

EFFECT OF PARTICLE SIZE AND SURFACE CHEMISTRY ON THE INTERACTIONS AMONG FINE METALLIC PARTICLES

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Abstract—The effect of different particle size (50–350 Å) and surface passivation on the magnetic behavior including interactions has been studied and correlated in Fe and Co particles. The effect of packing fraction on the above properties has also been investigated. The dc remanence (IRM and DCD) and ΔM curves have been used to calculate various interaction parameters and quantify them, respectively. Strong exchange coupling at the core-shell interface (intra-particle interactions) has a higher contribution to the overall interactions than the inter-particle dipolar interactions, especially in the smaller particles.

I. INTRODUCTION

The magnetic properties of small particles, including the modes of magnetization reversal, can be greatly affected by interparticle interactions. A knowledge of such interactions in a system of magnetic particles can help to understand and control their magnetic properties and applications. Remanence curves probe the irreversible component of magnetization and can supply important information about the intrinsic magnetic properties of a magnetic system. They are routinely used to characterize particulate media for magnetic recording applications.

The basic dc remanence curves of a magnetic system are called the isothermal remanent magnetization (IRM) and the dc demagnetization curve (DCD). The former is obtained by magnetizing an initially demagnetized sample by applying an increasing field (H) in small steps and measuring the remanence ($M_r(H)$) after the subsequent removal of the field. The latter curve is similarly measured by applying an increasing negative field to an initially saturated sample ($M_r(\infty)$) and remanence ($M_d(H)$) is obtained at the removal of the field. For an assembly of non-interacting, uniaxial, single-domain particles, Wohlfarth (1958) [1] showed that $M_d(H)$ and $M_r(H)$ are related according to the following expression:

$$M_d(H) = M_r(\infty) - 2M_r(H) \quad (1)$$

Any deviations from this relations are attributed to inter-particle interactions as long as the particles retain their single domain and uniaxial behavior.

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In this paper we will report on the magnetic behavior and remanence curves of Fe and Co particles with two different types of surface passivation. The effect of particle size, packing density and surface chemistry on interparticle interactions are studied. The magnetic data (H_c , “squareness” and magnetization) will be correlated with the interaction parameters.

II. EXPERIMENTAL METHODS

Particles of Fe and Co in the size range 50–350 Å were prepared by vapor deposition [2]. The particles were “passivated” in order to be protected from oxidation. Two methods of passivation were used. In one set, passivation was done in the evaporation chamber using a mixture of Ar with O_2 [3]; in the other method the particles were sandwiched between two thin films of Ag [4]. In both cases a core-shell type of morphology resulted where the core is made of the metal and the shell of the metal oxide. The oxide shell thickness in the latter set is much smaller as compared to the former. The chemical composition of oxide shell in Fe and Co particles is $\gamma\text{-Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ and $\text{CoO}/\text{Co}_3\text{O}_4$ respectively. We will refer to the former set as the “passivated” and the latter as $M(\text{Fe, Co})/\text{Ag}$.

Remanence measurements (at $T=10\text{K}$) were made on magnetically fresh powders. Passivated samples were fixed in paraffin wax and M/Ag samples were in the form of a thin layer of particles sandwiched between two Ag films on a Kapton substrate. Pressed samples were prepared by making pellets (very high density) of passivated powders.

Magnetic measurements were performed using a SQUID magnetometer in the temperature range 10–300 K, and in a maximum field of 55 kOe. The structure and morphology of the particles was characterized by X-ray diffraction, transmission electron microscopy (TEM) and electron diffraction.

III. RESULTS

The crystal structure of the Fe and Co metals in all the samples was bcc and fcc, respectively. Magnetic and remanence data of various Fe and Co samples with different particle sizes and surface chemistry are summarized in Ta-

TABLE I
SUMMARY OF THE MAGNETIC AND REMANENCE DATA OF Fe AND CO PARTICLES

Sample I.D.	D (Å)	M_r/M_s	H_c (Oe) at 10K	H_c (Oe) at 300K	H_r (Oe) at 10K	CF %	IFF %	1-S'
Fe-1	81	0.48	2906	0	5782	99	308	0.85
Fe-1 (pressed)	81	0.31	2528	0	6501	157	425	0.60
Fe-2	141	0.53	1716	657	2298	34	25	0.47
Fe-2 (pressed)	141	0.62	1260	350	1790	42	37	0.45
Fe-3	170	0.56	1706	650	2303	35	19	0.35
Fe/Ag-1	65	0.40	227	161	350	54	82	0.72
Fe/Ag-2	113	0.49	1172	570	1597	36	16	0.64
Fe/Ag-3	250	0.53	1706	1117	2303	35	17	0.38
Co-1	92	0.15	1042	100	11419	996	720	-
Co-1 (pressed)	92	0.19	3267	-	12485	282	211	-
Co-2	120	0.44	2870	150	4921	71.4	80	0.81
Co-3	310	0.51	2038	1210	2715	33.2	18	0.40
Co/Ag-1	82	0.43	1882	641	3547	88	135	0.99
Co/Ag-2	120	0.50	2387	1300	3485	46	30	0.45
Co/Ag-3	250	0.51	2506	1554	3371	34	21	0.36

ble I. "Squariness" defined as M_r/M_s increases with particle size. The maximum squariness obtained was ~ 0.5 in all the systems. The room temperature coercivity increases with size in contrast to that at 10 K which decreases as the size increases, except in M/Ag [4].

In all the systems, with the exception of Fe/Ag, the remanence coercivity H_r (at 10K), defined as the field where M_d becomes zero, decreases with increasing particle size. The behavior of H_r is similar to H_c in Fe system but not in the Co. The coercivity factor $CF = (H_r - H_c)/H_c$ [5], interaction field factor $IFF = (H_r' - H_r)/H_c$ [5], where H_r' is the field at which $M_r(H)$ reaches half its saturation value and $(1-S')$ [6,7] derived from DCD curve, were used to quantify the interactions and switching field distributions (SFDs). CF which is influenced by extrinsic factors and IFF which depends on intrinsic interactions decreased drastically as the particle size increased. The effect of packing was always to increase interactions except in the case of small Co particles. $1-S' = M_r / H_r (1/(dM_r/dH)_{H=H_r})$ which characterizes the distribution of energy barriers over which magnetization reverses, also decreases with increasing particle size. A zero value of $(1-S')$ indicates that the system has a square loop and reverses at a unique field.

Figure 1 shows the IRM, DCD and SFDs (obtained by differentiating IRM and DCD) for large (310 Å) and small (92 Å) particles of passivated Co. Figure 2 shows the ΔM curves [8] for Fe and Fe/Ag of different particle size. Figure 3 shows similar data for passivated Co particles. SFDs obtained by differentiating IRM curves of passivated Fe and Fe/Ag samples are shown in figure 4 in order to show the effect of size in addition to the effect of surface passivation.

IV. DISCUSSION

Interactions were always negative, implying that the net

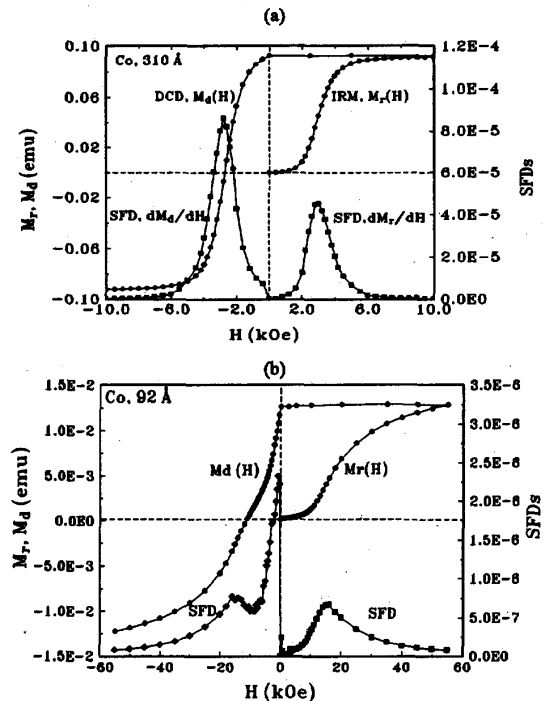


Figure 1. DC remanence curves and SFD of 310 Å (a), and 92 Å (b) passivated Co powders.

effect of intra-/inter-particle interaction is to help demagnetize the system (notice the degree of non-saturation in small Co particles, figure 1b). This also explains the decrease in coercivity with increased packing which in turn increases the interactions (ΔM increases). However this did not hold true in the case of small passivated Co ($D=92$ Å, Table I) and Fe particles, where an increase in H_c and H_r upon increased packing were observed. This behavior was usually observed in particles with size below 100 Å and above a certain surface passivation. This can be explained due to large fraction of surface moments in smaller particles which are canted [9] and upon pressing the powder, would result in a configuration which can oppose the demagnetizing fields, resulting in an effective increase of coercivity as well as decreased interactions.

Smaller particles had much higher interactions, low squariness, larger H_c and H_r , and very broad SFDs (figure 1b and figure 4). The increase in H_c and H_r with decreasing particle size has been attributed [3,4] to a larger anisotropy in small particles due to an increased fraction of oxide shell which is exchange coupled to the core, and also results in surface/interface pinning of moments. The double and very wide nature of the SFDs in smaller particles (fig. 1b and 4) can arise from the strongly pinned interface moments and non-uniform interfaces which would result in wide distribution of energy barriers. The double peak in SFD of small Co sample could be due to various reasons i) the particle size distribution, ii) two distinct type of anisotropic particles pre-

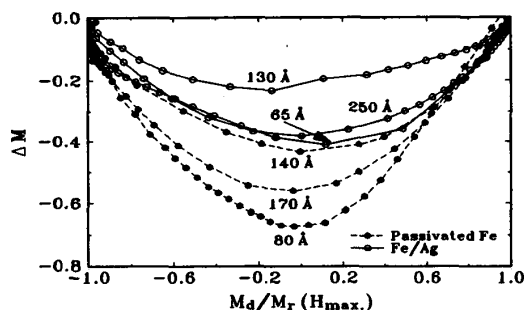


Figure 2. ΔM curves as a function of normalized M_d values, for various sizes of passivated Fe and Fe/Ag samples.

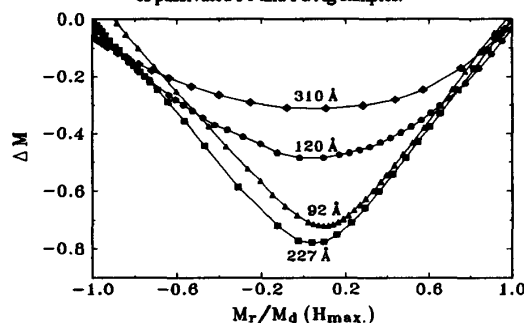


Figure 3. ΔM curves as a function of normalized M_d values, for various sizes of passivated Co samples.

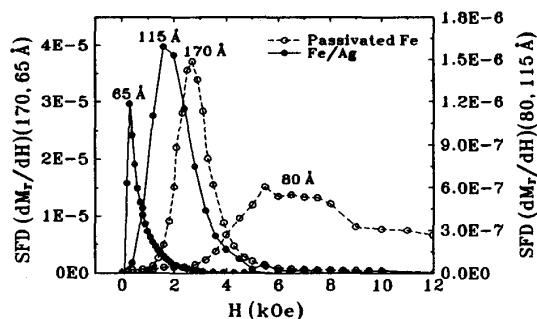


Figure 4. A comparison of the SFD of Fe particles with different size and surface chemistry.

sent in the sample, iii) two different magnetization reversals, an initial core magnetization reversal followed by the shell reversal at a much higher switching field. The first reason could not hold in this case, because of very narrow size distribution (log normal $\sigma \approx 0.1$). The second reason is possible if both "core-shell" type and completely oxidized particles were present together. The third scenario is possible, due to a large anisotropy difference of the core and the shell and very thick oxide shell. Either of the second or third reasons are possible. Similar results have also been predicted using micromagnetic modelling [10]. Large distribution of energy barriers can also explain the small squareness values in smaller particles. Thus the core-shell morphology is largely responsible for the large intrinsic SFDs in passivated small

particles.

Passivated Co or Co/Ag samples when compared to their Fe counterparts exhibit higher interactions. This can also be explained by considering the effect of exchange coupled core-shell. This coupling is much stronger in the case of Co/CoO as compared to Fe/ γ - Fe_2O_3 and/or Fe_3O_4 because of the higher anisotropy of CoO. The magnetic properties of Co particles are immensely affected by this exchange induced anisotropy and can result in anomalous coercivity and remanence behavior at cryogenic temperatures [11].

M/Ag samples, show much lower overall interactions (fig. 2) as compared to their passivated counterparts, even though they should exhibit higher dipolar interactions due to the higher magnetization (due to less Fe-oxides). SFDs in M/Ag samples are much more uniform but exhibit a tail at higher fields (fig. 4).

Though CF, IFF show a monotonic decrease with increasing particle size, the ΔM plots do not follow that. Instead an initial strong decrease with increasing particle size is followed by a subsequent increase which once more reverses its direction as the particle size is further increased (figure 3).

V. CONCLUSIONS

We have shown that an increase in the thickness of the oxide-passivation layer enhances interactions and this indicates that intra-particle interactions are stronger than the interactions among the particles. Strong surface pinning can result in wide energy barrier distributions causing non-uniform switching fields. Very reasonable values of CF and IFF, in addition to magnetic properties were obtained in bigger particles even though the particles were not dispersed and the temperature was low. Studies to correlate the ΔM plots with the IFF and the CF values are under progress.

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