Structural and magnetic characterization of Co particles coated with Ag

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Co fine particles coated with Ag have been synthesized through the microemulsion method in an inert atmosphere. The size of the particles is controlled by the water droplets of the microemulsions. Fine particles prepared by this method, consist of a magnetic core of Co covered by a layer of Ag. Samples containing from 3.3 to 40.5 vol % Co have been prepared. The average size of the particles obtained is in the nanometer range. The magnetic properties were studied by dc magnetization at 77 K and room temperature. The data show a strong dependence of the magnetic properties on the annealing temperature.

I. INTRODUCTION

Single domain magnetic particles show very interesting properties, such as high coercivity and remanence, which are of special interest to several applications in magnetic recording and permanent magnets. Different methods can be used in order to obtain small particles in the submicrometric range. Among these, chemical reactions and vacuum deposition are the most usual ones. Most studies of ultrafine metallic particles have been performed on granular materials in nonmetallic matrices.[1–3] Interest in single domain particles immersed in a nonmagnetic metallic matrix has increased recently.[4,5] The interest in granular materials, such as Fe-Ag, Co-Ag, $Ni_{81}Fe_{19}$-Ag, etc., is because they present a giant magnetoresistance (GMR).[6,7] Although much effort has been devoted during the last years studying the origin of their properties, a quantitative understanding of the phenomenon is still lacking.[8,9]

In this work we describe a new chemical method for the preparation of ultrafine Co particles covered by metallic silver. This method consists in mixing two water-in-oil (W/O) microemulsions containing the reactants dissolved in the aqueous phase in order to produce the Co core. The reaction takes place inside the droplets, which controls the final size of the particles. Subsequently, silver ions are adsorbed onto these particles and finally are reduced to produce a silver metallic shell.

II. EXPERIMENT

The microemulsions employed in the production of the particles were composed of *n*-heptane, aqueous solution, and aerosol-OT (AOT, sodium dodecylsulfosuccinate). The droplet size of these microemulsions was controlled by the ratio $R=[H_2O]/[AOT]$. This ratio was set to 10. The whole process for obtaining the particles, that was carried out in an inert glove box, can be divided into two stages.

(1) Formation of the magnetic cores: To carry out this first stage, two different microemulsions were prepared. The first one consisted in an aqueous solution of $Co(NO_3)_26H_2O$ (0.1 M) and the second one contained $NaBH_4$ (0.2 M). The two microemulsions were mixed and the magnetic particles were formed inside the microdroplets. The microparticles, separated from the microemulsion by ultracentrifugation, were washed later with *n*-heptane and ethanol several times and finally dried with acetone.

(2) Coating with Ag: The magnetic particles were redispersed with AOT in an aqueous solution containing $AgNO_3$ and EDTA (ethylendiaminetetracetic). Silver ions were then absorbed on the particles which acted as nucleation centers. This solution was later irradiated with UV light during 30 min to obtain a metallic cover of silver on the magnetic particles.[10] The amount of EDTA and $AgNO_3$ used depends on the Ag/Co ratio to be obtained. The coated microparticles were separated again from the solution by ultracentrifugation, washed several times with *n*-heptane and ethanol in order to remove the AOT surfactant, and finally dried with acetone. Then, the microparticles were examined before and after annealing in flowing Ar.

Most of the organic impurities were eliminated after annealing, followed by a process of oxidation and reduction. These were observed by differential thermogravimetric analysis measurements.

The samples were characterized analytically by inductive coupled plasma-atomic emission spectroscopy and the final composition of Co, Ag, and impurities were determined. The structural characterization was carried out by x-ray powder diffraction. These measurements were performed at room temperature, and matched with diffraction patterns from the total access diffraction database. In order to determine the size distribution, measurements of transmission electron microscopy (TEM) and dynamic light scattering (DLS) were carried out. For both TEM and DLS measurements, particles were dispersed in water using AOT. The average crystallite sizes were calculated from the shape of the x-ray diffraction peaks using the Debye–Scherrer formula. The magnetic properties of the samples were measured with a vibrating sample magnetometer in the temperature range of 80 K$<T<$300 K. The powder was introduced, loosely packed, in a cylindrical sample holder.

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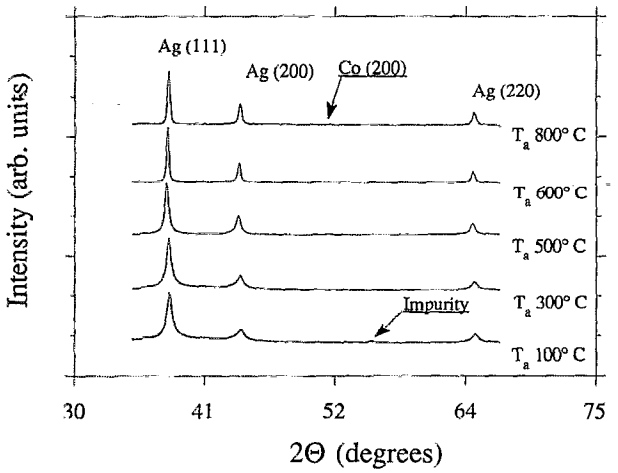

FIG. 1. X-ray diffraction pattern for $Co_{0.5}Ag_{0.5}$ after annealing at different temperatures. The arrows show the position of cobalt reflections.

III. RESULTS AND DISCUSSION

A. Structural characterization

X-ray diffraction on as-prepared Co particles (first chemical stage) shows a typical amorphous spectrum. Figure 1 shows the x-ray diffraction pattern for a typical Co/Ag sample at five temperatures of annealing (T_A=100, 300, 500, 600, and 800 °C). Long measurement times, counting times of 20 s per 0.002° step in 2θ, were needed in order to observe cobalt peaks in samples with high concentration of Co and high treatments of temperature. Only one Co peak is visible (200) because the others overlap with those due to silver. In Fig. 1 it can be observed how the width decreases with annealing temperature. Studies of the width of Ag (111) and Ag (220) peaks done as a function of annealing temperature yields the size of the Co/Ag particles grows from 15 to 60 nm.

Figure 2 shows the TEM electron micrograph for the sample with x=0.12 of Co_xAg_{1-x} treated at 500 °C. To obtain the micrograph, the samples were dispersed in water and then deposited onto Cu grid substrates. The average diameter was of about 30 nm, similar to the results obtained by DLS.

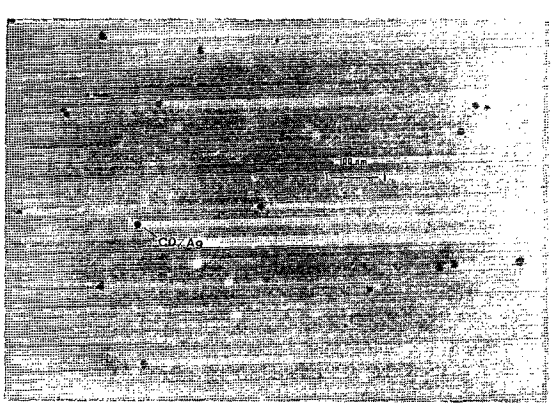

FIG. 2. TEM microphotograph of a sample of $Co_{0.12}Ag_{0.88}$.

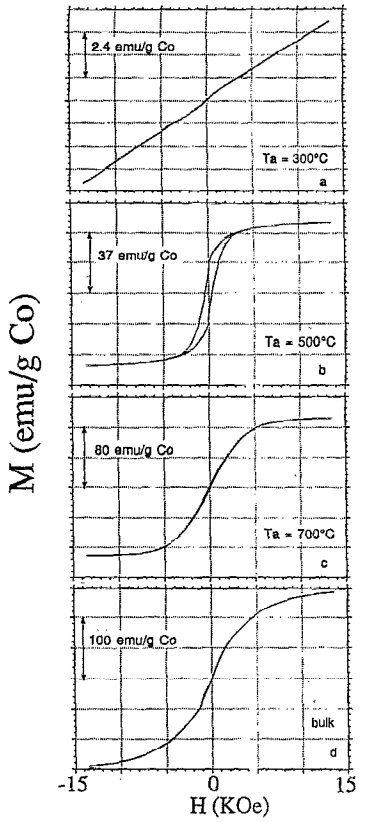

FIG. 3. In plane M-H loops at room temperature of Co_xAg_{1-x} with $x\approx0.12$ at different annealing temperatures in series A. (a) T_A=300 °C, (b) T_A=500 °C, (c) T_A=700 °C, and (d) bulk Co.

B. Magnetic properties

The temperature dependence of the magnetization has been measured after cooling in zero magnetic field (ZFC) and also after cooling in a field (FC). The M-T data show a splitting between the FC and ZFC curves. For the as-prepared samples, this splitting occurs close to room temperature (RT). For annealed samples, the sizes of cobalt cores grow and this splitting point is shifted towards higher temperature.

The magnetic hysteresis loops have been measured in three series of Co_xAg_{1-x} (A, B, and C). Series A and B are two separate fabrication runs with the same Co concentration (x=0.12±0.02) but with different annealing temperatures, 100 °C<$T_A T$<800 °C. Series C are samples of different compositions, from x=0 to x=0.66 annealed at T_A=500 °C. Figure 3 shows magnetization (M) as function of magnetic field (H) at RT for T_A=300 °C [Fig. 3(a)], 500 °C [Fig. 3(b)], and 700 °C [Fig. 3(c)]. Figure 3(d) is the M for cobalt powder (d<250 μm) and reflects the bulk properties of the material. The coercive field (H_c) as function of T_A is plotted in Fig. 4(a). The squareness, SQ, defined as M_r/M_s where M_r is the remanence magnetization and M_s is the magnetization at H=13.5 kOe, vs T_A, is shown in Fig. 4(b).

According to Fig. 4, for series A and B, it is possible to define three regions of annealing temperature. The first for low T_A, between 100 and 300 °C, shows a reversible M-H behavior. The second region, for 300<T_A<600 °C shows a hysteresis loop [Fig. 3(b)]. The dramatic change of the mag-

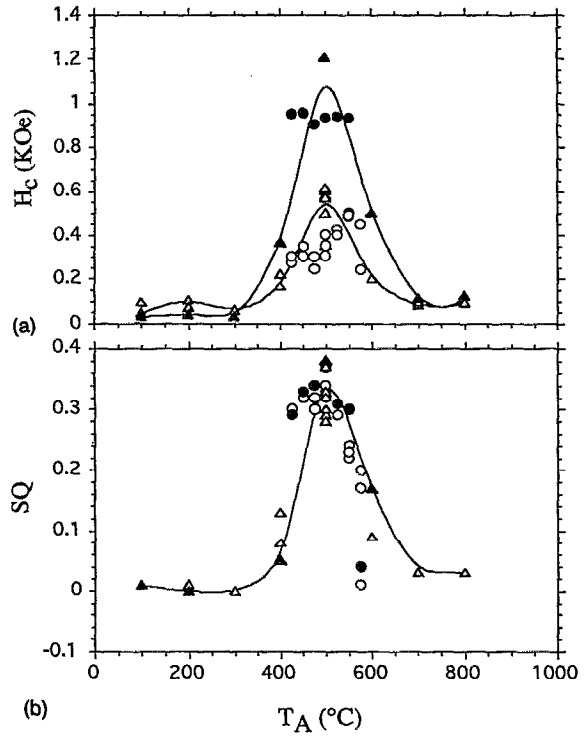

FIG. 4. (a) H_c vs T_A and (b) SQ vs T_A for two different runs of Co_xAg_{1-x} (x~0.12). Series A (△) RT, (▲) 77 K, series B (○) RT and (●) 77 K.

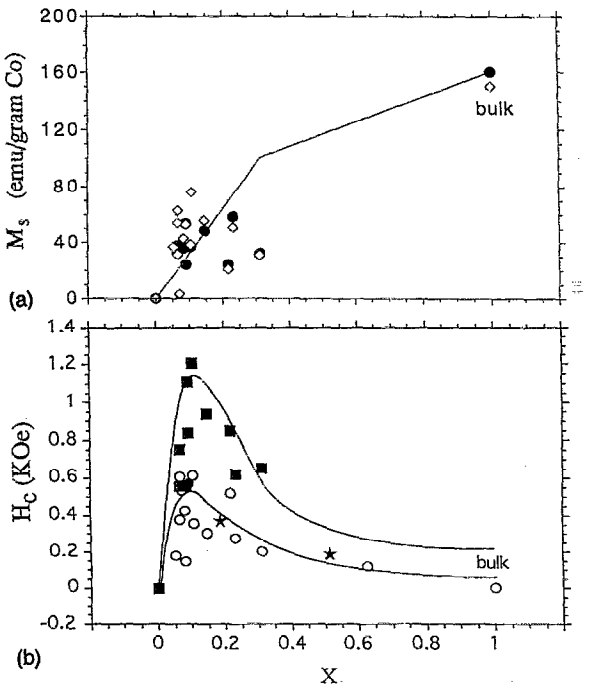

FIG. 5. Co_xAg_{1-x} samples (a) M_s vs x (experimental composition) after annealing at 500 °C (the solid line comes from Co_xCu_{1-x} in Ref. 5) and (b) H_c vs x. The solid lines are guides to the eye. Open and filled symbols show measurements at RT and 77 K, respectively. The filled stars are data from Ref. 11 of Co_xAg_{1-x} films.

netic properties in this range could be due to an increase of the Co nuclei and/or the crystallization of some amorphous portions of the Co cores as T_A increases. For $T_A \approx 500$ °C, H_c and SQ have maximum, as seen in Fig. 4. This maximum is similar to the one found by other authors in $Co_{19}Ag_{81}$ and $Co_{50}Ag_{50}$ granular magnetic thin films.[11] The third region ($T_A > 600$ °C) shows that the H_c and SQ decrease as T_A increases. The reason for it is that the interaction between the particles is strong and they are no longer single domains so their magnetic behavior approaches the one found for bulk Co.

Finally, in Fig. 5, we show M_s and H_c as function of experimental Co composition. The solid line is the data of Ref. 5 about Co_xCu_{1-x}. For the samples with low Co concentration ($x<0.12$), the magnetization does not saturate and the coercive field has a value close to zero. The long range magnetic order appears at high Co concentrations. For samples with $0<x<0.12$ the magnetization was found to saturate more easily and the systems exhibit a monotonic increase of H_c with increasing Co content. For $x>0.15$, the samples present a monotonic decrease of H_c with increasing x, which is consistent with a coupling effect of the Co particles.

IV. CONCLUSIONS

In summary, we have studied the structural and magnetic properties in a Co-Ag granular systems obtained by chemical reactions in microemulsions. The reaction takes place inside the droplets, which control the final size of the particles. By this method, magnetic ultrafine particles, in the nanometer range, of Co coated with Ag were obtained. From the x-ray analysis we observe that Ag crystallizes in the face centered cubic structure. The magnetic behavior of these samples after thermal treatments ($T_A \approx 500$ °C) shows coercive fields as high as $H_c \approx 600$ Oe at room temperature. These values are similar to those reported for granular materials which present GMR.[6,7] We are now in the process of measuring the MR in our samples.

ACKNOWLEDGMENTS

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