



ELSEVIER

Journal of Magnetism and Magnetic Materials 226–230 (2001) 1861–1863



www.elsevier.com/locate/jmmm

## Structure and magnetism of granular Fe–Al<sub>2</sub>O<sub>3</sub>

A. Santos<sup>a</sup>, J.D. Ardisson<sup>a</sup>, A.D.C. Viegas<sup>b</sup>, J.E. Schmidt<sup>b</sup>, A.I.C. Persiano<sup>c</sup>,  
W.A.A. Macedo<sup>a,\*</sup>

<sup>a</sup>Laboratório de Física Aplicada, Centro de Desenvolvimento da Tecnologia Nuclear, CP 941, 30123-970 Belo Horizonte, Brazil

<sup>b</sup>Instituto de Física, Universidade Federal do Rio Grande do Sul, 91501 Porto Alegre, Brazil

<sup>c</sup>Departamento de Física, Universidade Federal de Minas Gerais, 30161 Belo Horizonte, Brazil

### Abstract

The structural and magnetic properties of granular Fe–Al<sub>2</sub>O<sub>3</sub> 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 H<sub>2</sub> atmosphere. After reduction, our results indicated up to 78%  $\alpha$ -Fe, preserving the mean diameter of the metallic nanoparticles between 50 and 80 nm,  $\sim$ 16% Fe oxides and  $\sim$ 7% interstitial Fe<sup>2+</sup> and substitutional Fe<sup>3+</sup> cations in the Al<sub>2</sub>O<sub>3</sub> 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%  $\alpha$ -Fe and 51 vol% total Fe. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Metal–nonmetal granular system; Sol–gel; Magnetic properties; Magnetoresistance

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  $\alpha$ -Fe and insulator targets. Chemical routes have been also 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–SiO<sub>2</sub> [5], Ni–SiO<sub>2</sub> [6], and Fe–Al<sub>2</sub>O<sub>3</sub> with up to 2 vol% Fe [7]. Granular Fe–Al<sub>2</sub>O<sub>3</sub> prepared by sputter-

ing [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–Al<sub>2</sub>O<sub>3</sub> 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(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and FeSO<sub>4</sub>·7H<sub>2</sub>O as precursors, dropped slowly in a NH<sub>3</sub> 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 H<sub>2</sub> 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  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and some Fe<sub>3</sub>O<sub>4</sub> are detected. After H<sub>2</sub>-reduction, diffraction patterns due mainly to metallic Fe and to Fe<sub>3</sub>O<sub>4</sub> are observed, as illustrated in Fig. 1. The Al<sub>2</sub>O<sub>3</sub> matrix remains poorly crystallized and diffraction patterns due to this phase are

\* Corresponding author. Tel.: + 55-31-3499-3370; fax: + 55-31-3499-3390.

E-mail address: wmacedo@urano.cdtm.br (W.A.A. Macedo).

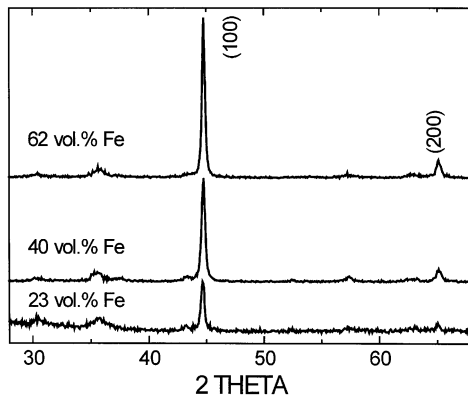


Fig. 1. XRD patterns of samples with different Fe content, after  $H_2$ -reduction at  $600^\circ\text{C}$  for 2 h.  $\alpha$ -Fe peaks are identified; other peaks correspond to  $\text{Fe}_3\text{O}_4$ .

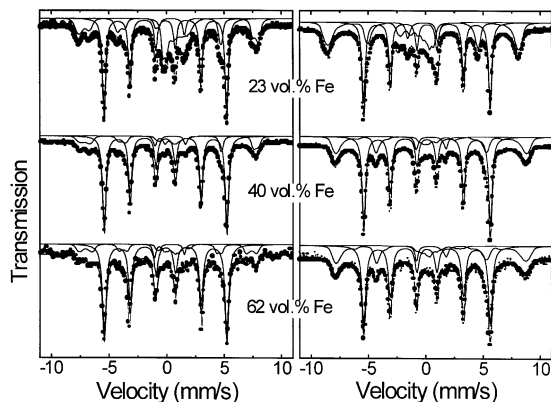


Fig. 2. Mössbauer spectra at room temperature (left) and at 20 K (right) of samples with different Fe content, after  $H_2$ -reduction at  $600^\circ\text{C}$  for 2 h.

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  $\alpha\text{-Fe}_2\text{O}_3$  particles.

Fig. 2 shows room temperature (left) and 20 K (right) Mössbauer spectra for samples with 23, 40, and 62 vol% total Fe, after  $H_2$ -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% (sextet,  $\alpha$ -Fe). In the spectra, remaining Fe-oxides ( $\sim 16\%$ ) are represented by a magnetic hyperfine field distribution at high fields ( $>40$  T). Approximately 10% of the spectral areas are attributed to  $\text{Fe}^{3+}$  ions occupying substitutional ( $\text{Al}^{3+}$ )

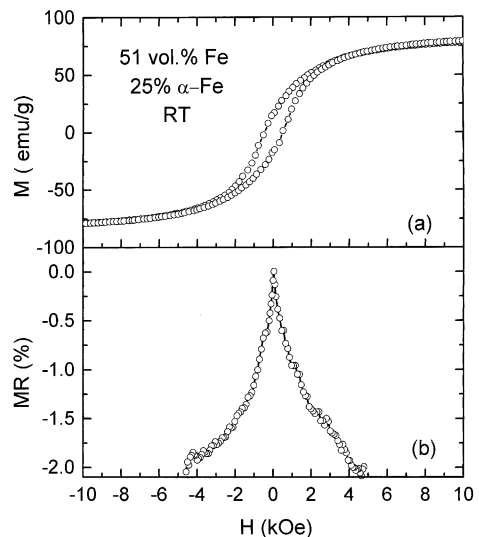


Fig. 3. Magnetization curve at 300 K (a), and room temperature magnetoresistance (b) for a sample with 51 vol%  $\text{Fe-Al}_2\text{O}_3$  (and 25%  $\alpha$ -Fe).

and  $\text{Fe}^{2+}$  ions occupying interstitial positions in the  $\text{Al}_2\text{O}_3$  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  $\text{Fe-Al}_2\text{O}_3$  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%  $\text{Fe-Al}_2\text{O}_3$  (25%  $\alpha$ -Fe, average particle diameter  $\sim 73$  nm), together with the magnetization curve presented by the sample. Equivalent codeposited  $\text{Fe-Al}_2\text{O}_3$  thin films reveal higher magnetoresistance, equal to 3% for 33%  $\text{Fe-Al}_2\text{O}_3$  [8].

In conclusion, we have investigated the synthesis and the structural and magnetic properties of granular nanocomposite  $\text{Fe-Al}_2\text{O}_3$  prepared starting from sol-gel processing. Samples with total Fe content ranging from 20 to 62 vol% were obtained by calcination at  $800^\circ\text{C}$  followed by  $H_2$ -reduction at  $600^\circ\text{C}$  for 2 h. We have achieved Fe reductions rates of up to 78%, preserving the mean diameter of the  $\alpha$ -Fe nanoparticles between 55 and 80 nm. Significant amount ( $\sim 16\%$ ) of  $\alpha$ - and  $\gamma\text{-Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  remains embedded in the alumina matrix, which presents some ( $\sim 6\%$ ) interstitial  $\text{Fe}^{2+}$  and substitutional  $\text{Fe}^{3+}$  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.

Financial support by CNEN, CNPq, FAPEMIG and FAPERGS (Brazilian agencies).

### References

- [1] J.Q. Xiao, J.S. Jiang, C.L. Chien, *Phys. Rev. Lett.* 68 (1992) 3749.
- [2] A. Berkowitz, J.R. Mitchell, M.J. Carrey, A.P. Young, S. Zhang, F.E. Spada, F.T. Parker, A. Hutten, G. Thomas, *Phys. Rev. Lett.* 68 (1992) 3745.
- [3] L.F. Schelp, G. Tosin, M. Carara, M.N. Baibich, A.A. Gomes, J.E. Schmidt, *Appl. Phys. Lett.* 61 (1992) 1858.
- [4] S. Honda, T. Okada, M. Nawate, *Phys. Rev. B* 56 (1997) 14566.
- [5] R.D. Shull, J.J. Ritter, A.J. Shapiro, L.J. Schwartzendruber, L.H. Bennett, *J. Appl. Phys.* 67 (1990) 4490.
- [6] C. Etoarnès, T. Lutz, J. Happich, T. Quaranta, P. Wissler, J.L. Guille, *J. Magn. Magn. Mater.* 173 (1997) 83.
- [7] A. Santos, J.D. Ardisson, E. Tambourgi, W.A.A. Macedo, *J. Magn. Magn. Mater.* 177–181 (1998) 247.
- [8] S.R. Teixeira, J.E. Schmidt, *J. Magn. Magn. Mater.*, to be published.
- [9] T. Ambrose, A. Gravin, C.L. Chien, *J. Magn. Magn. Mater.* 116 (1992) L311.
- [10] A.K. Giri, *Mat. Res. Bull.* 32 (1997) 523.