

Evolution of the Mössbauer recoilless fraction during mechanochemical activation of iron oxides

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The preparation and properties of ultrafine iron oxides continue to attract considerable interest and attention because of their importance in magnetic technologies and pigment applications [1–5]. Part of the interest comes from the fact that ball milling and related methods represent a novel alternative approach to the preparation of new materials and phases. Mössbauer spectroscopy represents a powerful method to characterize the sequence of magnetic phases formed during the ball milling process.

The most important parameter in a Mössbauer effect experiment is the recoilless fraction $f = \exp(-\mathbf{k}^2 \langle x^2 \rangle)$, where \mathbf{k} is the wavevector of the gamma rays and $\langle x^2 \rangle$ is the mean square vibrational amplitude of the resonant atom in the direction of observation. The only method available to date for the determination of the recoilless fraction relied on its temperature dependence and the determination of the Debye temperature from complicated equation plots. However, we have recently proposed a new method for the direct determination of the recoilless fraction by a single room-temperature transmission Mössbauer measurement. The method relies on a two-lattice comparative approach and made it possible to determine the recoilless fraction of various systems, from iron chlorides to nanoparticles [6, 7].

In the present paper we propose that the recoilless fraction represents an important parameter during the mechanochemical activation process. The magnetite precursor was milled in a hardened steel vial with six stainless-steel balls (type 440; four of 0.25 in. diameter and two of 0.5 in. diameter) in the SPEX mixer-mill for time periods ranging from 0–128 h. Room temperature transmission Mössbauer spectra were recorded using a constant acceleration spectrometer and a 50 mCi ^{57}Co source diffused in a Rh matrix. For the recoilless fraction determination experiments, we produced physical mixtures of iron powder with the powder whose fraction was to be determined. Least squares fitting of the Mössbauer spectra was performed with the NORMOS program [8].

Fig. 1a–c shows the room-temperature Mössbauer spectra of the magnetite powder, after 0, 30 and 70 h of ball milling, respectively. The precursor in Fig. 1a was fitted by considering two sextets, corresponding to the tetrahedral and octahedral magnetic sublattices in the sample. The intermediate products in Fig. 2b were analyzed with five sextets and this analysis was consis-

tent with the partial oxidation of magnetite to hematite and the formation of iron and superparamagnetic magnetite particles in the sample. It can be seen from Fig. 2c that the magnetite powder was completely converted to hematite after 70 h of milling time. The hematite is represented by a sextet with a hyperfine magnetic field of 52.7 T.

Fig. 2a–c shows the continuation of the ball milling process with the mechanochemical activation of hematite. The intermediate product after 111 h is wüstite (with traces of iron). The final milling phase after 128 h is wüstite, represented by a doublet with the typical quadrupole splitting of 0.98 mm/s.

In order to determine the recoilless fraction of the reaction products we made physical mixtures of each sample with iron powder and calculated the f factor from areal ratios [6, 7]. For example, Fig. 3 shows the transmission room-temperature Mössbauer spectrum of hematite with iron in a physical mixture. The spectrum was analyzed considering two sextets, for iron and hematite.

The area ratio derived from the spectral analysis corresponds to:

$$A_{\text{Fe}}/A_{\text{he}} = 74.39\%/25.61\% = 2.9 \quad (1)$$

On the other hand, one has from chemical arguments:

$$\begin{aligned} A_{\text{Fe}}/A_{\text{he}} &= (N_{\text{Fe}}f_{\text{Fe}})/(N_{\text{he}}f_{\text{he}}) \\ &= [\mu_{\text{he}}/(2\mu_{\text{Fe}})](\rho_{\text{Fe}}/\rho_{\text{he}})(f_{\text{Fe}}/f_{\text{he}}) \\ &= (159.692 \times 7.87 \times 0.7)/(2 \times 55.847 \times 5.3 \times f_{\text{he}}) \\ &= 1.48/f_{\text{he}} \quad (2) \end{aligned}$$

In this formula “he” stands for hematite. This leads to a value of $f_{\text{he}} = 0.51$ for the recoilless fraction in hematite. Estimated errors are $\pm 3\%$.

The values determined for the f factor are collected in Fig. 4. It can be seen that the recoilless fraction decreases from a value of 0.9 for magnetite to 0.51 for hematite and to 0.33 for wüstite, keeping constant values for the region of phase stability of the products and decreasing abruptly during the time period corresponding to the phase transformations. Therefore, we

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MAGNETITE BALL MILLING

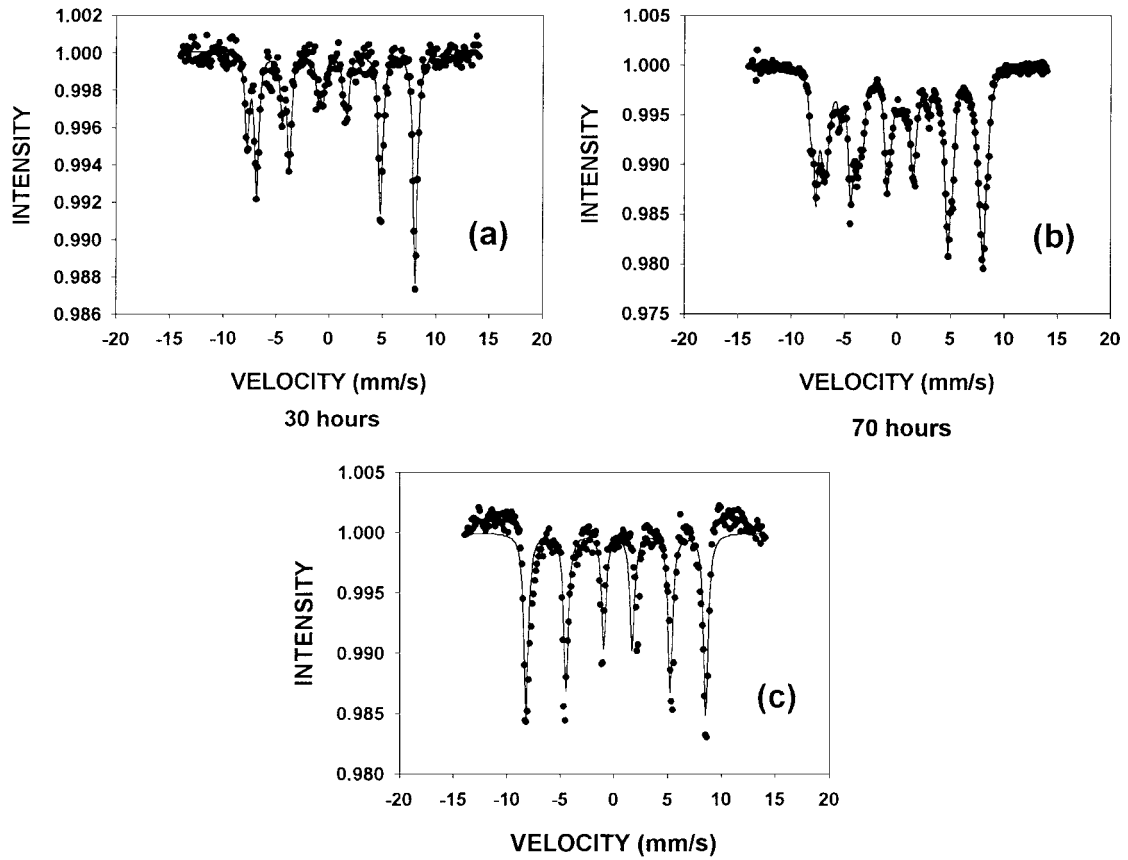


Figure 1 Room-temperature transmission Mössbauer spectra of magnetite after (a) 0; (b) 30 h and (c) 70 h of ball milling.

HEMATITE BALL MILLING

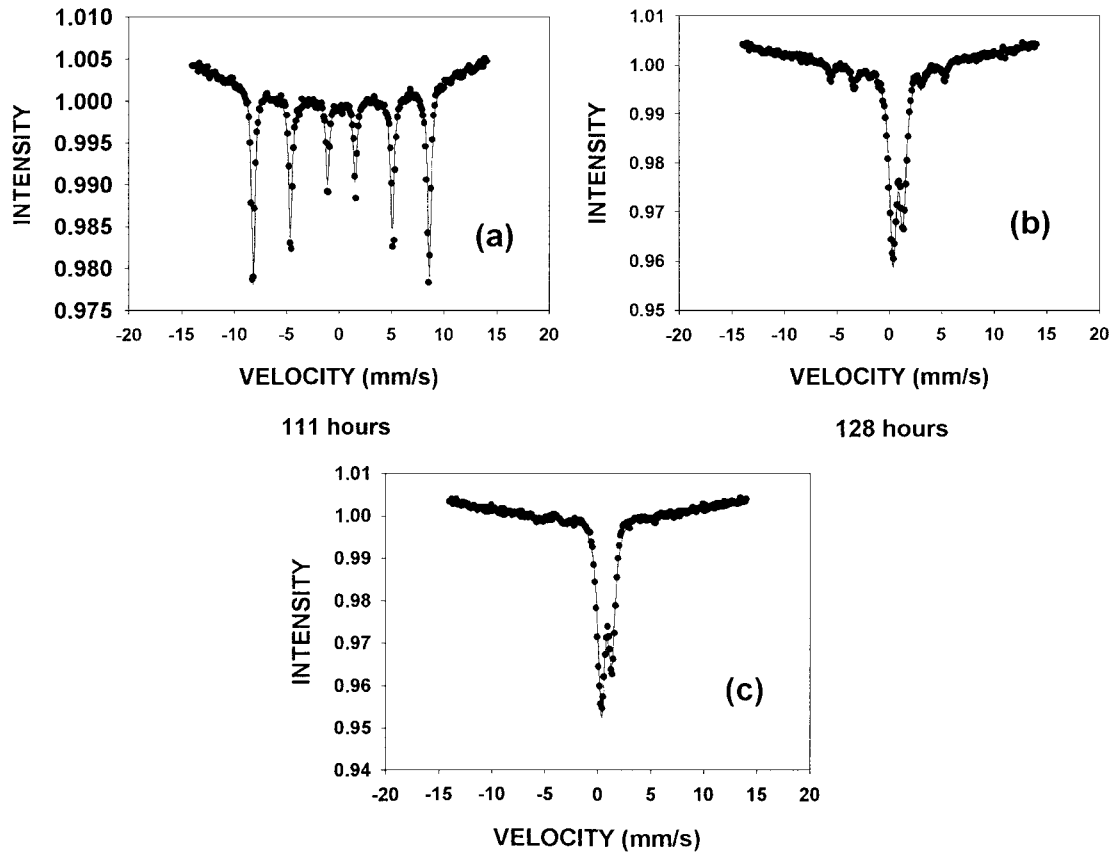


Figure 2 Room-temperature transmission Mössbauer spectra of hematite after a total of (a) 70 h; (b) 111 h and (c) 128 h of ball milling.

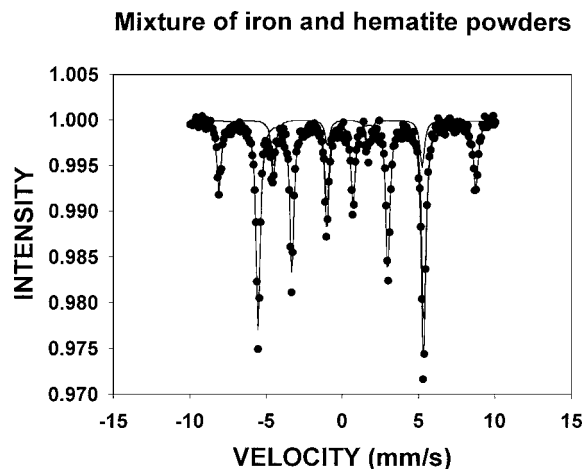


Figure 3 Room-temperature transmission Mössbauer spectrum of a physical mixture between hematite and iron, necessary for the determination of the recoilless fraction using the two-lattice method.

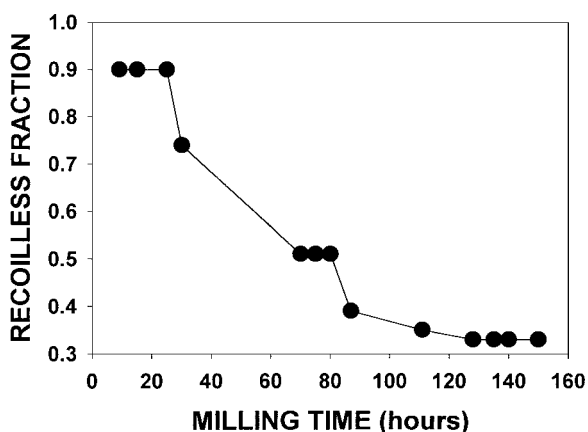


Figure 4 The dependence of the recoilless fraction on the total time of ball milling. The errors are considered in the marker size.

propose that the recoilless fraction is able to characterize the mechanochemical activation process, following the sequence of phases during the ball milling transformation. This result is possible only due to our new two-lattice method, which brings easy access to the values of the recoilless fraction in a wide class of materials.

Although in this experiment the recoilless fraction decreases, we expect that in other processes, such as the crystallization of amorphous magnets, the recoilless fraction will suffer an overall increase. It is interesting to follow its evolution during various processes and correlate its values with thermodynamic arguments.

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