



ELSEVIER



## Synthesis of granular Fe–Al<sub>2</sub>O<sub>3</sub> by the sol–gel method

A. Santos<sup>a</sup>, J.D. Ardisson<sup>a</sup>, E.B. Tambourgi<sup>b</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>Faculdade de Engenharia Química, Universidade Estadual de Campinas, Campinas, Brazil

### Abstract

We have investigated the structural and magnetic properties of a granular composite of iron particles dispersed in alumina matrix, obtained starting from an aqueous solution containing Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and FeSO<sub>4</sub>·7H<sub>2</sub>O. The samples were characterized by X-ray diffraction and fluorescence, Mössbauer spectroscopy (MS) and vibrating sample magnetometry (VSM). Samples with 7.8 wt% Fe were submitted to two different heat treatments with the aim of reducing the iron oxides into metallic iron. Series A was submitted to calcination between 100°C and 1200°C, followed by reduction in ultra pure H<sub>2</sub> at 600°C during 2 h; Series B was submitted to reduction at 600°C or at 1000°C directly after drying at 80°C. As determined by MS, we have obtained a maximum of 24% metallic Fe in series A and of 74% α-Fe in series B, after reduction at 1000°C. By VSM, at 300 K, the maximum coercivity of 819 Oe was obtained for the samples calcinated at 800°C before reduction and an almost constant saturation magnetization of 2 emu/g. In series B, samples with 74% α-Fe presented a coercivity of 370 Oe and a saturation magnetization of 9.0 emu/g. The applied synthesis method seems to be an interesting alternative way to obtain magnetic Fe nanoparticles in a non-magnetic alumina matrix. © 1998 Elsevier Science B.V. All rights reserved.

**Keywords:** Granular systems; Sol–gel synthesis; Mössbauer spectroscopy; Magnetometry

Granular solids composed of magnetic particles dispersed into insulating matrixes can show unusual properties and have been obtained by different synthesis methods like spark erosion, high energy ball milling, evaporation in an inert gas and chemical method [1–5]. In this work we are investigating the synthesis of the α-Fe/Al<sub>2</sub>O<sub>3</sub> granular solid by a sol–gel method and we present the obtained structural and magnetic properties.

We have used a sol–gel transformation to synthesize an alumina inorganic network containing iron. The samples were obtained starting from an aqueous solution with the precursors aluminum nitrate (Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) and ferrous sulfate (FeSO<sub>4</sub>·7H<sub>2</sub>O) at 5°C. The resulting solution were neutralized with NH<sub>4</sub>OH (~25 wt.%) and the gelatinous precipitates were adequately washed and dried at 80°C. We have obtained three batches of the Fe–Al<sub>2</sub>O<sub>3</sub> composite with increasing Fe contents, up to 7.8% Fe in the porous alumina matrix. As determined by X-ray diffraction (XRD), the resulting powders containing 3.0 and 5.8 wt% Fe show an amorphous structure

and a detectable crystallization occurs only in the powder containing 7.8 wt% Fe, composed of α-Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub> and hydrated alumina phases.

Powders with the highest Fe content (7.8 wt%) were submitted to different heat treatments in order to reduce Fe oxides into metallic Fe. Series A was submitted to calcination between 100°C and 1200°C, followed by reduction at 600°C/2 h. Series B was submitted to reduction at 600°C and 1000°C in ultra pure H<sub>2</sub>, during 2 h, directly after drying at 80°C. In Series A samples, the calcination thermal treatment was applied to promote the transformation of the hydrated alumina phases into intermediary transition alumina phases, in order to reach the stable phase α-Al<sub>2</sub>O<sub>3</sub> and also the formation of α-Fe<sub>2</sub>O<sub>3</sub> prior the reduction. The resultant samples were analyzed by XRD, X-ray fluorescence (XRF); <sup>57</sup>Fe Mössbauer spectroscopy (MS) and vibrating sample magnetometry (VSM).

Fig. 1 shows low-temperature Mössbauer spectra for (a) the dried powder, (b) a series A sample, after calcination at 800°C and reduction at 600°C, and (c, d) for a sample reduced directly at 1000°C (series B). The spectra were measured at 100 K (a–c) and 4.2 K (d). In (a) we have 64% of α-Fe<sub>2</sub>O<sub>3</sub>, 36% of the Fe<sub>3</sub>O<sub>4</sub> with a small

\* Corresponding author. Fax: +55 31 499 3390; e-mail: wmacedo@urano.cdtb.br.

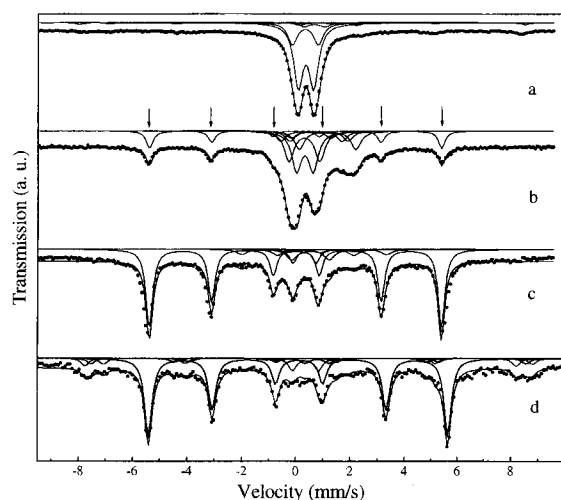


Fig. 1. Low-temperature Mössbauer spectra of (a) dried powder at 100 K, (b) series A sample at 100 K, after calcination at 800°C and reduction at 600°C and (c, d) series B sample after reduction at 1000°C, at 100 K (c) and at 4.2 K (d). The arrows indicate the lines of the  $\alpha$ -Fe subspectra.

quantity of these phase showing a resolved spectrum probably due to a particle size distribution. In (b) it is possible to identify  $\alpha$ -Fe (18%), superparamagnetic magnetite particles below the Verwey transition [7] (60%) and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (21%). Fig. 1c shows the high  $\alpha$ -Fe content (71%) together with superparamagnetic Fe oxides particles (2%  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, 27% Fe<sub>3</sub>O<sub>4</sub>). The  $\alpha$ -Fe lines are identified by arrows. The superparamagnetic behavior of the Fe oxide particles at 100 K becomes clear by lowering the measurement temperature, as illustrated in Fig. 1c and Fig. 1d for the Series B sample reduced at 1000°C, suggesting particles size in the submicron region.

For series A, as determined by MS and XRD, the heat treatments result in an almost constant fraction of  $\alpha$ -Fe ( $\sim$  24%) for calcination temperatures until 900°C and main spectral components corresponding to Fe oxides, i.e.,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (27–52%) and Fe<sub>3</sub>O<sub>4</sub> (53–24%). Calcination at temperatures higher than 900°C results in a decrease of the final  $\alpha$ -Fe fraction after reduction, due to densification effect at low temperature (1100°C), promoted in the alumina matrix by the Fe<sub>2</sub>O<sub>3</sub> particles [6]. By reduction directly after drying, without intermediate calcination (series B), a conversion rate as high as 16%  $\alpha$ -Fe was obtained for the heat treatment at 600°C and 74%  $\alpha$ -Fe for reduction at 1000°C during 2 h.

Fig. 2 shows representative magnetic hysteresis curves for series A and B samples at 300 and 80 K. For series A, VSM at 300(80) K show that the coercivity reaches a maximum of 819 (1142) Oe, for calcination at 800°C before reduction. The significant increase of the coercivity for that sample is supposed to be related to the different porosity of the Alumina transition phase in the

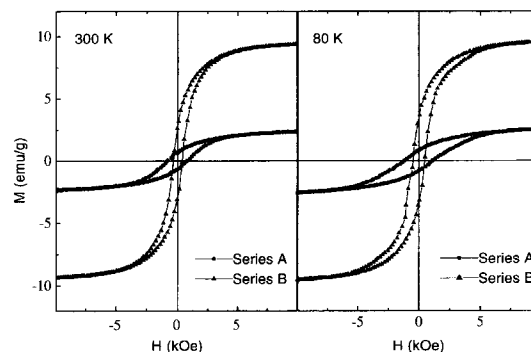


Fig. 2. Magnetic hysteresis at 300 and 80 K for series A sample after calcination at 800°C and reduction at 600°C and series B sample after reduction at 1000°C, obtained after sample alignment in a magnetic field of 1 T.

calcinated Alumina matrix; to the magnetic phases composition and to the particular morphology of our Fe/Al<sub>2</sub>O<sub>3</sub> system, similar to the observed for  $\alpha$ -Fe particles embedded in SiO<sub>2</sub> matrix [8]. The highest saturation magnetization was obtained for the sample calcinated at 1000°C equal to 3.8 (4.3) emu/g at 300 (80) K. The coercivity of the Series B samples presents decreasing values with the increase of the reduction temperature: 590 and 831 Oe for reduction treatments at 600°C and 363 and 473 Oe for reductions at 1000°C, as measured at 300 and 80 K, respectively. These results reflect the increase of the Fe particle size at higher temperatures. The obtained saturation magnetizations have shown almost constant values of  $\sim$  2 and  $\sim$  9 emu/g for the reductions at 600°C and 1000°C, respectively, independently of the measurement temperatures.

In conclusion, our results show that the applied sol-gel method, using an aqueous solution containing Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and FeSO<sub>4</sub>·7H<sub>2</sub>O, seems to be a promising method to synthesize Fe–Al<sub>2</sub>O<sub>3</sub> magnetic granular solids, allowing a high reduction of iron oxides into metallic iron directly after drying the precipitated gel. In continuing this work we will attempt to increase substantially the iron content in the alumina matrix.

The financial support of the FAPEMIG and of the CNPq/PADCT is gratefully acknowledged.

## References

- [1] K. Haneda, Can. J. Phys. 65 (1987) 1233.
- [2] J.L. Dormann, Mat. Sci. Eng. A Struc. Mater. 168 (1993) 217.
- [3] C.L. Chien, Ann. Rev. Mat. Sci. 25 (1995) 129.
- [4] G. Xiao, C.L. Chien, Appl. Phys. Lett. 51 (1987) 1280.
- [5] R.D. Shull et al., J. Appl. Phys. 67 (1990) 4490.
- [6] Y. Suwa, R. Roy, S. Komarneni, Mat. Sci. Eng. 83 (1986) 151.
- [7] R.S. Hargrove, W. Kündig, Solid State Commun. 8 (1970) 303.
- [8] R.D. Shull, H.M. Kerch, J.J. Ritter, J. Appl. Phys. 75 (1994) 6840.