Structure and magnetism of granular Fe–Al₂O₃

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Abstract

The structural and magnetic properties of granular Fe–Al₂O₃ nanocomposite obtained starting from sol–gel processing are presented. Samples with nominal Fe content ranging from 20% to 62% in volume were prepared. The conversion of Fe oxides into metallic Fe was obtained by calcination at 800 °C followed by reduction at 600 °C for 2 h in H₂ atmosphere. After reduction, our results indicated up to 78% α-Fe, preserving the mean diameter of the metallic nanoparticles between 50 and 80 nm, ~16% Fe oxides and ~7% interstitial Fe³⁺ and substitutional Fe⁵⁺ cations in the Al₂O₃ lattice. Vibrating sample magnetometry at 300 K resulted in coercivity between 400 and 630 Oe and saturation magnetization between 40 and 134 emu/g. From transport measurements, the highest magnetoresistance, close to 2% at room temperature, was observed for samples with 25% α-Fe and 51 vol% total Fe. © 2001 Elsevier Science B.V. All rights reserved.

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Granular magnetic heterogeneous materials with ferromagnetic metallic nanoparticles embedded in a non-magnetic matrix have attracted much attention in the last years since, similar to multilayers, these magnetic solids have been found to present giant magnetoresistance [1–3] due to spin-dependent tunneling [4] or spin-dependent scattering. Different deposition methods have been used to prepare magnetic granular Fe-ceramic systems in the form of granular thin films, starting from bulk α-Fe and insulator targets. Chemical routes have also been used to prepare granular Fe-insulator materials. Sol–gel is a chemical route that presents easy scale-up but needs an additional step for the reduction of oxide phases into metallic Fe. Sol–gel processing was applied, for example, to obtain granular nanocomposites such as Fe–SiO₂ [5], Ni–SiO₂ [6], and Fe–Al₂O₃ with up to 2 vol% Fe [7]. Granular Fe–Al₂O₃ prepared by sputtering [8] and by ball milling have also been investigated [9,10].

In this paper, we have investigated the synthesis and the structural and magnetic properties of granular Fe–Al₂O₃ nanocomposite obtained starting from sol–gel processing. The nominal total Fe content was in the range of 20–62% in volume. Samples were prepared starting from solutions with adequate concentrations of Al(NO₃)₃·9H₂O and FeSO₄·7H₂O as precursors, dropped slowly in a NH₃ solution. After precipitation, the gel was washed and dried at 80 °C for 12 h. The powder samples were then calcinated at 800 °C in air and reduced at 600 °C in H₂ atmosphere during 2 h. After calcination, the total Fe content was determined by atomic absorption spectroscopy. The obtained powder samples were characterized by X-ray diffraction (XRD), Mössbauer spectroscopy (MS) and vibrating sample magnetometry (VSM). XRD results have shown that after calcination only α-Fe₂O₃ and some Fe₅O₄ are detected. After H₂-reduction, diffraction patterns due mainly to metallic Fe and to Fe₃O₄ are observed, as illustrated in Fig. 1. The Al₂O₃ matrix remains poorly crystallized and diffraction patterns due to this phase are
not observed. As determined from the diffraction patterns, Fe nanoparticles present average diameter in the range of 50–80 nm, very close to the diameter of the precursor α-Fe₂O₃ particles.

Fig. 2 shows room temperature (left) and 20 K (right) Mössbauer spectra for samples with 23, 40, and 62 vol% total Fe, after H₂-reduction. At room temperature, the spectra are characterized by considerable superparamagnetic relaxation and at 20 K Mössbauer measurements allow a better fit by resolving superparamagnetic behavior of the nanometric particles. MS results indicated reduction rates as high as 70% (sixet, α-Fe). In the spectra, remaining Fe-oxides (∼16%) are represented by a magnetic hyperfine field distribution at high fields (>40 T). Approximately 10% of the spectral areas are attributed to Fe⁵⁺ ions occupying substitutional (Al³⁺) and Fe²⁺ ions occupying interstitial positions in the Al₂O₃ lattice, characterized by quadrupole splittings close to 0.85 and 1.75 mm/s, respectively, and represented by a hyperfine field distribution at low fields (<10 T).

As determined by VSM at 300 K, the magnetization presented by the samples at 2 T ranges from 40 to 134 emu/g. The maximum coercivity was 630 Oe, observed for a sample with 40 vol% Fe, value that is higher than that obtained by other authors for Fe–Al₂O₃ prepared by ball milling [9,10]. Magneto-transport measurements were performed for few samples. Fig. 3 shows the best result for the room-temperature magnetoresistance, obtained for a 51% Fe–Al₂O₃ (25% α-Fe, average particle diameter ∼73 nm), together with the magnetization curve presented by the sample. Equivalent codeposited Fe–Al₂O₃ thin films reveal higher magnetoresistance, equal to 3% for 33% Fe–Al₂O₃ [8].

In conclusion, we have investigated the synthesis and the structural and magnetic properties of granular nanocomposite Fe–Al₂O₃ prepared starting from sol–gel processing. Samples with total Fe content ranging from 20 to 62 vol% were obtained by calcination at 800°C followed by H₂-reduction at 600°C for 2 h. We have achieved Fe reductions rates of up to 78%, preserving the mean diameter of the α-Fe nanoparticles between 55 and 80 nm. Significant amount (∼16%) of α- and γ-Fe₂O₃ and Fe₃O₄ remains embedded in the alumina matrix, which presents some (∼6%) interstitial Fe²⁺ and substitutional Fe⁵⁺ ions diluted in its lattice. The highest value of giant magnetoresistance, close to 2% at room temperature, was measured for samples with 25% metallic Fe and 51 vol% total Fe.
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References