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Mechanochemical activation of a titanium–magnetite mixture: Mössbauer spectroscopy study

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Abstract

Mechanochemical activation has become a valuable tool in the design and synthesis of novel materials, due to the increased reactivity of activated solids, and the possibility of synthesizing metastable phases not obtainable by conventional methods. In this work, ac magnetic susceptibility, Mössbauer spectroscopy, X-ray diffraction (XRD) and scanning electron microscopy have been employed to study the structural and thermal evolution of a mechanochemically activated Ti–Fe_3O_4 mixture, with molar ratio Ti:Fe_3O_4 of 1:2. Upon activation in a high-energy planetary mill, the mixtures undergoes a redox reaction, in which the Ti reduces the Fe ions of the spinel, resulting in a solid solution of variable composition between magnetite (Fe_3O_4) and ulvospinel ($TiFe_2O_4$). The activation results in changes in the magnetic behavior of the mixture, and loss of crystallinity. Mössbauer spectroscopy and XRD show the progressive disappearance of the original phases, and the formation of Fe^0, Fe_2O_3 and ulvospinel.

Keywords: Milling; Spinels; Mössbauer effect; Powder–solid-state reaction; X-ray methods

1. Introduction

Mechanochemical processes involving reactions between metals and crystalline oxides have become of interest in the last decades. Due to the increased reactivity of the activated solids, these methods are applied to the design and synthesis of novel materials – like metastable and non-crystalline phases with controlled properties – which are not obtainable by conventional methods.[1,2] In addition to these applications of potential technological importance, the investigation of the reaction mechanisms and products add to the understanding of the natural occurring processes that lead to the formation of minerals and soils.

The natural series of minerals in the solid solution series between magnetite (Fe_3O_4) and ulvospinel (Fe_2TiO_4) and their intermediate members, titano-magnetites, lack a complete grasp of their magnetism and display incompletely understood differences in the degree of oxidation and their cation distribution among the spinel crystalline sites. Since they are the primary carriers of rock and soil magnetism, these systems have been intensively investigated in many experimental and theoretical studies.[3–5] The solid-state mechanochemically activated reactions induce cation displacements that make it possible to study in a controlled way how the distribution of cations takes place. This can help toward building a model to explain their magnetic properties.

To achieve a better understanding of the thermal, physicochemical, magnetic and hyperfine behavior, we have investigated a series of titanium and magnetite mixtures with diverse activation conditions. We have studied the development of new phases other than the initial ones, Ti and Fe_3O_4, by X-ray diffraction (XRD), scanning electron microscopy, ac magnetic susceptibility and Mössbauer spectrometry.

2. Experimental

Reactive mixtures were prepared from metallic Ti, commercial reagent, 98 wt%, and a concentrate of magnetite ore, from

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Sierra Grande (Chubut, Argentina), with ≥97.5 wt% Fe_3O_4. The major impurities found by XRD in the magnetite were a clay mineral (illite), and quartz (both in similar concentrations of ≈1 wt%). The particle size of both reactants was below 100 μm, and the mean particle size was 25 μm for Fe_3O_4, and 20 μm for Ti. The Ti/Fe_3O_4 molar ratio used was 1:2. The oxygen content of the Ti (as superficial oxide) was lower than 100 ppm.

The mechanochemical treatments were carried out in a planetary laboratory ball-mill (Fritsch Pulverisette 7) with vials and balls of hardened Cr-steel. The mixtures were prepared and activated in an Ar atmosphere ($PO_2 < 1$ Pa). The milling bowls were loaded with 5 g of powder and 7 balls of 15 mm diameter each, resulting in a ball-to-powder mass ratio of 20:1, and rotated at 1500 rpm during measured times.

The thermal treatments were performed under Ar atmosphere at temperatures ranging from 400 to 700 °C, using a heating rate of 10 °C/min, with 30 min soaking at the final temperature. Temperatures above 700 °C and soaking times longer than 30 min resulted in gradual oxidation to hematite (α-Fe_2O_3).

The particle morphology and composition of the starting mixtures and of the activated samples were examined by scanning electron microscope (SEM) Philips 505, equipped with an electron probe micro-analyzer (EPMA). Prior to the observation, the samples were coated with gold.

Phase identification and structural characterization by XRD were made from data taken with a Philips 3020 goniometer with a PW 3710 controller, Cu Kα (λ = 1.5406 Å) radiation and Ni filter at 40 kV to 20 mA. In some samples, the powder diffraction patterns were analyzed with the program FullProf,[6] which is a multipurpose line-profile fitting program that performs Rietveld refinement. The starting crystallographic data for each phase were extracted from the literature.[7]

Magnetic measurements were carried out in a LakeShore 7130 ac susceptometer, with an excitation field of 1 Oe and 825 Hz, with null static field. The measurements were taken at temperatures between 13 and 325 K on heating at a constant rate of 1.5 K/min.

The Mössbauer spectra were taken at room temperature in a constant acceleration spectrometer with transmission geometry. The absorber thickness was chosen to be the optimum according to the Long et al. criterion.[8] The spectra were fitted to Lorentzian line-shape components with a least-squares program with constraints. The isomer shifts are referred to metallic iron at room temperature.

3. Results

The ac susceptibility thermal behavior for all milling times displays a response that increases with temperature (Fig. 1). This is indicative of a reversible movement of magnetic domain walls and of the greater ease with which the system magnetic states can be reached with increasing temperature, which decreases with the ball-milling time. This is in good agreement with a reduction of the particle size and the transformation of the ferrimagnetic material (magnetite) into para- or antiferromagnetic species. The Verwey transition at ≈110 K is an outstanding feature of the initial mixture. However, the behavior of the susceptibility changes as the activation time increases; for the 0.5 h sample, at 110 K only a bump can be seen, which gradually disappears for longer milling times. After 1.5 h of milling, no clear magnetic transition can be observed. However, the relative high value of χ' denotes the arising of ferro- or ferrimagnetic phases with high T_c that conceal signals coming from species with other magnetic regimes.

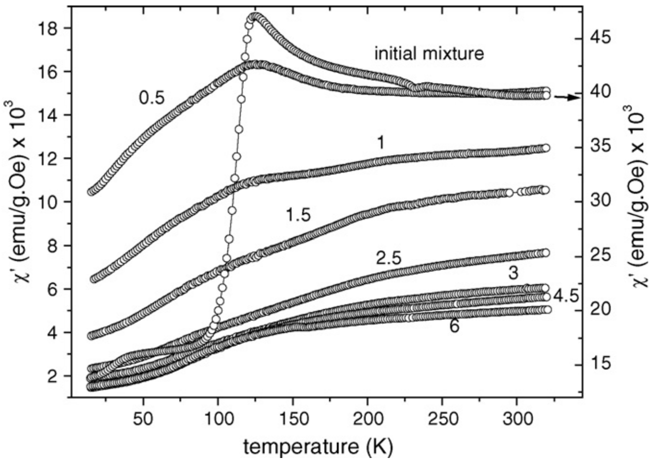

Fig. 1. In-phase ac susceptibility of the Ti–Fe_3O_4 mixture ball-milled for the times shown in the figure. The susceptibility of the initial mixture is much higher than the milled samples and is referred to the left axis. The solid lines are only a guide for the eye.

The Mössbauer spectrum of the initial Fe_3O_4–Ti mixture (Fig. 2) displays the typical spectrum of magnetite in addition to a signal – whose relative area is ≈1% – which can be assigned to already existing illite in the initial mixture.

Fig. 2 shows as well the spectra taken after different milling times. They display a gradual decrease in the areas of the magnetite sextets and the emergence of two central doublets, whose areas increase with activation time, and an α-Fe signal with a relative area of ≈10%, which remained constant for all milling times. One of the doublets at the center of the spectra have parameters similar to those reported for Ulvospinel at room temperature, that we assign to non-stoichiometric forms of this species. The other central doublet belongs to an unidentified species of Fe^{2+}. Fig. 3 shows the relative areas of the signals and the species to which their parameters approximately belong. Table 1 displays the results of the fittings as described in Section 2.

In addition to the signals whose parameters are similar to the reported species, it was necessary to include a signal belonging to an unidentified Fe^{3+} compound to improve the fitting to χ^2 values according to the data statistics. This species remains constant over the milling at approximately less than 10% relative area. The Fe^{3+} species is likely originated in defective grain boundaries and not fully formed phases caused by the ball milling.

3.1. X-ray diffraction

Fig. 4 displays the XRD patterns of the samples. As the milling progresses, the intensity of the diffracted peaks decrease

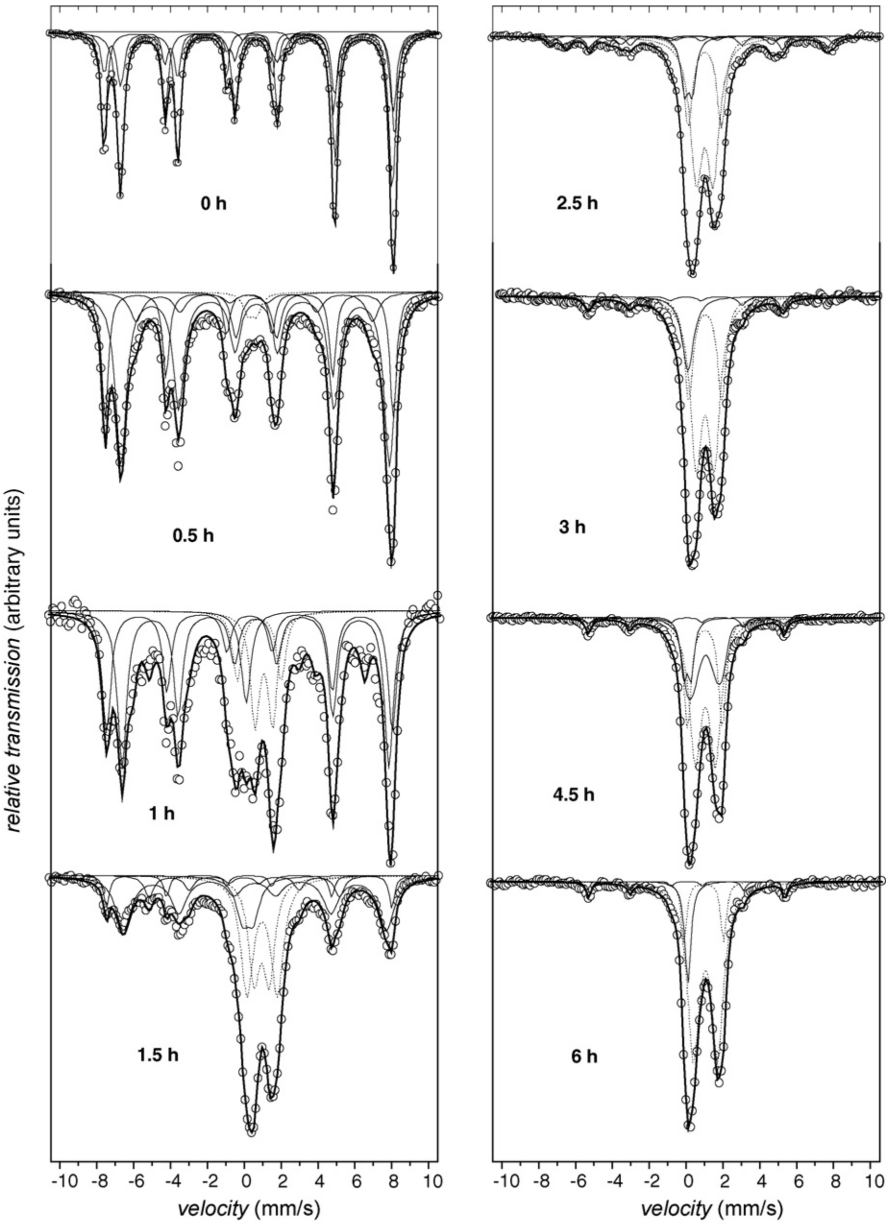

Fig. 2. Room temperature Mössbauer spectra of the Ti–Fe_3O_4 mixture ball-milled for the times shown in the figure. The dotted lines are the components of the doublets assigned to non-stoichiometric Ulvöspinel and of the unidentified Fe^{2+} species mentioned in the text. The thin solid lines are the sextets and the unidentified Fe^{3+} species of the described fitting that together with the doublets make up the total spectrum displayed in thicker lines.

and their line-width broadens (The crystallite size, determined by FWHM measurement and using the Scherrer equation, was: >200 nm for TiM0, 9 nm for TiM1, and 7 nm for TiM1.5. For longer activation times, the disappearance of the original phases made impossible the determination.). This effect is expected because of the decrease of the crystal size and the deterioration of the crystalline structure. The evolution of the diagrams also shows a shift of the peaks corresponding to the structure of spinel.

At the early steps of the activation, the Rietveld analysis suggests a structure of low crystallinity compatible with a (FeO + TiO) structure. Metallic iron becomes detectable after 1 h of activation, as a little shoulder overlapped to the (4 0 0) peak of the Fe_3O_4 spinel, which increases its intensity up to 3 h.

The experimental measurements show that with increasing activation times, the value of the a_0 parameter of the cubic structure increases. This is due to the progressive disordering of the structure and to the incorporation of Ti in the spinel lattice, which generates a precursor with a composition included in a continuous series of solid solutions, from magnetite (before any reaction with Ti has occurred) to ulvospinel (although it does not reach its full stoichiometry under our experimental conditions). This was confirmed by XRD analyses after thermal treatments (30 min at 700 °C) during which the crystallinity of this phase was developed.

At activation times longer than 3 h, the relative concentrations of the different phases stabilize. The presence of a significant amount of remnant Fe^{2+} is possibly related to the total concen-

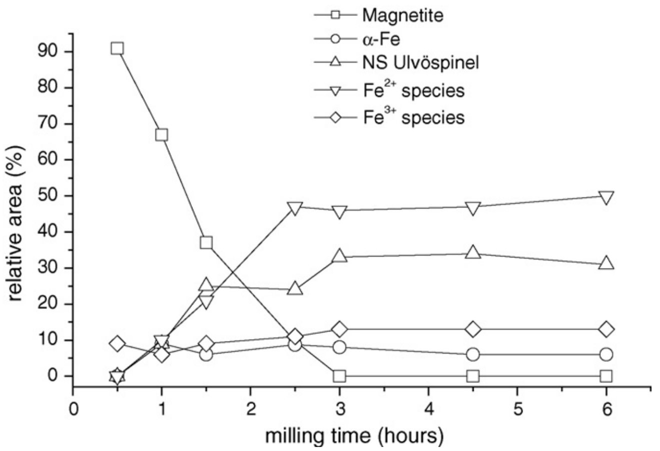

Fig. 3. Relative areas of existing iron species in the samples identified through their Mössbauer parameters. NS stands for non-stoichiometric. The solid lines are a guide for the eye.

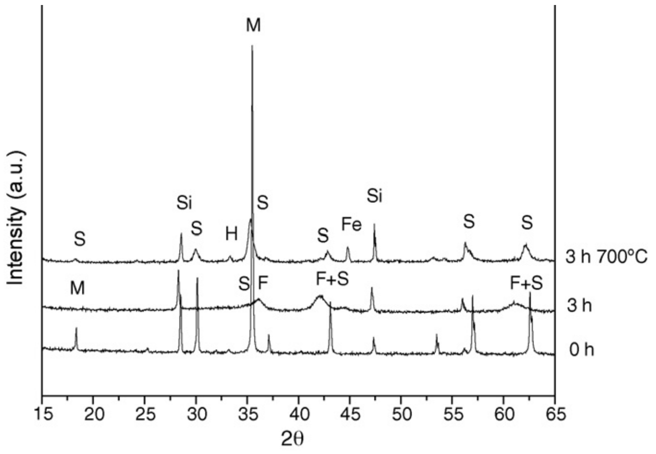

Fig. 4. XRD pattern. F: FeO + TiO, Fe: iron, H: hematite, M: magnetite, S: solid solution (ulvospinel–magnetite).

tration of Ti, which is 50% of that needed to form ulvospinel with all the Fe contained in the initial mixture.

3.2. SEM–EPMA

The scanning electron micrographs (Fig. 5) show that the particle size decreases with the time of activation, reaching an average particle size of about 0.5 μm after 3 h of activation.

We can also observe the loss of the original particle morphology, with production of a relatively fine and homogeneous microstructure, with rounded and poorly crystalline particles and considerable tendency to agglomeration. The latter effect is due not only to their small size, but specially to the high surface energy that results from the high concentration of structural defects brought about by the activation.

The analysis by EPMA of the original mixture made it possible to distinguish between the Ti and Fe_3O_4 particles. On the

Table 1
Hyperfine parameters of the samples milled for the time indicated in the left column, obtained after the least squares fittings described in the text

Milling time (h)		δ (mm/s)	Δ or ε (mm/s)	H (kOe)	RA (%)
0	Illite	1.2_3	2.56_6		$1_{0.5}$
	Magnetite site A	0.28_2	0.00_1	489_2	37_2
	Magnetite site B	0.66_2	0.00_1	457_1	62_2
1	Ulvospinel NS	0.83_4	2.3_1		9_2
	Fe^{2+} species	0.99_4	1.1_1		10_2
		0.44_8	0.7_2		6_1
	Magnetite	0.29_2	0	482_2	23_3
		0.60_2	0	449_1	34_2
		0.26_6	0	393_4	10_1
	α-Fe	0	0	330	9_2
2.5	Ulvospinel NS	1.02_6	1.79_3		24_4
	Fe^{2+} species	1.02_1	0.91_4		47_4
		0.13_1	0.42_2		3.2_6
	Magnetite	0.32_5	0	476_4	3.2_6
		0.55_3	0	439_3	6.5_7
	α-Fe	0	0	323_3	9_1
3	Ulvospinel NS	0.97_7	1.90_4		30_7
	Fe^{2+} species	0.964_8	1.05_6		53_7
		0.50_2	0.43_4		10_7
	α-Fe	0.00_5	-0.05_5	327_3	7_2
	Ulvospinel NS	0.98_4	1.95_2		34_4
	Fe^{2+} species	0.972_6	1.20_5		47_5
6	Ulvospinel NS	0.99_1	1.96_4		33_8
	Fe^{2+} species	0.95_2	1.32_6		50_{10}
		0.54_5	0.33_7		12_1
	α-Fe	0.04_4	-0.01_3	331_2	6_1

The sub indexes denote the uncertainties in the least significant figures of the reported values.

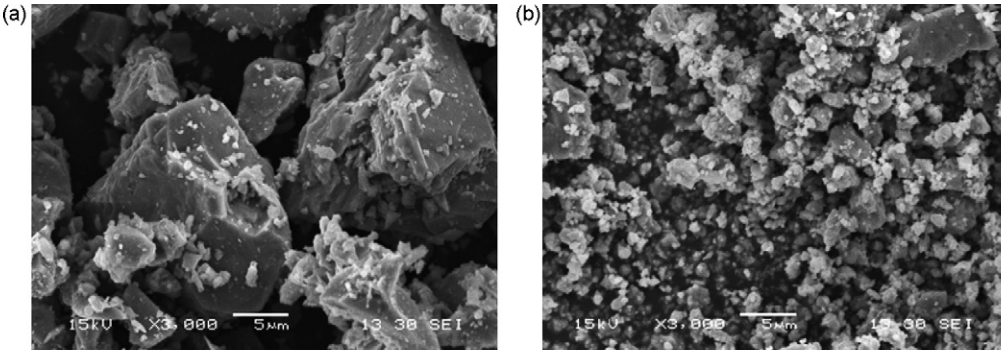

Fig. 5. Scanning electron micrographs of the starting (a) and the 3 h ball-milled sample (b).

other hand, the analysis of individual particles of the activated samples yielded a constant particle composition over all activation times, with a homogeneous distribution of Fe and Ti in the whole sample.

4. Discussion

The activation of Ti–$\mathrm{Fe_3O_4}$ mixtures produces a reduction of the particle size and the transformation of the ferrimagnetic material (magnetite) into the para- or antiferromagnetic species at very short activation times. The Verwey transition is an outstanding feature of the initial mixture.

After 3 h of ball milling, the magnetite signal no longer contributes to the Mössbauer spectrum. Both ulvospinel and the unidentified $\mathrm{Fe^{2+}}$ species are not initially present. The ulvospinel relative area increases up to 2.5 milling hours and remains constant until the longest times. At short times, XRD shows a loss of crystallinity and a shift of the spinel cell parameter indicating that Ti is incorporated in the structure, with the emergence of unidentified phases that adjust to a (FeO + TiO) structure.

The same happens with the $\mathrm{Fe^{2+}}$ species, except that the saturation percentage is achieved at 1.5 h. It is worth mentioning, that by Mössbauer spectroscopy the oxidation state of the Fe atoms belonging to a certain species can be assessed straightforwardly, but that it is not so easily possible to identify the compound in which the Fe ion is present. Therefore, the $\mathrm{Fe^{2+}}$ signal observed in the spectra could belong to more than one species or a mixture of them. Moreover, because of the local sensitivity of Mössbauer spectroscopy, the signal might belong to seeds of newly formed species that do not have yet the size to diffract coherently X-rays and hence cannot be detected by XRD. For both techniques it is observed that the main changes in the structure and the reactions occur up to activation times of 3 h. Further thermal treatments (in Ar atmosphere) at 700 °C bring forth an increase of the crystallinity of the existing phases. When the annealing is made in air, hematite appears as the principal crystalline phase.

The parameters of ulvospinel are not exactly the same as those reported for the stoichiometric species. However, because of the way it has arisen, this can be expected. According to the Mössbauer parameters, the ulvospinel doublet approaches the expected values with milling time.

The results show that over the mechanochemical activation produced by ball milling the mixtures in Ar atmosphere at room temperature, the Ti atoms reduce the Fe atoms in the $\mathrm{Fe_3O_4}$ spinel, partly to $\mathrm{Fe^{2+}}$ and partly to metallic Fe. Fe ions are partly substituted for Ti in the structure, leading to a stoichiometry of the type $\mathrm{Fe^{3+(IV)}Fe^{2+(VI)}}_{1+x}\mathrm{Fe^{3+(VI)}}_{1-2x}\mathrm{Ti^{4+(VI)}}_{x}\mathrm{O_4}$, where, according to,[6] we have assumed that $\mathrm{Ti^{4+}}$ incorporates mainly into octahedral (VI) sites and that part of the $\mathrm{Fe^{2+}}$ ions (x) is produced by reduction of the octahedral $\mathrm{Fe^{3+(VI)}}$ ions.

5. Conclusions

The mechanical activation for times up to 6 h of a mixture of Ti and $\mathrm{Fe_3O_4}$ lead to the development of new phases. The ac magnetic susceptibility results show that the conversion of the starting ferrimagnetic material (magnetite) into para- or antiferromagnetic species occurs at very short activation times, and, when the loss of crystallinity observed by XRD takes place after ≈1.5 h, clear magnetic transitions are no longer observed.

By Mössbauer spectroscopy and XRD, we have been able to monitor quantitatively the evolution of the changes in the contents of the main phases, α-Fe, ulvospinel, and non-stoichiometric $\mathrm{Fe^{2+}}$ and $\mathrm{Fe^{3+}}$ species, which appear as the activation progresses.

In addition, the activation causes Ti atoms to reduce the Fe atoms in the $\mathrm{Fe_3O_4}$ spinel, partly to $\mathrm{Fe^{2+}}$ and partly to metallic Fe. Fe ions are partly substituted for Ti in the structure, leading to a stoichiometry of the type $\mathrm{Fe^{3+(IV)}Fe^{2+(VI)}}_{1+x}\mathrm{Fe^{3+(VI)}}_{1-2x}\mathrm{Ti^{4+(VI)}}_{x}\mathrm{O_4}$.

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