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Structural alterations during mechanochemical activation of a titanium–magnetite mixture

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ABSTRACT

In this work, mechanochemical activation and thermal behaviour of (Ti + Fe_3O_4) mixtures in Ti/Fe_3O_4 molar ratios 0.5, 1, and 1.5, are studied. The samples were activated under Ar atmosphere, thermally treated at temperatures ranging between 400 and 700 °C, and analyzed by XRD and Rietveld analysis, SEM and EPMA. By XRD, a progressive decrease in crystallinity with the activation time of was observed. For the samples with lower Ti contents, the system evolved towards the formation of a ulvospinel (Fe_2TiO_4)–magnetite (Fe_3O_4) solid solution, while for higher Ti contents the major phase obtained was ilmenite ($FeTiO_3$). During the activation at room temperature, low crystalline intermediate phases (FeO + TiO, FeO, pseudobrookite [Fe_2TiO_5]) were generated, depending on the initial mixture composition. Thermal treatments resulted in a progressive structural ordering, with lattice parameters slightly greater than those of the original spinel.

These results suggest that during the activation at room temperature, the Ti reduces the Fe of the spinel and partially replaces it in the lattice.

1. Introduction

Mechanochemical activation of crystalline solids using high-energy mills 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 [1,2]. 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 metal-oxide systems, it has been reported that is possible to obtain, by ball milling activation, precursors in conditions milder than those needed in conventional methods, or even, in the cases in which the reactive enthalpic change allows it, to trigger the above mentioned reactions at room temperature or slightly above it, making them self-sustained [3,4].

The study of magnetite–ulvospinel (Fe_3O_4–Fe_2TiO_4) solid solutions is stimulated by their interest to the materials science community (Fe metallurgy, ferrites) and Earth science community (indicators of magnetic, redox, and thermal history of rocks) [5].

Titanomagnetites have been synthesized by soft chemistry and by mechanochemical methods, using stoichiometric mixtures of iron, iron oxide and titanium oxides [6,7], studying their structure and cation distribution as a function of the composition and the experimental variables.

In this work, we have investigated the mechanochemical activation of Ti–magnetite mixtures and their physicochemical and thermal behaviour in different atomic ratios, using information yielded by X-ray diffraction (XRD), Rietveld analysis, scanning electron microscopy (SEM) and electron probe microanalysis (EPMA).

2. Experimental

2.1. Preparation of samples

Reactive mixtures were prepared from metallic Ti, commercial reagent, 98 wt%, and a concentrate of magnetite ore, from Sierra Grande (Chubut, Argentina), with ≥97.5 wt% Fe_3O_4. The major impurities in magnetite were a clay mineral (illite), and quartz (both in similar concentrations). The particle size of both reactants was below 100 μm. Three Ti/Fe_3O_4 molar ratios were used: 1:2(TiM0.5), 1:1(TiM1) and 3:2(TiM1.5). A planetary laboratory ball-mill (Fritsch Pulverisette 7) with vials and balls of hardened Cr-steel was used for the mechanochemical treatments.

The mixtures were prepared and activated under Ar atmosphere ($PO_2 < 1$ Pa). The milling bowls were loaded with 5 g of powder and 7 balls of 15 mm diameter

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each, resulting in a ball-to-powder mass ratio of 20:1, and rotated at 1500 rpm during measured times. The obtained samples were labelled TiM *x*–*y*–*z*, were *x* is the molar Ti/Fe_3O_4 ratio, *y* is the activation time in hours and *z* is the temperature of the thermal treatment done after milling.

The thermal treatments were performed under Ar atmosphere at temperatures ranging from 400 to 700 °C using a heating rate of 10 °C min^{-1}, and a soaking time of 30 min 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).

Also, an ulvospinel sample was synthesized by solid-state reaction [8] to serve as a reference in the lattice parameter measurements. A stoichiometric ($Fe + Fe_2O_3 + TiO_2$) reactive mixture was pressed into a 5 mm diameter pellet and enclosed in an evacuated silica glass tube. The tube was heated at 950 °C during 168 h.

2.2. Analysis and characterization of samples

The particle morphology and composition of the starting mixtures and of the activated samples were examined by SEM (Philips 505) equipped with an electron probe microanalyzer (EPMA).

Prior to the observations, the samples were coated with gold. The EPMA analyses were carried out in an EDAX analyzer attached to the electron microscope.

Crystalline phases were characterized by X-ray diffraction with a Philips 3020 goniometer with PW 3710 controller, using Cu Kα radiation and Ni filter at 40 kV–20 mA. The samples were scanned between 15° and 65° 2θ with a step size of 0.04° and a step counting time of 4 s. Silicon was added as internal standard.

The powder diffraction patterns were analyzed with the program FullProf, which is a multipurpose profile-fitting program, including Rietveld refinement [9]. The starting crystallographic data for each phase were extracted from the literature [10–13].

2.3. Effects of mechanochemical and thermal treatments

2.3.1. Series TiM0.5

The X-ray diffraction patterns of the TiM0.5 series of samples are shown in Fig. 1. Here, a decrease of the diffracted intensities is observed, 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 a shift of the peaks corresponding to the original structure of spinel.

In the early steps of the activation, Rietveld analysis suggests the presence of a poorly crystalline structure compatible with (FeO + TiO), which have the same structure and while the redox reaction take place, they can exist separated or in solid solution. Metallic iron becomes visible after 1 h of activation, as a little shoulder overlapped to the (4 0 0) peak, at approximately 44° 2θ, increasing 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 also 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). 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 due to the fact that the concentration of Ti, is 50% of that needed to form ulvospinel with all the Fe contained in the initial mixture.

The appearance of Fe^0 in the early stages of the activation, together with the Mössbauer spectroscopy observations [14] suggest that the redox reaction between Ti and Fe_3O_4 is comparatively fast in relation to the generation of the solid solution. At longer times, the Ti^{4+} would be progressively incorporated to the structure, probably by growth of the solid solution upon the remaining spinel crystals. This possibility could also explain the observation, and posterior disappearance, of the low-crystalline (FeO–TiO) phases.

The diminution of the magnetite signal at longer activation times, observed by X-ray diffraction as well as by Mössbauer spectroscopy, could be accounted for by its progressive deterioration, and by the "shielding" effect eventually produced by the solid solution growth on the surface of the remaining magnetite particles.

Millot et al. [15] studied the spinel structure of the titanomagnetites, and they found that when the ferrite contains some substitutional cations, the cation distribution is not as simple as it is in magnetite at room and near-room temperatures, where all the Fe^{2+} ions are on octahedral sites. In the case of titanium ferrite, the distribution of cations has been extensively studied. All the authors have found the Ti^{4+} cations residing in octahedral sites but the location of Fe^{2+} cations is still controversial even when results are derived from the same technique. Moreover, a change of the cation to anion ratio is possible in the spinel phase leading to a deviation (δ) from stoichiometry $(Fe_{3-x}Ti_x)_{1-\delta}O_4$.

Wechsler et al. [8] determined the relationship between a_0 and *U* (*U* = % Ti in the solid solution/% Ti in the ulvospinel × 100) over a wide composition range in the solid solution series, and reported that the variation of a_0 is not linear, but follows a sigmoidal curve, similar to those proposed by Lindsley [16] for samples synthesized at 800 °C by hydrothermal methods, and Banerjee et al. [17] for samples sinterized at 1100 °C in silica glass tubes under vacuum.

Their results strongly suggest that the trend is continuous between $x = 0$ and $x = 0.75$, with the curvature gradually decreasing towards $x = 0.75$, and showing a quasilinear behaviour up to $x = 1.0$. This discontinuity could indicate the presence of non-stoichiometric compounds when $x > 0.75$. Also, titanomagnetites undergo a paramagnetic–ferromagnetic transition at room temperature in the vicinity of $x = 0.75$; this could also contribute to the change of slope in this region of the curve.

As a result of the thermal treatments (Fig. 2), an increase in crystallinity and an additional increase of a_0 are observed (Table 1). It could be expected that during the heating, the structural defects would be healed, and the lattice dimensions made smaller; however, this increase suggests that more Ti is being added to the structure.

Also, the peak corresponding to Fe became narrower, and its integrated intensity (area under the peak) increased. However, this does not necessarily mean that the quantity of Fe^0 increases during the thermal treatment. It is possible that in the early stages of activation, the Fe^0 resulting from the redox reaction with Ti being in small clusters, not easily detectable by XRD; at longer activation times and/or after thermal treatment, these dominions would become ordered and their diffracted intensity increases. This would be in accordance with the Mössbauer results [14] which show that all the Fe^0 is produced in the first hour of activation.

In this series, Ti is in defect with respect to the stoichiometry of ulvospinel, but the solid solution, being more stable than a biphasic ulvospinel–magnetite system, is formed.

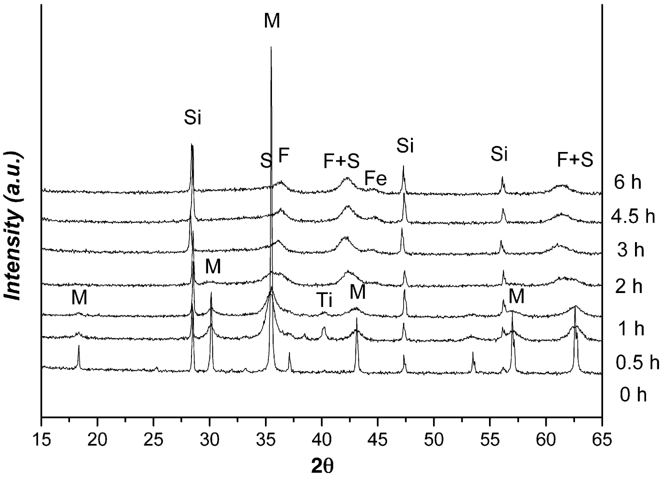

Fig. 1. XRD patterns of sample TiM0.5 for different activation times. F: FeO–TiO; Fe: iron; M: magnetite; S: solid solution; Si: silicon; Ti: titanium.

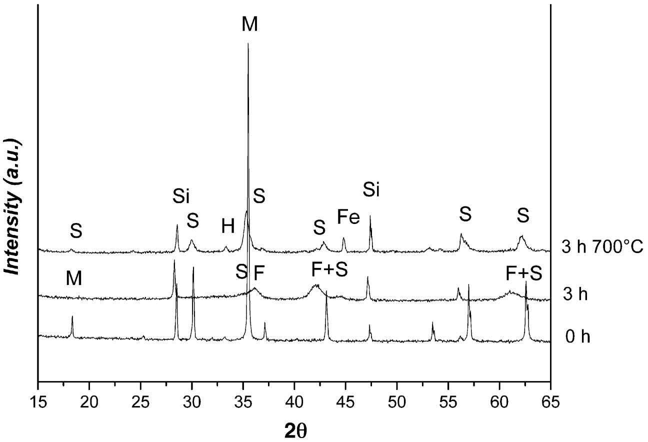

Fig. 2. XRD patterns of samples TiM0.5-0, TiM0.5-3 and TiM0.5-3-700. F: FeO–TiO; Fe: iron; H: hematite; M: magnetite; S: solid solution; Si: silicon; H: hematite.

Table 1
a_0, d, and U parameter for TiM0.5 series

Sample	a_0 (Å)	$d_{(3\,1\,1)}$ (Å)	(% Ti in the solid solution/% Ti in ulvospinel) × 100 (U parameter)
TiM0.5-0	8.394(1)	2.530(1)	0
TiM0.5-0.5	8.396(7)	2.531(2)	2.5
TiM0.5-1	8.399(7)	2.532(2)	5.4
TiM0.5-1.5	8.411(6)	2.536(2)	16.1
TiM0.5-2	8.431(5)	2.542(2)	31.4
TiM0.5-2.5	8.433(8)	2.543(2)	33.1
TiM0.5-3	8.443(9)	2.546(3)	39.0
TiM0.5-3-700	8.459(8)	2.551(2)	48.9
TiM0.5-4.5	8.452(8)	2.548(2)	44.7
TiM0.5-6	8.477(7)	2.556(2)	59.1
TiM0.5-6-700	8.460(8)	2.551(2)	49.3
Magnetite	8.396	2.531	
Ulvospinel	8.535	2.573	

Values in parenthesis represent estimated standard deviations in the last quoted place.

2.4. SEM–EPMA

The scanning electron micrographs (Fig. 3) 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.

Also, it has been observed the loss of the original morphology of the particles, 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 provoked by the activation.

The analysis by EPMA of the original mixture allowed to distinguish between the particles of Ti and Fe_3O_4. On the other hand, the analysis of individual particles of the activated samples gave as result that the composition of the particles after different times of activation is constant, with a homogeneous distribution of Fe and Ti in the whole sample.

2.4.1. Series TiM1

As in the case of the series TiM0.5, several low-crystalline intermediate phases (FeO–TiO, ilmenite) are compatible with a satisfactory adjustment by the Rietveld method between the first and third hour of activation, which generates a precursor with a composition included in a continuous series of solid solutions, from magnetite to ulvospinel, together with the metallic Fe generated by reduction (Fig. 4).

After the thermal treatment at 700 °C (Fig. 4), the only crystalline phases present in appreciable concentration are the ulvospinel–magnetite solid solution and the metallic iron. Also, some oxidation products are observed in very small quantity, mainly Fe_2O_3 (the stoichiometry of the initial mixture in this series corresponds to that of ulvospinel).

From the relationship of proposed by Wechsler et al. [8], the value of U was determined from the a_0 values obtained by XRD, and plotted as a function of activation time (Fig. 5) for TiM0.5 and TiM1. During the first hour of activation, no significant variation in a_0 value is was observed; this is attributed to the fact that at short times, the supplied mechanical energy is employed in plastic deformation and distortion of the crystal structure. At longer times, a_0 increases due to the incorporation of Ti in the spinel cubic lattice. This increase is faster for TiM1 than for TiM0.5, reaching the same values at shorter activation times.

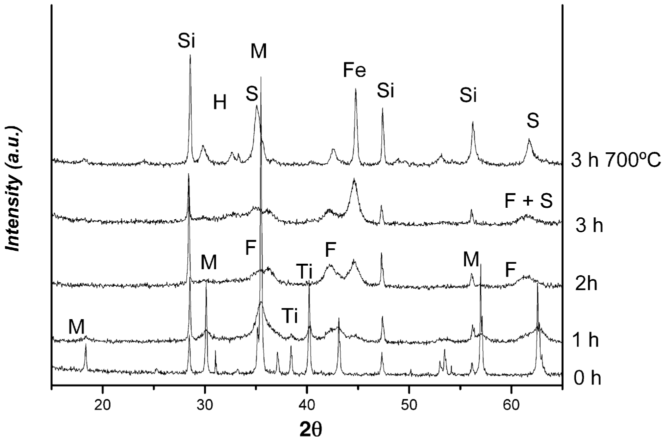

Fig. 4. XRD patterns of TiM1-0; TiM1-1; TiM1-2; TiM1-3 and TiM1-3-700. F: FeO–TiO; Fe: iron; H: hematite; M: magnetite; S: solid solution; Si: silicon; Ti: titanium.

For TiM1, as observed for TiM0.5, the displacement reaction progresses during the heat treatment at 700 °C, as revealed by a further increase in a_0, despite the reordering of the crystal structure brought about by the heating (Table 2).

The values of the U parameter for samples TiM1-3 and TiM1-6 show that the reaction is completed during the first 3 h of activation. Longer milling times only increase the deterioration of the crystalline structure; this is supported by the fact that after thermal treatment, these samples (TiM1-3-700 and TiM1-6-700) have similar values of U.

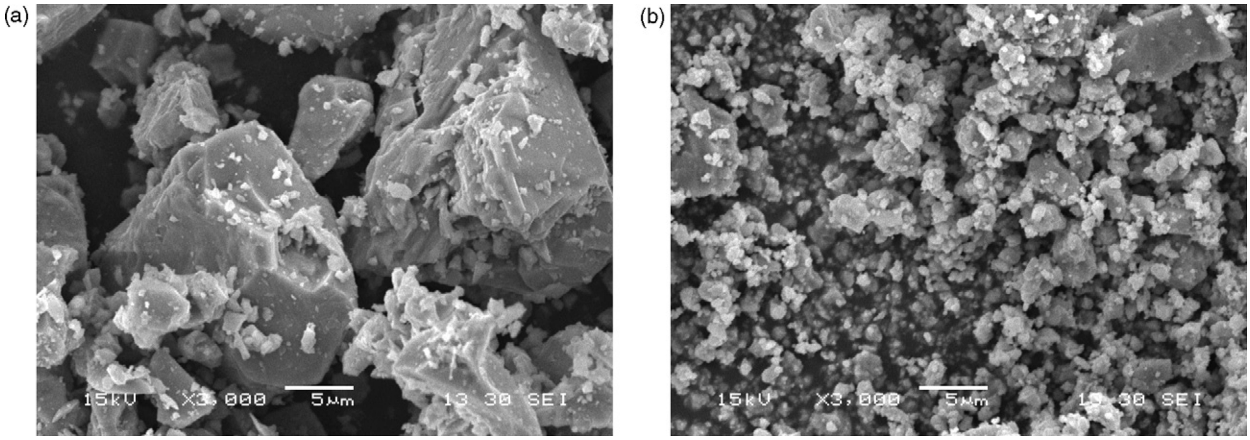

Fig. 3. SEM micrographs of the samples (a) TiM0.5-0; (b) TiM0.5-3.

Table 2
a_0, d, and U parameter for TiM1 series

Sample	a_0 (Å)	$d_{(3\,1\,1)}$ (Å)	(% Ti in the solid solution/% Ti in ulvospinel) × 100 (U parameter)
TiM1-0	8.398(5)	2.531(2)	0
TiM1-0.5	8.400(6)	2.532(2)	5.7
TiM1-1	8.400(5)	2.532(2)	5.7
TiM1-1.5	8.421(8)	2.539(2)	24.1
TiM1-2	8.452(9)	2.548(3)	44.7
TiM1-3	8.477(7)	2.556(2)	58.6
TiM1-3-700	8.508(7)	2.565(2)	76.7
TiM1-4.5	8.471(5)	2.554(2)	55.5
TiM1-6	8.477(4)	2.556(1)	58.6
TiM1-6-700	8.502(1)	2.563(1)	73.2
Magnetite	8.396	2.531	
Ulvospinel	8.535	2.573	

Values in parenthesis represent estimated standard deviations in the last quoted place.

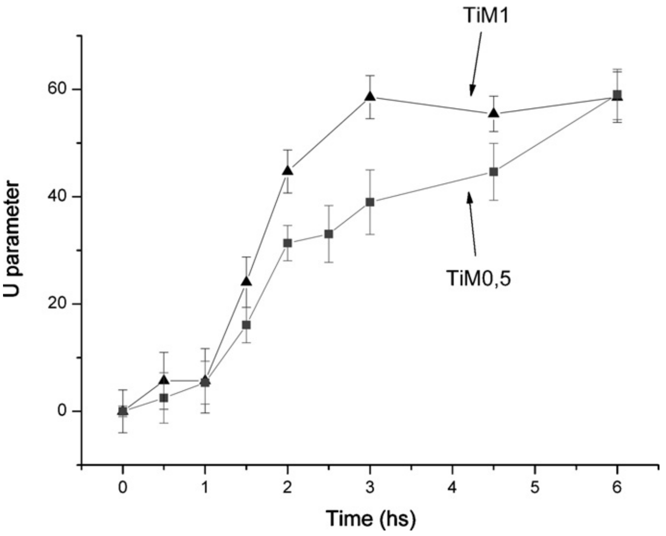

Fig. 5. U parameter vs. activation time for TiM0.5 and TiM1 (the lines are drawn only as a guide to the eye).

2.4.2. Series TiM1.5

During the activation of this series of samples, the intermediate phases observed by the Rietveld method were poorly crystalline FeO, ilmenite and pseudobrookite (Fe_2TiO_5), together with metallic iron. The thermal treatment resulted in an increase in crystallinity, with iron and ilmenite as the only crystalline phases present (Fig. 6).

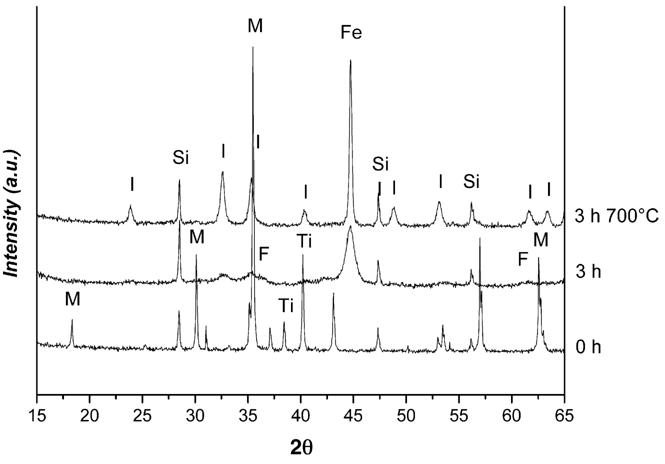

Fig. 6. XRD patterns of samples TiM1.5-3 and TiM1.5-3-700. F: FeO–TiO; Fe: iron; I: ilmenite; M: magnetite; Si: silicon; Ti: titanium.

The analysis of the main phases obtained from the different series of samples shows that as a result of the activation, TiM0.5 and TiM1 form a solid solution with spinel structure, while TiM1.5, with a higher Ti/Fe_3O_4 ratio, evolves to the formation of ilmenite.

In a study of the mechanochemical reaction $2Ti + Fe_3O_4 \rightarrow 3Fe + 2TiO_2$, Takacs [18] reported that the reaction proceeds in a self-propagating way. However, this was not the case under our experimental conditions. In the three series of samples, the amount of Ti is lower than that required for the complete reduction of the Fe; also, the main reaction product is the solid solution, instead of Fe and TiO_2. Also, the milling conditions were different: We used a milling media/powder mass ratio of 20 (7 milling balls), vs. 8.4 used by Takacs (3 milling balls). In our system, more heat has been used to heat up the milling balls, and also the vials, which in our case are heavier than those used by Takacs with the Spex mill. All these effects could result in increased heat dissipation. Furthermore, it might be possible that the higher number of balls make more difficult their movement inside the vial, lowering the “efficiency” of the impacts.

3. Conclusions

The obtained results show that during mechanochemical activation of Ti–Fe_3O_4 mixtures at room temperature under Ar atmosphere, the reduction of Fe by titanium takes place. During the reduction–oxidation process, Fe^{2+}, metallic Fe and Ti^{4+} are produced. Titanium replaces the octahedral Fe^{3+} ions in the original spinel structure forming $Ti_xFe_{3-x}O_4$ solid solutions when mixtures with Ti/Fe_3O_4 molar ratios 1:2 and 1:1 are activated. With Ti/Fe_3O_4 molar ratio 1.5, ilmenite appears as the main crystalline phase. Ti^{4+} is incorporated in octahedral sites while part of the Fe^{2+} is produced by reduction of the octahedral Fe^{3+}. In this way, the octahedral/tetrahedral occupation ratio remains constant.

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 μm.

The thermal treatment at 700 °C of the activated samples produces a partial recovery of the crystallinity of the phases present. This effect is more noticeable in the XRD peak intensity of metallic iron. An increase of the a_0 parameter is observed during thermal treatment, showing that the Ti incorporation in the structure still increases with the thermal treatment.

The fact that by changing the experimental conditions of the mechanochemical activation, it is possible to control not only the reaction rate, but also the nature of the reaction products, is a very remarkable one.

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