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Structural and Mössbauer spectroscopy characterization of bulk and nanostructured $TiFe_{0.5}$ $Ni_{0.5}$/graphite compounds and their hydrides

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Abstract The structural and hyperfine properties of bulk $TiFe_{0.5}Ni_{0.5}$ intermetallic and ball-milled $TiFe_{0.5}Ni_{0.5}$/graphite compounds and their hydrides have been studied. The bulk and nanostructured $TiFe_{0.5}Ni_{0.5}$ compounds crystallize in the cubic crystal structure of CsCl (B2). After hydrogenation, the formation of hydrogen-poor phase ($\propto$-phase) and hydride phase (β-phase) have been determined for the bulk compound. However, the formation of the $\propto$-phase and the hydrogen-richest phase (γ-phase) and other secondary phases have been determined for the ball-milled $TiFe_{0.5}Ni_{0.5}$/graphite sample. It has been determined that the ball-milled $TiFe_{0.5}Ni_{0.5}$/graphite sample presents a large amount of the γ-phase which indicates that the presence of graphite nearby nanostructured intermetallic grains enhances the absorption of hydrogen. Mossbauer results are consistent with the structural results. Meanwhile, no significant changes in the isomer shift (IS) value has been determined for the α-phase with respect to the intermetallic compound, a strong increase in the IS value has been determined for the β- and γ-phases with respect to the $\propto$-phase. That increase indicates a decrease of the s-electron density at the Fe nuclei due to the charge transfer from the metal to the nearby hydrogen atoms.

Keywords Intermetallic · Ball-milled nanostructured compound · Hydrides · Graphite nanocomposites

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1 Introduction

Nowadays, one of the biggest global problems is the anomalous global warming caused by the human-made greenhouse gases coming from fossil fuel burning. It demands to research for clean energy sources in order to avoid that environmental problem. The hydrogen used as a fuel is one of the alternatives, since after the energy release we will have just heat and water as the residual products. However, the problem of how to store the hydrogen in favourable thermodynamic conditions and low cost still remains. Despite the intense research on solid-state hydrogen storage materials, the hydrogen absorption capacity of intermetallic compounds is not high enough yet.

One of the intermetallics that provides a high storage capacity is the TiFe alloy (∼1.9 wt%) [1]. The substitution of Fe by Ni can improve the activation of grain surface, reduce the equilibrium pressure of the hydride, and provide a strong catalytic action for the hydrogenation reaction [2–5]. One promising way to improve that absorption capacity is by using nanostructured materials. Reports in the literature indicate the formation of the hydride phase (β-phase) in ball-milled intermetallic compounds [16] and the hydrogen-rich phase (γ-phase) is only obtained by applying high hydrogen pressures (∼40 atm). Moreover, that improvement can lead to drastic modifications on the structural, morphological and magnetic properties of the intermetallic matrix. It is also known that the presence of carbon-based clusters can improve the hydrogen absorption capacity of Ti-Fe-Ni nanostructured compounds [6, 17], but the role of the carbon-based component on the activation characteristics is not well known yet.

In order to assess the effect of carbon-based clusters on the hydrogen absorption properties of Ti-Fe-Ni nanostructured compound in this work we present a comparative study of the structural and hyperfine properties of the bulk intermetallic compound and carbon-modified $TiFe_{1-x}Ni_x$ ($x = 0.5$) nanostructures and their hydrides.

2 Experimental

$TiFe_{0.5}Ni_{0.5}$ bulk alloys were prepared by using a commercial arc-voltaic furnace and stoichiometric amount of high purity elements Fe (99.99 %), Ti (99.99 %) and Ni (99.95 %) melted under argon atmosphere. The arc-melted button was remelted several times for composition homogenization. After that, samples were sealed in evacuated quartz capsule and subjected to heat treatment at 900 °C for 20 hours. The milling process has been carried out using a high energy ball milling (SPEX 8000) under argon atmosphere for 5 hours. Hardened steel vial and balls have been used in a ball-to-powder weight ratio of ∼4:1. After that, a 10 wt% of graphite powder was added to the milled sample and an additional milling for 10 minutes was carried out. Hereafter, this sample will be named as a graphite-milled sample. The hydrogenation process was carried out by the Sievert's method using a high purity hydrogen gas (99.9999 %). Previous to hydrogenation, the samples have been subjected to a thermal annealing at 800 °C for 30 min, in a vacuum. The structural properties of the obtained powders have been studied by using a commercial diffractometer (Rigaku, MiniFlex 600) with Cu-Kα radiation. The diffractograms were recorded in the 2θ range from 25° to 90° and a step size of 0.05° . Mössbauer spectroscopy (MS) measurements were performed at room temperature using the transmission mode in a constant acceleration spectrometer with a triangular waveform and using a ^{57}Co/Rh source. Isomer shifts are quoted relative to the value of α-Fe thin film.

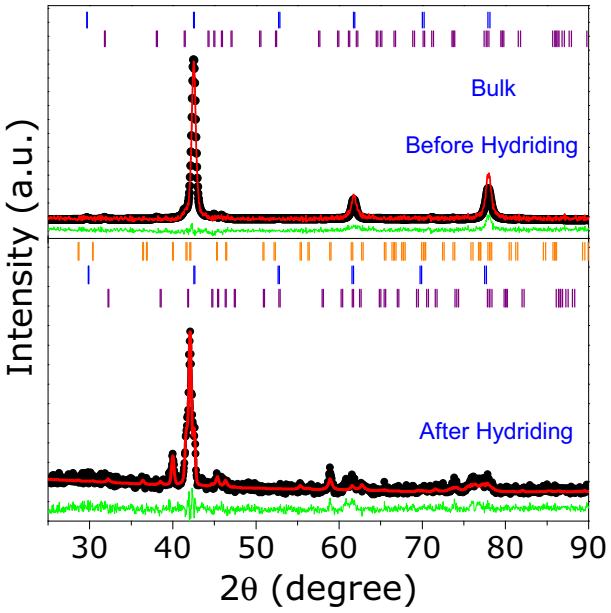


Fig. 1 Room temperature XDR patterns of $TiFe_{0.5}Ni_{0.5}$ bulk intermetallic alloy and its hydride. The observed and calculated data are represented by the points and solid line, respectively. The Bragg's reflections are represented by the vertical tick marks in the upper part of the graphs. Before hydriding: $TiFe_{0.5}Ni_{0.5}$ and $TiNi_2$ and after hydriding: $TiFe_{0.5}Ni_{0.5}H_{1.03}$ (β-phase), $TiFe_{0.5}Ni_{0.5}H_{0.2}$ (α-phase) and $TiNi_2$ phase, respectively

3 Results and discussion

The XRD patterns of the bulk sample before and after hydrogenation are shown in Fig. 1. Similarly, in Fig. 2 are shown the XRD patterns of the nanostructured sample before and after hydrogenation. Before the hydrogen absorption, the observed Bragg reflections of bulk and nanostructured samples are consistent with the cubic $TiFe_{0.5}Ni_{0.5}$ phase (space group Pm3m) [3]. The strong peaks broadening observed in the XRD diffraction pattern of the graphite-milled sample suggests a reduction in the coherent diffraction domains (crystallites). Further analysis of the XRD pattern of the bulk sample carried out with the Rietveld refinement method indicates the presence of extra reflection peaks which correspond to the $TiNi_2$ phase [7]. Similar analysis carried out for the graphite-milled sample indicates the presence of $\sim$17 % of a metallic iron phase. The presence of metallic iron has been assigned to the release of iron from the vial set during the milling process.

After the hydrogen absorption, the bulk sample shows the coexistence of two main phases: the $TiFe_{0.5}Ni_{0.5}H_{1.03}$ (β-phase), which absorbs a larger amount of hydrogen, and forms in an orthorhombic structure with space group $P222_1$ and the $TiFe_{0.5}Ni_{0.5}H_{0.2}$ (α-phase), which absorbs a small amount of hydrogen, and remains in the cubic structure. The percentage of phases is $\sim$73 % for the β-phase, $\sim$12 % for the $\propto$-phase and $\sim$15 % for the $TiNi_2$ phase. However, for the graphite-milled sample, besides the $\propto$-phase ($TiFe_{0.5}Ni_{0.5}H_{0.34}$), the formation of the hydrogen richest phase $TiFe_{0.5}Ni_{0.5}H_{2.0}$ (γ-phase) has been determined, which forms in an orthorhombic structure (space group *Cmmm*). It is worth noting that after the hydrogenation, the unit cell expansion for the $\propto$-phase is esti-

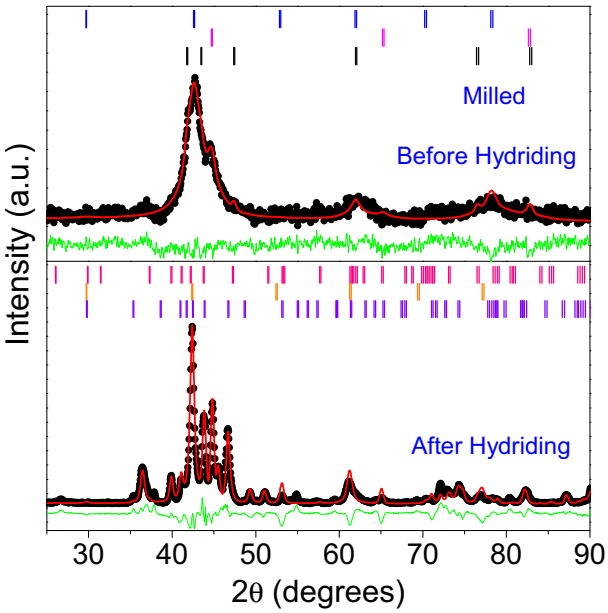


Fig. 2 Room temperature XDR patterns of the graphite-milled $TiFe_{0.5}Ni_{0.5}$ compound and its hydride. The observed and calculated data are represented by the points and solid line, respectively. The Bragg's reflections are represented by the tick marks in the upper part of each graph. Before hydriding, the identified phases were: $TiFe_{0.5}Ni_{0.5}$, metallic iron and graphite phases and after hydriding: $TiFe_{0.5}Ni_{0.5}H_{2.0}$ (γ-phase), $TiFe_{0.5}Ni_{0.5}H_{0.34}$ (α-phase) and Ni_3Ti phases

mated to be 2.8 and 5.4 % in the bulk and graphite-milled samples, respectively. Moreover, for the graphite-milled sample, the percentage of phases is ∼22 % and ∼10 % for the ∝-and γ-phase, respectively. Reports in the literature indicate the formation of only the β-phase in ball-milled Ti-Fe-Ni compounds [16]. Therefore, our results indicate that the presence of graphite in the graphite-milled sample favors to the formation of the richest hydrogen containing phase (γ-phase) instead of the formation of the β-phase as determined for the hydride sample obtained for the bulk intermetallic powder in this work. Moreover, the presence of graphite also leads to the formation of other extra phases such as TiC (18 %), Ni_3Ti (29 %) and others in tiny amounts. It has been reported that the nanostructured graphite could store a large amount of hydrogen forming a stable hydride due to its chemisorption properties [8, 9]. In our sample, the graphite seems to play the role of a catalytic agent that helps with the hydrogen dissociation and improves the hydrogen uptake kinetics for the intermetallic.

In Fig. 3 are shown the room-temperature Mössbauer spectra of the bulk intermetallic and its hydride. The Mössbauer spectrum of the bulk intermetallic has been modeled with one singlet. This is in accordance with reports in the literature [10, 11], wherein the Mossbauer spectrum of the TiFe alloy is well-modeled with one single peak. Since the crystal symmetry does not change when Fe atoms are substituted by Ni atoms, it is expected that the spectrum of the bulk sample were well-modeled with only one singlet (as observed in Fig. 3). Therefore, the isomer shift value (IS = −0.18 mm/s) obtained for the bulk intermetallic $TiFe_{e0.5}Ni_{0.}5$ alloy is the same range of that one reported for TiFe alloy (IS = −0.15 mm/s),

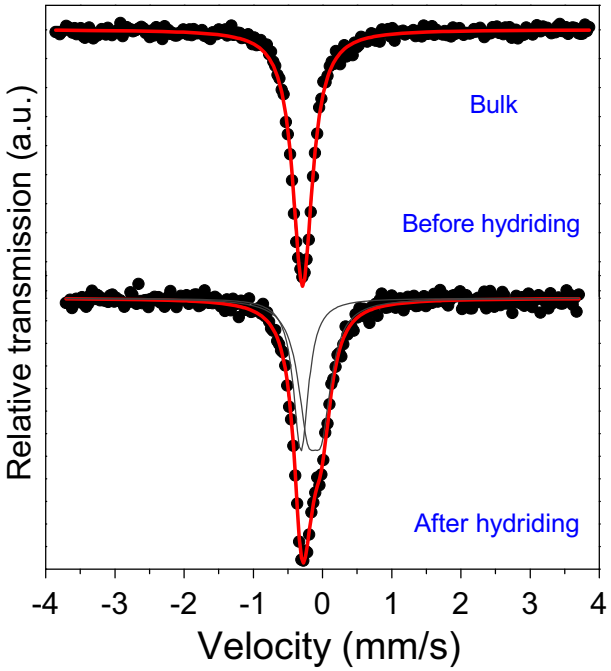


Fig. 3 Room temperature Mossbauer spectra of the bulk $TiFe_{0.5}Ni_{0.5}$ intermetallic and its hydride. The solid line represents the best fit and dotted lines represent the subspectra used in the fit

Table 1 Mössbauer parameters determined from the fit of Mössbauer spectra of the bulk sample and its hydride

Sample	Phase	IS (mm/s)	QS (mm/s)	Γ (mm/s)	A(%)
$TiFe_{0.5}Ni_{0.5}$	α	-0.18	–	0.34	100
$TiFe_{0.5}Ni_{0.5}H_x$	α	-0.2	–	0.26	36
	β	-0.05	0.21	0.34	64

The maximal experimental errorsof hyperfine parameters (IS and QS) and linewidh (Γ) are estimated to be ±0.03 mm/s and ±2 % for the spectral area (A)

within the uncertainty range. However, the Mössbauer spectrum of the hydrogenated sample was well-fitted with two components: one singlet and one doublet, as can be observed in Fig. 3. These components were associated with the α and β-phases, respectively. In Table 1 are listed the hyperfine parameters of the bulk sample and its hydride.

It seems that the increase of H atoms in the lattice structure causes a saturation effect and drives to the instability of the cubic structure of the hydrogen-poor phase $\propto$-phase). That instability leads to a phase transition from a cubic to orthorhombic phase, which correspond to the β-phase. It is known that the main axes (a, b, c) of the β-phase correspond to directions [001], [110] and [1$\bar{1}$0] of the cubic lattice host [12, 13]. The distortions introduced due to the realignment of axes break the symmetry around the Fe atom and produces an electric field gradient which is probed by the ^{57}Fe nuclei and drives to the appearance of a Mössbauer

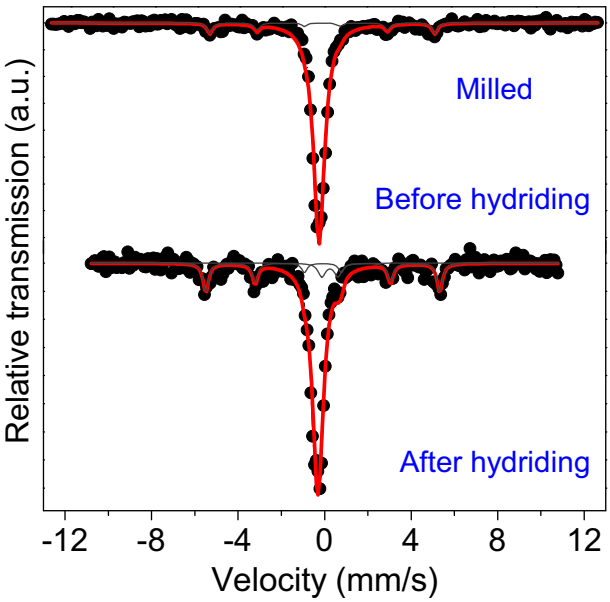


Fig. 4 Room-temperature Mössbauer spectra of the graphite-milled sample and its hydride. The solid line represents the best fit and dotted lines represent the subspectra used in the fit

component with a nonzero quadrupole splitting (QS) corresponding to the β-phase. No remarkable change was observed for the IS of the α-phase; however, the IS of the β-phase shows a relative increase of +0.20 mm/s with respect to the intermetallic compound without hydrogen. This increase has been associated with a decrease in the s-electron density visiting the Mössbauer nucleus caused by the presence of nearby hydrogen atoms.

We can express the IS change by:$\Delta IS_t = \Delta IS_{vol} + \Delta IS_{el} = \left(\frac{\partial IS_t}{\partial lnV}\right)\frac{\Delta V}{V} + \Delta IS_{el}$, where the first term corresponds to the volume change contribution and the second one to the electronic contribution. Considering an estimated expansion of $\Delta V/V \sim 0.1$ in the unit cell volume of the β phase and using the values of $\left(\frac{\partial IS}{\partial lnV}\right)$ reported in the literature [14, 15], a change in the IS value associated with the volume expansion in the range of $\Delta IS_{vol} \sim +0.13$–$0.15$ mm/s is determined. These values are smaller than that experimentally determined ($\Delta IS_t = +0.20$ mm/s) which means that an electronic contribution is needed to explain that IS change.

The Mössbauer spectrum of the graphite-milled sample is well-resolved by considering one singlet and one sextet (see Fig. 4). Those components correspond to the $\propto$-phase and the metallic iron, respectively. After hydrogenation, the Mössbauer spectrum is well-resolved by considering three components: one singlet, one doublet and one sextet as shown in Fig. 4. The presence of the doublet for the hydride sample has been related to the γ-phase in consistency with the XRD data. The hyperfine parameters of that doublet are IS = +0.35 mm/s and QS = 0.74 mm/s (see Table 2) which is in consistency with values reported in the literature [10]. The positive value of IS indicates a strong reduction in the s-electron density after the hydrogenation. It is worth mentioning that the significant change of IS from negative to positive after the hydrogenation is associated to a strong charge transfer from Fe atoms to the nearby H atoms which localize s-electrons due to the relatively large difference

Table 2 Mossbauer parameters and spectral areas obtained from the fit of the Mössbauer spectra of graphite-milled sample before and after the hydrogenation

Graphite-milled Sample	Phase	IS (mm/s)	QS (mm/s)	B_{hf}(T)	Γ (%)	A (%)
$TiFe_{0.5}Ni_{0.5}$	α	-0.26	–	–	0.63	92
	$\alpha-$Fe	0.00	–	33.0	0.30	8
$TiFe_{0.5}Ni_{0.5}H_x$	α	-0.19	–	–	0.60	75
	γ	+0.35	0.74	–	0.40	6
	$\alpha-$Fe	+0.02	0.00	33.5	0.30	19

The maximal experimental errorsof hyperfine parameters (IS and QS) and linewidh (Γ) are estimated to be ±0.03 mm/s. The maximal experimental errors for the hyperfine field (B_{hf}) are ±0.1T and ±2 % for the spectral area (A)

in electronegativity between Fe and H atoms. According to the concept of electronegativity, the low affinity of Ti to Fe atoms is the responsible for the charge transfer from Ti to Fe atoms and provokes an increase in the s-electron density in the TiFe alloy. The presence of H atoms modifies that scenario in the hydride phases (β and γ); therefore, it will be easier to take up electrons from the Fe atoms to nearby hydrogen atoms. Although these results are qualitatively explained based on differences in electronegativity of metals, the role that graphite plays in the formation and on the resulting hyperfine parameters of the γ-phase is not clear yet and more detailed study is needed. Currently, a detailed study of $TiFe_{0.5}Ni_{0.5}$/graphite nanocomposites is carried out to clarify this issue and those results will be published elsewhere.

4 Conclusions

The bulk and graphite-milled $TiFe_{0.5}Ni_{0.5}$ compounds and their hydrides were successfully synthesized in this work. Meanwhile, the formation of $\propto$ and β hydride phases have been determined for the bulk intermetallic compound, the formation of the $\propto$ and γ hydride phases have been formed in the graphite-milled compound. It has been stablished that the graphite plays the role of a catalytic agent that helps with the hydrogen absorption. It means that the presence of graphite near to the nanostructured grains of the intermetallic favors to the formation of the γ-phase which avoids applying high hydrogen pressures in order to get the richest hydride phase (γ-phase) in the Ti-Fe-Ni intermetallic. Mossbauer spectra of the bulk and graphite-milled $TiFe_{0.5}Ni_{0.5}$ compounds are well-resolved by considering one singlet in agreement with XRD data. After the hydrogenation, the change in value of IS observed for the hydrogen-rich phases with respected to the intermetallic compound has been accounted for in terms of the lattice expansion and electronic effects introduced by the presence of hydrogen atoms. The non-zero quadrupole splitting (QS) determined for the β and γ phases has been assigned to the strong symmetry changes provoked by the entrance of H atoms which drive to a phase transition from cubic to orthorhombic phase in accordance with XRD data analysis. The significant change of the IS of the γ-phase with respect to the intermetallic suggests a strong charge transfer from Fe atoms to the nearby H atoms due to the large difference in electronegativity between the metals and H atoms.

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