Effect of oxide layer on the hysteresis behavior of fine Fe particles

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The effects of surface oxidation on the structural and magnetic properties of fine Fe particles prepared by the evaporation technique have been studied using transmission electron microscopy, x-ray photoelectron spectroscopy, superconducting quantum interference device magnetometry, and Mössbauer spectroscopy. By varying the argon pressure, particles were obtained with sizes in the range of 60–350 Å. The hysteresis behavior was found to be strongly dependent on the variation in the amount of surface oxidation. The differences in the magnetic behavior due to variation in size and oxidation have been explained by considering a shell/core model for the particle morphology with the shell consisting of Fe oxides surrounding the α-Fe core.

I. INTRODUCTION

Ultrafine particles (UFPs) of Fe are among the most promising candidates for high density recording media[1] due to their high saturation magnetization and coercivity. Experimental and theoretical investigations are underway to understand the origin of the high coercivity and its temperature dependence. The knowledge derived from these studies can be used to further improve the magnetic properties and develope high density recording media using Fe-based particles.

Fe particles in the nanometer scale are pyrophoric, and need a protective coating (passivation) to resist oxidation when exposed to the ambient. Passivated Fe particles can have a coercivity as high as 3400 Oe[2] at 10 K (for particles with 60 Å diameter) which is three orders of magnitude higher than the bulk Fe value (about 5 Oe). It is not yet clear whether this enhancement in coercivity is due to the small size of the particles or the protective oxide shell around the Fe core. Very little experimental work has been done to probe the effect of the changes in the oxide layer on the hysteresis behavior of Fe particles. Micromagnetic calculations[3] and experimental studies[4] on passivated and unpassivated γ-Fe_2O_3 particles have shown that the thickness and the magnetic state of the oxide layer affect the switching fields and hence the coercivity.

In the present paper, we investigate the changes in the temperature dependence of coercivity in Fe particles by reducing the surface oxidation.

II. EXPERIMENTAL METHODS

UFPs can be produced by various techniques,[5,6] including gas evaporation. With this method, the particles are formed by evaporation and condensation of the bulk metal in an inert atmosphere.

Fine particle samples were made in a bell-jar system, the details of which are given elsewhere.[7] The base pressure used was $\sim 10^{-6}$ Torr. A reasonably good control of the particle size was obtained by varying the argon pressure (10^{-4} to 30 Torr) and (or) the temperature of the evaporation source during formation of the particles. Agglomerates of fine particles were collected on a water-cooled copper plate.

Two groups of samples with different extent of oxidation were prepared. In the first group the particles were passivated by creating an oxide coating on their surface. This was achieved by exposing the particles to a well-controlled argon–air mixture in the bell jar (the ratio of argon: O_2 being ~ 300) for a few hours after evaporation. In the other group, however, effort was made to minimize the extent of oxidation. This was accomplished by sandwiching the Fe particles between two thin films of Ag. These sandwiches were prepared, by first depositing a thin film of silver metal on a kapton substrate, which in turn was adhered to the cold copper substrate; the Fe UFPs were then deposited on the silver film (under suitable argon flow), and then, another silver thin film was deposited on the freshly formed fine particles (referred to as Fe/Ag from now on).

A superconducting quantum interference device (SQUID) magnetometer was used in the temperature range of 10 to 300 K with a maximum applied field of 55 kOe to study the magnetic properties and their temperature dependence. Transmission electron microscopy (TEM) was used to determine the particle size and its morphology. Selected area diffraction (SAD) patterns and x-ray diffraction (XRD) were employed for the crystal structure studies. X-ray photoelectron spectroscopy

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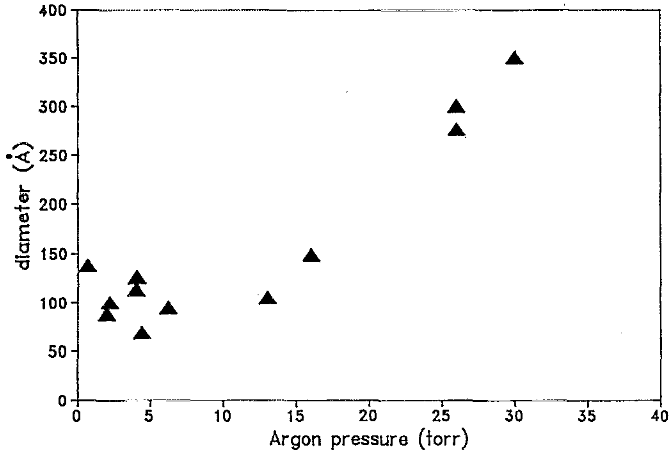

FIG. 1. Change in particle size as a function of argon pressure during evaporation, for passivated Fe particles.

(XPS) was used to find the surface composition and depth profile in the Fe/Ag sandwitches. A Mössbauer spectrometer with a constant acceleration source [^{57}Co(Rh)] was used in the temperature range of 4.2 to 300 K to study the magnetic state of the core and its shell and also to determine the relative amounts of Fe and Fe oxides present.

III. RESULTS AND DISCUSSION

The particle size was found to increase with argon pressure. Figure 1 shows the change in particle size with pressure for the passivated Fe samples.

Particles obtained in this study were roughly spherical. XRD and SAD showed the presence of α-Fe and its oxides Fe_2O_3 and Fe_3O_4 in the passivated Fe samples. The lines due to α-Fe were much sharper in the larger particles as compared to the smaller ones (as expected). The oxide lines were always diffused and broad and this has been attributed to their very fine grain structure[8] in the shell surrounding the Fe core. No evidence of Fe oxides was made from the XRD or SAD patterns on Fe/Ag samples.

XPS is a very sensitive technique to detect different chemical species in a sample with amounts $\geqslant$4 at. %. A typical x-ray photoelectron spectrum of a passivated Fe sample is shown in Fig. 2. The position of the Fe oxides as marked in the spectrum was obtained by deconvoluting the asymmetric broadening of the higher energy edge of the metallic Fe peak. The chemical composition was determined from the relative intensities of Fe and Fe-oxide peaks in the XPS spectrum. For a passivated Fe sample with a median diameter of 214 Å the composition was found to be 68.6% α-Fe, 16.2% Fe_3O_4, 10.6% FeO, and 4.7% Fe_2O_3. After argon etching for 2 min, the amount of α-Fe increased and the amounts of Fe oxides decreased. The increase in the amount of α-Fe indicates that the oxides reside on the surface of the particles. The same surface oxides were obtained when XPS was performed on Fe/Ag particles. The presence of oxides on the surface was not unexpected, since there is always some residual O_2 present in the chamber ($\sim 7 \times 10^9$ molecules/cm^3 even at 10^{-6} Torr) which would result in a thin oxide coating during particle formation. However, this amount was not large enough to show up in either the SAD or XRD patterns.

A typical Mössbauer spectra of a passivated Fe sample with median diameter of 130 Å is shown in Figs. 3(a) and 3(b). At $T = 4.2$ K the spectrum consists clearly of two magnetic hyperfine patterns; the sharp and narrow lines with an effective field near 34 T is due to α-Fe and the others due to Fe_3O_4/γ-Fe_2O_3.[9] At 300 K a broad spectra due to superparamagnetic oxides was observed superimposed on the α-Fe sextet. The absence of the expected quadropole splitting at 300 K from the superparamagnetic Fe oxides may arise from an exchange interaction at the interface of ferromagnetic Fe core and superparamagnetic oxide shell.[8,9] For passivated Fe particles with a diameter of 130 Å [Figs. 3(a) and 3(b)] the relative amounts of Fe and Fe oxides as determined from the areas under their respective Mössbauer spectra were, 28% and 72%, respectively. However, the relative amounts of Fe and its oxides was 90% and 10%, respectively, in a Fe/Ag sample [Fig. 3(c)] ($D = 117$ Å), indicating a strong reduction in oxidation as compared to the passivated Fe samples.

The coercivity of passivated Fe samples was found to depend strongly on both the particle size and temperature.

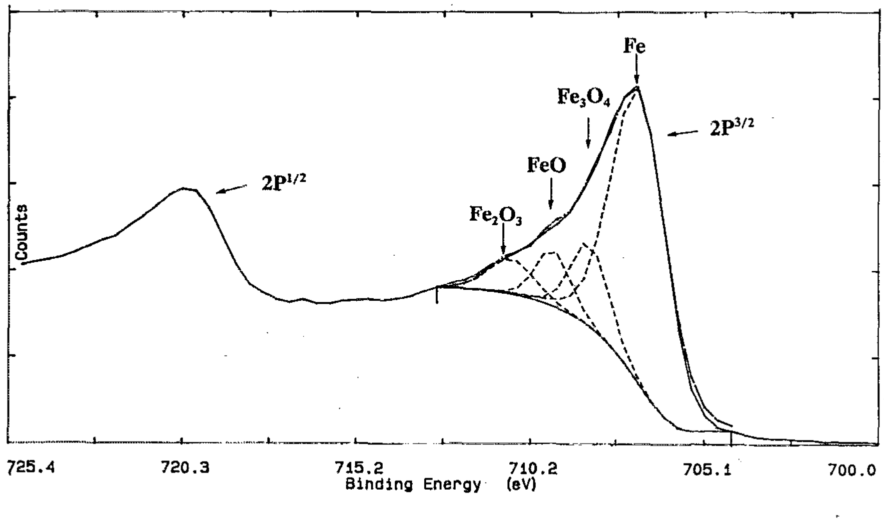

FIG. 2. $2p$ x-ray photoelectron spectrum of a passivated Fe sample with diameter 214 Å, showing the presence of metallic Fe and its oxides.

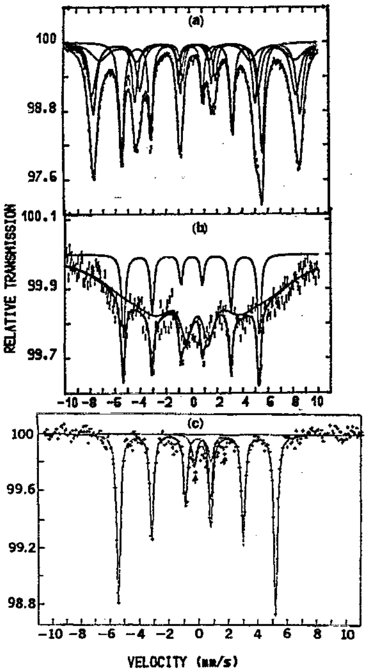

FIG. 3. Mössbauer spectra of passivated Fe particles with 130 Å diameter at (a) $T = 4.2$ K, (b) $T = 300$ K, (c) Mössbauer spectrum of a Fe/Ag sample with 117 Å diameter at $T = 300$ K.

In Fig. 4 the coercivity is plotted as a function of temperature for different core diameters.[9] At low temperatures, the coercivity was higher for smaller particles as compared to the bigger ones. However, this trend was quite reversed at higher temperatures. Furthermore, the temperature dependence of coercivity in smaller particles was much more drastic as compared to the bigger particles. This drastic temperature dependence in smaller particles and the size dependence of coercivity can be explained by considering a core/shell type of model where the core consists of α-Fe and the coating of Fe oxides. The ratio of the Fe oxide to metallic Fe is much higher in smaller particles because of the large percentage of atoms residing on the surface. We believe that in passivated particles the magnetic interaction at the core-shell interface is responsible for the high coercivity. In smaller particles the Fe core feels much more the effects of the Fe–O shell and the absolute temperature coercivity is higher and changes drastically with temperature because of the superparamagnetic behavior of the Fe–O shell. In bigger particles the volume fraction of oxide to Fe is not so large and therefore the influence of the superparamagnetic shell on the Fe core, is not as strong, resulting in much slower temperature dependence of coercivity.

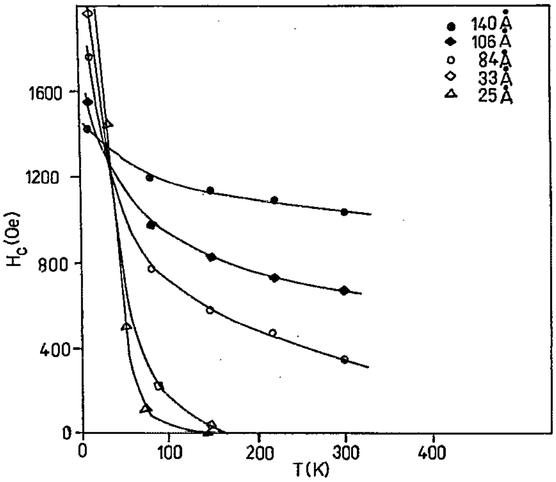

FIG. 4. Temperature dependence of coercivity in passivated Fe samples with different core diameter[2] (where core consists of only α-Fe and is surrounded by its oxides).

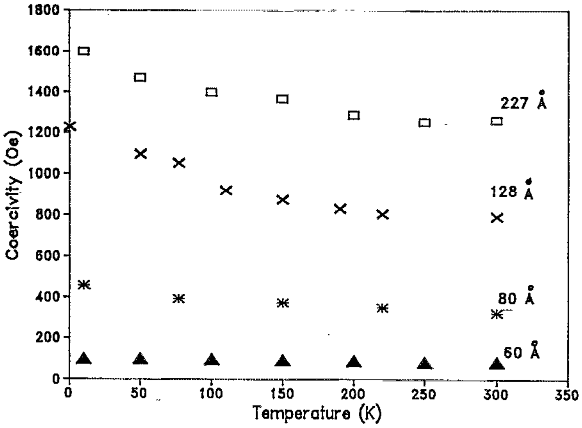

FIG. 5. Temperature dependence of coercivity in different sized Fe/Ag samples.

One would expect to see a different size and temperature dependence for H_c if the surface oxides were removed. This was almost accomplished in the case of Fe/Ag samples. Figure 5 summarizes the same data for Fe/Ag samples where the trend in coercivity with size is totally different from what was observed in passivated Fe samples at cryogenic temperatures (Fig. 4). In fact, the strong temperature dependence of coercivity is also not observed anymore. The same argument as used to explain the hysteresis behavior of passivated particles could also be applied here to explain the size and temperature dependence of coercivity.

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