

Magnetic and structural properties of vapor-deposited Fe-Co alloy particles

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The structural and magnetic properties of two Fe-Co alloy particles with composition $\text{Fe}_{100-x}\text{Co}_x$ ($x=45,65$) were studied using x-ray diffraction, x-ray photoelectron spectroscopy, transmission electron microscopy, superconducting quantum interference device magnetometry, and Mössbauer spectroscopy. The particles were nearly spherical in shape with an average particle size around 350 Å. Particles formed long chains and showed a core/shell particle morphology. X-ray diffraction and Mössbauer studies showed the presence of bcc α -Fe-Co and CoFe_2O_4 phases with the former as the majority phase in $\text{Fe}_{55}\text{Co}_{45}$ and the latter the majority phase in $\text{Fe}_{35}\text{Co}_{65}$. The room-temperature coercivities of both of these samples were much higher than those in Fe particles with values exceeding 2.2 kOe. The $\text{Fe}_{35}\text{Co}_{65}$ sample showed a drastic temperature dependence of coercivity from 1.5 kOe at 300 K to 15 kOe at 10 K. The structural and magnetic data suggest a core/shell morphology with the surface oxide layer having a very important impact on both the magnitude and temperature dependence of the coercivity of the whole particle.

Previous studies on Fe, Co, and Ni particles prepared by gas evaporation have shown large coercive forces with values of 1050, 1200, and 100 Oe, respectively.¹ Transmission electron microscopy (TEM) and Mössbauer studies indicated a core-shell particle structure with a metallic core surrounded by the corresponding oxide shell. Micromagnetic calculations² and experimental studies³ on passivated and unpassivated $\gamma\text{-Fe}_2\text{O}_3$ particles have shown that the thickness and magnetic state of the oxide layer affects the switching fields and hence the coercivity of the particle. In passivated Fe and Co particles the hysteresis behavior was found to be strongly dependent on the amount of surface oxidation and the magnetic interaction at the core-shell interface was claimed to be responsible for the high coercivity.⁴ Previous work⁵ on Fe-Co alloy particles has shown coercivities exceeding 2.5 kOe which are much higher than those of either Fe or Co particles. A similar behavior has been observed on elongated Fe-Co particles prepared by electrodeposition⁶ and the high coercivity was attributed to the presence of a cobalt ferrite oxide layer on the surface of the particle.

In the present paper we try to understand the origin of the high coercivity of Fe-Co alloy particle samples by comparing their structural, microstructural, and magnetic properties.

Two Fe-Co alloy particle samples prepared by the gas evaporation method were obtained from Vacuum Metallurgical Co., Japan.

The structure of the particles was determined by x-ray diffraction (XRD) and selected area diffraction (SAD) patterns. The particle size was determined by transmission electron microscopy (TEM) and their composition was deter-

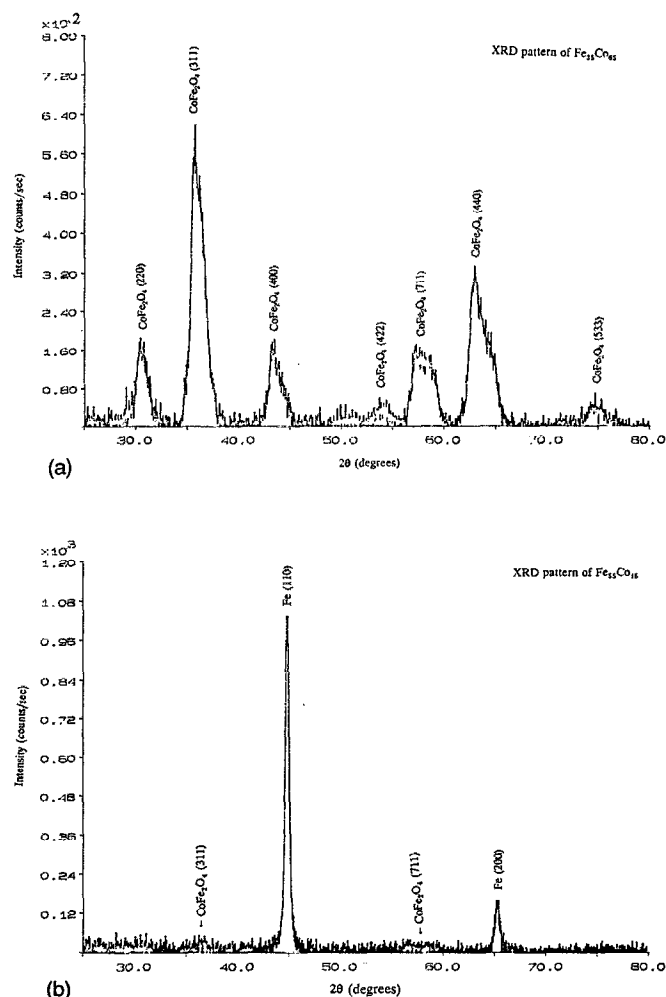


FIG. 1. XRD patterns of the Fe-Co samples: (a) $\text{Fe}_{35}\text{Co}_{65}$, (b) $\text{Fe}_{55}\text{Co}_{45}$.

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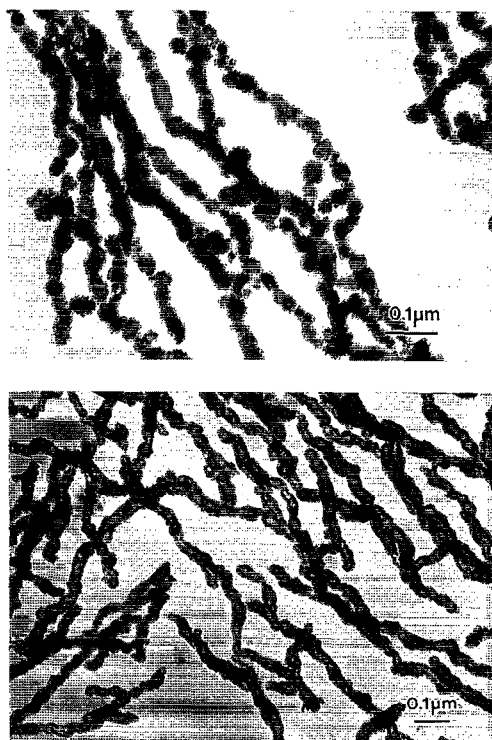


FIG. 2. Bright-field TEM micrographs of (a) $\text{Fe}_{55}\text{Co}_{45}$ and (b) $\text{Fe}_{35}\text{Co}_{65}$.

mined by energy dispersive x-ray analysis (EDAX). X-ray photoelectron spectroscopy (XPS) was used to probe and characterize the surface of the particles. The magnetic properties were measured by both a vibrating sample magnetometer (VSM) and a superconducting quantum interference device (SQUID) magnetometer. Mössbauer spectroscopy was also carried out to determine the type of the oxides present.

The two samples studied had a nominal composition $\text{Fe}_{100-x}\text{Co}_x$ with $x=45$ and 65 . EDAX measurements gave the x values of 43 and 64 , respectively.

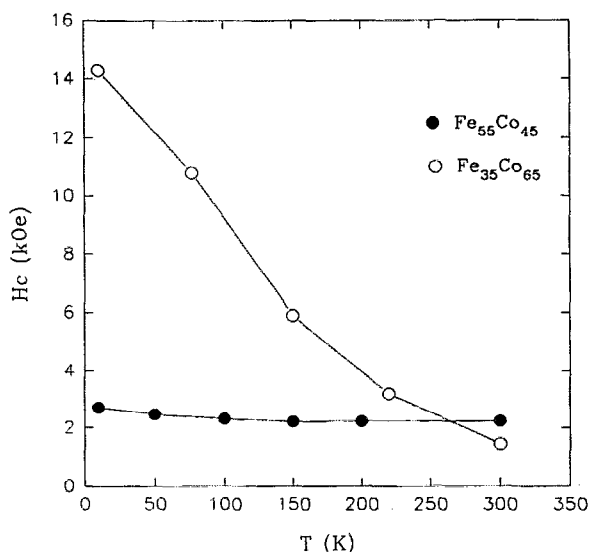


FIG. 3. Temperature dependence of coercivity in the two Fe-Co samples.

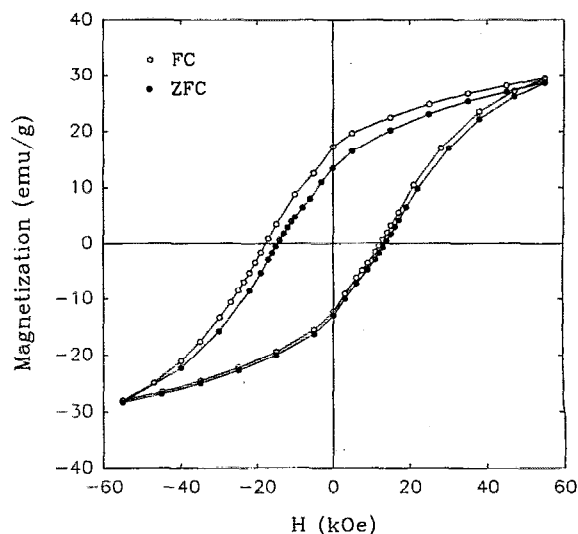


FIG. 4. Zero-field-cooled (ZFC) and field-cooled (FC) hysteresis loop in an $\text{Fe}_{35}\text{Co}_{65}$ sample.

The x-ray diffraction pattern of $\text{Fe}_{55}\text{Co}_{45}$ was dominated by bcc Fe-Co, with few extremely weak and broadened peaks corresponding to CoFe_2O_4 [Fig. 1(a)], while the pattern of $\text{Fe}_{35}\text{Co}_{65}$ showed strong and relatively broadened peaks corresponding to CoFe_2O_4 [Fig. 1(b)]. The asymmetric broadening of the CoFe_2O_4 peaks may be due to the small grain size and the off-stoichiometric composition of CoFe_2O_4 . The presence of an Fe/FeCo phase could not be detected unambiguously due to the overlap of its d spacing with that of the asymmetric broadened peaks of the CoFe_2O_4 phase. Selected area diffraction (SAD) patterns agreed with the XRD results.

Bright-field micrographs obtained for the two samples revealed that the particles were about spherical in shape and formed a long chain-like structure. The average grain size of the two samples was about the same and ~ 350 Å (Fig. 2). The particles in the $\text{Fe}_{35}\text{Co}_{65}$ sample showed a very distinct contrast between the inside core area and surface shell region as shown in Fig. 2(b).

The magnetic properties of these samples were measured in the temperature range from 10 to 300 K. $\text{Fe}_{35}\text{Co}_{65}$ showed an M_s around 30 emu/g while in $\text{Fe}_{55}\text{Co}_{45}$ M_s was much

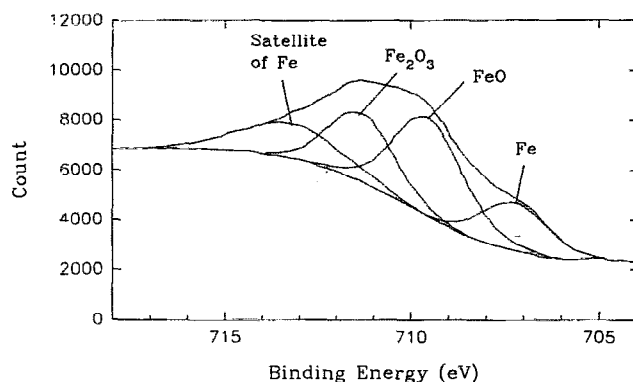


FIG. 5. XPS spectra of $\text{Fe}_{55}\text{Co}_{45}$.

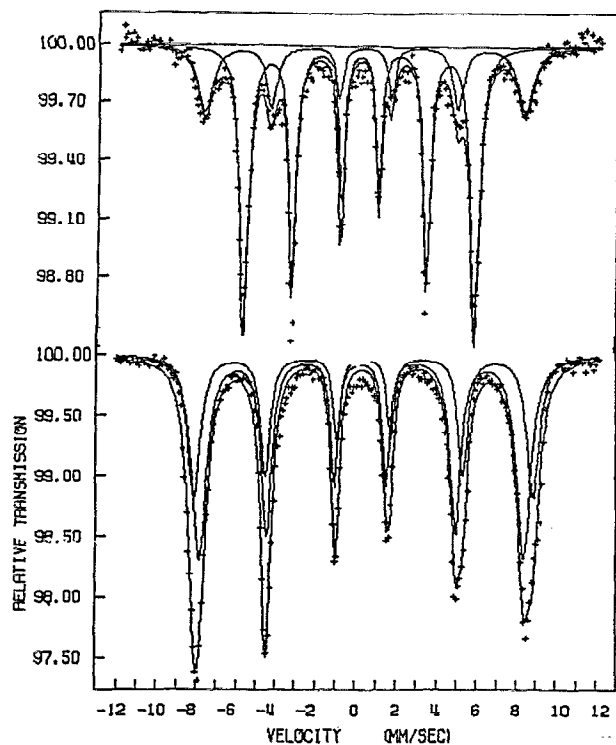


FIG. 6. Mössbauer spectra of the two Fe-Co samples (a) $\text{Fe}_{55}\text{Co}_{45}$, (b) $\text{Fe}_{35}\text{Co}_{65}$.

higher, over 170 emu/g. Such a difference in the magnetization of the two samples could be due to the presence of a large amount of CoFe_2O_4 in $\text{Fe}_{35}\text{Co}_{65}$ as compared to $\text{Fe}_{55}\text{Co}_{45}$, and to possible surface spin pinning in the former because of a thicker cobalt ferrite shell. The decrease in M with increasing T (10–300 K) was only about 5%. The remanence was about 0.5 in both the samples. The temperature dependence of coercivity for the two samples was quite different, as shown in Fig. 3. The coercivity of the $\text{Fe}_{35}\text{Co}_{65}$ sample was ~ 1.5 kOe at 300 K and increased to 15 kOe at 10 K (about 900% increase) while the coercivity of the $\text{Fe}_{55}\text{Co}_{45}$ sample was 2.2 kOe at 300 K and increased slightly to 2.7 kOe at 10 K (only 25% increase).

Field-cooled hysteresis loops on both samples showed a shift to the left (Fig. 4) with the value of the shift much larger in the $\text{Fe}_{35}\text{Co}_{65}$ sample (about 3 kOe in $\text{Fe}_{35}\text{Co}_{65}$ and 0.5 kOe in $\text{Fe}_{55}\text{Co}_{45}$ at 10 K). The shift in the field-cooled (FC) loops ($H_{\text{cool}}=20$ kOe) is believed to be the result of exchange interaction at the interface of a core-shell particle morphology. The larger amount of shift in $\text{Fe}_{35}\text{Co}_{65}$ is consistent with the presence of a thicker cobalt ferrite shell.

XPS is a sensitive technique to detect the type of oxides on the surface of the particles. The presence of the Fe-Co oxides was determined by deconvoluting the asymmetric broadening of the higher-energy edge of the metallic Fe and Co peaks. Figure 5 shows the spectrum of $\text{Fe}_{55}\text{Co}_{45}$ around the binding energy of Fe. These data show clearly the presence of surface oxides in both samples. Because XPS probes the surface layer, a thin Fe-O layer on the surface can result in a corresponding peak in the spectrum.

TABLE I. Mössbauer parameters. δ is the isomer shift. ΔE_Q is the quadrupole splitting. H is the hyperfine field.

Sample	δ (mm/s)	ΔE_Q (mm/s)	H (kOe)	ΔH (kOe)	%	Phase
$\text{Fe}_{55}\text{Co}_{45}$	0.40	0.02	504	20	28	$(\text{Fe},\text{Co})_3\text{O}_4$
	0.14	-0.004	362	80	72	Fe-Co
$\text{Fe}_{35}\text{Co}_{65}$	0.37	0.018	506	15	A	$(\text{Fe},\text{Co})_3\text{O}_4$
	0.51	-0.02	529	12	B	

Mössbauer spectra for $\text{Fe}_{55}\text{Co}_{45}$ showed a mixture of Fe-Co alloy and cobalt ferrite while the spectrum of $\text{Fe}_{35}\text{Co}_{65}$ showed only CoFe_2O_4 (Fig. 6). The ratio of Fe^{3+} at the A and B site was 1.6:1 instead of 1:1, indicating an off-stoichiometric CoFe_2O_4 . The Mössbauer parameters are listed in Table I. The fact that no FeO has been observed with Mössbauer indicates a small percentage of this oxide (<5%). This is different in XPS, where a thin FeO layer on the surface can result in a corresponding peak in the spectrum.

The XRD and Mössbauer results on the Fe-Co alloy particles indicated a core-shell particle morphology. In $\text{Fe}_{55}\text{Co}_{45}$ the core is a bcc Fe-Co alloy while the shell consists of Fe-Co oxides with CoFe_2O_4 as the majority oxide. In $\text{Fe}_{35}\text{Co}_{65}$ the core/shell morphology is composed of stoichiometric and off-stoichiometric CoFe_2O_4 , respectively.

Based on the present and our previous experiments with passivated Fe particles,⁴ we believe that the CoFe_2O_4 oxide layer plays an important role in the magnetic properties of the particles. It results in a large surface-pinning force, which impedes the rotation of magnetization near the interface layer toward the direction of the external field, and thus it leads to the high coercivity and nonsaturation effects even at 55 kOe. The anisotropy constant K_1 of CoFe_2O_4 is much higher than that of Fe_3O_4 (the values are 2×10^6 and -1.1×10^5 erg/cm³ at room temperature, respectively⁷) and has a strong temperature dependence: K_1 (0 K) is almost an order of magnitude higher than K_1 (300 K).⁸ This large temperature dependence of K_1 explains the drastic temperature dependence of the coercivity in $\text{Fe}_{35}\text{Co}_{65}$.

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