

Effects of the Ti/Fe ratio on the phase composition and magnetic properties of mechanochemically activated Ti–Fe₂O₃ mixtures

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ABSTRACT

The mechanochemical activation of Ti/Fe₂O₃ powder mixtures with molar ratio 1 and 1.5 was performed with the aim of understanding the effects of the starting composition on the reactivity and structure of the produced phases. The solid mixture was characterized by scanning electron microscopy, X-ray diffraction, vibrating sample magnetometry and Mössbauer spectroscopy. The consumption of the reactants and the formation of metallic iron are observed at short activation times. After 3 h, the redox reaction completes, yielding a composite powder formed by nanocrystalline Fe particles dispersed in an oxide matrix. The mixture with the highest Ti/Fe ratio leads to the formation of a TiO₂ matrix, whereas the other composition forms FeTiO₃. Both composite materials have very high saturation magnetization and moderate coercivities. Under subsequent thermal treatment at 700 °C, the activated solids show a progressive crystalline ordering with partial oxidation of Fe (mainly to FeTiO₃ and Fe₂O₃) and crystallization into the rutile phase of TiO₂. This leads to a significant decrease of magnetization and coercivity.

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1. Introduction

Mechanochemical activation is a powder-processing method conducted in high-energy ball-mills which results in the generation and storage of excess energy in crystalline solids, through a significant accumulation of structural defects and strains which affect the chemical reactivity of the studied system. High-energy ball-milling has acquired great importance during the last years as a tool for the preparation of precursors in the synthesis of new materials and metastable phases not obtainable by conventional techniques [1–3]. The formation of precursors in comparatively mild conditions, or even, the ignition of self-sustained reactions close to room temperature has been reported for metal–oxide systems [4,5]. The reactions between inorganic oxides and active metals have been used for decades in the production of metal–ceramic composite materials [6–8]. Also, the use of metals instead of simple oxides as starting materials has proved to favor the reactivity in the formation of complex oxides, such as spinels or perovskites [9,10]. During the milling, plastic deformation of metal particles on the oxide particles takes place, increasing the contact interface between both solid reactants.

In particular, the Fe–Ti–O system displays a very rich phase diagram, which contains a variety of continuous solid solutions including ulvöspinel-magnetite (Fe_{3–x}Ti_xO₄), ilmenite-hematite (Fe_{2–x}Ti_xO₃) and pseudobrookite (Fe_{1+x}Ti_{2–x}O₅) [11–13]. Most of these compounds show magnetic properties which are strongly dependent on the composition and cation distribution in the crystal structure [14]. Recently, we have published two articles reporting the mechanical activation of the Ti/Fe₂O₃ system in a molar ratio of 0.5 [15,16]. In those mixtures, two solid solutions of composition Fe_{3–x}Ti_xO₄ were obtained: one with a Ti content higher than 0.5 and the other one containing a Ti fraction lower than 0.5. A small amount of metallic iron was also formed during the milling. Considering those results, the increase of the Ti/Fe₂O₃ molar ratio could be advantageous to produce solid solutions of composition Fe_{3–x}Ti_xO₄ which are richer in Ti. Besides, the increase of metal Ti could favor the reduction of iron, leading to materials composed by a dispersion of metal Fe in an oxide matrix. This kind of systems could exhibit high magnetization and coercivity, making them potentially useful as materials for information storage devices and permanent magnets [17,18].

In this work, Ti/Fe₂O₃ solid mixtures with two molar ratios (1 and 1.5) were mechanochemically treated with the aim of determining the effect of the Ti/Fe ratio on the reactivity of the system and the magnetic properties of the obtained materials.

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2. Experimental

2.1. Samples preparation

The reactive mixture was prepared from metallic Ti (98 wt.%) and hematite (97 wt.%), both commercial reagents. The initial mixtures Ti:Fe₂O₃ – with molar ratio 1 and 1.5 – were activated in a laboratory planetary ball-mill (Fritsch Pulverisette 7) with vials and balls of hardened Cr-steel. The mixtures were prepared and activated under Ar atmosphere ($P_{O_2} < 1$ Pa) during 1, 2 and 3 h. The experimental method assured there was no incorporation of oxygen from the outer atmosphere into the vials. 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. The vials were rotated at 1500 rpm during measured time intervals. The activated powders were then submitted to a thermal treatment at 700 °C under flowing Ar, using a heating rate of 10 °C min⁻¹, and a soaking time of 30 min at the final temperature. The series of activated samples were labeled TiH1–*x* and TiH1.5–*x* for Ti/Fe₂O₃ molar ratio 1 and 1.5 respectively, being *x* the activation time in hours.

2.2. Samples characterization

The microstructure of the activated samples was examined by scanning electron microscopy (SEM) with a Philips 505 microscope.

The crystalline phases were characterized by XRD on a Philips 3020 goniometer with a PW 3710 controller, using Fe-filtered CoK α radiation and operating at 40 kV and 30 mA. The scanings were performed between 10° and 80° in 2θ . The instrumental width was determined measuring the (3 1 1) peak of a silicon pattern, giving a value of 0.15° 2θ . Mössbauer spectra were taken at room temperature (RT) in a conventional constant acceleration spectrometer in transmission geometry with a ⁵⁷Co/Rh source. The absorber thickness was chosen to be the optimum according to the Long et al. criterion [19]. Least-squares fitting of the spectra was performed by using the Normos program [20]. Isomer shift (IS) values are given relative to that of α -Fe at room temperature. Magnetic measurements were performed at RT using a vibrating sample magnetometer Lakeshore 7300. The powders were shaped into disks of 6 mm diameter by 1 mm height and uniaxially compacted at 7.5 ton cm⁻². Hysteresis loops were obtained varying the applied field between ± 15 kOe.

3. Results and discussion

XRD patterns of the TiH1 series and the one for TiH1-3-700 are shown in Fig. 1a. The vanishing of the peaks corresponding to the reactant components (Ti and hematite) is complete after 1 h of activation. At that moment, intense signals corresponding to metallic iron (α -Fe) and ilmenite (FeTiO₃) can be observed. This oxide has a rhombohedral structure with lattice parameters slightly higher than those of hematite. Since Ti is a stronger reducing agent than Fe, the presence of ilmenite can be related to the partial reduction and replacement of Fe³⁺ in the hematite structure by Ti⁴⁺, during the activation.

Fig. 1b shows XRD diagrams for samples TiH1.5. A decrease of the diffracted intensities is observed as the activation time increases. Similarly to samples TiH1, 1 h of mechanical treatment produced the complete consumption of both reactants. Diffractograms exhibit very intense peaks corresponding to metallic iron (main peak at $2\theta \sim 52.6^\circ$), but there is no evidence of ilmenite in the solid. The absence of peaks belonging to phases with titanium suggests that metallic Ti has been oxidized to a low-crystalline phase, probably TiO₂.

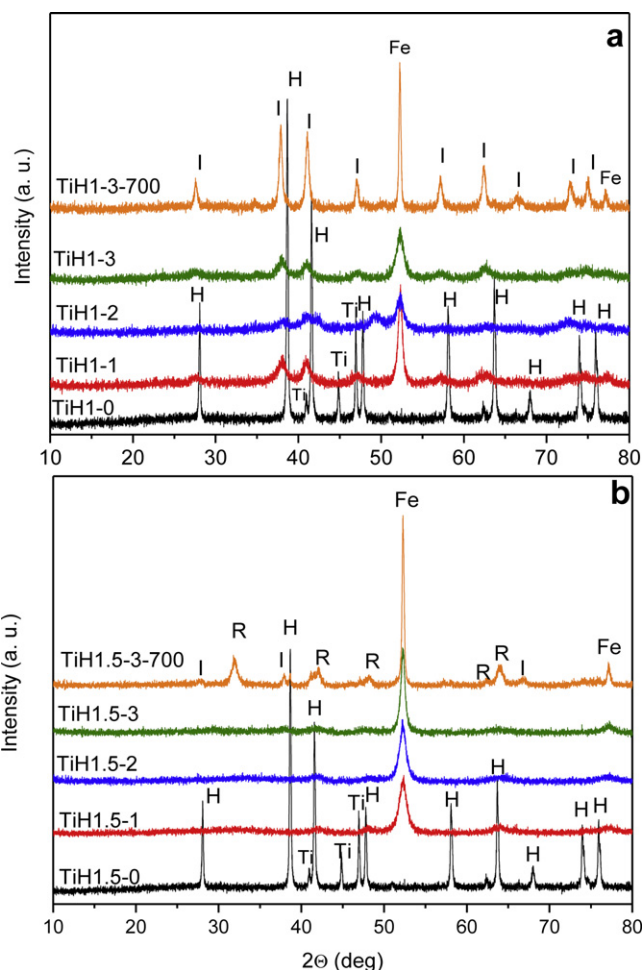


Fig. 1. (a) XRD patterns for the series of samples TiH1–*x* and TiH1-3-700. (b) XRD patterns for the series of samples TiH1.5–*x* and TiH1.5-3-700. Fe: metallic iron, H: hematite, I: ilmenite, R: rutile, Ti: titanium.

In this way we can propose mechanochemical reactions (1) and (2) for the two series of samples TiH1 and TiH1.5, respectively:



These equations indicate that in both cases a redox reaction between Ti and Fe₂O₃ proceeded, but a different Ti/Fe ratio of the starting mixtures led to unlike materials.

In both series of samples, for activation times longer than 1 h there are no significant changes except for the decreasing intensity and widening of the iron peaks. The crystallite size calculation performed using Scherrer's equation reveals values of around 20 and 10 nm for samples activated for 1 and 3 h, respectively.

Calcination at 700 °C produced the narrowing of the diffracted peaks as a consequence of the growth of crystallite size (for Fe crystals Scherrer's equation gives around 50 nm), the healing of structural defects and a significant increase of the crystalline order. Both mixtures TiH1-3-700 and TiH1.5-3-700 show small peaks corresponding to hematite, probably formed by partial oxidation of metallic iron. The pattern of sample TiH1.5-3-700 also shows peaks corresponding to ilmenite, formed by reaction between Fe and TiO₂ in an air atmosphere. Another phase detected after the heat treatment is rutile (TiO₂), whose presence is explained by the crystallization of the poorly crystalline or amorphous TiO₂ formed during the reaction (Eq. (2)). In fact, the examination of the TiH1.5-3 diffractogram shows broad

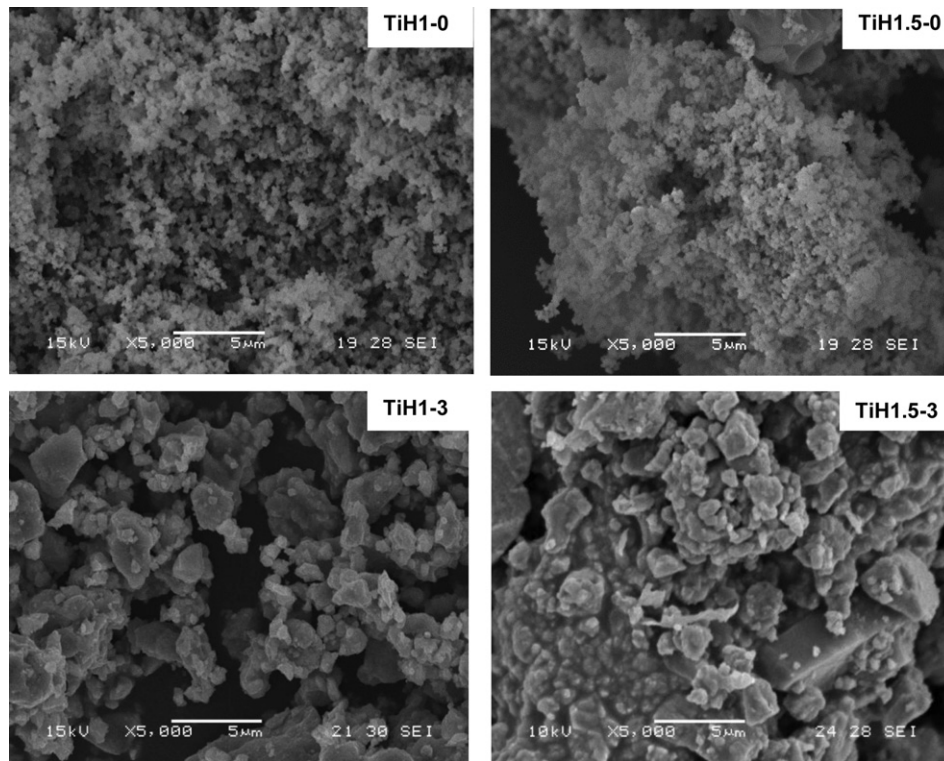


Fig. 2. Scanning electron micrographs of un-milled (TiH1-0 and TiH1.5-0) and milled samples for 3 h (TiH1-3) and (TiH1.5-3).

and low-intensity peaks which could be assigned to this titanium oxide (rutile).

The effect of mechanical activation on the microstructure of the powders can be observed in Fig. 2. SEM micrographs of the unmilled samples reveal a small size of both Ti and hematite particles, being smaller than 500 nm. After 3 h of mechanical treatment the microstructure of the system notably changes towards

agglomerates of a few microns constituted by micrometric rounded particles. This is a consequence of the formation of metallic Fe at expenses of hematite and Ti (according to XRD results). A more exhaustive observation of samples TiH1-3 and TiH1.5-3 suggests that the particles which form the agglomerates are stuck by a more plastic phase (probably Fe). This is more evident for TiH1.5-3, where the metal content is higher than in TiH1-3. It is worth remarking

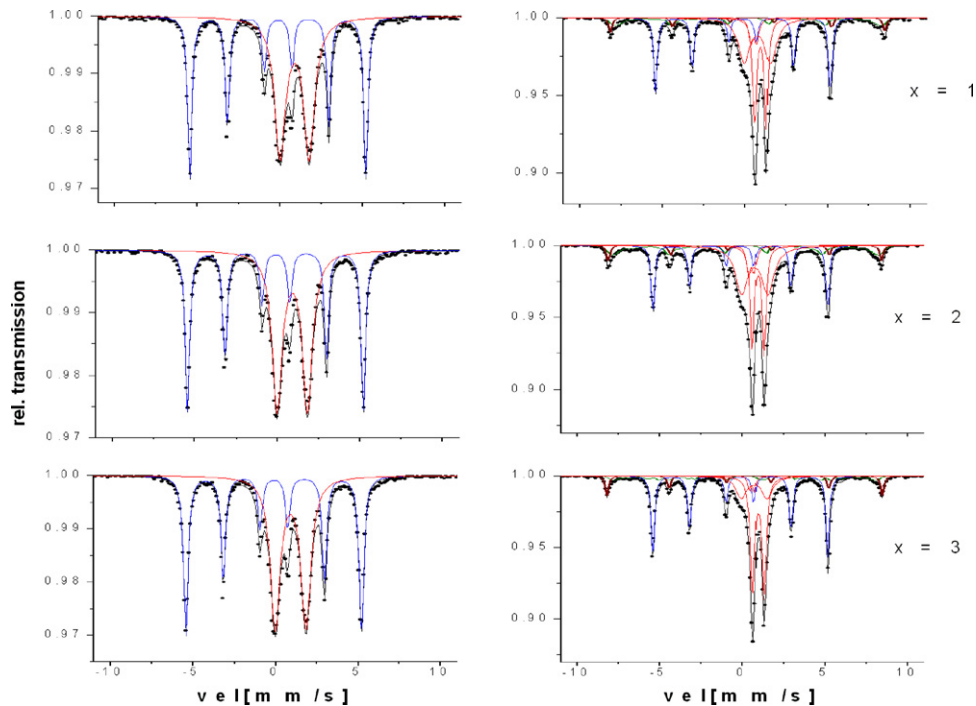


Fig. 3. Fitted RT Mössbauer spectra of TiH1- x (left column) and TiH1- x -700 (right column). • Experimental points, — convolution of the subpeaks, — α -Fe, — FeTiO_3 , — α - Fe_2O_3 , — T-M. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

that the average particle size is much larger than the mean crystallite size determined by Scherrer's equation (10 nm), indicating that Fe particles are polycrystalline.

Fig. 3 shows the Mössbauer spectra at RT for samples TiH1 obtained at different milling times (1, 2 and 3 h), with and without heat treatment at 700 °C. It is important to keep in mind that Mössbauer spectroscopy only detects Fe-bearing compounds (because in this case a ^{57}Co source was used). For the as-milled samples, spectra were fitted to a sextet with a hyperfine magnetic field around 33 T, typical of metallic Fe, and a quadrupole-split doublet. From Table 1, where the relative abundances of Fe-bearing compounds detected in each one of the samples is displayed, it can be seen that α -Fe percentage is nearly constant at about 50% for the different activation times. The other 50% is represented by a wide quadrupole-split doublet with hyperfine parameters characteristic of ilmenite mechanically treated in a high energy ball-mill [21], whose quadrupole splitting value is almost three times greater than that from an ilmenite without mechanical process. Then, it can be concluded that Ti reduces Fe ions in the hematite lattice to Fe^{2+} and to metallic iron in equal amounts and that the crystalline hematite reduction is completed in only 1 h of activation.

On the other hand, the heat-treated samples were fitted to a hyperfine field distribution with two sextets and three quadrupolar doublets. In every case the hyperfine field distribution with maxima at 37 T, 43 T and 49 T was assigned to the presence of titanomagnetite (T-M) [22]. Table 1 displays the median value of the distributions. The sextets with hyperfine field values of 51 T and 33 T correspond to hematite and to metallic Fe respectively. One of the three doublets, having the characteristic hyperfine parameters of natural ilmenite, appears together with the other two which only come out in ilmenite obtained by high-energy ball milling [23]. This effect could be due to the distorted structure and the small crystalline grains induced by the mechanical process. In these heat-treated samples, metallic Fe is in a lower proportion than that present in the as-milled samples, remaining the ilmenite amount about one half of the total iron-bearing compounds. In addition, Fe–Ti mixed-oxides were formed.

Table 1

Hyperfine parameters and relative abundances of Fe-bearing compounds obtained by Mössbauer spectroscopy analysis for samples TiH1. *: median value of the distribution. IS: isomer shift, QS: quadrupole splitting, 2ϵ : quadrupole shift, B_{hf} : hyperfine magnetic field, Rel. Ab.: relative abundance, T-M: titanomagnetite.

Sample	IS (mm s^{-1})	QS (mm s^{-1})	2ϵ (mm s^{-1})	B_{hf} (Tesla)	Assignment	Rel. Ab. (%)
TiH1-1	0.00	–	0.00	33.05	α -Fe	48
	1.01	1.76	–	–	FeTiO_3	52
TiH1-2	0.00	–	0.00	33.05	α -Fe	48
	1.00	1.84	–	–	FeTiO_3	52
TiH1-3	0.00	–	0.00	32.98	α -Fe	50
	1.01	1.86	–	–	FeTiO_3	50
	0.38	–	–0.26	51.85	α - Fe_2O_3	8
	0.00	–	0.00	32.85	α -Fe	35
	1.08	0.68	–	–	–	–
	0.84	1.53	–	–	FeTiO_3	47
TiH1-1-700	0.72	0.30	–	–	–	–
	0.32	–	0.00	47.61*	T-M	10
	0.42	–	–0.31	51.43	α - Fe_2O_3	6
	0.00	–	0.00	32.85	α -Fe	24
	1.08	0.68	–	–	–	–
TiH1-2-700	0.88	1.56	–	–	FeTiO_3	57
	0.69	0.33	–	–	–	–
	0.31	–	0.00	48.88*	T-M	13
	0.42	–	–0.28	51.60	α - Fe_2O_3	5
	0.00	–	0.00	32.85	α -Fe	29
TiH1-3-700	1.08	0.68	–	–	–	–
	0.88	1.58	–	–	FeTiO_3	55
	0.68	0.34	–	–	–	–
	0.31	–	0.00	49.10*	T-M	11

Fig. 4 displays the Mössbauer spectra of the series of samples TiH1.5 acquired at RT, while Table 2 shows the corresponding hyperfine parameters and the relative abundances of each Fe-bearing compound present in the samples. Spectra corresponding to TiH1.5-2 and TiH1.5-3 were computer-fitted using one sextet and a quadrupole-split doublet, while the spectrum corresponding to TiH1.5-1 was better fitted adding also an extra quadrupole doublet. The sextet with hyperfine magnetic splitting around 33 T observed in all the samples denotes the presence of metallic iron. From Table 2 it follows that its relative abundance grows with increasing activation time and it is always the predominant phase. After 3 h of activation, the Mössbauer spectrum shows metallic Fe as being practically the only phase present in the system (95% of relative abundance). The spectrum also reveals a small contribution of FeTi_2O_5 as the only Ti-bearing phase detected. This fact agrees with XRD results (Fig. 2), which indicate that most of the Ti appears as poorly crystalline TiO_2 . Taking these results into account, it can be concluded that the displacement reaction (2) is almost complete after 3 h of mechanochemical activation. Both doublets included in the fitting procedure were assigned to a solid solution with general formula $\text{Fe}_{1+y}\text{Ti}_{2-y}\text{O}_5$ ($0 \leq y \leq 1$). The end compounds are known as ferropseudobrookite (FeTi_2O_5) and pseudobrookite (Fe_2TiO_5), being the former a ferrous compound and the latter a ferric one. For intermediate compositions both phases coexist [11]. In our case, this coexistence is evident in TiH-1.5-1, whose spectrum was fitted with a quadrupolar doublet associated to a ferrous (Fe^{2+}) ion and another one related to a ferric (Fe^{3+}) ion. For TiH1.5-2 and TiH1.5-3 instead, the only solid solution detected is FeTi_2O_5 . From Table 2 it follows that the relative abundance of this minor phase decreases to almost disappearance at 3 h of activation time. For TiH1.5-1-700 two sextets and two doublets were used in the fitting routine. The sextet with hyperfine field around 51 T corresponds to α - Fe_2O_3 whereas the other sextet corresponds to α -Fe, which remains as the major phase just as in the samples without heat-treatment (Table 2). The parameters of the quadrupole doublets are compatible with divalent and trivalent iron sites. The first doublet (corresponding to Fe^{2+}) has the hyperfine parameters characteristic of ilmenite (FeTiO_3) while the second one (corresponding to Fe^{3+})

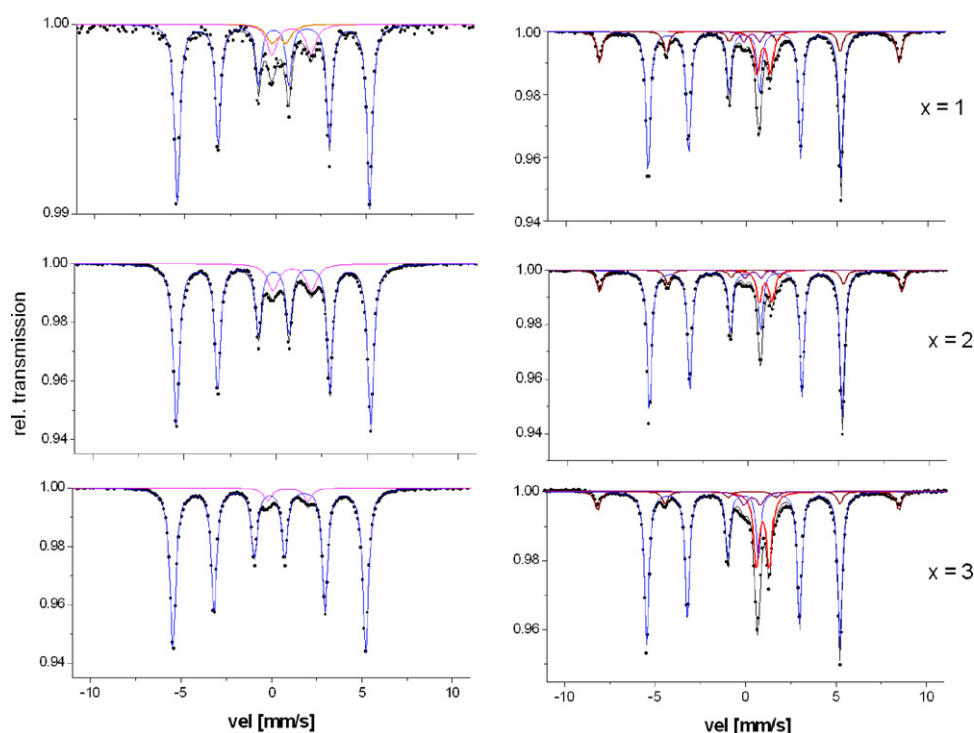


Fig. 4. Fitted RT Mössbauer spectra of TiH1.5- x (left column) and TiH1.5- x -700 (right column). • Experimental points, — convolution of the subspectra, — α -Fe, — FeTiO₃, — α -Fe₂O₃, — FeTi₂O₅, — Fe₂TiO₅, — Ti(Fe)O₂/Fe₂TiO₅. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

could be associated to the presence of a pseudorutile-type phase, as reported in [24] for a high-energy ball-milled natural ilmenite. Nevertheless, taking into account the obtained hyperfine parameters, a mixture of Fe in rutile and in pseudobrookite (Ti(Fe)O₂/Fe₂TiO₅) – difficult to resolve due to their very low proportions in the sample – appears as more probable, as it was also observed in mechanical alloyed Fe-doped TiO₂ [25].

Fig. 5 shows the magnetic hysteresis loops of samples TiH1 and TiH1.5 activated for 1 and 3 h. Clearly, TiH1 series has saturation magnetization (M_s) values lower than those for TiH1.5 series. The explanation for this is the difference in the iron content. According

to Mössbauer spectroscopy, the relative abundance of α -Fe in samples TiH1-1 and TiH1-3 is about 50%, whereas for samples TiH1.5-1 and TiH1.5-3 this is 80 and 95%, respectively (Tables 1 and 2). For the series TiH1.5, very large M_s values (higher than 100 emu g⁻¹) can be noticed.

Considering that reactions (1) and (2) occur completely after 3 h of milling, it is then possible to calculate the weight percentage of each component in the whole mixtures. For sample TiH1 this calculation gives 27% Fe and 73% FeTiO₃, and for sample TiH1.5 the composition is 48% Fe and 52% TiO₂. Assuming that iron is the phase which mainly contributes to the total magnetic moment (FeTiO₃

Table 2

Hyperfine parameters and relative abundances of Fe-bearing phases for the samples TiH1.5. IS: isomer shift, QS: quadrupole splitting, 2ϵ : quadrupole shift, B_{hf} : hyperfine magnetic field, Rel. Ab.: relative abundance.

Sample	IS (mm s ⁻¹)	QS (mm s ⁻¹)	2ϵ (mm s ⁻¹)	B_{hf} (Tesla)	Assignment	Rel. Ab. (%)
TiH1.5-1	0.01	–	0.00	33.0	α -Fe	80
	0.31	0.81	–	–	Fe ₂ TiO ₅	8
	0.99	2.16	–	–	FeTi ₂ O ₅	12
TiH1.5-2	0.00	–	0.00	33.04	α -Fe	88
	1.01	2.10	–	–	FeTi ₂ O ₅	12
TiH1.5-3	0.00	–	0.00	33.04	α -Fe	95
	1.01	2.23	–	–	FeTi ₂ O ₅	5
	0.37	–	–0.22	51.42	α -Fe ₂ O ₃	16
TiH1.5-1-700	0.00	–	0.00	33.05	α -Fe	70
	1.08	0.72	–	–	FeTiO ₃	11
	0.42	0.87	–	–	Ti(Fe)O ₂ /Fe ₂ TiO ₅	3
	0.40	–	–0.28	51.89	α -Fe ₂ O ₃	12
TiH1.5-2-700	0.00	–	0.00	33.05	α -Fe	76
	1.10	0.69	–	–	FeTiO ₃	9
	0.42	0.90	–	–	Ti(Fe)O ₂ /Fe ₂ TiO ₅	2
	0.39	–	–0.24	51.74	α -Fe ₂ O ₃	9
TiH1.5-3-700	0.00	–	0.00	33.13	α -Fe	69
	1.09	0.71	–	–	FeTiO ₃	18
	0.51	0.93	–	–	Ti(Fe)O ₂ /Fe ₂ TiO ₅	4

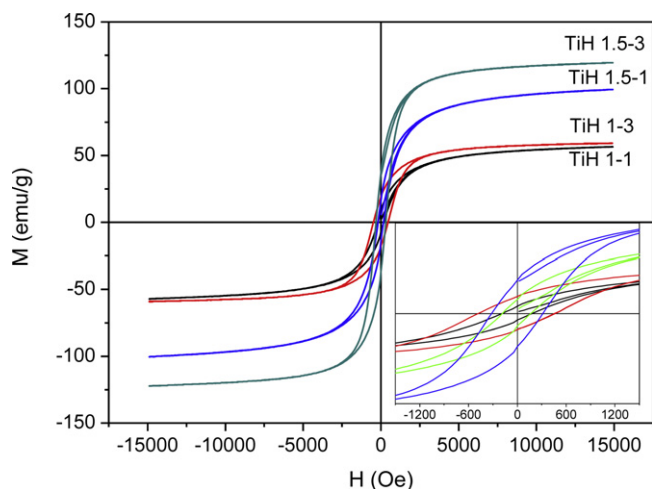


Fig. 5. *M* vs *H* curves for the series of activated samples TiH1 and TiH1.5. The inset displays an enlargement of the low-field zone showing differences in coercivities.

is paramagnetic and TiO₂ diamagnetic), and taking the *M_s* of bulk α-Fe as 220 emu g⁻¹ at 293 K [26] it can be concluded that the compositions of samples TiH1-3 and TiH1.5-3 nicely agree with the stoichiometric calculations. For both series of samples, coercivity measurements show a significant increment between the first and third hour of activation. This increase could be due to the large amount of defects generated by the activation in the early stages which hinder the mobility of magnetic domain walls, originating a higher coercive field.

When the activated samples were heated at 700 °C, a marked decrease in *M_s* was observed (Fig. 6). This fact is explained by the partial oxidation of metallic iron and the formation of oxides with lower magnetization. According to Mössbauer spectra, in both systems some hematite is formed as a consequence of atmospheric oxidation of α-Fe. On the other hand, metallic iron is oxidized to Fe²⁺, giving rise to mixed oxides such as ilmenite (TiH1 and TiH1.5) and titanomagnetite (TiH1). These phases are formed together with a mixture of Ti(Fe)O₂ and Fe₂TiO₅ (in a much lower proportion), as Table 2 shows. The very weak ferromagnetic response of these oxides leads to a magnetization decrease with respect to the as-milled samples. Coercivities of the calcined samples are significantly lower than those measured for the as-milled

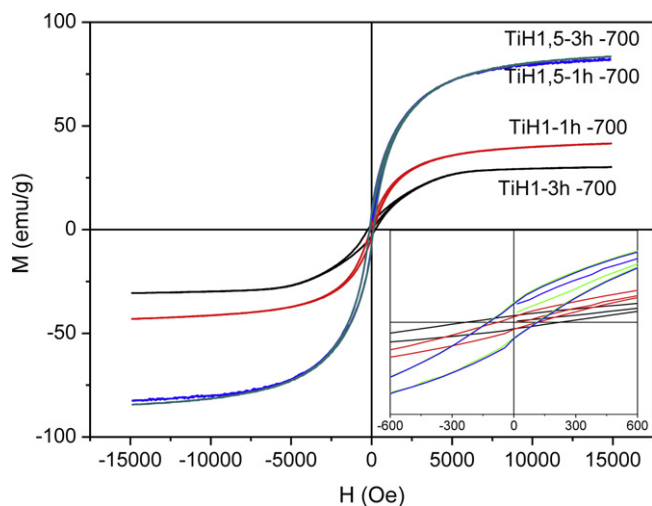


Fig. 6. *M* vs *H* curves for samples TiH1-*x*-700 and TiH1.5-*x*-700. The inset displays an enlargement of the low-field zone showing differences in coercivities.

powders. Thermal treatments produce elimination of defects and grain boundaries, lowering the magnitude of the coercive field.

4. Conclusions

Mechanochemical activation of Ti/Fe₂O₃ mixtures in molar ratio 1 and 1.5 induces rapid redox solid-state reactions at room temperature. For the system with the lowest Ti/Fe ratio the complete reduction of hematite occurs in only 1 h of mechanical treatment. The so obtained material is composed of 27% α-Fe and 73% FeTiO₃, showing a saturation magnetization of 60 emu g⁻¹ and a coercivity between 180 and 470 Oe, depending on the milling time. On the other hand, the mixture with molar ratio 1.5 reacts more gradually, yielding a composite powder of α-Fe particles dispersed in a low-crystallinity TiO₂ matrix, after 3 h of milling. Mössbauer spectroscopy analysis also reveals the formation of phases with intermediate oxidation states (Fe₂TiO₅ and FeTi₂O₅) whose concentration is reduced by extending the milling time. This powder exhibits a high saturation magnetization (120 emu g⁻¹) and a relatively high coercivity (300 Oe).

For both systems, the heat treatment in Ar atmosphere at 700 °C increases the crystallinity of the activated solids and favors the oxidation of the metallic Fe and its reaction with TiO₂ to form small quantities of Fe_{2-x}Ti_xO₄, Fe₂O₃ and/or FeTiO₃. This fact produces a marked decrease of the magnetization and coercivity of the materials.

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