MAGNETIC AND MORPHOLOGICAL PROPERTIES OF NANOPHASE METALLIC PARTICLES OF Fe, Co, AND Ni

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ABSTRACT

A vapor deposition technique has been used to prepare nano-size particles of Fe, Co and Ni using argon gas. The particles were passivated from further oxidation using a small volume of air. The range of particle size obtained in these systems was 47-200 Å. The saturation magnetization of Fe particles varied between 25-200 emu/g with the higher values corresponding to larger particles and the highest coercivity achieved at room temperature was 1050 Oe. In the case of Co and Ni, the magnetization varied in the range 35-100 emu/g and 14-45 emu/g, respectively. The highest room temperature coercivity was 1200 and 41 Oe for Co and Ni, respectively. A shell-type structure consisting of a metallic core surrounded by an oxide shell has been proposed for the particles.

INTRODUCTION

Fine particles produced by evaporation are superior from those prepared by various other methods [1-3] due to the high purity achieved by the evaporation and condensation process and the greater control on the design of particles for application purposes. The magnetic properties of fine particles are drastically different from those of bulk. For instance, fine particles of Fe-Co alloys have been reported [4] to have a coercivity as high as 2300 Oe and a squareness of 0.81, whereas bulk Fe and Co are virtually magnetically soft (Hc < 100 Oe).

Because of their very small size and enhanced hard magnetic properties, such ultrafine particles (UFPs) have vast applications, e.g., as catalysts, pigments, paints, inks, medical supplies, organic photo conductors and most importantly as high density magnetic recording media [4,5].

In the present study we will concentrate on the magnetic and structural properties of ferromagnetic fine particles of Fe, Co and Ni metals prepared in an argon atmosphere.

EXPERIMENTAL

Fine particles of Fe, Co and Ni were prepared using a gas-condensation technique. The metal was evaporated near its melting point from a resistively heated alumina-coated tungsten boat in a pyrex bell-jar chamber. The system was pumped down to a pressure < 10^{-3} torr before evaporating the sample. A dynamic pressure of argon gas in the range 0.5-8.0 torr was maintained during evaporation, whereas the upper bound in case of Ni was 27 torr. The evaporated metal atoms cool down through collisions with the gas molecules, and coalesce to form clusters of atoms called particles.

Mat. Res. Soc. Symp. Proc. Vol. 206. ©1991 Materials Research Society

thermophoresis

Given enough time, such particles form agglomerates, and through convection currents (that result due to the enormous difference in temperature between source and substrate) deposit themselves on a water-cooled Cu substrate. Since the evaporation rate is proportional to the vapor pressure, the impurities tend to evaporate before or after the mother substance. The typical distance used between the source and substrate was 2 cm.

Particles formed by this method are highly pyrophoric, hence they need passivation to be protected from further oxidation. An argon-air mixture was used to cover the surface of the particles with their respective oxides, before taking them out to the atmosphere. A carbon-covered Cu grid was used to collect small samples for transmission electron microscopy. The black colored smoke-like powder was scraped off the substrate using a glass slide. Samples were weighed and packed in quartz holders using paraffin wax for magnetic measurements.

The magnetic properties were studied using a SQUID magnetometer in the temperature range of 4.2-300 K, and a maximum field of 55 kOe. Transmission electron microscopy (TEM), selected area diffraction (SAD), X-ray diffraction, X-ray photo-electron spectroscopy (XPS) and Mössbauer spectroscopy were used to determine the morphology, crystal structure and surface composition of the particles.

STRUCTURE AND MORPHOLOGY

Particle size, shape and morphology play the key role in determining the magnetic properties of UFPs, which initiate the need for a greater control and deeper understanding of these parameters.

The particle size depends on many factors during evaporation, e.g., the source-substrate separation, source evaporation temperature, substrate temperature, molecular weight of the inert gas, and inert gas pressure during evaporation.

A reasonable control over the first four parameters could allow us to vary the particle size by only varying the argon pressure. This behavior is shown in Fig. 1 for Co and Ni UFPs. A similar trend was also observed in Fe particles where the particle size could be varied from 50-200 Å by changing the argon pressure

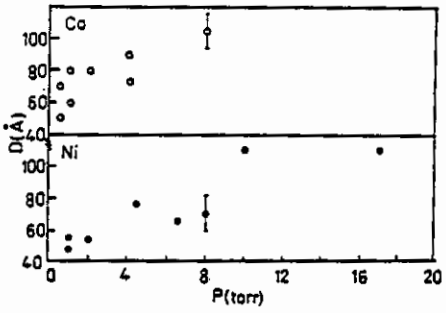
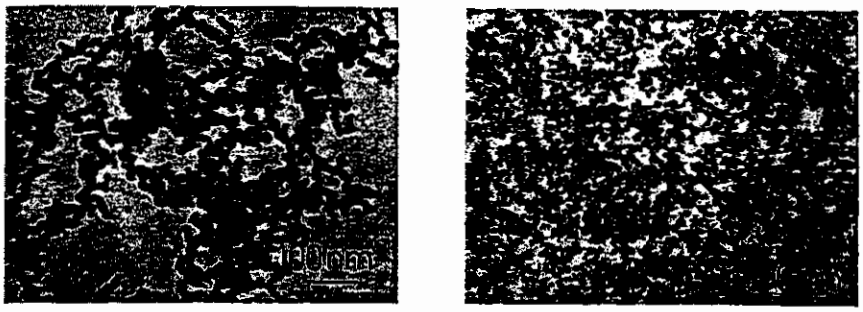


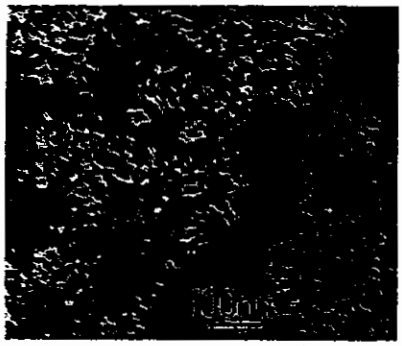
Fig. 1. Median diameter versus argon pressure for Ni and Co particles.



(a) (b)

in the range of 0.5-8 torr. All the samples were found to have a log-normal distribution in their particle size.

The shape of particles, observed was less spherical in the case of Fe and Co as compared to that of Ni. Typical transmission electron micrographs for the three metal particles are shown in Fig. 2. Tendency for chain formation was observed to be greater in samples with higher magnetization and this could be due to enhanced dipolar interactions.



(c)

Fig. 2. Bright field pictures for Fe, Co and Ni particles. (a) Fe: D(median) = 130Å; (b) Co: D(median) = 90Å; (c) Ni: D(median) = 110Å.

The passivation process (after sample preparation) is believed to have caused a shell-type structure, where each particle consists of a metallic core covered by an oxide coating. This model is clearly evident in the TEM micrograph of Fig. 2(a). Furthermore this is also supported by the fact that, the diameters determined from dark-field pictures were smaller than those determined using the bright-field pictures.

XPS studies were performed on few samples (D(median) ≥ 100 Å) of each metal powder, in order to investigate the surface composition. These studies showed the presence of FeO and Fe_2O_3 in Fe, NiO in Ni and CoO in Co. These data agree with the X-ray diffraction and SAD patterns which also confirm the presence of the above oxides in addition to their respective metals. The oxide rings in the SAD patterns were broad and diffuse indicating the presence of amorphous or extremely fine grain oxides.

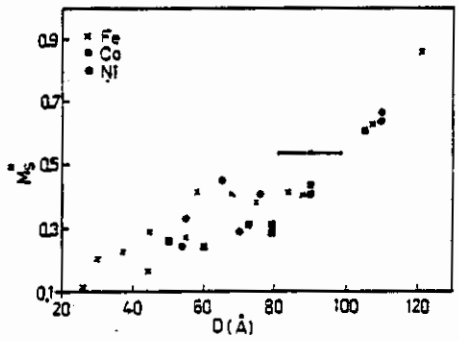


Fig. 3. Magnetization Ms* vs median diameter. (Ms* = Ms (of sample at T = 10K)/Ms (of bulk at T = 0K)

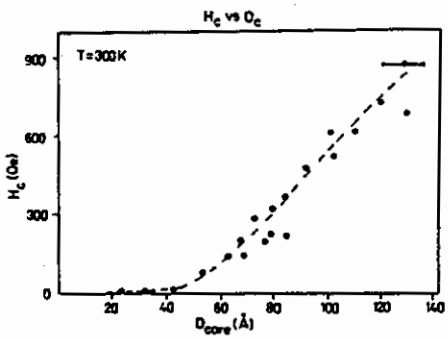


Fig. 4. Coercivity versus core diameter for Fe particles at 300 K.

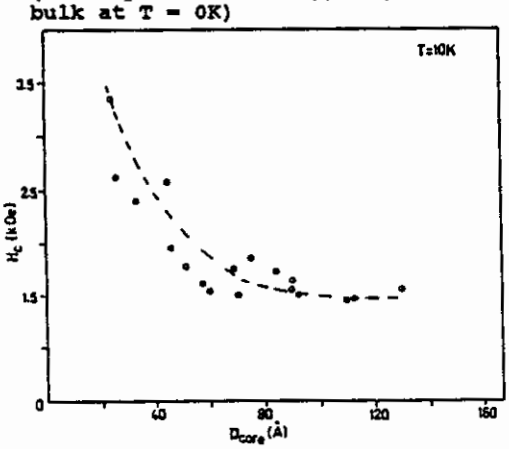


Fig. 5. Coercivity versus core diameter for Fe particles at 10K.

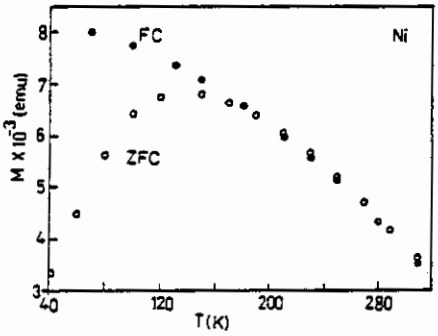


Fig. 6. Thermomagnetic data for a Ni powder of 55 Å diameter particles.

MAGNETIC PROPERTIES

The magnetic properties of fine particles are strongly affected by their size. The size dependence of magnetization is shown in Fig. 3. The decrease in M with decreasing particle size can be due to both surface oxidation and surface canting of moments. Both of these contributions are increased as the particle size is made smaller. This is due to the large surface fraction of atoms present in small particles as compared to the bigger ones. Also it has been observed [6], that in Fe fine particles the shell thickness is nearly constant as the total diameter of the particle is increased, which would result in larger surface fraction of atoms in smaller volumes.

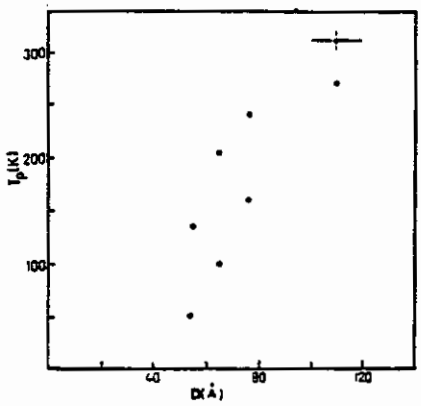


Fig. 7. Peak temperature T_p (in ZFC curve) versus particle diameter for Ni.

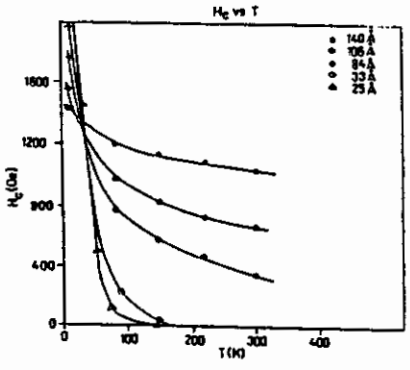


Fig. 8. Coercivity versus temperature for Fe particles of different size.

The dependence of coercivity on particle size at room temperature (Fig. 4) follows the classical single domain particle behavior. A reverse trend was observed at 10K (Fig. 5), because of the negligible thermal effects present at that temperature. The increase in coercivity with decreasing particle size is believed to be due to the large surface anisotropy effects in the small particles.

Particles of Fe and Ni with a size below 70 and 76 Å diameter respectively, exhibited a superparamagnetic behavior for T < 300 K, whereas, Co particles as small as 50 Å still had a finite coercivity at room temperature. Thermomagnetic measurements performed on Ni samples in a small DC field were featured with a broad peak in zero-field-cooled (ZFC) curve, Fig. 6. This peak temperature was found to increase with particle size, Fig. 7. The fact that the field cooled (FC in a small field of 100 Oe) data in all samples below the peak temperature show a negative slope indicates that this peak is the result of superparamagnetic behavior rather than a spin glass behavior. This is further supported by the fact that the peak temperature was found to be very close to the blocking temperature in all the samples.

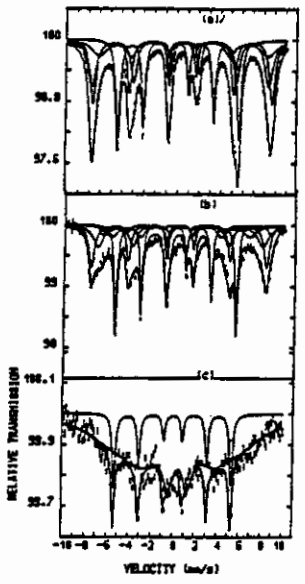


Fig. 9. Mössbauer spectrum of Fe at (a) T=4.2K; (b) T=85K; (c) T=300K.

The temperature dependence of coercivity shows a decrease in coercivity with increasing temperature, Fig. 8. The slope of the curve was found to increase for smaller particles. This behavior

can be explained by considering the results of the typical Mössbauer spectra performed on an Fe sample of D(median) = 130 Å (Fig. 9). At low temperatures both the metallic core and the oxide coating are ferromagnetic giving rise to a large coercivity. As the temperature increases, the oxide coating becomes superparamagnetic [7-10] (Fig. 9(c)) and the magnetic moment fluctuates randomly in time. Due to the exchange coupling between the core and the shell, the core also becomes softer resulting in a smaller coercivity at higher temperatures. This effect is much stronger in smaller particles resulting in zero coercivity even below room temperature. This is because the volume fraction of atoms present in the oxide shell is much larger in smaller particles.

CONCLUSIONS

The magnetic properties of Fe, Co, Ni fine particles were found to be strongly dependent on particle size and morphology. A shell-type structure is proposed for the passivated metal particles which explains successfully the magnetization and temperature dependence of coercivity. A detailed study of the surface properties of particles including high resolution TEM is imperative in order to fully understand the origin of giant coercivity in the ultrafine particles.

ACKNOWLEDGEMENTS

This work has been supported by NSF-CHE-8706954. We are very thankful to Dr. Kostikas and Dr. Papaefthymiou at Demokritos, Athens, Greece for their help in Mössbauer studies. We are also very grateful to Dr. I. Shah for his contribution in XPS results.

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