

Magnetic Properties of Ultrafine Co Particles

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Abstract—Fine particles of Co have been prepared in the size range of 50 - 350 Å by the vapor deposition technique. The dependence of magnetization on size and temperature has been studied. A maximum coercivity of 1500 Oe was obtained for a particle size of 350 Å. The magnetic and structural measurements indicate a shell-type structure with a fcc Co core surrounded by a Co-oxide shell. The effect of exchange interactions between the antiferromagnetic Co-oxide shell and the ferromagnetic Co core on the magnetic behavior of the powders has been investigated.

I. INTRODUCTION

Research in the area of fine magnetic particles has been very active because of the potential applications in high density magnetic recording media [1, 2]. Due to their very small sizes (10's to 100's of Å) fine particles possess properties, which are drastically different from the bulk and pose an extremely stimulating scientific problem to study.

Metallic magnetic fine powders prepared under controlled environment can have high magnetization, high coercivity, a narrow size distribution which are required for magnetic recording. Their resistance against environmental and mechanical degradation can be controlled by appropriate preparation conditions. Magnetic interactions among and within the particle clusters are also of immense importance and require special investigation.

In this paper we will report the studies performed on the magnetic and structural properties of Co fine particles prepared by the vapor deposition technique.

II. EXPERIMENTAL

In the vapor deposition method [3, 4], the metal is evaporated in the presence of an inert gas (argon) atmosphere to form aggregates of atoms called particles which can further agglomerate to form clusters of particles. Particles in the size range of 50 - 350 Å were obtained by

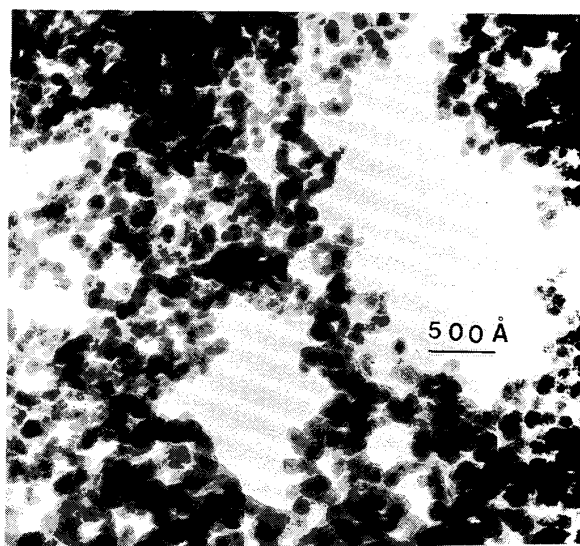


Fig. 1. Bright field TEM of Co particles with an average size of 120 Å. Particles formed were roughly spherical in shape.

varying the residual gas pressure in the chamber during evaporation from 1 to 30 torr and were collected on a water-cooled substrate. An air-argon mixture was used to passivate the particle's surface before exposing them to atmosphere. Crystal structure and morphology were studied using selected area diffraction (SAD), X-ray diffraction and transmission electron microscopy (TEM). Magnetic properties were studied using a SQUID magnetometer in the temperature range of 10 - 300 K and with a maximum field of 55 kOe.

III. STRUCTURAL AND MAGNETIC RESULTS

A. Structure and morphology

By controlling the argon pressure during evaporation and the temperature of the source, particles in the size range of 50 - 350 Å could be prepared. The crystal structure of all the powder samples matched with that of fcc Co. In

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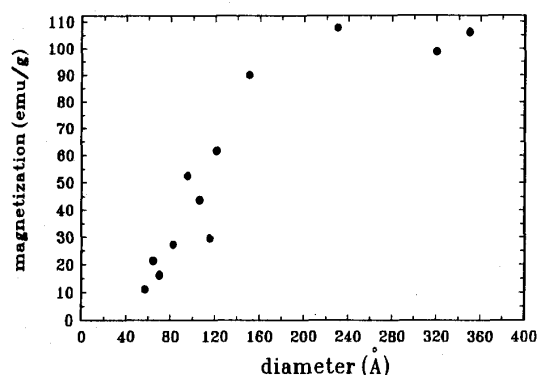


Fig. 2. Saturation magnetization as a function of particle size at 10 K.

addition to Co, small amounts of CoO and Co_3O_4 were also found. Morphology of the particles was very close to being spherical (fig. 1). Deviation from sphericity increases as the particle size is increased. The extent of poly-dispersion in the samples also increased as the average particle size increased.

B. Magnetization

The saturation magnetization (M_s) of the powders increased with particle size as shown in fig. 2. For particle sizes above 200 Å the value of magnetization was found to saturate to about 108 emu/g (961 kA/m). The decrease in magnetization with decreasing particle size is due to the increased volume fraction of oxide in smaller particles and to the canting of the surface moments [4, 5] whose

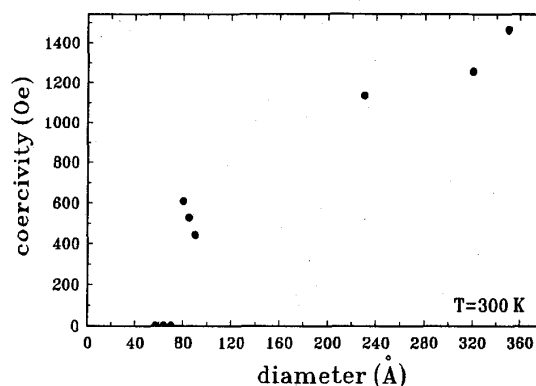


Fig. 4. Coercivity as a function of particle size at $T=300$ K.

contribution is also higher in smaller particles. The sharper increase in M_s (fig. 3) in the lower temperature regime (10–100 K) is caused by the presence of Co_3O_4 which undergoes an anti-ferromagnetic transition at 40 K (for bulk Co_3O_4). This increase is enhanced in smaller particles due to increased volume fraction of Co-oxide (fig. 3) and superparamagnetism.

Particles below 70 Å exhibited superparamagnetism at temperatures below 300 K. The blocking temperatures (T_b) were found to be 190 and 240 K for 57 and 70 Å particles. Their superparamagnetic behavior was confirmed by the presence of a peak in the zero-field-cooled (ZFC) thermo-remanent magnetization data. Also, the magnetization curves above (T_b) were superimposed when plotted against H/T .

C. Coercivity

At room temperature the coercivity was found to increase with particle size (fig. 4) consistent with the fact that their particle size is below the single domain particle size. Particles below 70 Å did not show any coercivity and remanence. The maximum value of coercivity was 1500 Oe (120 kA/m) and was obtained for the largest size particles (350 Å). At cryogenic temperatures the magnetization of the smaller particles could not be saturated even with fields as large as 55 kOe. The maximum coercivity found at 10 K for a given amount of passivation was 3200 Oe. The coercivity at 10 K decreased with increasing particle diameter, which is in contrast to its behavior at 300 K. Similar behavior has also been observed in fine Fe particles and is satisfactorily explained with the core/shell morphology [6].

The dependence of coercivity on temperature is shown in fig. 5. As the samples age, the value of coercivity below 80 K starts to decrease, with the amount of decrease being dependent on particle size and the extent of aging. The

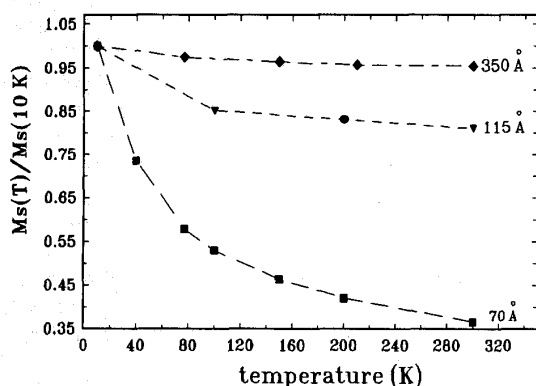


Fig. 3. Temperature dependence of saturation magnetization (normalized to its value at $T=10$ K) for samples with different particle sizes.

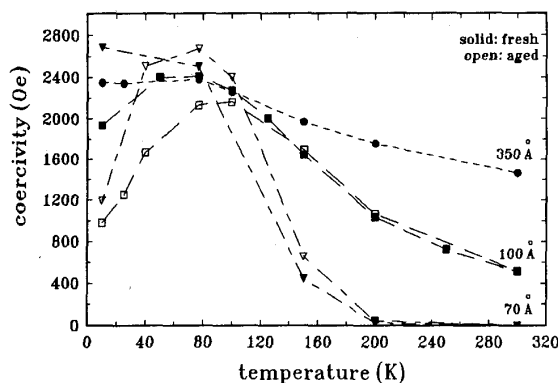


Fig. 5. Temperature dependence of coercivity for different particle sizes. Solid markers display the data taken on freshly prepared sample and the open markers display aged sample.

temperature (about 80 K) below which the coercivity starts decreasing is close to that where the magnetization increases faster (fig. 3). Furthermore the values of coercivity above 200 K were not affected by aging or by the increase in the amount of Co-oxide.

The exchange interaction between the particle's metallic core and its oxide shell (Co-oxide), which undergoes a magnetic transition (from anti-ferromagnetic to paramagnetic) at 291 K (for bulk CoO) was studied from displaced hysteresis loops [7]. First the coercivity of ZFC sample was measured at 10 K, the sample was then warmed to 300 K and subsequently cooled in a field of 20 kOe and the coercivity at 10 K was measured again (fig. 6). The shift

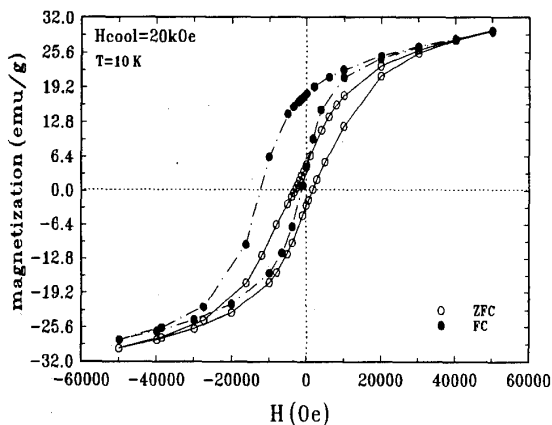


Fig. 6. Zero-field-cooled and field-cooled ($H_{cool} = 20$ kOe) loop at 10 K; showing a shift of 9.4 kOe in a Co sample of 115 Å diameter.

in the loops was measured by subtracting the ZFC coercivity from the FC coercivity. Shifts as large as 10 kOe were found in the smaller particle samples (70 Å). The larger shifts may also result from minor loops because of non-saturation effects. In the biggest particle sample (350 Å) the amount of shift was only 1200 Oe. The shift in the FC loops of all the samples, irrespective of their particle size, disappeared between 150 and 200 K.

IV. DISCUSSION AND CONCLUSIONS

The stronger increase of magnetization at cryogenic temperatures is believed to be due to Co_3O_4 which orders magnetically below 40 K. Based on the magnetic results, the particles may have different morphologies, with the Co core surrounded by a shell of Co_3O_4 , CoO or a mixture of the two. This core/shell structure [4] is responsible for the large coercivities present at cryogenic temperatures and the non-saturation effects, which increase with decreasing particle size and with higher oxidation. The disappearance of the shift at 150 K marks the loss of exchange interaction between the Co-core and its CoO oxide coating. So the 150 K temperature could either be the blocking temperature or the Néel temperature of CoO crystallites present in the oxide shell. Presently we are studying the magnetic properties of Co-oxide particles to better understand the magnetic behavior of passivated Co particles.

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