolization of aqueous solutions and vapor deposition, to create fine particles of iron and iron-oxides. We study the phase, morphology, magnetic hysteresis, and magnetic moment of the particles. Knowledge gained from the creation of these well-known particles will be useful when the techniques are applied to more unusual materials.

II. EXPERIMENTAL METHOD

Iron-oxide particles were prepared by an aerosol technique. A solution of 10 g/ℓ $FeSO_4$ in H_2O was nebulized using N_2 gas. The aerosol was forced to pass through a quartz tube, which was heated to 800 °C. Decomposition of aerosol in the quartz tube produced fine particles of iron-oxides.[3] These fine particles were collected on cellulose millipore filters with 0.22-μm pore size. By varying the residence time (t_R) of the aerosol in the quartz tube, different samples of color varying from red to brown were obtained.

The Fe ultrafine particles (UFPs) were prepared by vapor deposition.[4] Bulk iron was evaporated from an Al_2O_3-coated tungsten basket in an Ar pressure of 4–10 Torr. The system was evacuated to a base pressure of 0.013–0.015 Torr, purged twice with argon at ~1/2 atm, then pumped to the final pressure while maintaining a slow flow of Ar. A water-cooled copper substrate was used to collect the samples. The distance between the substrate and the tungsten basket was about 2.3 cm. Particle size depends on this distance and on the pressure.[5] To prevent total oxidation of these Fe particles, an iron oxide layer was created on their surface, as suggested in Ref. 1. This was done by adding 1/2-Torr air with the low pressured Ar and waiting 10 min before bringing the particles to air.

TABLE I. Summary of data for Fe-oxide particles.

Sample	t_R (s)	Phases	Flowrate (L/min)	M_s (emu/g); H_c (Oe) T(K)				
				10	77	150	220	300
1	0.94	29% γ-Fe_2O_3 71% α-Fe_2O_3	2.0	46; 550	28.5; 280	25.7; 185	24.6; 110	22.5; 80
2	1.26	21% γ-Fe_2O_3 79% α-Fe_2O_3	1.5	25; 700	19.6; 310	18.4; 180	17.5; 120	16.5; 80
3	1.88	21% γ-Fe_2O_3 79% α-Fe_2O_3	1.0	20.7; 75	15.4; 90	14.8; 60	14.4; 45	16.2; 75
4	3.76	9% γ-Fe_2O_3 91% α-Fe_2O_3	1.0	11.6; 90	8.4; 80	7.9; 50	7.5; 60	7.1; 60
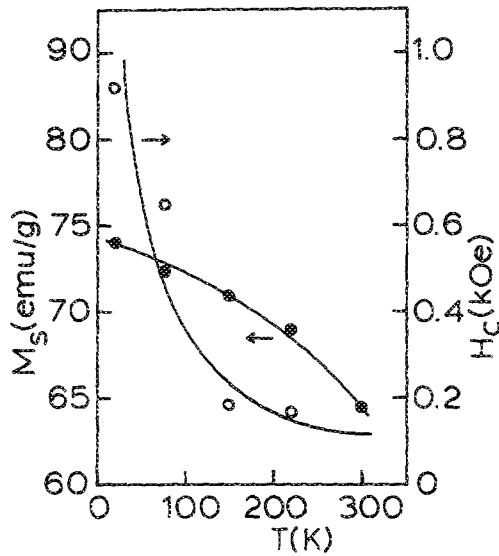
FIG. 1. Saturation magnetization and coercivity as a function of temperature for Fe_3O_4 particles.

FIG. 2. Fit of magnetization to the $T^{3/2}$ law in Fe particles.

A SQUID magnetometer was used to measure the magnetic properties of the particles. A Jeol 100 CX scanning transmission electron microscope was used to examine the microstructure of the fine particles.

III. RESULTS AND DISCUSSION

A. Aerosol particles

X-ray diffraction studies showed that more red colored powders, produced with long t_R, were predominantly α-Fe_2O_3 and those more brown colored were mostly γ-Fe_2O_3. A third sample of black color was obtained by adding H_2 gas to the N_2 gas. It was predominantly Fe_3O_4.

As t_R increases, M_s and H_c decrease (Table I). The maximum M_s (46 emu/g at 10 K) and H_c (550 Oe at 10 K) were obtained for the brown particles of $t_R = 0.94$ s. Table I shows the temperature dependence of saturation magnetization (M_s) and coercivity (H_c) for the red and brown (long t_R and short t_R) samples. Figure 1 also shows the temperature dependence of M_s and H_c for the black colored aerosol sample (Fe_3O_4).

The approximate composition of the particles was determined by the x-ray results. An estimate of the amount of α-

Fe_2O_3 and γ-Fe_2O_3 of the particles was also obtained by considering the total M_s of the particles and the known values of M_s for γ-Fe_2O_3 (76 emu/g at 300 K) and for α-Fe_2O_3 (0.6 emu/g at 300 K) for the bulk materials. These measurements, confirmed by x-ray diffraction, indicate that the relative amount of α-Fe_2O_3 increases wtih the residence time t_R (Table I). When t_R is large, the particles get enough time to go to the more stable α-Fe_2O_3 state. Since M_s and H_c were larger for smaller t_R, M_s, and H_c can be controlled by controlling t_R.
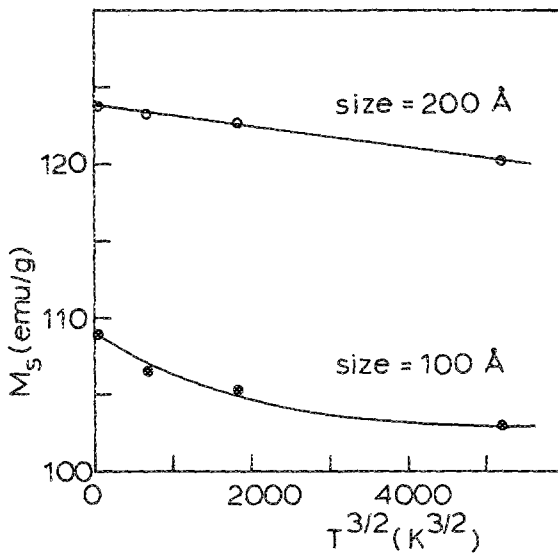
Electron micrographs showed a spherical particle shape with an average size of 200 nm in diameter which was independent of t_R.

B. Vapor deposited particles

Table II shows the data for Fe particles produced by vapor deposition. Larger Ar pressure during evaporation resulted in bigger particle sizes. The M_s values obtained varied from 47% to 55% of the bulk iron moment when the particle size increased from 10 to 20 nm. The smaller particles, on the other hand, had a larger coercivity, equal to 1540 Oe at 10 K.

Both M_s and H_c decreased with increasing temperature. The $BT^{3/2}$ temperature dependence[6] of M_s is obeyed for the larger Fe particles but not for the smaller ones (Fig. 2). The

TABLE II. Summary of data for vapor-deposited Fe particles.

Sample	Pressure (Torr)	Particle size (Å)	Phase (%)	M_s(emu/g); H_c(Oe)			
				T(K)			
				10	77	150	300
1	4	100	47% α-Fe 53% α-Fe_2O_3	108.8; 1540	106.5; 1130	105.4; 930	103.0; 730
2	10	200	55% α-Fe 45% α-Fe_2O_3	123.9; 915	123.3; 670	122.7; 650	120.4; 550
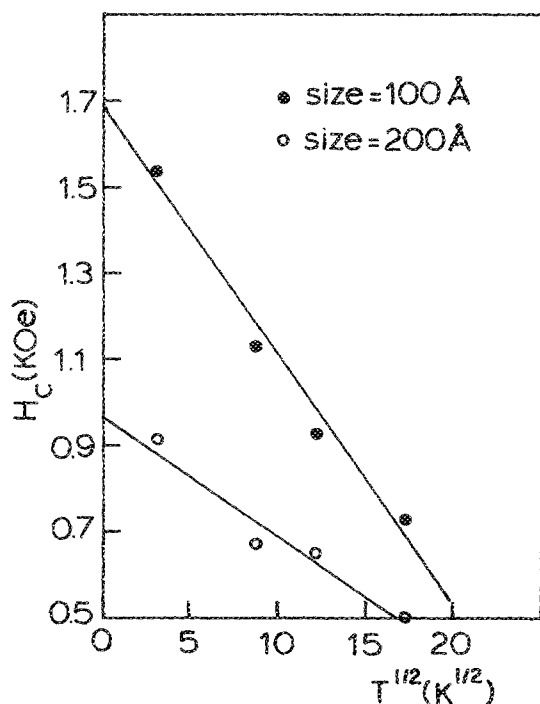
FIG. 3. Coercivity fit to $T^{1/2}$ law predicted for superparamagnetic particles.

(a)

(b)

FIG. 4. (a) Electron diffraction pattern and (b) microstructure of particles evaporated at 4 Torr.

coefficient B is found to be $B = 5.5 \times 10^{-6}$ K$^{-3/2}$ as compared to the value of 3.4×10^{-6} K$^{-3/2}$ for bulk iron.[6]

The temperature dependence of H_c is quite different from that reported by Tasaki, Takao, and Tokunaga.[1] The coercivity of their samples increased slightly from 1100 to 1350 Oe upon cooling from 300 to 77 K. This kind of behavior indicates that the superparamagnetic blocking temperature of their samples is much higher than that of the samples in this study. The coercivity data at different temperatures can be fitted to the $T^{1/2}$ relation predicted for superparamagnetic particles[7] (Fig. 3). From the slope of the straight line, KV can be found where V is the particle volume and K is the magnetic anisotropy. Since the size of the particles is known a value of K can be determined. K is found to be larger, $K = 5.7 \times 10^6$ erg/cm^3, in the smaller Fe particles (100 Å) decreasing to 9.86×10^5 erg/cm^3 in larger Fe particles (200 Å). For bulk Fe,[7] $K = 4.8 \times 10^5$ erg/cm^3. It is clear from these data that both M_s and anisotropy K show strong size effects.

Figure 4 shows the electron diffraction pattern and microstructure of particles evaporated at 4 Torr. The d spacings found from the diffraction pattern were similar to those of α-Fe. It was expected that there would be a coating of α-Fe$_2$O$_3$ on the surface of the particles as α-Fe$_2$O$_3$ is the most stable state of the iron-oxides. However, no lines were observed for α-Fe$_2$O$_3$ in the electron diffraction pattern indicating that any oxides that may be present are in the amorphous state. Assuming a constant M_s value for Fe independent of particle size, a rough estimate of the amount of oxide can be made (Table II). This assumption may be reasonable because the particles are bigger than those for which size effects are predominant. The amount of α-Fe so calculated is
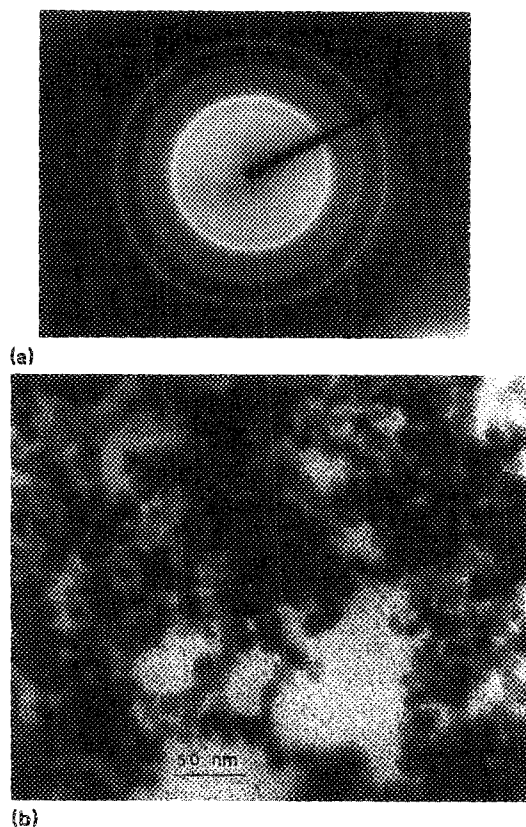
about 50%. Further work is required to determine unequivocally the amount of oxides present.

IV. CONCLUSION

In conclusion, it is shown here that both the aerosol and vapor deposition techniques are viable methods for creation of iron and iron-oxide particles. The aerosol method leads to fairly large particles (200 nm) which can be modified in phase and composition during production. No size-dependent magnetic properties were seen. The vapor deposition method can be used to create smaller particles of iron with controllable size. Size-dependent magnetic properties are seen at this size level (10–20 nm). Use of these preparation techniques for future studies of iron and more unusual materials is warranted and shows promise.

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