Transactions of the Materials Research Society of Japan 29 [1] 351-356 (2004)

Magnetic behaviour of Co@Ag nanoparticles prepared by the microemulsion technique

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Ag covered nanoparticles, *Co@Ag*, have been prepared in microemulsions by the successive reaction technique and their magnetic behaviour was studied as a function of the heat treatment. It was observed that, under the experimental conditions of this study, the size of the Co nuclei is limited by the reactant concentration, whereas the Ag covering is templated by the microemulsion droplet size. The as-prepared particles mainly contain nuclei in the form of Co_3O_4, which evolves to Co as the samples are annealed in reducing atmosphere at different temperatures (T_a). Four different regimes for the magnetic behaviour are observed and explained taking into account intra- and inter-particle reorganizations. At high temperatures (T_a > 300°C) the passivating surfactant layer decomposes with the subsequent growth of the Co nuclei and the convergence of their magnetic properties to bulk Co.

Key words: Co@Ag, magnetic nanoparticles, microemulsions.

1. INTRODUCTION

Magnetic nanoparticle systems play an important role from a scientific point of view, but also due to their great potentiality in technological applications [1]. The properties of these nanosystems are, in many cases, very different from the bulk materials and also from the isolated atoms, which gives rise to a very reach variety of new mesoscopic phenomena. From a technological point of view, nanoparticles are found today in many devices, such as magnetic recording, ferrofluids, medical diagnosis, paint pigments, ceramics, etc. For these reasons, magnetic nanoparticles has been an interesting topic during the second half of the last century, but in the last decade it was a boom mainly due to the technological demand of more and more device miniaturization (nanotechnology). Furthermore, the development of new preparation and characterization techniques allows nowadays, by simple techniques, a very precise control of the composition, size and shape of nanoparticles. This interdisciplinary research field evolves very rapidly and it is believe that in the new future spectacular applications will appear, like hybrid nanostructures (films/wires/particles), nanocomposites (magnetic/non magnetic material), etc. A good example of the last type of materials is the granular magnetic solids. These are formed by magnetic nanoparticles of different transition metals immersed in a non-miscible matrix. Although a lot of theoretical and experimental work has been done in the last years, the explanation of the complex magnetic and electrical behaviour shown by these materials still is challenge which remains to be clarified [2].

Among the different preparation methods of nanostructured magnetic systems, the use of soft chemical reactions in compartmentalized media is one of the most promising techniques allowing, in a simple way, the size control of the produced nanomaterials. In particular, the successive reaction technique in microemulsions has been employed to prepare "onion"-like particles with a sub-nanometer resolution [3,4,5], but many aspects of the technique, as well as of the magnetic and electrical properties of the synthesized nanomaterials remain to be elucidated. In this work we have carried out a study of the magnetic properties of Co nanoparticles covered by Ag, synthesized by the *microemulsion technique*.

2. SAMPLE PREPARATION

The microemulsions employed in the production of the particles were composed of n-heptane, aqueous solution, and aerosol-OT (AOT, sodium dodecylsulphosuccinate). The droplet size of these microemulsions was controlled by the ratio $R=[H_2O]/[AOT]$. This ratio was set at 10 (d= 6.6 nm) [6]. The whole process for obtaining the particles was carried out in an inert glove box. For the formation of the magnetic cores two different microemulsions were prepared. The first one consisted of an aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ and the second one contained $NaBH_4$. The two microemulsions were mixed and the Co magnetic particles were formed inside the nanodroplets.

In a second step, solid $NaBH_4$ was added in excess and then an aqueous solution containing $AgNO_3$ with a previously established molar ratio was poured over this microemulsion containing the magnetic cores. The Ag^+ ions can only be reduced within the nanodroplets containing the Co particles. This process prevents surfactant from being present at the Co/Ag interface. The nanoparticles were separated from the solution by ultracentrifugation, washed several times with n-heptane and ethanol, and finally dried with acetone.

In this work we will focus on samples with a fixed Co/Ag molar ratio of 1/10. Samples of Co without Ag covering were also prepared in order to compare their magnetic properties. The as-obtained particles were subsequent annealed in reduced (H_2) or inert (Ar) atmospheres at different temperatures in the range 100≤T_a(°C)≤700.

2. EXPERIMENTAL

For the chemical analysis of the samples, the neutron activation technique (Centro Atómico de Bariloche, Argentine) was employed. Thermogravimetric analysis (TGA, Perkin Elmer) was used to study the evolution of the samples treated at different temperatures.

The local structure of the nanoparticles was studied by X-ray absorption (EXAFS) and diffraction (XRD), and transmission electron microscopy (TEM).

For the XRD measurements, a Philips PW-1710 diffractometer with a Cu anode operating at 40 kV was employed. The radiation used corresponds to the $K_{\alpha 1}$ and $K_{\alpha 2}$, transitions, with an average λ=1.542 Å. All the XRD measurements were carried out at room temperature.

EXAFS experiments were carried out in the DCI ring of the synchrotron at LURE, Paris, employing a Si(111) crystal monochromator. The measurements were performed at the K Co edge with compacted samples (pressed at 10Tm) using the TY detection mode at 80 K. Samples were fixed to the sample holder using a Ag paint. In order to get a good signal to noise ratio 4 scans per sample were performed with 2eV steps in a 1000eV range over the de absorption threshold.

Two TEM equipments were used to get microphotographs and diffraction patterns: A Phillips CM200 and a JEOL 2010 both running at 200 kV. Samples were prepared dispersing the particles in ethanol depositing one drop onto a carbon-coated Cu grid (simple-screen distance: 1.5 m).

For the magnetic measurements two equipments were used: a SQUID (Quantum Design) magnetometer operating in the 2<T(K)<300 temperature range up to 50 kOe, and a vibrating sample magnetometer (VSM 1660 Digital Measurements Systems Inc.) for the measurement of isothermal hysteresis loops at room temperature up 13.5 kOe. A home made Faraday balance was employed for magnetization measurements at high temperatures (room temperature up to 300°C) working up to 10 kOe.

3. ANALIYTICAL AND STRUCTURAL ANALYSIS

Table I shows the chemical analysis of the samples. It can be observed the presence of Co and Ag with a composition which agrees with the theoretical one (the composition fixed by the used reactant concentrations). Besides that, the existence of other substances, corresponding to the some hydration water and surfactant (see Figure 1) protecting the particles is also observed.

Table I: Analysis of the samples (in weight percentage)

	%Co	%Ag	Rests
Co	5.77±0.07	0	94.23±0.07
Co@Ag	2.48±0.05	41.2±0.8	56.3±0.8
Co@Ag*	2.90±0.06	59.1±0.8	38.0±0.8

*Sample treated at T_a=300°C during 5 hours

Figure 1 shows that at ≈ 300°C the surfactant decomposes. The elimination of the surfactant protection layer leads to the particle aggregation (Fig. 2b).

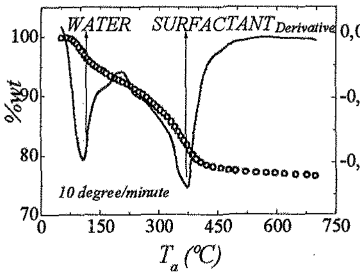

Fig. 1: Weight loss of the samples after heat treatment (TGA).

TEM micrographs (Fig. 2a) of as-prepared Co@Ag particles show that the particles are spherical with similar sizes (<d> = 7.1nm) of the used microemulsion droplets (6.6 nm). The heat treatment of the particles promotes first their agglomeration (Fig. 2b) because of the surfactant loss and, finally, their growth (Fig. 2c) because of the lack of protection.

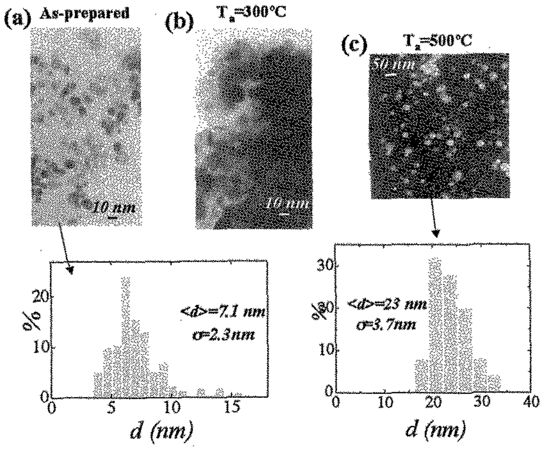

Fig. 2: TEM micrographs and histograms of Co@Ag particles treated at different temperatures

X-ray and electron diffraction patterns clearly show the existence of Ag (Fig. 3). The increase of the crystallization degree by increasing the temperature can also be seen.

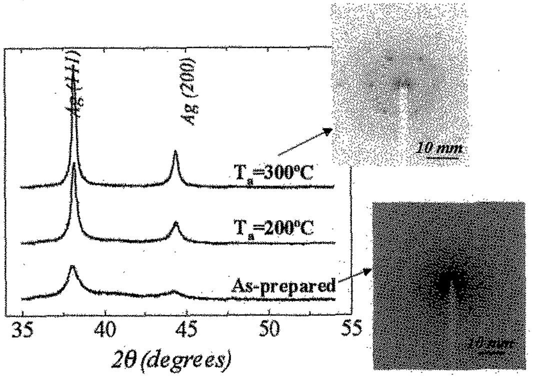

Fig. 3: X-ray diffraction and electron diffraction patterns of Co@Ag particles treated at different temperatures.

By TEM and X-ray diffraction is very difficult to distinguish the Co particles without Ag covering due to their very small size (< 1 nm). The reduced dimensions of the Co "clusters" explain also the shape of the X-ray diffraction patterns obtained for these samples (Fig. 4a).

Although the particle synthesis was carried out in an inert glove box, XRD and EXAFS measurements (Fig. 4b) show that Co in the as-prepared samples is oxidized in the form of Co_3O_4 [7], and that metallic fcc Co is only obtained after heat treatment (T_a > 300°C) under inert or reducing atmospheres.

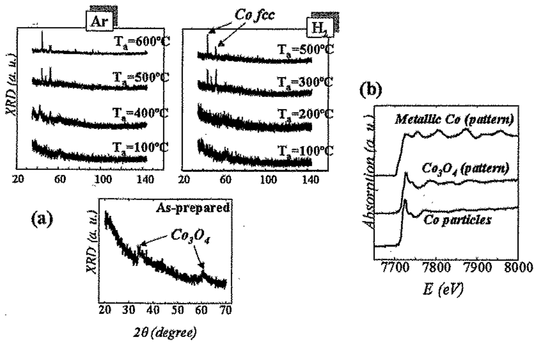

Fig. 4: X- ray Diffraction (a) and Absorption (b) of Co particles treated at different temperatures

4. MAGNETIZATION MEASUREMENTS

Residual Magnetization: Firstly, the residual magnetization of the samples due to all but Co material was measured. Figure 5 shows the isothermal magnetization curves with magnetic applied fields up to 50kOe and dc zero-field-cooling/field cooling (ZFC-FC) curves measured under and applied field of H=50 Oe in the temperature range 2<T(K)<200. It is observed that, although Co is present in the samples in a quantitative small proportion (see Table 1), this compound is the only one which appreciably contributes to the sample magnetization.

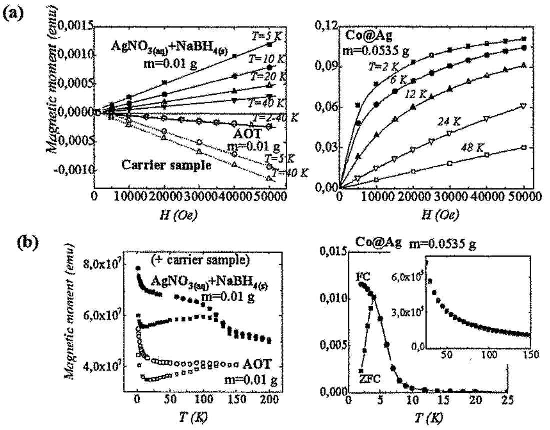

Fig. 5: (a) Isothermal magnetization and (b) ZFC and FC magnetization curves at low fields (H=50 Oe), for the non-Co compounds which are present in the samples, compared with similar measurements carried out with a Co@Ag sample with low Co content (Co/Ag=1/15).

Magnetization of Co@Ag samples (as-prepared and treated at temperatures T_a≤200°C): In order to compare the magnetization behaviour of Co@Ag and Co samples (as-prepared and heat treated) Figure 6 shows measurements of M vs. H at low temperatures.

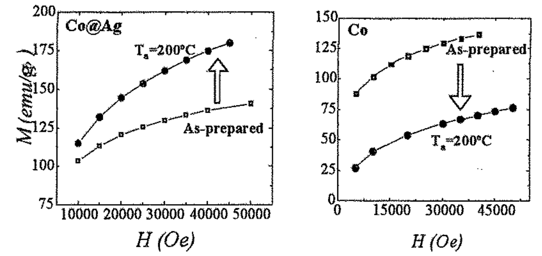

Fig. 6: Isothermal magnetization (T=2 K) vs applied magnetic field

It is observed that the saturation magnetization increases with the heat treatment for the Ag-coated Co particles, but it decreases for the unprotected Co particles. This can be attributed [7] to a surface effect, e.g. the presence of a ligand [8] (surfactant) in the Co surface which is inhibited when the Co is covered by Ag, and it can be taken as another proof of the good quality of the Co covering Ag layer.

Figure 7 shows ZFC-FC curves measured under an applied field of H = 50 Oe in the temperature range 2≤T(K)≤20. It can be observed that the ZFC magnetization shows a maximum typical of an ensemble of magnetic particles. This maximum is associated with the blockade of the superparamagnetic state [7, 9, 10]. The low temperatures at which this blocking is observed clearly show the very small size of the magnetic clusters. The heat treatment leads to an increase in the temperature of the maximum and a diminution of the magnetization of the peak. This can be associated with an increase of the particle size dispersion.

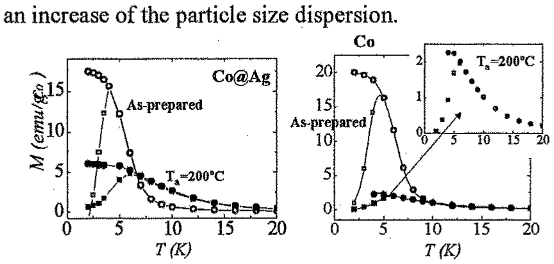

Fig. 7: Dependence of the magnetization with the temperature (ZFC-FC) at low fields (H=50 Oe).

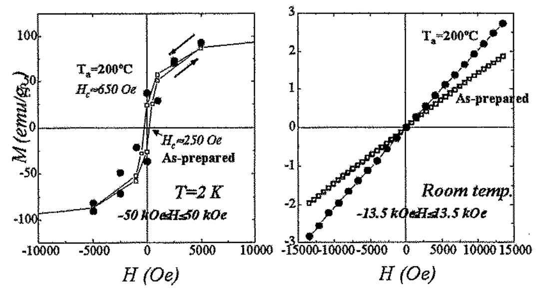

Fig. 8: Hysteresis curves for the Co@Ag sample (as-prepared and heat treated) below (a) and above (b) the blocking temperature.

In Figure 8 it is observed that, at T = 2K, the magnetization shows irreversibility which is not observed at higher temperatures, in agreement with what is shown in Fig. 7.

In order to study the "in situ" evolution of the magnetization with the heat treatment, we have measured the magnetization of a Co@Ag sample in an reducing atmosphere of N_2+H_2(4%) with a Faraday balance. In Figure 9 it is shown the results for T_a≤200°C.

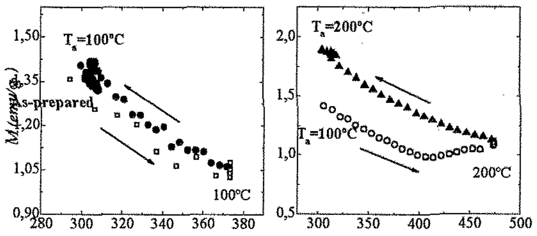

Fig. 9: Magnetization cycles at H=10kOe for a Co@Ag sample (3 hours process).

It can be observed that the magnetization processes are not reversible, being this irreversibility larger at 200°C. The magnetization increases after the heat treatment.

Magnetization of samples treated at high temperatures (T_a>200°C): As we have seen the magnetization of Co@Ag particles increases with temperature at low temperatures (T_a≤200°C) and high fields. However, when T_a increases over 200°C the magnetization decreases with temperature as it can be seen in Fig. 10a. Moreover, this magnetization decrease is more important as the annealing time increases (Fig. 10b).

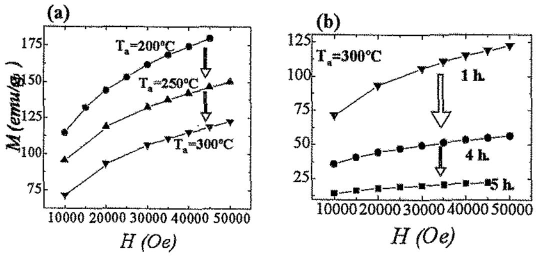

Fig. 10: High field Isothermal magnetization (T=2 K) of Co@Ag samples treated at different temperatures (a) and annealing times (b).

In Figure 11 it can be seen that, when the samples are heated above 200°C, there is a clear separation of the ZFC and FC curves which shows an irreversible behaviour. Besides that, it appears a "soft" peak in the ZFC curve at high temperatures which grows as the low temperature peak decreases. This is an indication of a rapid growing cluster population giving rise to a bimodal distribution of particle sizes.

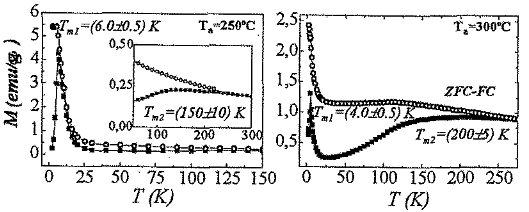

Fig. 11: Low field (50 Oe) magnetization vs temperature for Co@Ag particles treated at temperatures T_a>200°C

"In situ" magnetization measurements were (see Fig. 9) also performed at high temperatures and the results are shown in Fig. 12.

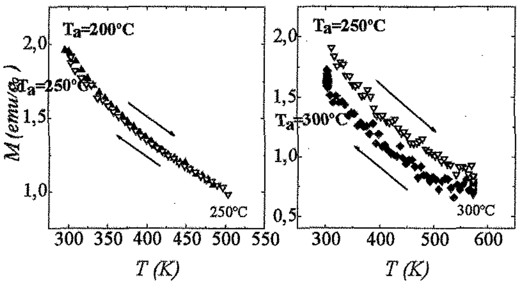

Fig. 12: Magnetization cycles at H=10 kOe for a Co@Ag sample (≈5 hours process)

From this experiment it can be concluded that the magnetization decrease observed for T_a>200°C is not due to a sample deterioration and therefore should be attributed to a structural evolution of the samples. Moreover, it has been observed that a heat treatment under oxidant conditions does not appreciably change the magnetic properties, although at high temperatures the non-reducing atmosphere treatment gives rise to an even more magnetization drop (see Fig. 13 T_a=400°C).

In Fig. 13 we compare room temperature hysteresis loops of the same Co@Ag sample subjected to different thermal treatments. It can be observed that now treatments at temperatures above 300°C do not induce a magnetization drop, but just the opposite. The behaviour of the sample treated at the highest temperature is similar to bulk Co in agreement with the results shown in Fig. 4a.

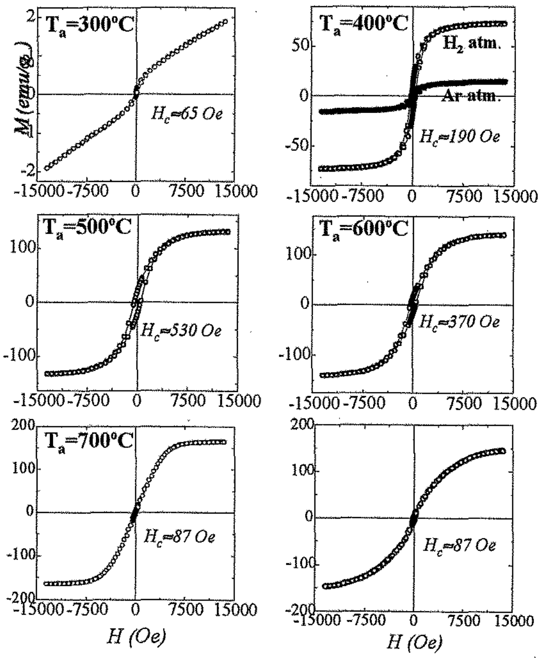

Fig. 13: Hysteresis loops at room temperature for a Co@Ag sample treated at different temperatures. It is also shown the hysteresis loop for a Co bulk sample.

5. DISCUSSION AND CONCLUSIONS

According to the magnetic behaviour of the samples when they are treated at different temperatures, one can distinguish three different regions.

Region 1: T_a≤200ºC. In Co@Ag samples fired at these temperatures the saturation magnetization increases attaining a maximum value at approx T_a=200ºC. The maximum saturation magnetization is much higher than bulk Co (Fig. 14). This behaviour observed in Co@Ag simples is very different from that observed in Co simples without the Ag covering. In the later case the saturation magnetization decreases.

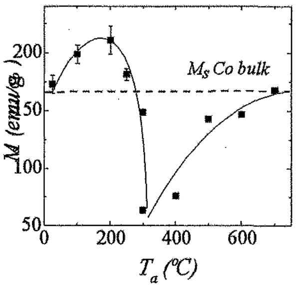

Fig. 14: Saturation magnetization extrapolated from the M vs H isotherms for Co@Ag samples fired at different temperatures.

In this region Co@Ag samples show a reversible behaviour in a large temperature range. Magnetic particle sizes are extremely low, in the cluster range, with a number of atoms per cluster (≈ 10 [5]) which perfectly agrees with the concentration used in the synthesis: 9 Co ions per nanodroplet of the microemulsion. Then, the size of the obtained Co clusters is limited by the reactant concentration, whereas the Ag covering size is restricted by the nanodroplet volume. This different templating behaviour is well known and has already been reported [5]. It has been theoretical explained as a complex interplay of several parameters, among which the most important are: reactant and concentration exchange rate, reaction rate, surfactant film rigidity, droplet size and surfactant adsorption [5, 11]. It has been observed that, although the heat treatment increases the particle size dispersion, there is no appreciable change of the mean particle size. This can be attributed to two competing processes: a small cluster growth due to the diffusion and coalescence of clusters inside the Ag matrix (which is more important at high temperatures) and a cluster fragmentation, for those clusters which are pinned and do not have enough energy to diffuse, due to the segregation tendency of Ag and Co. This process allows explaining the observed increase of the saturation magnetization because when the cluster size decreases the uncompensated number of antiparallel spins increases very fast ($\approx N^{1/2}$ [12]). One should remember that in the as-prepared samples Co is present as Co_3O_4 which is antiferromagnetic at low temperatures.

Región 2: 200<T_a(ºC)≤400. M_s drastically drops and the irreversibility properties are now dominant in a large temperature range. Hysteresis loops clearly appear now at room temperature. Clustering growth is not uniform and a bimodal distribution appears. It is interesting to note that the appearance of this type of size distributions is also observed in Co/Ag thin films when they are subjected to similar temperatures [13].

The magnetization drop may be due to the (still oxidised) particle growth because of an spin compensation and/or the influence of the ligands (surfactant molecules) on the surface of the smallest particles which emerge from the Ag see. This situation is favoured in the uncovered Co clusters.

Region 3: 400<T_a(ºC)<600. High field magnetization increases again with temperature due to a favourable combination of factors: Co oxide reduction and Co growth. As it can be observed in Fig. 13, for T_a=500ºC, H_c shows a maximum value. The existence of this maximum at this temperature is again similar to that found in thin films of granular Co/Ag samples obtained by different procedures [14] showing GMR [15].

Region 4: For T_a ≥600ºC, the coercive field decreases and slowly evolves to the values characteristics of Co bulk, being the reason for this decrease the formation of multidomains [7, 16].

Acknowledgements The authors wish to thank the financial support of the Ministerio de Ciencia y Tecnología, Spain (Project MAT 2002-00824) and the Secretaría Xeral de Investigación e Desenvolvemento, Galicia (Project PGDIT03PXIC20907PN).

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(Received October 13, 2003; Accepted November 28, 2003)