Preparation, Characterization, and Magnetic Properties of Fe-Based Alloy Particles with Elongated Morphology

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Fe-based elongated particles of about 120 × 20 nm protected with an alumina coating have been obtained by dehydration and further thermal reduction of undoped and Co-doped goethite precursors. The precursors were obtained by oxidation−precipitation of a mixture of $FeSO_4$ and $Co(NO_3)_2$ in the presence of NaOH and Na_2CO_3. Prior to the thermal treatment, the particles were coated with a homogeneous thin layer of alumina by taking advantage of the different surface charge densities of the compounds in selected pH regions. The nature and location of Co in the goethite precursors, as well as in the final metallic particles, have also been studied. Finally, the magnetic properties of the Co-doped samples have been measured and compared to that of the undoped samples in order to explain their differences. Values of the coercivity around 1200 Oe have been found in the FeCo metallic particles protected with the alumina layer.

Introduction

Magnetic recording systems are one of the most rapidly developing areas of high technology.[1,2] Particularly, since the introduction of metallic particles, important progress has been reported in the area of advanced flexible media (tapes or disks) used for the storage of digital and analogue signals.[3−6] These particulate media consist of Fe-based elongated particles deposited longitudinally on a film. Elongated particles are preferred over equiaxial particles because of the low value of the demagnetizing field along the major axis. Additionally, because of the need to improve bit-packing densities, small particle sizes (above the superparamagnetic size limit) are required for high-density recording media.[1]

The main reason for using Fe metals and Fe-based alloys, rather than iron oxide, for recording applications is that they have higher values of saturation magnetization and coercivity. The main disadvantage of these media is the intrinsic chemical instability of finely divided metal, which requires after reduction a controlled oxidation of particles surfaces. The only commercially significant process for the production of iron metallic elongated particles is the thermal reduction of α-FeOOH (goethite) particles.[7] This thermal treatment can promote interparticle sintering and therefore the loss of the elongated shape. Both silica and alumina are common elements added to the system to prevent sintering of the particles during the required heat treatment.[8,9]

Cobalt is another important element added to the system that has been found to improve the coercivity of the material, and it also has been suggested to increase the chemical stability.[10] However, few studies have been reported about the exact location of Co in the Fe-based alloys compounds, and therefore, the precise role of the Co in improving the magnetic characteristics of the Fe-based metallic particles still remains unclear. For example, if the Fe-based alloys have a surface enriched in Co, the magnetic anisotropy of the coating is varied and this might have a possible influence on the magnetic interaction between the core and the shell of the particles (exchange interaction). Moreover, interparticle interactions of dipolar origin can also be strongly influenced and this can affect the coercivity value.[11,12]

Ultimately, the recording density achievable with these magnetic particles is limited by the coercivity and particularly the distribution of coercivities or switching

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fields within the material, which are closely associated with the crystallochemical characteristics of the particles (mainly particle size distribution, coating homogeneity, and particle microstructure).[1] Therefore, it seems necessary to create new synthetic routes or to develop the existing ones to better understand the role that the different additives could play in improving the magnetic characteristics of the materials such as coercivity and saturation magnetization. These synthetic routes should produce highly uniaxial and uniform doped goethite particles (say, for example, Co-doped goethite) in a rather simple way and with the adequate particle size and microstructure. Recently, we have reported the synthesis of uniform acicular goethite particles by a modified-carbonate route.[13] The synthesis essentially consists of two sequential oxidation processes (two-step method) that intend to separate the formation of primary particles and their subsequent growth to avoid heterogeneous particle distributions. This method, if applicable, should be the ideal route to produce uniform elongated FeCo particles, from which we could obtain information about the precise role of the Co.

Thus, the aim of this work was first to extend the two-step method for the production of Co-doped goethite particles to correlate the chemical and structural modifications of the precursors with the magnetic properties of the resulting metallic particles. Then, the particles so-obtained have been characterized in terms of morphology, and chemical and phase compositions with special attention in determining the location of cobalt. Finally, the magnetic properties of the metallic particles obtained by reduction of the goethite precursors have been measured and related to their microstructure. On the basis of previous studies on the Al−goethite system,[9] we have also added this element in some experiments to study how the combined effect of Al and Co helps to improve the coercivity of the final material. In particular, the antisintering effect of aluminum will help us to better understand the role of cobalt in improving the magnetic properties of the metallic particles.

Experimental Section

Sample Preparation. Analytical-grade reagents ferrous sulfate $Fe(SO_4)\cdot 7H_2O$ (Fluka), cobalt nitrate $Co(NO_3)_3$ (Aldrich), aluminum nitrate $Al(NO_3)_3\cdot 9H_2O$ (Aldrich), sodium carbonate Na_2CO_3 (Carlo Erba), and sodium hydroxide NaOH (Aldrich), and doubly distilled water previously deaerated with N_2 were used in all experiments.

Uniform Co−goethite particles were obtained by oxidation−precipitation of $FeSO_4$ and $Co(NO_3)_3$ solutions following a method described earlier for the preparation of undoped goethite particles.[13] First, sodium hydroxide (0.35 OH/Fe equivalent ratio) was added to a solution (kept at 40 °C under N_2) that contained $FeSO_4$ in a concentration of 0.1 M and the desired amount of $Co(NO_3)_3$. Immediately after the addition of the base, the N_2 gas was replaced with air (5 L min^{-1} flow rate) until a constant pH was reached (∼3.5). Then, an appropriate amount of sodium carbonate was added to raise the pH (1.5 CO_3^{2-}/Fe equivalents) and the oxidation was extended 4 h at the same temperature. Finally, once the reaction was completed, all the samples were cooled, centrifuged, washed several times with doubly distilled water, collected by filtration, and dried at 50 °C before analyses. Samples synthesized by this method are named G−Co. For comparison, we have also used this method to prepare pure goethite particles (named G).

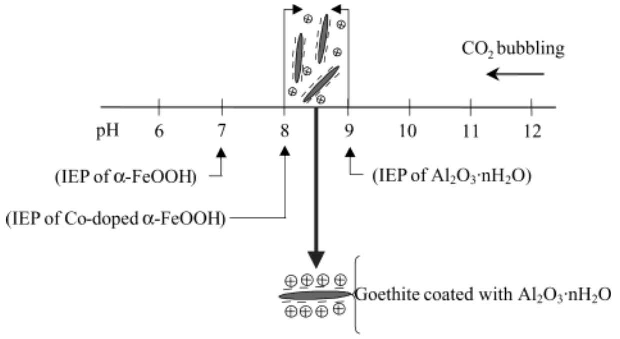

Figure 1. Schematic representation of the coating process. IEP stands for isoelectric point.

Once the pure and Co-doped goethite particles were obtained, they were further coated with a hydrated aluminum oxide (Al/(Al+Fe) molar ratio of 10%). The coating process involved first the dissolution of $Al(NO_3)_3$ (10^{-2} M) in 100 mL of water followed by the addition of a 10% NaOH aqueous solution to reach a pH of 12.5. Then either undoped or Co-doped goethite particles (1.0 g) were homogeneously suspended in the solution and carbon dioxide gas was blown into the slurry to lower the pH to a value of 8.5. In this way, a hydrated aluminum oxide ($Al_2O_3\cdot nH_2O$) layer was deposited onto the surface of the goethite particles.[6] It was found that rigorous pH control was essential for the production of homogeneous alumina coatings. Thus, the initial pH was set to 12.5 because in this region the surface charge density of the goethite particles is very high and electrostatic forces can stabilize the suspension.[14] For the coating process, the pH was lowered to 8.5 because the isoelectric points (IEP) of aluminum hydroxide, pure goethite, and Co-doped goethite are 9, 7.3, and 8.1, respectively.[14,15] Therefore, at pH 8.5 the surface of the undoped or the Co-doped goethite particles remains negative, while the surface of the aluminum hydroxide nuclei is positively charged, favoring the heterocoagulation process (electrostatically induced coagulation of particles having opposite charge density) and the formation of a homogeneous coating. A schematic representation of the heterocoagulation process is displayed in Figure 1. We could have started from an acidic pH, instead of basic, to stabilize the goethite particles, but in this case when increasing the pH to the optimum value to produce heterocoagulation (8.5), the goethite particles have to pass through their isoelectric point, which induces particle aggregation, resulting in nonhomogeneous coatings. Another parameter that affects the homogeneity of the coating is the initial concentration of the $Al(NO_3)_3$, which was found to be optimum at 10^{-2} M. Higher concentrations drive the segregation of aluminum hydroxide in the form of separate particles. Meanwhile, lower concentrations result in the partial coverage of the particles as detected by transmission electron microscopy. Samples synthesized by this method are named G−Al and G−CoAl.

Thermal Reduction. To obtain the final metal particles, the goethite samples were dehydrated in air at 400 °C for 3 h (after this treatment we can also expect the transformation of the hydrated aluminum oxide layer in alumina) and then reduced at 450 °C in a hydrogen stream of 40 L h^{-1} for 4 h. The samples were then cooled to room temperature under the hydrogen atmosphere. Finally, nitrogen gas was blown into a flask containing ethanol and the resulting stream was passed through the sample (∼1 h) to slightly passivate the iron particle surface. Without passivation samples could rapidly oxidize upon exposure to air. Dehydration and reduction temperatures were optimized in each case to achieve a

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(15) Isoelectric points for undoped and Co-doped goethite samples were experimentally obtained by measuring the electrophoretic mobility as a function of pH with a Coulter Delsa 440.

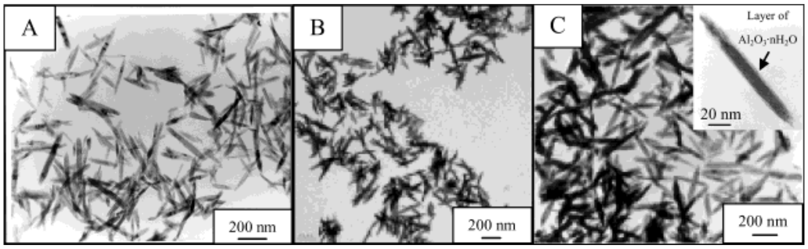

Figure 2. TEM images of (A) undoped goethite particles; (B) Co-doped goethite particles; and (C) a typical microstructure of the Al-coated samples showing no evidence of the possible segregation of the hydrated aluminum oxide in the form of separate particles and details of the coating.

decrease in internal porosity of the particles while preserving the acicular morphology of the final metallic particles. Samples prepared by this method are named Fe (after reduction of G), Fe−Co (after reduction of G−Co), Fe−Al (after reduction of G−Al), and Fe−CoAl (after reduction of G−CoAl).

Characterization Techniques. Phase identification was carried out by X-ray diffraction (XRD) in a Philips PW1710 using the Cu Kα radiation. An estimation of the crystallite size was determined from the full width at half-maximum of the XRD selected reflection by using the Scherrer equation. Cell parameters were determined by using the FULLPROF program. To determine the position of the diffraction peaks, single-peak fittings using a pseudo-Voigt profile were carried out and silicon was used as internal reference standard. Particle size and sample shape were examined by transmission electron microscopy (TEM, JEOL 2000 FX). The mean length (L) and width (W) were evaluated from the electron micrographs by counting around one hundred particles. From these data, the degree of polydispersity, defined as SD/mean size, was evaluated. The mean and the SD values associated with the axial ratio (L/W) were evaluated from the L/W ratios obtained for each particle.

The cobalt content in the goethite samples was determined by plasma emission (ICP, Perkin-Elmer 5500). For this analysis, 100 mg of powder was first dissolved with concentrated HCl and then diluted with doubly distilled water. Chemical analyses at particle level were done with an energy dispersive spectrometry analyzer (EDX, Oxford Link QX 2000) integrated in the transmission electron microscope.

Surface analyses of samples that include X-ray photoelectron spectroscopy (XPS) and Auger spectroscopy were carried in a VG Escalab 220 using the Mg Kα excitation source. The magnetic characterization was carried out in a vibrating sample magnetometer (VSM, MLVSM9 MagLab 9 T of Oxford Instrument). Hysteresis loops were recorded at 298 K after applying a saturating field of 3 T. Magnetic parameters, such as saturation magnetization (M_s), coercivity (H_c), and squareness (M_r/M_s, where M_r is the remanent magnetization) were obtained from the loops for each sample. The M_s values were evaluated by extrapolating to infinite field the experimental results obtained in the high field range where the magnetization linearly increases with 1/H.

Results and Discussions

Samples Preparation and Characterization. The addition of Co during the synthesis in a 10 mol % under the conditions described in the Experimental Section led to single-phase goethite particles with a cobalt content (determined by ICP) equal to that initially added. Chemical analyses carried out on single particles by EDX showed a composition similar to that of the overall solid, which indicates chemical homogeneity at particle level. Co-doped goethite particles were smaller (190 × 25 nm) than those that were undoped (240 × 30 nm) but they had similar axial ratios (Figure 2 and Table 1). Thus, the Co-doped goethite precursors are, in principle, more appropriate to obtain metallic particles with smaller particle sizes, which result in larger packing densities, and therefore better magnetic recording characteristics. We can also observe in Figure 2 that the coating procedure carried out under the conditions described in the Experimental Section led to homogeneous coatings with no evidence of the presence of hydrated aluminum oxide in the form of separate particles. Supporting this result, chemical analyses carried out on single particles by EDX showed that the aluminum content was similar to that of the overall solid.

Table 1. Morphological Characteristics for the Goethite Precursors Determined by TEM and XRD

sample	particle size (TEM) (nm) length	width	axial ratio	crystallite size (RX)[a] (nm)
G	240 (60)	30 (7)	8 (3)	25
G−Co	190 (40)	25 (6)	8 (3)	21

[a] Crystallite size was determined from the (020) reflection of goethite.

The smaller particle size of the Co-doped sample seems to suggest that the presence of cobalt retards the formation of goethite. Foreign species can retard goethite formation by interference at two stages of its formation: (1) by retarding dissolution of intermediate phases (for example lepidocrocite) and (2) by hindering nucleation and growth of goethite in solution.[16] Supporting this idea, the addition of higher amounts of cobalt leads to powders constituted by mixtures of goethite and lepidocrocite. Attempts were made to increase the amount of cobalt added by changing the experimental conditions (temperature, time, and OH/Fe and CO_3^{2-}/Fe equivalent ratios), however, we were not successful to obtaining samples constituted by only goethite. It seems that there is an upper limit to the amount of Co (∼10 mol %) that can be incorporated within the goethite structure. Therefore the presence of additional amounts of this element probably retards even longer the dissolution of the lepidocrocite and hinders the nucleation and growth of the goethite phase. In fact, previous studies have shown a similar limit to the amount of Co forming a solid solution within the goethite structure.[16] Crystal sizes obtained from the (020) XRD reflection of goethite for the Co-doped and undoped samples were similar to the particle width observed by TEM (Table 1), suggesting that the [001] crystallographic axis is along the longest particle dimension, in accordance with the goethite crystal habit of growth.[17]

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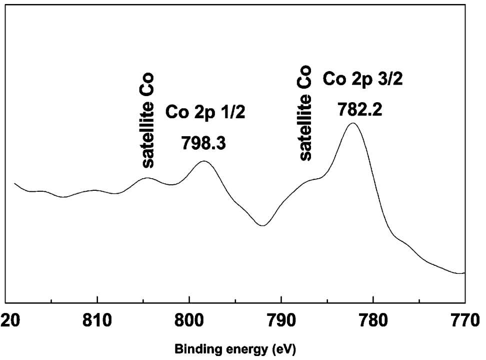

Figure 3. XPS diagram for the sample G−Co showing only the bands associated with Co.

Table 2. Cell Parameters of Pure and Co-Doped Goethites

sample	*a* (nm)	*b* (nm)	*c* (nm)	volume (nm^3)
G	0.4622 (2)	0.9955 (2)	0.3027 (1)	0.1393 (1)
G−Co	0.4630 (2)	0.9982 (3)	0.3030 (1)	0.1400 (2)

The XPS spectrum of sample G−Co was registered to determine the nature and location of the Co cations (Figure 3). The spectrum was characterized by two broad main peaks at 782.2 and 798.3 eV due to Co 2p and two strong associated satellites located at the high binding energy side of the main peaks. The position and intensity of these peaks are typical of the presence of Co(II).[18−21] In addition, the XPS spectrum (data not shown) displayed bands associated with the presence of Fe(III) cations and oxygen anions. The presence of an Auger band due to oxygen, which appears close to the main peak for cobalt, precludes the use of XPS to determine the Co/(Co + Fe) molar ratio on surface. Thus, we registered the Auger spectrum of the sample (data not shown) to estimate this value.

The Co/(Co + Fe) molar ratio on the surface obtained by Auger spectroscopy (11%) was similar to that obtained by ICP and EDX analyses (10%). This result suggests that Co(II) cations are homogeneously distributed in the goethite particles probably forming a solid solution due to the fact that the goethite particles are single crystals.[22] It is worthy of note that the incorporation of divalent cations up to a limit of 10 mol % in the goethite structure (similar to the one here reported for Co(II)) has been previously reported.[23] Additional confirmation of the presence of Co(II) inside the goethite structure was obtained after comparing the unit-cell parameters of the undoped and Co-doped samples (Table 2). First, it is important to mention that in most oxide structures high-spin Co(II) and low-spin Co(III) cations occur in the octahedral sites whereas iron cations are always found in the high-spin configuration.[24] The ionic radii of these cationic species in octahedral positions are 0.65, 0.74, and 0.55 Å for high-spin Fe(III), high-spin Co(II), and low-spin Co(III), respectively.[25] Therefore, we should observe an increase in unit-cell parameters if Co(II) forms a solid solution within the goethite structure and a decrease if Co(III) is the cation forming a solid solution within the goethite structure. In our samples, we observe an increase in unit-cell parameters (Table 2), which confirms both the existence of Co(II) cations and that these cations are found forming a solid solution within the goethite structure.[26]

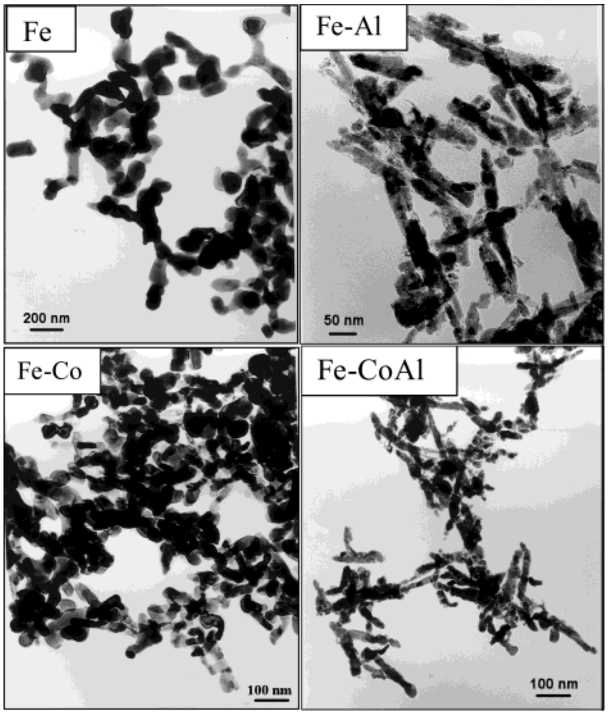

Figure 4. TEM images of the metallic particles.

Thermal Reduction. Metallic particles obtained from thermal reduction of the goethite precursors show very different morphological characteristics (Figure 4). Samples Fe and Fe−Co lost their elongated shape by sintering as a consequence of the heating process. In accordance, a particle volume increase instead of the theoretically expected decrease was observed when going from goethite to metallic iron (Tables 1 and 3). Unlike this, the samples with the alumina coating retained the acicular morphology after reduction because this oxide helps to prevent sintering. Considering that there is approximately a factor of 3 between the amount of iron in a unit volume of goethite and the same volume of iron (there are about 29 Fe atoms in 1 nm^3 of goethite and about 83 Fe atoms in 1 nm^3 of α-Fe), we should expect, in the absence of interparticle sintering, a shrinkage of the volume of about a factor of 3 in the samples that keep the morphology (axial ratio) after reduction (Fe−CoAl and Fe−Al). Indeed, this is the case (Tables 1 and 3), which clearly indicates the absence of interparticle sintering.

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(22) Electron diffraction carried out on a selected area of the Co-doped and undoped samples gave clear diffraction spots characteristic of goethite, confirming the single-crystal character of the samples.

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(26) In our samples we do not observe by XPS the presence on surface of adsorbed cations such as Na$^+$ that could balance the charge. Thus, it seems reasonable to assume that the charge balance occurs by uptake of protons (see ref 23). The Co(II) cations are probably found in the goethite structure homogeneously distributed and not forming Co(II)-enriched clusters that present low solubility.

Table 3. Morphological (determined by TEM) and Magnetic Properties of the Metal Particles

sample	length (nm)	width (nm)	axial ratio	H_c (Oe)[a]	M_s (emu/g)[b]	M_r/M_s[c,d]
Fe	~150			390	181	0.24
Fe-Co	~50			580	190	0.30
Fe-Al	170 (30)	22 (5)	8 (2)	1050	130	0.45
Fe-CoAl	120 (30)	18 (5)	7 (2)	1160	132	0.48

[a] H_c = coercivity. [b] M_s = saturation magnetization. [c] M_r = remanent magnetization. [d] M_r/M_s = squareness.

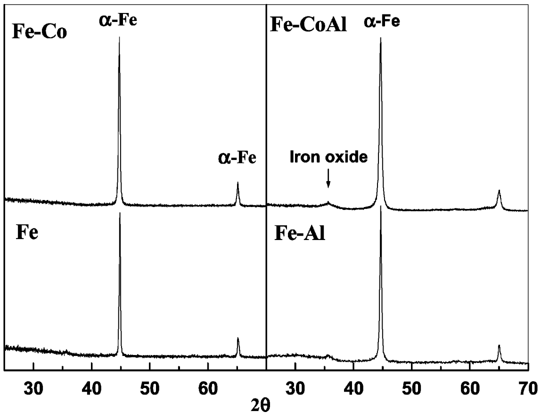

Figure 5. XRD patterns for the metallic particles.

XRD patterns for all the reduced samples are shown in Figure 5. Samples Fe and Fe–Co display a similar pattern with only diffraction peaks due to α-Fe, while samples Fe–Al and Fe–CoAl show, in addition to the main diffraction peaks associated with α-Fe, the presence of a broad diffraction peak around 35° (2θ), which could be due to the presence of small crystallites (estimated to be ~2 nm by the Scherrer equation) of an iron oxide with a spinel structure.[9] The fact that the samples remaining elongated (no interparticle sintering) have the highest iron oxide content could indicate that this phase has been formed during the passivation process carried out to stabilize the particles (small particles have high surface area and therefore are more susceptible to be oxidized). Further confirmation of the presence of oxidized iron was established by registering the XPS spectra of samples Fe and Fe–Co (data not shown).[27] The quantitative analyses of sample Fe–Co carried out by Auger spectroscopy showed that the Co/(Fe + Co) molar ratio on the surface was similar to that obtained in the goethite precursors, which indicates that the thermal treatment did not lead to any preferential segregation of the Co, and therefore that Fe and Co form an alloy with the Co randomly distributed in the Fe metallic core. Supporting the absence of segregation, chemical analyses carried out by EDX at particle level showed a composition similar to that of the overall solid, which indicates that all Co is found on the elongated particles.

Magnetic Behavior of Samples. Hysteresis loops of samples are displayed in Figure 6. The magnetic parameters obtained from the hysteresis loops are shown in Table 3. The M_s values were, in all cases, lower than that of bulk Fe (~220 emu/g) and Fe–Co (230 emu/g for 10 mol % of Co),[10] which is associated with the above-mentioned presence of a certain amount of iron oxide spinel. It is important to mention that Fe and Fe–Co particles of these sizes are expected to have values of M_s similar to those of bulk,[28,29] and therefore any diminution from the expected value must be unequivocally associated with the presence of the oxide passivation layer. Supporting this interpretation, the sintered samples (Al-free samples), which have smaller surface area and therefore lower iron oxide content, present the higher M_s values.[30] By taking into consideration the M_s value for bulk Fe (220 emu/g) and the Fe–Co alloy (230 emu/g) and a value of 10–20 emu/g for the iron oxide spinel (assumed to be nanocrystals of maghemite of about 2 nm),[31] we could estimate an iron oxide content of ~20% for samples Fe and Fe–Co and ~50% for samples Fe–Al and Fe–CoAl.

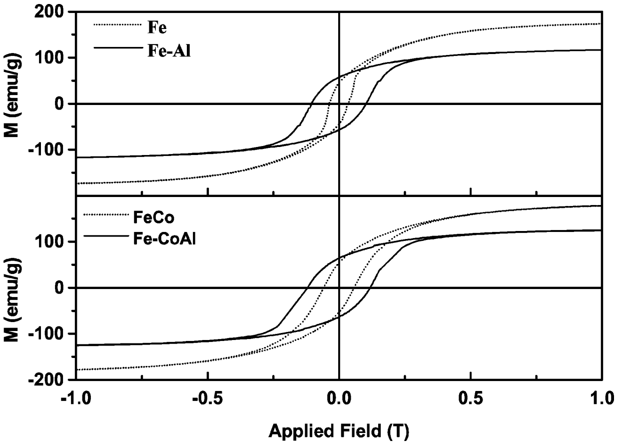

Figure 6. Hysteresis loops at room temperature of the metallic particles.

The H_c value for sample Fe–Co was significantly higher (580 Oe) than that obtained for the sample containing only Fe (390 Oe). Such an increase could be attributed to the role that Co played during the goethite synthesis. As mentioned above, Co retards the formation of goethite, and thus Co-doped goethite particles were smaller than undoped goethite particles (Table 1); and what is more important is that after reduction Fe–Co particles remained smaller (Table 3). The smaller particles have a size much closer to the one that corresponds to a magnetic monodomain and thus it seems realistic to conclude that this is the reason for which they present higher H_c values. Supporting this idea the value of M_r/M_s was higher for sample Fe–Co (Table 3). Additional support of this idea can be obtained

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(27) The absence of the iron oxide diffraction peak in samples Fe and FeCo is probably due to their low content combined with the small particle size of the generated nanocrystals (with a grain size lower than ~2 nm, diffraction effects are diffuse and close to the background noise).

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(30) The amount of nonmagnetic material (alumina) represents only 8% in weight and thus cannot account for the observed decrease in M_s values.

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from the samples containing alumina. These particles have similar axial ratios and similar values of M_s (similar shape anisotropy contribution), however we observe a slight increase in the value of H_c in sample Fe−CoAl (1160 Oe) when compared to that of sample Fe−Al (1050 Oe). This increase, even though is low, could be again associated with the small particle size of sample Fe−CoAl. In agreement, the value of M_r/M_s was higher for sample Fe−CoAl (Table 3). Finally, the increase in H_c values in the alumina-coated samples (as expected for their higher axial ratio) confirms that additions of elements that prevent sintering, such as alumina, are essential to obtain metallic particles adequate for magnetic recording.

Conclusions

We have shown that a method based on a modified-carbonate route produces elongated Fe-based particles of interest for magnetic recording applications. This synthetic route is especially adequate to obtain information about the role that different elements such as cobalt play in improving the magnetic properties of the Fe-based metallic particles used in recording applications. We have observed that the addition of cobalt retards the formation of the goethite precursors and that there exists a limit in the amount of Co that can be incorporated to the goethite structure (∼10 mol %). We have also determined that this retarding effect is in the base of the production of smaller metallic particles. This decrease is directly related to the improvement of magnetic properties in the Co-doped samples. Finally, it has been determined that even in the samples containing cobalt, the presence of the alumina coating is essential to avoid interparticle sintering and therefore to achieve higher values of coercivity.

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