Handling the particle size and distribution of Fe$_3$O$_4$ nanoparticles through ball milling

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Abstract

A series of samples consisting of spinel Fe$_3$O$_4$ nanoparticles with controlled particle sizes and increasing concentration has been obtained through ‘mild’ ball milling (BM) experiments by using an organic carrier liquid. We have succeeded in producing quite narrow particle size distributions with mean values $d \sim 7$–10 nm by an appropriate choice of the milling time for each concentration. The method proved to be practical to tailor the final particle size without formation of undesirable phases. All samples showed superparamagnetic behavior at room temperature, with transition to a blocked state at $T_B \sim 10$–20 K. The mean value and distribution width of the size distributions for the three samples studied were obtained from $M(H)$ cycles recorded at $T > T_B$ showing good agreement with X-ray diffraction and electron microscopy results. The effect of increasing interparticle interactions was to shift $T_B$ upwards, as inferred from magnetization measurements. Mössbauer spectra at low temperatures showed no evidence of enhanced spin disorder.

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1. Introduction

High-energy ball milling (HEBM) is known to induce chemical reactions in powder mixtures, a process usually termed mechanochemistry. During the last decade, HEBM has proved to be an exciting technique for the transformation of known materials and the synthesis of new ones. A broad range of ceramics and cermets composites, amorphous and nanocrystalline alloys as well as high temperature phases of nitrides, carbides and silicides have been produced by applying the HEBM technique with different experimental setups [1–3]. Self-sustained combustion can also occur for exothermic mixtures of reactants, provided the transferred mechanical energy is enough to put the starting powders to a critical metastable state [4].

For lower energy ranges, this technique has been applied to solid/liquid mixtures as a tool for making homogeneous dispersion at industrial scales, such as paint and coating production techniques [5,6]. However, a limitation for this approach is related to the chemical reactions that yield non-desired surface phases or even dissolution of the solid phase onto the liquid carrier.

Regarding the magnetic properties of nanostructured systems, the study of the mechanisms linking particle shape, size distribution and surface structure to the resulting magnetic properties is hindered by the concurrency of several mechanisms on the observed properties [7]. Relaxation effects are strongly dependent on the magnetic dipolar interactions between particles, and thus it is crucial to isolate the influences of dipole–dipole interactions, surface disorder, shape anisotropy, cluster aggregation, etc. In this work, we present a study on the magnetic properties and interactions in Fe$_3$O$_4$ nanoparticles synthesized through ‘mild’ ball milling (BM) experiments, using methanol as an organic liquid carrier in different concentrations.

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2. Experimental procedure

Three samples consisting of magnetite (Fe₃O₄) particles dispersed in a liquid carrier (CH₃OH), with different concentrations, have been prepared by BM in a planetary mill (Frisch Pulverisette 4). A mixture of magnetite powder (99.99%, mean particle size $\sim 0.5$ μm) and methyl alcohol (between 20 and 40 ml) were introduced in a hardened steel vial and sealed in an Ar atmosphere (Fig. 1). All samples were ground for times up to 125 h, extracting partial amounts after selected intervals to follow the evolution of the mean particle size ($d$) of the magnetite phase, and stopping the experiment after reaching a value of $d \sim 6–10$ nm. The milling parameters and the resulting properties are summarized in Table 1.

X-ray diffraction (XRD) measurements were performed using a commercial diffractometer with Cu Kα radiation in the 2θ range from 10 to 80°, and the morphology of the milled samples was analyzed by transmission electron microscopy (TEM) in a JEOL JEM-1230 microscope. Mössbauer spectroscopy (MS) measurements were performed between 20 and 294 K in dried samples. A conventional constant-acceleration spectrometer was used in transmission geometry with a 57Co/Rh source. The recorded spectra were fitted by single-site and distribution programs, using α-Fe at 294 K to calibrate isomer shifts and velocity scale. For magnetic measurements, all samples were conditioned in closed containers before quenching the magnetite/methyl-alcohol mixture below its freezing point ($\sim 265$ K) from room temperature. A commercial SQUID magnetometer was employed to perform static and dynamic measurements as a function field, temperature and driving frequency. Zero-field-cooled (ZFC) and field-cooled (FC) curves were taken between 5 and 250 K, to avoid the melting of the solid matrix (solvent).

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R$ (wt%)</th>
<th>BM time (h)</th>
<th>$d_{\text{TEM}}$ (nm)</th>
<th>$d_{\text{XRD}}$ (nm)</th>
<th>$d_{\text{MAG}}$ (nm)</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
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<td>3</td>
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<td>8.1</td>
<td>6.4</td>
<td>7.4</td>
<td>0.55</td>
</tr>
<tr>
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<td>18</td>
<td>9.3</td>
<td>7.1</td>
<td>8.0</td>
<td>0.77</td>
</tr>
<tr>
<td>F50</td>
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<td>28</td>
<td>9.2</td>
<td>7.4</td>
<td>9.6</td>
<td>0.68</td>
</tr>
</tbody>
</table>

3. Results and discussion

Three continuous BM experiments, up to 125 h, were carried out for concentrations $R = 3, 10$ and 50 wt% of magnetite. For each experiment, about 20 fractions were extracted along the process, from the first minutes up to $\sim 120$ h, and X-ray diffractograms were taken to follow the evolution of the average crystallite size ($d$) with milling time (inset of Fig. 2). The Scherrer formula was used to estimate the ($d$) values from the three more intense peaks of each diffraction pattern, without considering possible contributions of crystal stress to the observed linewidth. The three series of patterns showed essentially the same evolution of the diffraction lines: starting from well-defined peaks (for the initial $\sim 0.5$ μm particles) the linewidth increased steadily with increasing milling time, reaching a maximum value after some 10–20 h (depending on the sample) that remained constant up to $\sim 120$ h.

In the following we will focus on three samples, selected from each of the series with different concentrations. The samples with 50, 10 and 3 wt% of magnetic material will be labeled F50, F10 and F3, respectively. The arrows in the inset of Fig. 2 shows that the milling times for each sample were chosen at the beginning of the plateau defined by the constant ($d$) values, avoiding the possibility of different degrees of structural disorder or re-crystallization processes [8]. It can be observed that for increasing concentration of magnetic particles, a longer milling time was needed for reaching the beginning of the plateau of minimum crystallite size. On the other side, the minimum values of ($d$) attained...
were almost independent of the particle concentration. The values of crystallite sizes for the samples studied in this work are displayed in Table 1.

TEM images showed that all samples consisted of agglomerates of particles with average grain size \( d \sim 7-10 \) nm (Fig. 1 and Table 1). The clusters of particles observed in the TEM images were difficult to break with ultrasonic treatment, and thus it is likely that these clusters also exist in the as milled dispersion. All XRD patterns could be indexed with the Fe\(_3\)O\(_4\) single phase (Fig. 2) without any evidence of new phases formed during milling. It is worth to notice that previous results (not shown here) on the same particles showed the oxidation to Fe\(_2\)O\(_3\) after some minutes of milling when milled in open vials. This fact is in agreement with previous reports on the hematite–magnetite transformation during milling in open/closed vials [9], and shows that the liquid carrier does not prevent gas (oxygen) exchange during milling. Estimations of \( d \) from TEM data indicated good agreement with XRD data, although the latter slightly underestimates the average diameter, probably due to the contribution of structural stress to the linewidth in milled samples.

The Mössbauer spectra at room temperature (Fig. 3) showed for all samples a doublet with the same hyperfine parameters within experimental error (quadrupolar splitting \( Q_S = 0.52(2) \) mm/s, and isomer shift \( IS = 0.29(2) \) mm/s). These parameters are typical of magnetite nanoparticles in the SPM state, as expected for the present samples. This doublet is originated in the fast relaxation of the particle magnetic moment in the SPM state. As the temperature is decreased and the blocking temperature \( T_B \) is crossed, a magnetic sextet develops due to the slowing of the relaxation rate. For \( T = 20 \) K, the spectra showed only one sextet with broadened lines (Fig. 3), which could be fitted using a hyperfine field distribution with mean values \( B_{hyp} \sim 51.9 \) T for all samples.

Magnetite has a cubic spinel structure (space group \( Fd3m \)) that contains Fe\(^{3+}\) ions at tetrahedral sites (A) and Fe\(^{3+}/Fe^{2+}\) at octahedral sites (B), yielding ferrimagnetic order below \( T_C \) [10]. At low temperature, the system undergoes a structural transition (the Verwey temperature, \( T_V \sim 120 \) K), and concurrently the magnetic and transport properties undergo a sudden change at this temperature. It is known that this transition temperature is shifted to lower temperatures in small particles [11], disappearing for values of \( d \) of about 10 nm. In agreement with the previous ideas, the ZFC/FC curves (Fig. 4) of the three samples show clearly that the Verwey transition measured in a well-crystallized sample (solid line in Fig. 4) is absent, and a peak at low temperatures signals the transition to the ordered state. It was found that this blocking transition increase for increasing particle concentration, suggesting the contribution of interparticle interactions to the effective magnetic anisotropy of the nanoparticles.

Magnetization measurements vs. applied field performed at \( T = 5 \) K (Fig. 5) showed that the magnetization does not saturate at high fields. Thus, the \( M_S \) values were obtained after extrapolating to infinite field were about 15–19%
lower than the saturation value of bulk magnetite ($M_s = 88–90$ emu/g) at the same temperature. The possibility of the observed decrease in $M_s$ being due to changes in A- and B-site population was discarded since this would require an almost full inversion. For ball-milled particles, spin disorder at the surface is a more likely reason for the observed reduction.

Hysteresis loops performed above the blocking temperature (inset of Fig. 6) showed that the three samples were in the SPM state, having null coercivity within experimental accuracy. Furthermore, the magnetization data could be collapsed onto a single curve for any $T > T_B$; as expected for SPM nanoparticles. For non-interacting and monodispersed SPM particles, this universal function is given by

$$M_{sp}(H; T) = N_m L(x)$$

where $N_m$ is the number of particles of magnetic moment $m$, and $L(x)$ is the Langevin function of argument $x = \mu H/k_B T$ i.e., the ratio of magnetic to thermal energy. A more realistic model \cite{12,13} should include the effects of particle size distribution resulting along the milling process, so the magnetization can be better described as a weighted-sum of Langevin functions

$$M^p = M^\text{bulk}_s \int_0^\infty L \left( \frac{\mu H}{k_B T} \right) f(\mu) d\mu$$

where $f(\mu)$ is a log-normal distribution

$$f(\mu) = \frac{1}{\sqrt{2\pi}\sigma\mu} \exp\left(-\frac{(\ln \mu/\mu_0)^2}{2\sigma^2}\right)$$

of magnetic moments $\mu$. In this equation, $\sigma$ is the distribution width and $\mu_0$ is the median of the distribution related to the mean magnetic moment $\mu_m$ by $\mu_m = \mu_0 \times \exp(\sigma^2/2)$. The distribution function satisfies the normalization condition

$$M_s = \int_0^\infty f(\mu) d\mu.$$

The results of the fitting procedure of the $M(H, T)$ curves using Eqs. (1) and (2), and the resulting particle size distributions are shown in Fig. 6. For the fitting procedure the saturation magnetization values $M_s$ measured for each sample have been used. The resulting magnetic moment distribution values have been related to size distributions by assuming spherical geometry for particles, i.e., $V = \pi (\bar{d})^3/6$ where $\bar{d}$ is the particle diameter, and a saturation magnetic moment of bulk material. The radii estimated calculated from the respective magnetic moment values, by assuming spherical particles, are in excellent agreement with TEM observations (Table 1).

The control on the final particle size and dispersion of ball-milled magnetite particles, achieved through the use of an organic solvent as a dispersant, is probably related to the existence of this carrier phase that tends to homogenize the spatial distribution of the granular solid at the initial stages of the BM. This in turn allows a more homogeneous
collision rate between particles and balls within the milling containers. Although we did not observed the formation of undesired phases up to 140 h of milling with methanol as dispersant, chemical reactions did occur for all other organic solvents after ~60 to 100 h, depending on the molecular weight. Therefore, the control of the crystallite evolution along the whole process could be useful to prevent these phases by stopping the experiment just after reaching the steady \(d\) values, and before chemical reactions start.

Although the distribution width values found here are evidently larger than for most of equilibrium synthesis routes (i.e., sol–gel, coprecipitation, molecular epitaxy, etc…), the present distributions are the narrower yet reported, to the best of our knowledge. Furthermore, the results obtained turned out to be highly reproducible, which is a crucial requisite for taking advantage of this technique that is potentially expansible up to industrial scales.

This control allowed us to find that, as the concentration of magnetic phase increases, the system requires more energy transfer to reach the (minimum) steady values of crystallite size \(d\). Since this minimum value is essentially the same for all concentrations, the observed increase of the blocking temperatures with higher particle concentrations suggests the influence of interparticle interactions on the ordering process. The existence of spin disorder in all samples, inferred from the diminished saturation magnetization at low temperatures, does not seems to be related to the milling process but to intrinsic properties of the surface in these nanoparticles.

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References