

Mechanically induced instability in Fe₂Ti and mechanical alloying of Fe and Ti

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Mechanical alloying (MA) of Fe and Ti elemental powder mixtures has been reported in studies mainly related to the preparation of nanocrystalline FeTi intermetallic compound [1–8]. In all these studies amorphous and/or nanocrystalline phases have been reported as end products of the milling process. The atomic composition 2Fe:1Ti has received less attention. For this composition the formation of amorphous phase on milling has been reported [2]. The amorphous phase was characterized by a broad X-ray diffraction peak and its crystallization was observed on heating above 800 K [2].

A more recent paper on mechanical milling (MM) of Fe₂Ti reports the occurrence of certain structural disorder in the C14 hexagonal structure of this Laves phase but without the formation of an amorphous material [9]. The structural disorder is related to the occurrence, under milling, of planar defects such as stacking faults. According to X-ray diffraction (XRD) annealing at 873 K of this disordered phase restores the crystal structure of Fe₂Ti. However, from the Mössbauer spectrum of the annealed of MM Fe₂Ti sample about 5% of bcc iron is reported [9], which could be interpreted as an incipient decomposition process of Fe₂Ti due to the milling process. In that case, on prolonged milling a higher amount of bcc iron would be formed. In this contribution we report the resulting intermediate and end products of 2Fe:1Ti elemental mixtures and Fe₂Ti powder samples when they were submitted to prolonged milling. In both cases in the end products a solid solution of Ti in α -Fe, α -Fe(Ti) (bcc), was detected.

The intermetallic compound Fe₂Ti was prepared by melting the appropriate mixture of elemental Fe (99.9% nominal purity) and Ti (99.9%) coarse powders in an electric arc-furnace under an argon atmosphere. After melting, the alloy was sealed in a quartz tube filled with argon and then annealed for 48 h at a temperature of 1173 K to aid homogeneity and crystallinity. Its elemental and phase composition was determined using energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD), respectively.

Prior to milling, the Fe₂Ti ingot was cut into small pieces using a diamond saw. The powder resulting from the cutting process was collected and used as representative of the starting Fe₂Ti sample (without milling).

For the MA of 2Fe:1Ti elemental mixtures, iron and titanium powders of 3 and 250 μ m of particle size, respectively and with a nominal purity of 99.9 wt% were used. The milling process of both, the intermetallic Fe₂Ti and the mixtures of 2:1Ti mixed powders was carried out using a high energy ball mill (Spex 8000D) with balls and vials made of hardened steel. The powders were loaded and sealed into the vials inside a glove box filled with argon (99.99% of purity). Removal of milled samples at different milling times was also performed under argon atmosphere. The weight ratio of balls to powders varied from 10:1 to 5:1 in our experiments.

The ball-milled powders were characterized by X-ray diffraction (XRD) and Mössbauer techniques. XRD powder patterns were recorded using a Siemens D-500 diffractometer with monochromated Cu K α radiation. Mössbauer spectra were obtained at room temperature using a ⁵⁷Co in Rh source and a constant acceleration spectrometer (from Wissel) operated in the transmission mode. All Mössbauer spectra were fitted with distributions of hyperfine magnetic field (B_H) and quadrupole splitting (Δ) [10]. In the fitting of Mössbauer spectra with a distribution of B_H , a linear correlation between the isomer (δ) and quadrupole splitting (Δ), $\delta = a + b\Delta$, was assumed. This means that the obtained value of δ can be used to follow the trend in the electronic interactions of the involved metals (Ti and Fe) but not as an exact measure of these interactions. Some spectra were also fitted with an iterative least-squares minimization algorithm using pseudo-Lorentzian line shapes. Isomer shift values are reported relative to metallic iron (α -Fe).

According to its composition and crystal structure Fe₂Ti belongs to the Laves phase C14 (hexagonal MgZn₂ type cell). In this structure there are eight iron atoms per unit cell located in two different structural sites, 2(a) and 6(f). This compound has an antiferromagnetic behavior with a layered spin structure where the magnetic moments on Fe(6f) are antiparallel along the c axis while Fe(2a) remains non-magnetic [11]. The Mössbauer spectra of Fe₂Ti at room temperature can be interpreted as a single quadrupole doublet with $\delta = -0.34$ mm/s (relative to α -Fe) and $\Delta = 0.49$ mm/s

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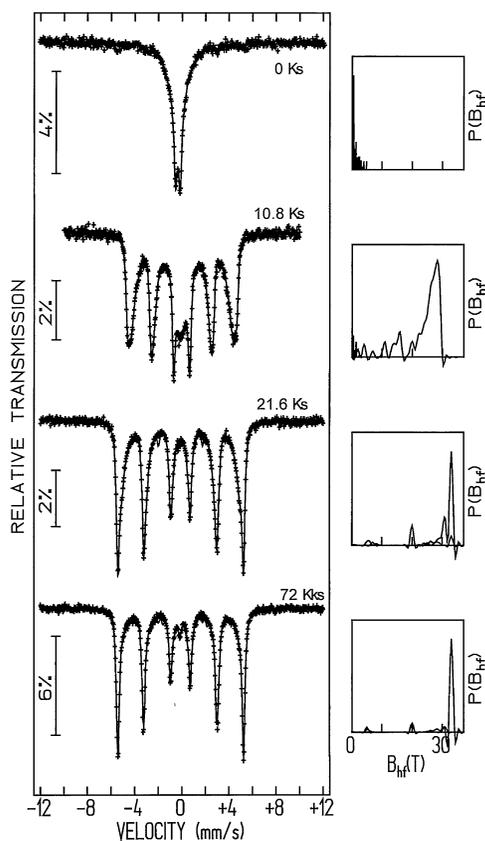


Figure 1 Mössbauer spectra and the corresponding hyperfine magnetic field distributions of Fe_2Ti before and after different milling times which are indicated.

[12, 13], which suggests that the two iron sites are practically equivalent.

Mössbauer spectra of Fe_2Ti after different milling times are shown in Fig. 1. The Mössbauer spectrum of the as-melted and then annealed Fe_2Ti sample consists of a quadrupole doublet with a minor magnetically ordered contribution (a decomposition product of Fe_2Ti , as discussed below). According to its parameters (Table I), that doublet corresponds to the Laves phase Fe_2Ti [13]. The milling of this phase leads to its decomposition. The Mössbauer spectra of the intermediate and end products correspond to a magnetically ordered phase (a six absorption lines pattern, a sextet) plus a minor non-magnetic phase (Fig. 1b–d). The appearance of that six lines pattern means that the local order, and probably also the local composition, around the iron atoms have changed on milling relative to those

observed in Fe_2Ti . The change in the local composition is suggested by the variation of isomer shift, from -0.27 mm/s in Fe_2Ti to ~ -0.1 mm/s in the emerging magnetic phase.

Self-consistent band calculations for conduction electrons in FeTi alloys have shown that 0.18 electrons are transferred from Ti to Fe, and that 2/3 of these are d-like [14]. This means a higher s-electron density at the iron nucleus which is detected as a smaller isomer shift (δ) value, which explains the relatively low value of δ in Fe_2Ti (-0.27 mm/s relative to $\alpha\text{-Fe}$). From this fact the observed change in the value of δ on milling was interpreted as a depopulation in Ti for the emerging magnetic phase relative to Fe_2Ti . For 3 h (10.8 Ks) of MM the quadrupole doublet only represents 13% (of relative area) of the Fe-bearing phases (Table I). The six lines pattern (sextet) corresponding to the magnetically ordered phase shows a pronounced lineshape asymmetry, particularly in the outer lines, which is usually observed in disordered or amorphous magnetic materials [15]. In these materials the iron nuclei are sensing different hyperfine magnetic fields due to differences in the local composition of their first neighbors. In a crystalline magnetic material, like bcc iron, all the iron nuclei are in equivalent environments and, in consequence, they are sensing a well-defined hyperfine magnetic field (B_H), in this case of 33.3 T [16].

The calculated B_H distribution, $P(B_H)$, for this milling time (3 h, 10.8 Ks), shows a marked shoulder at the low B_H side ($\sigma = 4$ T), from an average B_H value of 26 T (Fig. 1b), which is interpreted as existence of a wide range of local compositions around the iron atoms in that phase, particularly, iron atoms with different population of Ti atoms in their shell of first neighbors. The maximum B_H value of 29 T must correspond to local environments rich in iron atoms. For a milling time of 6 h (20.8 Ks) or higher, the observed shape asymmetry decreases and the corresponding B_H distribution sharpens ($\sigma = 1$ T). This corresponds to a more homogeneous phase at atomic level where practically no difference is observed between the local composition at a given site and the average one in the bulk sample. The observed increase in B_H , practically up to that observed in $\alpha\text{-Fe}$ (33.3 T) (Table I), suggests the existence of a relatively low Ti population in the shell of first neighbors of the iron atoms. These results indicate that the MM of Fe_2Ti leads to formation of a solid solution of Ti in $\alpha\text{-Fe}$, $\alpha\text{-Fe}(\text{Ti})$, which is also inferred

TABLE I Calculated Mössbauer parameters at room temperature of Fe_2Ti and of intermediate and products of its mechanical milling. All the spectra were fitted using a distribution of hyperfine magnetic field (B_H) plus a distribution of quadrupole splitting (Δ)

Milling time Hours (Ks)	Distribution of hyperfine magnetic field (B_H)					Distribution of quadrupole splitting (Δ)			
	δ^a (mm/s)	Δ (mm/s)	$\langle B_H \rangle^b$ (T)	σ_B (T)	A (%)	δ^a (mm/s)	$\langle \Delta \rangle^b$ (mm/s)	σ_Δ (mm/s)	A (%)
0 (0)	–	–	–	–	–	-0.27	0.49	0.09	100
3 (10.8)	-0.08	0.01	25	4	87	-0.15	0.35	0.10	13
6 (21.6)	-0.10	0.01	30	1	99	-0.18	–	–	1
20 (72)	-0.09	0.01	31	0.5	97	-0.15	–	–	3

^aError in δ and Δ are no higher than 0.01 mm/s. δ values are reported relative to $\alpha\text{-Fe}$.

^b $\langle B_H \rangle$ and $\langle \Delta \rangle$ are the average values of the corresponding distributions and σ_B and σ_Δ their standard deviations, respectively.

from XRD results (discussed below). The decomposition process is already appreciable in the powder sample obtained from the cutting process of the starting Fe₂Ti ingot. The Mössbauer spectrum of that sample shows a weak contribution of a magnetically ordered phase (Fig. 1a).

In equilibrium conditions, the solubility of Ti in bcc Fe is only about 4 at.% [17]. By vapor quenching method this solubility limit can be extended up to near 15 at.% of Ti, with a systematic decreasing in its hyperfine magnetic field, B_H [18]. The average value of B_H , 25 T, at 3 h of milling suggests that about a 10 at.% Ti remains dissolved in the α -Fe host structure, which corresponds to a supersaturated solid solution.

In the Mössbauer spectra of prolonged MM of Fe₂Ti samples also a weak single line appears which is interpreted as formation of a small fraction of the intermetallic FeTi. The Mössbauer spectrum reported for this phase is a single absorption line with an isomer shift value of -0.25 mm/s [19], similar to that found for one of the end products of MM Fe₂Ti (Table I). A minor fraction of this phase could be present in the sample of 3 h since the signal attributed to Fe₂Ti remains unresolved and its δ and $\langle\Delta\rangle$ values are slightly smaller than those found for the starting Fe₂Ti sample.

XRD powder pattern of the initial Fe₂Ti sample entirely corresponds to the reported PDF file 15-0336 for this Laves phase [20] (Fig. 2a). The MM of this phase leads to its decomposition and formation of a material with a cubic (bcc) structure but with relatively large peak width and cell edge (Fig. 2b–d). These two features are consistent with the formation of a solid

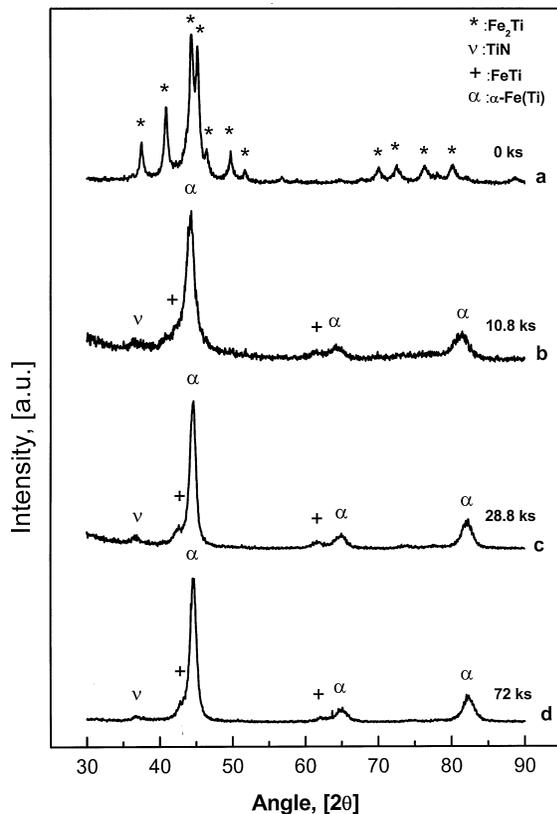


Figure 2 XRD powder patterns of Fe₂Ti after different milling times: (a) Fe₂Ti (no milled sample), (b) milled 10.8 Ks, (c) milled 28.8 Ks, and (d) milled 72 Ks. Indicated are the observed phases.

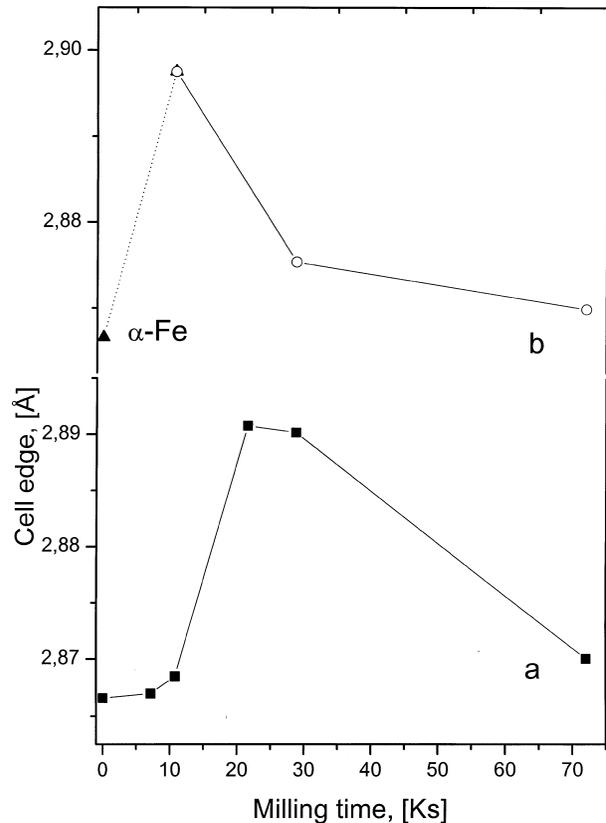


Figure 3 Variation in the cell parameter “a” for the solid solution α -Fe(Ti) obtained from: (a) mechanical milling of Fe₂Ti and (b) mechanical alloying of an elemental mixture of Fe and Ti in an atomic ratio of 2Fe:1Ti.

solution of Ti in α -Fe. A large peak width could result from different factors, for instance: a small crystallite size, local distortions in the crystal cell, or structural disorder caused from inhomogeneous local compositions. In our case the first factor was discarded since for the largest milling time a peak sharpening was observed. These facts suggest the formation of a supersaturated solid solution which on milling segregates the excess of solute atoms (Ti) to a more stable phase. The metallic radius of Ti is about 120% that of Fe [21]. A supersaturated α -Fe(Ti) solid solution with 33 at.% of Ti would have a cell parameter above 0.300 nm. However, such α -Fe(Ti) solid solution would be very unstable and very unlikely to form. The maximum “a” value that we have observed for milled Fe₂Ti samples is 0.2897 nm, for 3 h (10.8 Ks) of milling (Fig. 3). With subsequent milling this supersaturated solid solution evolves to a more ordered system segregating Ti atoms to form other minor phases, and reducing its lattice parameter. If the MM process is further prolonged a fraction of the segregated Ti atoms could be newly dissolved in the α -Fe(Ti) matrix forming a more uniform solid solution which could be stable in the milling conditions. The dependence of the lattice parameter “a” of α -Fe(Ti) on the milling time shows an excellent agreement with that evident behavior of the formed solid solution (Fig. 3a). The final value of “a” does not correspond to pure α -Fe, which indicates that certain amount of Ti atoms remains dissolved in the bcc structure of α -Fe. As minor phases TiN and FeTi are observed, however, a significant fraction of Ti must remain as an amorphous phase to account for the 33.3 at.% in the initial material.

The Laves phases to which the intermetallic compound Fe_2Ti belongs correspond to a narrow range of composition, nominally AB_2 . The existence of these “stoichiometric” phases is closely related to the size and ordering of A and B atoms to obtain a maximum space filling. Ideally this is possible when the ratio of the atomic radii is $R_A/R_B = \sqrt{3/2} = 1.225$ [22]. In the C14 structure (hexagonal MgZn_2 type cell) of Fe_2Ti eight Fe atoms are located in 2(a) and 6(h) sites while four atoms of Ti are found in 4(f) sites. The atomic array is such that the first neighbors of a titanium atom are four Ti and twelve Fe. Thus giving a total number of 16 first neighbors. Likewise, the first coordination shell around both iron sites is composed of six iron atoms and six Ti atoms. This results in a packing of the atomic planes represented by the general sequence ABABAB. . . . The plastic deformation of this structure due to the repeated compression of the Fe_2Ti particles between the colliding balls or between these last ones and the mill walls, leads to the appearance of a large number of structural defects and related stacking faults. While the short range order of the milled sample remains within the stability limit of the corresponding Laves phase, its initial structure can be restored through an appropriate annealing. For partially disordered Fe_2Ti by MM the recovery of the original hexagonal structure, through an annealing at 873 K, has been reported [9]. Our results suggest that drastic plastic deformation leads to an irreversible process and finally to the formation of a bcc solid solution of Ti and Fe. This phase transformation on milling, from a hexagonal closed packed (hcp) structure to form a body center cubic (bcc) ordered solid solution (hcp \rightarrow bcc) behaves as the inverse of that reported for lanthanides (bcc \rightarrow hcp) for which the corresponding displacive transformation mechanisms (shift of the involved atomic layers) has been already reported [23]. In principle, these mechanisms must also be valid in the inverse transformation, hcp \rightarrow bcc, induced by the drastic plastic deformation in the Fe_2Ti phase when it is submitted to a prolonged milling.

The milling of a mixtures of elemental powders in order to obtain the Fe_2Ti intermetallic compound is the inverse route of that discussed above. However, for prolonged milling, and under the same conditions, the same end products must be obtained. The high energy ball milling is a very drastic process which practically destroy the material memory concerning its initial state.

Mössbauer spectra of the 2Fe:1Ti milled mixtures show the six absorption lines pattern typical of a magnetically ordered phase plus a central signal corresponding to a non-magnetic phase (Fig. 4). The central signal can be interpreted as an unresolved doublet or a single absorption line and was tentatively assigned to formation of the intermetallic FeTi during the MA process. The amount of this phase increases up to 6 h (21.6 Ks) of milling and then decreases and practically disappear for 20 h (72 Ks) of treatment. The six absorption lines pattern initially corresponds to metallic iron (α -Fe) with a hyperfine magnetic field of 33.3 T, and then on milling Ti is progressively dissolved in α -Fe forming a solid solution, α -Fe(Ti). The dissolution of Ti in

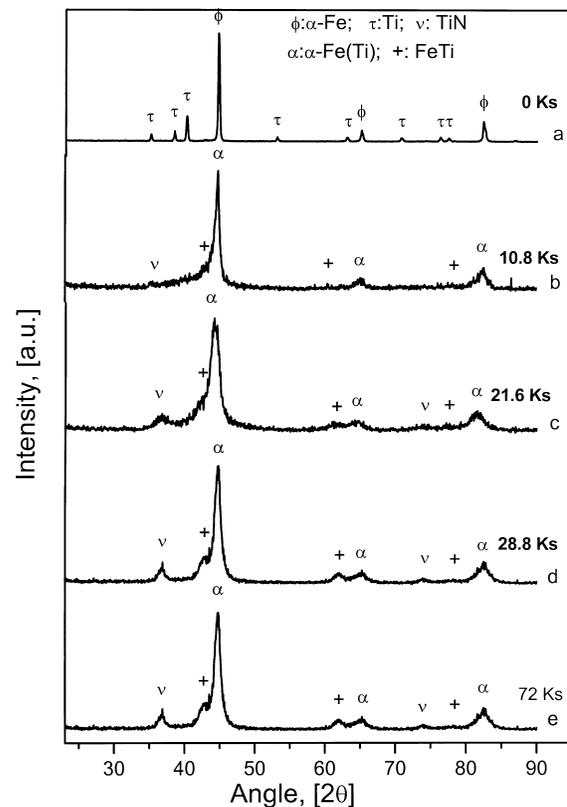


Figure 4 Mössbauer spectra and the corresponding hyperfine magnetic field distributions of an elemental mixture of Fe and Ti in an atomic ratio of 2Fe:1Ti after different milling times which are indicated.

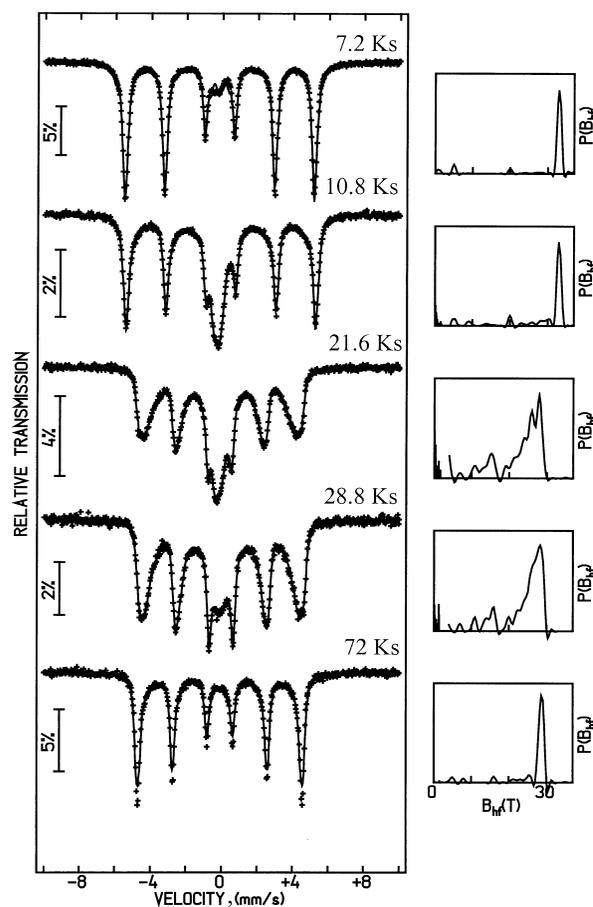


Figure 5 XRD powder patterns of an elemental mixture of Fe and Ti in an atomic ratio of 2Fe:1Ti before and after different milling times which are indicated.

TABLE II Calculated Mössbauer parameters at room temperature of the milled mixture of elemental powders. All the spectra were fitted using a distribution of hyperfine magnetic field (B_H) plus a distribution of quadrupole splitting (Δ)

Milling time Hours (Ks)	Distribution of hyperfine magnetic field (B_H)					Distribution of quadrupole splitting (Δ)			
	δ^a (mm/s)	Δ (mm/s)	$\langle B_H \rangle^b$ (T)	σ_B (T)	A (%)	δ^a (mm/s)	$\langle \Delta \rangle^b$ (mm/s)	σ_Δ (mm/s)	A (%)
0 (0)	0.00	0.00	33.3	0.2	100	–	–	–	–
2 (7.2)	0.00	0.00	33	0.5	96	–0.19	0.36	0.05	4
3 (10.8)	0.00	0.00	32	0.5	86	–0.19	0.36	0.05	14
6 (21.6)	–0.10	0.02	26	3.5	84	–0.18	0.37	12.7	16
8 (28.8)	–0.10	0.02	28	3.0	91	–0.18	0.34	12.7	9
20 (72)	–0.07	0.02	31	0.5	98	–0.18	0.08	–	2

^aError in δ and Δ are no higher than 0.01 mm/s. Isomer shift values are reported relative to α -Fe.

^b $\langle B_H \rangle$ and $\langle \Delta \rangle$ are the average values of the corresponding distributions and σ_B and σ_Δ their standard deviations, respectively.

α -Fe leads to a reduction in the average magnetic hyperfine field sensed by the iron nuclei, and also to a shape asymmetry in the absorption lines. The shape asymmetry results from a continuous distribution of magnetic hyperfine field due to the existence of a wide range of local composition around the iron atoms. Within the solid solution, those particles or local zones with the highest amount of dissolved Ti correspond the minimum values of B_H . For 6 h (21.6 Ks) of milling, the dilution of Ti in α -Fe reaches its maximum with 26 T as average value of B_H (Fig. 4d). From this milling time, if the MA process is continued, the formed supersaturated solid solution progressively decomposes ejecting Ti atoms previously dissolved. For 20 h (72 Ks) of milling, the solid solution contains a relatively small amount of Ti, probably close to 4 at.%, the solubility limit of Ti in α -Fe in equilibrium conditions [17]. The variation in the isomer shift value for the magnetically ordered phase also suggests the above discussed progress of the formed solid solution. δ decreases with the amount of Ti atoms diluted in α -Fe and then practically returns to its initial value (~ 0 mm/s in α -Fe, the reference) when the formed supersaturated solid solution decomposes (Table II).

The XRD powder patterns of the milled elemental mixtures are shown in Fig. 4. On milling the Ti peaks disappear suggesting that Ti is rapidly disordered or it becomes into an amorphous phase, a behavior which has been already reported [9]. For 3 h (10.8 Ks) of milling, the main diffraction peaks correspond to α -Fe(Ti) accompanied of a minor peaks associated with FeTi and TiN (PDF files 83-1635 and 74-1214, respectively) [20]. On the formation of the supersaturated solid solution α -Fe(Ti), an increase in the peak width is observed up to 6 h (21.6 Ks) of milling and then, when this phase progressively decomposes, a peak refinement takes place. This means that the peak broadening is directly related to a large local disorder generated by an excess of Ti dissolved in the bcc cell of iron. The cell size also follows this trend (Fig. 3), which reaches its maximum value for 6 h of milling, when, according to the Mössbauer spectra, the amount of dissolved Ti in the α -Fe structure is a maximum. The cell size variation is a direct evidence of the progress of the formed solid solution with the milling time.

In both processes, MM of Fe₂Ti and MA of a 2Fe:1Ti elemental mixture, the formation of TiN was detected. It seems the milling process favors a high reactivity of

Ti which reacts with the atmospheric nitrogen during the sample handling, probably during the XRD data acquisition.

In summary, the intermetallic Fe₂Ti phase is unstable upon mechanical milling producing a mixture of supersaturated α -Fe(Ti) solid solution and FeTi intermetallic phase. This solid solution decomposes for prolonged milling ejecting a large fraction of the Ti atoms that were previously dissolved in the α -Fe structure. The mechanical alloying of 2Fe:1Ti leads to the same intermediate and end products. These results suggest that Fe₂Ti cannot be obtained through a mechanical alloying process. The instability of the compound could be related to the accumulation of a many stacking faults on prolonged milling which favors a hcp \rightarrow bcc structural transition.

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