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Characterization of a mechanochemically activated titanium-hematite mixture: Mössbauer spectroscopy study

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ABSTRACT

Mechanochemical processes involving reactions between metals and crystalline oxides are of interest because of their potential technological applications in structural, magnetic or electric materials. In addition they can contribute to the understanding of the natural occurring processes that lead to the formation of minerals and soils. The controlled studies of how the distribution of cations in the titanomagnetites takes place can help toward building a model for the nature of their magnetism and, since they are the primary carriers of rock and soil magnetism, are therefore intensively investigated in many experimental and theoretical studies.

In behalf of a better comprehension of the thermal, physical–chemical, magnetic and hyperfine behavior, we have considered a titanium and hematite mixture, with molar ratio Ti:Fe₂O₃ of 1:2, mechanochemically activated during different activation times. We have studied the development of new phases by X-ray diffraction, scanning electron microscopy and Mössbauer spectroscopy. The evolution from the starting materials affected by different milling times and subsequent annealing shows that Ti reduces the Fe ions in the Fe₂O₃ lattice, partly to Fe²⁺ and partly to metallic Fe.

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1. Introduction

Intensive mechanochemical activation on crystalline solids using high-energy mills produces the development of new surfaces, plastic deformation and accumulation of structural defects, which may induce reactions with a kinetic and thermodynamic behavior very different from that of thermally initiated reactions [1,2]. Mechanochemical activation has been used during the last decades as a powerful tool for the preparation of metastable crystalline and amorphous phases and nanostructured materials not obtainable through conventional methods [3,4]. This is due to three fundamental reasons: shortening of reaction times, reduction of the high temperatures usually required for developing solid state reactions and the possibility of obtaining materials with special properties. Mechanical activation increases the reactivity of the solid reactants through the generation of extended crystal defects, new surfaces and lattice distortions, thus facilitating the occurrence of transformations in the solid state.

In this work, following a series of previous studies [5], we have investigated the mechanochemical activation of a Ti–hematite mixture and their physicochemical and thermal behavior, using information yielded by X-ray diffraction (XRD), Mössbauer spectroscopy and scanning electron microscopy (SEM).

2. Experimental

2.1. Preparation of samples

The reactive mixture was prepared from metallic Ti (98 wt%) and hematite (99 wt%) both commercial reagents. The particle size of both reactants was 20 and 5 μm for Ti and hematite, respectively. The initial mixture, with molar ratio Ti/Fe₂O₃ 1:2, was activated in a planetary ball-mill (Fritsch Pulverisette 7) with vials and balls of hardened Cr-steel.

The mixture was prepared and activated under Ar atmosphere (PO₂ < 1 Pa). The experimental method assured there was no leaking of oxygen from the outer atmosphere into the vials. The milling bowls were loaded with 5 g of powder and seven balls of 15 mm diameter each, resulting in a ball-to-powder mass ratio of 20:1 rotating at 1500 rpm.

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The thermal treatment was performed on the samples under Ar atmosphere at 700 °C with a heating rate of 10 °C/min, and a soaking time of 30 min at the final temperature. The obtained sample was labelled TiH x - y , where x is the activation time in hours and y is the temperature of the subsequent thermal treatment.

2.2. Analysis and characterization of samples

The particle morphology and composition of the starting mixture and of the activated sample were examined by SEM (Philips 505). Crystalline phases were characterized by XRD (Philips PW 3710), using CoK α radiation and Fe filter at 40 kV–30 mA.

Mössbauer spectra were taken at room temperature (RT) and in one case at 15 K in a conventional constant acceleration spectrometer in transmission geometry with a $^{57}\text{Co}/\text{Rh}$ source. Least squares' fitting was performed by using the Normos Program [6]. Isomer shift values referred to αFe at RT.

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 displays a gradual reduction of the crystallinity evidenced by a notable decrease in the diffracted intensity together with a widening of the peaks (due to the decrease of the crystal size and the disordering of the crystalline structure). The evolution of the diagrams shows the formation of the titanomagnetite structure. In the early steps of the activation process the presence of Ti and hematite (corresponding to the original sample) was evidenced. In addition new phases were formed by activation. With increasing activation times, apart from the values of the a_0 parameters of the rhombohedral structure of hematite, it is clear the emergence of a cubic structure in accordance with the formation of titanomagnetite. This is due to the progressive disordering of the hematite structure and also to the incorporation of Ti in its lattice. This was confirmed by XRD analyses after a thermal treatment (30 min at 700 °C) during which the crystallinity of this solid solution was developed. By means of the thermal treatment (Fig. 1) the structural defects would be healed, and the system would be rearranged leading to the formation of titanomagnetite.

At 2 h of activation a peak corresponding to metallic iron became visible ($2\theta \sim 52.6^\circ$) meanwhile at 3 h of activation, its

intensity (area under the peak) decreased. This effect is attributable to microstrains generated by the milling. After the thermal treatment the peak became narrow. However, this does not necessarily denote that the quantity of αFe increased.

3.2. Mössbauer spectroscopy

Fig. 2 shows the RT Mössbauer spectra of the studied samples (TiH x - y). They were fitted by considering five sextets and two quadrupole-split doublets in the case of TiH1, TiH2, TiH3 and TiH1-700 meanwhile a hyperfine field distribution contributed to resolve TiH2-700 and TiH3-700 because of the presence of an extra distribution of minor hyperfine fields in the range 15–29 T.

The sextet with a hyperfine field of ~ 51 T corresponds to hematite. The following three sextets were assigned to titanomagnetite ($\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$), which conforms a solid solution of the two end members of Fe_3O_4 (magnetite) and Fe_2TiO_4 (ülvöspinel). It was fitted to three different sites corresponding to different Fe surroundings [7]. The Fe^{3+} sextet with a magnetic hyperfine splitting of ~ 48 T and the $\text{Fe}^{2.5+}$ sextet with a magnetic hyperfine splitting of ~ 45 T represent the tetrahedral and octahedral sites of magnetite, respectively. The third one instead, with a magnetic hyperfine splitting of ~ 42 T, arises from the Fe substitution by Ti in the magnetite structure. In all of the samples, except in TiH1, a sextet characteristic of αFe also appeared.

A doublet with a quadrupole splitting in the range 0.5–1.0 mm/s and an isomer shift of about 0.32 mm/s was added to all the fitted spectra. Taking into account the hyperfine parameters obtained, they could be assigned to various possible compounds.

To properly identify this phase, an additional spectrum at 15 K was performed for one of the samples (TiH2). Comparing the spectra at RT and 15 K (Fig. 3), it follows that the RT quadrupole

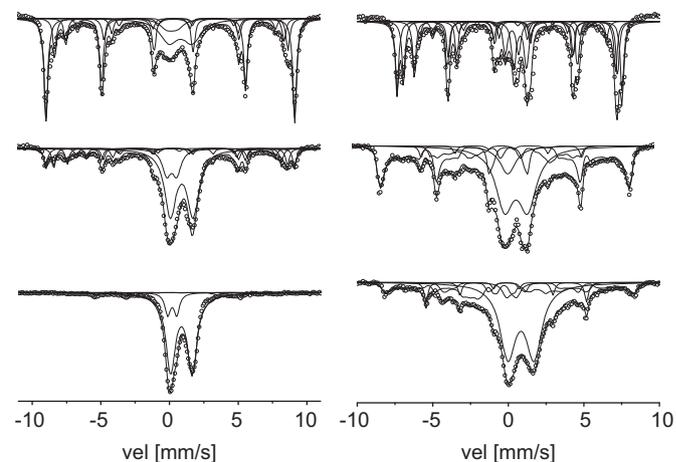


Fig. 2. RT Mössbauer spectra: TiH1, TiH2, TiH3 from up to down (right column) and TiH1-700, TiH2-700, TiH3-700 from up to down (left column).

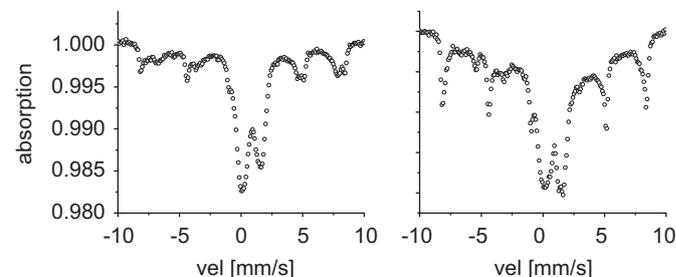


Fig. 3. Comparison between RT and 15 K spectra for TiH2.

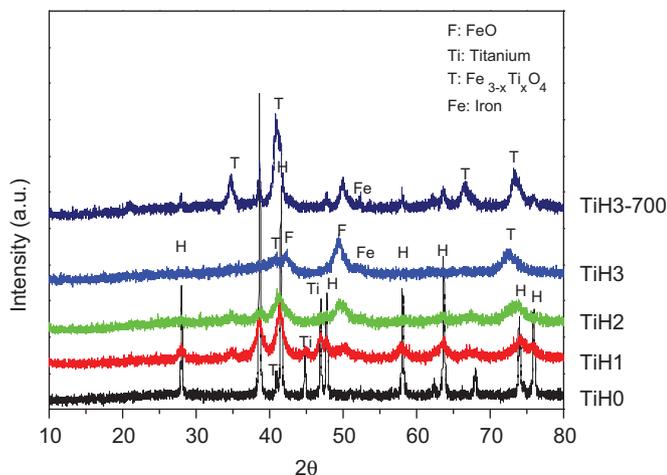


Fig. 1. XRD patterns of the sample for different activation times.

Table 1
Relative abundancies of Fe-bearing phases obtained by Mössbauer analyses.

| Sample | H | T-M | α Fe | sH | n-s U | gp |
|----------|---------|---------|-------------|----|-------|----|
| TiH1 | 42 | 29 | – | 7 | 22 | – |
| TiH2 | 9 | 20 | 5 | 14 | 52 | – |
| TiH3 | $\ll 1$ | $\ll 1$ | 2 | 14 | 84 | – |
| TiH1-700 | 26 | 48 | 6 | 8 | 12 | – |
| TiH2-700 | 18 | 17 | 4 | 8 | 39 | 14 |
| TiH3-700 | 6 | 10 | 7 | 5 | 54 | 18 |

H: hematite, T-M: titanomagnetite, sH: superparamagnetic hematite, n-s U: non-stoichiometric ulvöspinel, and gp: grain boundary phases.

split doublet converts to a sextet with the typical hyperfine parameters of hematite at 15 K. Therefore, we conclude that the doublet corresponds to the occurrence of superparamagnetic hematite, almost certainly due to the ball milling process. It is likely the presence of a distribution of particle sizes such that a part of them remains in a non-superparamagnetic state contributing to a sextet and the others, the very small particles (sizes in the order of a few nm), give a superparamagnetic doublet in the spectra. On the other hand, another doublet characteristic of Fe^{2+} species was evidenced. Its RT hyperfine parameters are close to those available in literature for stoichiometric ulvöspinel [8], thus it was assigned to non-stoichiometric ulvöspinel. A minor FeO contribution (seen by XRD) cannot be discarded.

The relative abundancies of each phase obtained by Mössbauer analysis are displayed in Table 1. It is important to remind that this technique only detects Fe-bearing compounds.

From the spectra and Table 1 values it is noticeable that the non-stoichiometric ulvöspinel increases at the expense of hematite and titanomagnetite with increasing ball-milling time. The reduction of crystalline hematite is complete after 3 h of activation, however, superparamagnetic hematite remains (about 14%). It is also interesting to note that the ulvöspinel hyperfine parameters become closer to the stoichiometric values with increasing activation time.

The α Fe relative abundance shows a maximum of about 7% for TiH3-700.

The spectra corresponding to TiH2-700 and TiH3-700 also present not identified minor hyperfine fields components (between 15 and 29 T), maybe arising from grain boundary phases produced due to milling.

2.3. Scanning electron microscopy

SEM micrographs (Fig. 4) show the decreasing of the particle size with activation time, reaching an average particle size of about $0.5 \mu\text{m}$ after 3 h of activation. It is also perceptible the loss

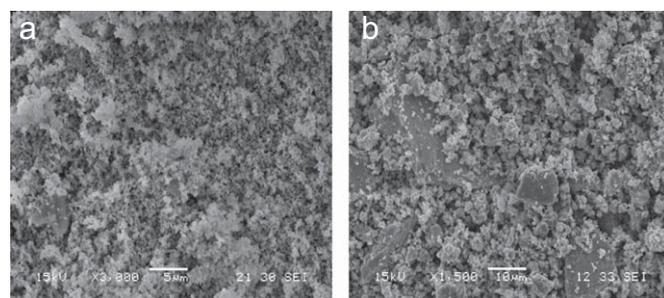


Fig. 4. (a) Scanning electron micrographs of the starting and (b) the 3 h ball-milled sample.

of the original morphology of the particles with the production of a relatively fine and homogeneous microstructure, presenting rounded and poorly crystalline particles tending toward agglomeration. The latter effect is due not only to their small size, but specially to the high surface energy resulting from the high concentration of structural defects provoked by the activation.

3. Conclusions

The obtained results show that during mechanochemical activation of a Ti- Fe_2O_3 mixture at room temperature under Ar atmosphere, the reduction of Fe by Ti takes place. During the reduction-oxidation process mainly Fe^{2+} and Ti^{4+} are produced as non-stoichiometric ulvöspinel and titanomagnetite and also metallic iron. Titanium changes the original structure of hematite when a mixture with Ti/ Fe_2O_3 molar ratio 1:2 is activated. From a textural and microstructural point of view, the mechanochemical activation produces a loss of crystallinity of the solid, which reaches a mean particle size lower than $1 \mu\text{m}$.

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