



Magnetic characterization of the mechanically induced thermite reaction between Fe_2O_3 and Al

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Abstract

We have investigated the mechanically induced self-propagating reaction between Fe_2O_3 and Al. In this reaction the final phases, Al_2O_3 and Fe, are formed by an in situ chemical reaction. The evolution of the system was characterized as a function of the milling time using X-ray diffraction, magnetometry (300 and 5 K) and Mössbauer spectroscopy (300 and 77 K). After reaction, Fe particles in a crystalline Al_2O_3 matrix have been formed. At larger milling times, a rather wide Fe grain size distribution of around 20 nm was obtained according to the diffraction patterns. Mössbauer spectra were constituted of both paramagnetic and ferromagnetic contributions. The former was attributed to small grains of superparamagnetic Fe (within the Mössbauer characteristic time $\tau_M \approx 10^{-8}$ s) and FeAl_2O_4 , whereas the latter was associated to larger Fe grains. Saturation magnetization, coercivity field and remanent magnetization rapidly reached a stationary value with the milling time. A correlation between the microstructural characteristics of the sample and its magnetic properties before and after reaction is described.

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PACS: 75.50; 81.20.W; 82.30

Keywords: Magnetometry; Mössbauer spectroscopy; Ball milling; X-ray diffraction

Small magnetic particle systems are interesting due to their applications in recording media, pigments, ferrofluids, etc. Single domain magnetic particles embedded in an insulating matrix have

also received attention. For practical uses of small magnetic particles, a high saturation magnetization (M_S) and coercivity (H_C) are required [1]. Iron has the required magnetization, but also a low coercivity. However, maximum coercivity of Fe particles occurs at about 15 nm, decreasing rapidly for smaller particles, and slowly for larger particles [2].

Ball milling is a suitable tool for the preparation of these materials [3]. Here, we investigate the

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mechanically induced self-propagating reaction (MSR) between hematite (Fe_2O_3) and aluminum. In this reaction the final phases, Al_2O_3 and Fe, are formed by an in situ chemical reaction in which Al reduces the oxide [4]. The ball-milled mixture composition was prepared according to the following stoichiometric reaction:



This exothermic, non-gradual reaction proceeds in a well-defined milling time (the ignition time, IT). Magnetic measurements (300 K and 5 K) of these nanocomposites, together with X-ray diffraction (XRD) and Mössbauer spectroscopy (MS) at 300 and 77 K, were used to obtain information on the milling process and on the properties of the resulting materials.

The mixture was analyzed at different milling times, before and after ignition: 1.8 ks (0.34IT), 3.6 ks (0.68IT), 5.1 ks (0.96IT), 5.3 ks (IT), 7.1 ks (1.34IT), 9.2 ks (1.73IT), 14.3 ks (2.7IT) and 30.8 ks (5.8IT). Further details about these experiments and instrumental specifications are available [4].

Only Fe_2O_3 and Al coexist in the samples before IT as seen by XRD [4]. Fig. 1 shows the hysteresis curves of these pre-ignition samples. As it could be observed at 5 K, all samples present remanence and a hysteretic behavior. Hematite is canted anti-ferromagnetic and this could be an indication of a

bulk suppressed Morin transition as well as uncompensated moments due to surface anisotropy and symmetry breaking. Suppression of the Morin transition has been already described as related to the microstructural changes in ball-milled samples [5,8]. Hematite average crystallite sizes were calculated from XRD diffraction patterns, passing from 69 nm (0.34IT) to 52 nm (0.68IT) and then to 56 nm (0.96IT). Further, dark-field transmission electron microscopy images (not shown here) reveal a broad distribution of coherent diffraction domains around the calculated XRD values (i.e. as low as 10 nm). Fig. 1 also shows that the coercivity does not vary as a function of the milling time, contrary to the remanent magnetization M_R , which attains a maximum value after 0.68IT and slightly decreases with further milling. This non-monotonous trend was also exhibited by the Fe_2O_3 crystallite size as mentioned above. Earlier studies have shown that, depending on the microstructure of the hematite particles, H_C ranges between 0.03 and 0.4 T. The values reported here, ~ 0.09 T, are between these limits. In the same figure, a 300 K hysteresis curve of the 0.96IT sample is also presented. A significant change in the hysteresis parameters is easily seen, i.e. a lower coercivity, remanence and saturation; this could be taken as an indication of a superparamagnetic (SPM) behavior (within the time window that characterizes these experiments $\tau_M \approx 100$ s). One possibility is that hematite is in the SPM state, becoming blocked at low temperatures. For spherical monosized hematite, a threshold diameter of ~ 41 nm has been reported, below which the particles could behave SPM [6]. In the present study, the hematite particles are not monosized and it is expected that a certain fraction of particles have an average grain size below that limit, as discussed above. Although the presence of this SPM Fe_2O_3 cannot be disregarded it could hardly justify by itself the low-temperature magnetization increment detected. Another possibility is that this low-temperature high-saturation signal belongs to SPM Fe present in the sample before ignition that becomes magnetically blocked, in a sufficiently low quantity to preclude its detection by XRD. Furthermore, the MS at 300 K of the 0.96IT sample is consistent with 6₂% of α -Fe,

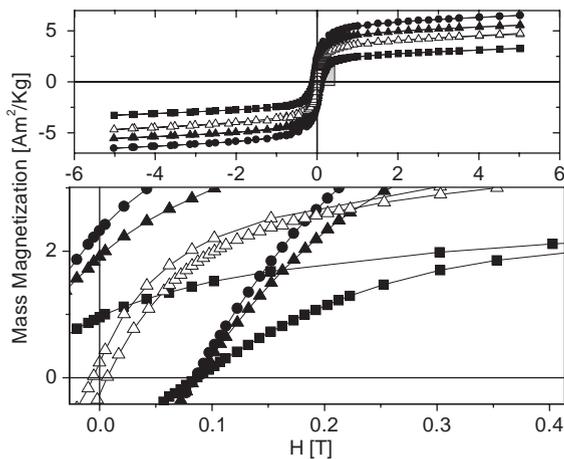


Fig. 1. Hysteresis plots of different pre-ignition milled samples: 0.34IT (5 K) (square), 0.68IT (5 K) (circle), 0.96IT (5 K) (full triangle) and 0.96IT (RT) (open triangle).

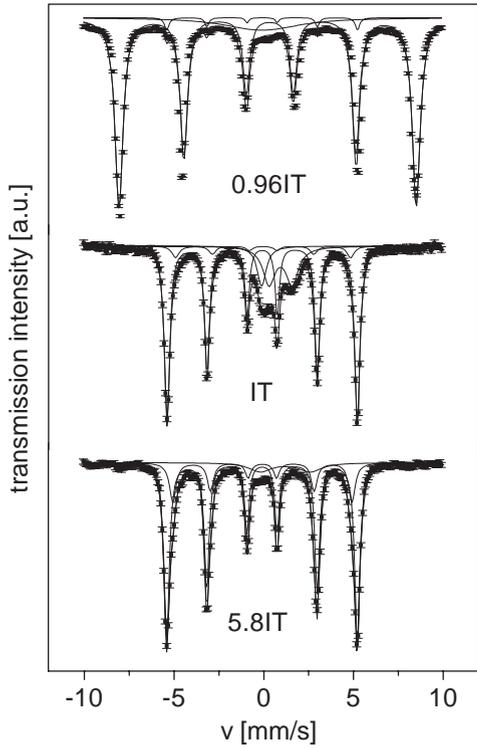


Fig. 2. Mössbauer spectra at 300 K before (0.96IT), immediately after (IT) and long after (5.8IT) reaction.

Fig. 2. This demonstrates that before IT a given amount of iron could be formed as a result of an incomplete reaction between Fe_2O_3 and Al, where a certain fraction could be in the SPM state. If this hypothesis is correct, we could try to find the fraction of Fe by means of the following assumption:

$$M_T(H) = f_{\text{Hem}} M^{\text{Hem}}(H) + f_{\text{Fe}} M_S^{\text{Fe}},$$

where $M_T(H)$ is the magnetization experimentally measured from the hysteresis plot at a given H , i.e. 5 T, f_{Hem} (f_{Fe}) is the wt% of hematite (iron) present in the sample, $M^{\text{Hem}}(H)$ is the magnetization of hematite at a given H , and M_S^{Fe} is the saturation magnetization of iron at the given temperature (5 K). Under these assumptions, we found 1 wt% (0.34IT), 2.4 wt% (0.68IT) and 2 wt% (0.96IT) of SPM iron. Both SPM contributions (Fe and Fe_2O_3) probably are responsible for the single line contribution at 300 K that decreases at

77 K according to SPM relaxation in the MS of pre-ignition samples, i.e. from 6% to 2% for the 0.96IT.

Post-ignition milled samples show a saturation mass magnetization at 5 K (Fig. 3), about 21% less than the magnetization estimated by assuming that all the iron present is in the form of bulk α -Fe at IT. This may be the consequence of a fraction of SPM Fe particles and/or the presence of iron-containing non-magnetic oxides. The hypothesis of SPM iron particles could be difficult to sustain on IT samples, because during ignition, there is a very pronounced growth in grain size as a consequence of the temperatures attained (i.e. $>3\text{E}3\text{ K}$) [4], which is contrary to the known trend of SPM behavior at low grain sizes. On the other hand, the iron-containing non-magnetic oxide was detected in the XRD patterns (hercynite, FeAl_2O_4) [7], and suggested in the 300 K MS by the presence of a quadrupole splitting (QS) of 1.29_3 mm/s and an isomer shift (δ_{Fe}) of 1.03_2 mm/s , Fig. 2 [8]. With further milling of the reaction products (from 1.34IT and henceforth), the diffraction lines of this ternary oxide are no longer discernible, suggesting its reduction or amorphization. From 300 K MS, we see that a combination of both processes could be the most probably sound, because the high QS and positive δ_{Fe} associated with hercynite persists with the milling time from the initial 24% (at IT) to a stationary value of $\sim 9\%$ of resonant area fraction. The

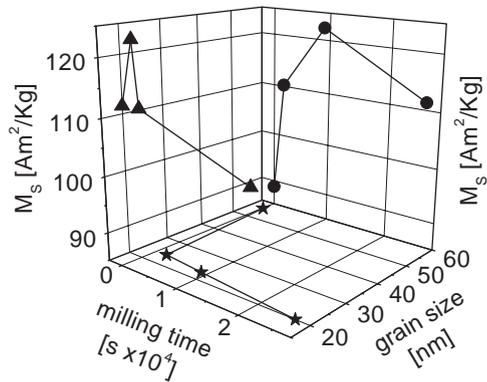


Fig. 3. The milling time (circle) and grain size (triangle) dependence of saturation magnetization M_S . Additionally, the milling time dependence (star) of grain size (post-ignition samples).

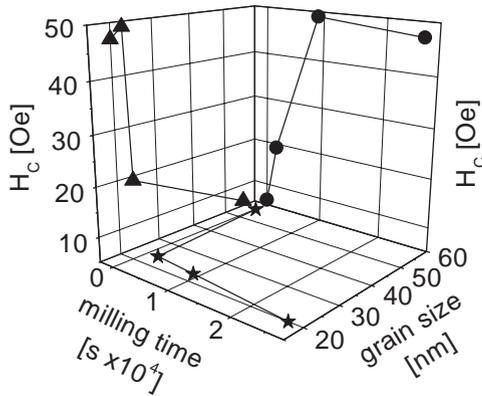


Fig. 4. The milling time (circle) and grain size (triangle) dependence of coercivity H_C . Additionally, the milling time dependence (star) of grain size (post-ignition samples).

increase in magnetization on prolonged milling indicates the partial conversion of the non-magnetic oxide to α -Fe and/or, less probably, the collapse of SPM Fe particles. XRD patterns show a simultaneous increase of the intensity of α -Fe lines relative to α -Al₂O₃ lines with the milling time [7]. According to the decreasing particle size, a distinct magnetic hardening process takes place on milling. The remanent magnetization increases from 0.27 to ~ 4 A m²/kg with the milling time. The coercivity of samples increases from the initial 6 to ~ 50 Oe, slightly decreasing again with further milling (Fig. 4). As mentioned above, this non-monotonous dependence of coercivity with grain size is well known. The behavior was followed by these samples, however at a slightly higher grain

size, as is shown in Fig. 4, in which a smaller decrease is present for the sample with larger milling time.

We conclude that minor amounts of Fe could be formed before IT. After IT, magnetic properties rapidly reached a stationary value with the milling time. MSR is a relatively inexpensive technology to produce small magnetic particles systems, but many details of the process are yet to be understood. It is demonstrated that magnetic measurements can be reliably used, in combination with other techniques, to gain a better understanding of the process.

CCL acknowledges the help of SECYT-CAPES (Argentina) and LME/LNLS (Campinas, S.P., Brazil) for technical support during electron microscopy work, LMS the help of Brazilian agency FAPESP.

References

- [1] M. Pardavi-Horvath, et al., *IEEE Trans. Magn.* 28 (1992) 3186.
- [2] W.H. Meiklejohn, *Rev. Mod. Phys.* 25 (1953) 302.
- [3] A.K. Giri, *Mater. Res. Bull.* 32 (1997) 523.
- [4] C. Cuadrado-Laborde, et al., *Hyperfine Interactions* 134 (2001) 131.
- [5] S.J. Stewart, et al., *J. Magn. Mater.* 260 (2003) 447.
- [6] T.P. Raming, et al., *J. Colloid. Interf. Sci.* 249 (2002) 346.
- [7] C. Cuadrado-Laborde, et al., submitted.
- [8] E. Murad, et al., *Mössbauer spectroscopy applied to inorganic chemistry: iron oxides and oxyhydroxides*, in: G.J. Long (Ed.), Plenum, Netherlands, 1981, pp. 507–582.