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Synthesis of Fe/SiO_2 and iron oxides/SiO_2 nanocomposites by long-term ball milling

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ABSTRACT

Iron oxide/SiO_2 nanocomposites are synthesized by dry ball-milling a mixture of *bcc* Fe and α-quartz powders for prolonged times. A sequence of nanocomposites is obtained, with small magnetic particles dispersed in a non magnetic, amorphous matrix. The powders are characterized by X-ray diffraction and transmission electron microscopy. The magnetic hysteresis properties are investigated in the range 50–300 K. After 120 h milling, deformed, non-spherical, α-Fe nanocrystallites of about 10 nm in size and very few small (<10 nm) maghemite particles are found. At room temperature, iron particles are ferromagnetic and a large effective magnetic anisotropy is estimated, which is mainly attributed to surface effects. Between 160 and 200 h milling, maghemite nanoparticles are observed while after 220 h grinding, hematite phase appears; after 340 h milling, the sample consists of ferromagnetic hematite particles with a broad size distribution (5–50 nm) embedded in an amorphous matrix.

1. Introduction

Magnetic nanocomposite materials based on iron and iron oxides dispersed in ceramic matrixes have attracted great interest mainly because of their many and broad applications [1]; these include data storage, magnetic resonance contrast-enhancing media, gas sensors, magnetic fluids, magnetic refrigeration, magneto-optics and bioprocessing, among others. Size effects become important in these nanoscale featured materials, giving rise to complex magnetic behaviours often requiring a different approach as compared to bulk materials [2,3]. The main features determining the magnetic behaviour of these composite systems are the particle size distribution, the large volume fraction of atoms in and nearby the surface, the eventual appearance of a superficial oxide layer and magnetic interactions, strongly dependent on the dispersion of magnetic particles into the non-magnetic host [4].

For Fe/SiO_2 nanocomposites, many authors report unexpectedly high room temperature coercivities, ranging from $\mu_0 H_C = 35$ mT to over 150 mT [4,5], as compared to the value predicted by the Stoner–Wohlfarth model assuming anisotropy values close to the bulk one. Another interesting property of Fe nanoparticles dispersed or embedded in different matrixes, is that they exhibit a strong uniaxial effective anisotropy, in spite of their cubic crystal symmetry [6,7]. Surface anisotropy due to broken symmetry or spin disorders at the particle surfaces is believed to play a dominant role in such fine particulate systems [8].

Nowadays, composites containing γ-Fe_2O_3 (maghemite) nanocrystals are also intensively investigated for their potential applications in magnetic-tape media, colour imaging, magnetic memories for computers, magneto-optical devices, bioprocessing, catalysis and ferrofluids. Maghemite is a ferrimagnetic material which represents the low temperature phase of iron oxide, and it easily transforms to the more stable phase, hematite (α-Fe_2O_3), when submitted to temperatures above 653 K [9–11]. The development of new synthesis routes for maghemite nanoparticles is still of great interest. The usual technique needs two steps: the synthesis of nanoparticles by coprecipitation in alkaline solution of ferrous and ferric cations and then, the particle oxidation by a treatment in air, at temperatures between 373 K and 523 K [12].

Different methods have been reported in the literature for preparing iron and iron oxide nanocomposites, such as wet chemical synthesis, sol–gel processing and sputtering. In recent years, high energy mechanical milling has been used as a versatile and non-expensive technique for producing non-equilibrium

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phases in several ways, such as nanostructured and amorphous materials with a broad range of chemical compositions, nanocomposites and extended solid solutions [13,14]. This relatively simple synthesis technique, with only a few operation parameters, is suitable for large scale commercial production [15]. Maghemite nanoparticles and maghemite/silica nanocomposites have been already prepared by high energy mechanical alloying, using hematite (α-Fe_2O_3) [12] and chemistry-derived α-Fe_2O_3/SiO_2 gel powders [16] as precursors, and also from grinding iron powders in water [12].

In this paper we report the results obtained with an alternative route to produce iron/and iron oxide/SiO_2 composites. Two basic crystalline precursors, α-Fe and SiO_2 powders are dry milled in a medium energy planetary mill for long times, under air atmosphere. In this case, large amounts of energy are also supplied to the powder but at a low rate promoting the formation of different metastable phases. It was possible to sequentially obtain composites containing iron, maghemite and hematite nanoparticles dispersed in amorphous silica, directly from iron and quartz powders. The microstructure evolution, the different iron containing phases forming during milling and the magnetic hysteresis properties of the different composites are then described.

2. Experimental procedures

Analytical grade α-Fe (99.4% purity) and SiO_2 (99% purity) crystalline powders, were used as starting materials for ball milling. The milling was carried out in a Fritsch Pulverisette 5 planetary ball-mill equipped with hardened steel balls and vials. These precursor powders were first milled separately to reduce their particle size, until both had a similar mean crystallite size, of about 65 nm for α-Fe and 50 nm for quartz. Then, these pre-milled powders were mixed to achieve the proportion: 50 wt.% α-Fe + 50 wt.% SiO_2. The initial ball to powder mass ratio was 10:1 and the mixture was milled at a speed of 200 rpm, for times up to 340 h, in air atmosphere without any additive (dry milling). The milling process was interrupted after selected times to take out small amounts of powder for characterization. Samples were then labelled Sx, where x refers to the total milling time in hours.

Crystalline phases and the microstructure of the milled products were monitored by X-ray diffraction (XRD) and transmission electron microscopy (TEM) respectively. X-ray diffraction profiles were recorded by a Philips PW 3830 diffractometer, operated in Bragg–Brentano geometry, with Cu Kα radiation (λ = 1.5418 Å) in the $10^\circ \leq 2\theta \leq 100^\circ$ range. XRD results were used to determine the phases present in the powders and their lattice parameters and average crystallite sizes. The morphology of the nanocomposite powders was observed by a Philips CM200UT TEM operating at 200 kV. Samples for TEM observation were prepared by dispersing a small amount of the powders in ethanol and depositing a drop of each emulsion on a holey carbon-coated copper grid.

Samples for magnetic measurements were prepared by cold-pressing the as-milled powders under 5 tons pressure, into cylinders of 6.5 mm in diameter and typically 2 mm in height. The magnetic field was applied parallel to the sample diameter and the actual internal field was calculated as $\mu_0 H_i = \mu_0 H_a - N J$, with $\mu_0 H_a$ the applied field, N ($\cong$0.18) the demagnetizing factor and J the magnetic polarization. Room temperature hysteresis curves were recorded by a vibrating sample magnetometer (VSM) Lakeshore 7300, with a maximum field up to 1.5 T. The magnetization as a function of temperature was studied in a Quantum Design SQUID magnetometer, in the range between 5 K and 300 K, following the zero field cooling (ZFC) and field cooling (FC) protocols. The sample is first cooled from room temperature to 4 K, without any applied field and the ZFC curve is recorded during heating under an applied field of 10 mT. The FC curve is then measured during a second heating run, keeping the external field applied. In addition, isothermal hysteresis loops were traced in the same temperature range up to 1.5 T.

3. Results and discussion

3.1. Microstructures

Fig. 1 shows the XRD patterns of the powders after different milling times. Sample S0 only shows the precursor oxides characteristic lines (α-Fe (bcc) and α-quartz); after 120 h milling, these diffraction peaks become less intense and significantly broadened, as expected for a continuous reduction in particle/crystallite size and a progressive microstrain (defects) during the milling process. A new phase appears in sample S160, but due to the large structure distortions induced by milling, the identification by X-ray diffraction is not conclusive. This new phase is also found in sample S180, but as the crystalline structure of maghemite is almost identical to that of the inverse spinel magnetite [10,17] it could not be identified with this technique as magnetite (Fe_3O_4) nor maghemite (γ-Fe_2O_3).

This phase was further investigated by measuring the room temperature Mössbauer spectrum, in transmission geometry, using a constant acceleration spectrometer with a 10-mCi ^{57}CoRh source. Fig. 2 shows the results for samples S120, S160 and S180; points are experimental data and the thick continuous line is the fitting curve, obtained by the addition of the different contributions shown. The fitting parameters as the isomeric shift (δ) referred to the metallic iron, the quadrupole splitting (ΔQ), the hyperfine field (B) and the percentage (P) are listed in Table 1.

Sample S120 is the only one exhibiting a weak magnetic interaction at room temperature, evidenced by a sextet (Zeeman splitting). It also shows two paramagnetic signals while a doublet is not observed because of a fast superparamagnetic relaxation. The first paramagnetic interaction has an isomeric shift near that of Fe^{3+} while in the second one it is about that of Fe^{2+}. These interactions are likely to arise in mixed Fe and Si oxides. The parameters corresponding to the magnetic interaction are similar to those of metallic iron (α-Fe). No traces of magnetite are

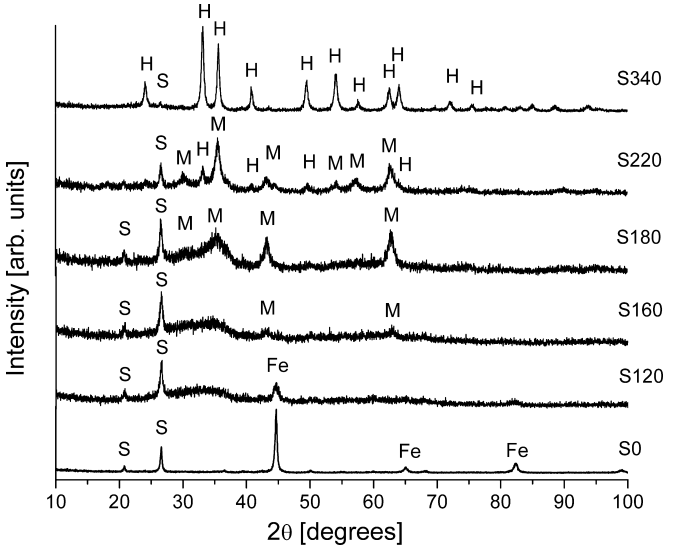

Fig. 1. X-ray diffraction patterns of samples Sx after different milling times. The principal diffraction lines of the α-Fe (Fe), α-quartz (S), maghemite (M) and hematite (H) are indicated.