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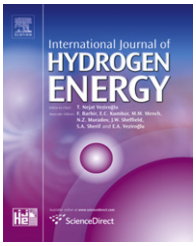

Mechanically alloyed Mg–Ni–Ti and Mg–Fe–Ti powders as hydrogen storage materials

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ABSTRACT

Recent research on coevaporated thin gradient films $Mg_{1-x-z}Ni_xTi_z$ have detected, using optical hydrogenography, a compositional region centered around $Mg_{69}Ni_{26}Ti_5$, with low absolute values of the hydride formation enthalpy. These destabilized hydrides would present then sorption kinetics more favorable for their use as hydrogen reservoirs. In order to check if these relevant properties extend to massive samples we attempted an investigation on mechanically alloyed powder mixtures $Mg_{1-x-z}Ni_xTi_z$ of similar composition and also on mixtures $Mg_{1-x-z}Fe_xTi_z$, with Fe instead of Ni. Thus, powder mixtures of nominal composition: $Mg_{69}M_{26}Ti_5$, $Mg_{64}M_{26}Ti_{10}$ and $Mg_{64}M_{31}Ti_5$ (M = Ni, Fe) were milled in a H_2 ambient till a steady state, with no further H_2 absorption, was attained and the hydriding kinetics was determined from the H_2 intake. Each hydrided sample was discharged by increasing the temperature at a given starting H_2 pressure and recharged by decreasing the temperature under the same conditions. The resulting P vs T curves were analyzed to extract approximate values of the equilibrium (T,P) data for H_2 desorption and absorption. Before and after their cycling in H_2 the samples were characterized by X ray diffraction and those containing Fe, by Mössbauer spectroscopy. The results are analyzed in connection with possible mechanisms for the transition metals catalytic action and the influence of the sample microstructure.

1. Introduction

Solid hydrides as hydrogen reservoirs are thought to be of crucial importance in the global energy prospects based in the use of hydrogen as an energy vector. MgH_2 is nominally a good candidate for hydrogen storage in that form, due to its high volumetric and gravimetric capacity, but its sorption kinetics should be considerably improved for it become of practical use. The reduction of grain sizes to the nanometer scale and the addition of small quantities of transition metals, such as Fe, Ni and Ti, as catalysts, have demonstrated to be useful for that purpose [1–3].

Mg also combines with Ni or Fe and hydrogen to form the complex ternary hydrides Mg_2NiH_4 [4] and Mg_2FeH_6 [5]. The former have somewhat smaller hydrogen volumetric content than MgH_2 but a lower dissociation enthalpy. On the contrary, Mg_2FeH_6 has one of the highest volumetric hydrogen content (150 kg H_2/m^3) but also a high dissociation enthalpy (77 kJ/mol) and for that reason has been considered as a candidate for energy storage also [6]. While Mg_2NiH_4 may be thought as the hydride of the intermetallic Mg_2Ni, Mg_2FeH_6 does not have a hydrogen-free intermetallic precursor and when it decomposes Mg and Fe must mutually segregate. These complex hydrides may be obtained by heat treatments at moderate

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temperature and high H_2 pressure [4,5] or by mechanical milling of the metallic constituents in H_2 atmosphere at moderate pressure and room temperature [7–10]. In previous papers we have described the mechanosynthesis of ternary (Mg_2FeH_6, Mg_2CoH_5 and Mg_2NiH_4) as well as quaternary hydrides (combining Mg with two of the transition metals Fe, Co and Ni in several proportions) [11,12], all of them prepared by mechanical milling of the constituent metals in a H_2 ambient.

Recent research on films of continuously varying composition in the system Mg–Ni–Ti have found, using optical hydrogenography [13], a compositional region centered around $Mg_{69}Ni_{26}Ti_5$, with low absolute values of the hydride formation enthalpy. Thus the hydrogen sorption kinetics became optimized in films with that composition [14] and it would be interesting to explore these properties in bulk materials of similar composition.

With that purpose we started an investigation on mechanically alloyed Mg–Ni–Ti powder mixtures of nominal composition similar to those mentioned above and also on Mg–Fe–Ti mixtures, with Fe instead of Ni. We milled the samples in a H_2 ambient, till a steady state with no further H_2 absorption was attained and followed the mechanosynthesis process through the analysis of the hydrogen absorption kinetic curves. The resulting hydrides were then submitted to several H_2 discharge–charge cycles. Before and after their cycling in H_2 the samples were characterized by X ray diffraction and those containing Fe, by Mössbauer spectroscopy on ^{57}Fe. The results will be analyzed in the framework of possible mechanisms for the transition metals catalytic action on the H_2 sorption processes and the influence of the sample microstructure.

2. Experimental

Pure metallic powders: Mg (Sigma–Aldrich, 99.98), Ni (Fluka puriss gt; 98.5), Fe (Merk, 99.5) and Ti (Cerac, 99.98) were mixed in molar ratios adequate to the desired stoichiometry, i.e. $Mg_{69}M_{26}Ti_5$, $Mg_{64}M_{26}Ti_{10}$ and $Mg_{64}M_{31}Ti_5$ with $M = Ni$ or Fe. Samples weighing 500 mg were filled in a cylindrical steel milling vial together with one steel ball ($\Phi = 12$ mm), yielding a ball to sample mass ratio around 14:1. The milling vial was connected to a gas reservoir (total volume $V = 20\ cm^3$) and sealed with an O-ring. All sample handling was performed in a glove box under a controlled protective atmosphere, keeping the oxygen content below a few ppm.

After washing the vial several times, the mechanical milling of each powder mixture was conducted in H_2 atmosphere (N50, $P_i = 0.3$ MPa) using a horizontal mill oscillating at a fixed frequency of 32 Hz. The H_2 pressure was measured continuously during the process with a strain gauge (Sensyn SX30; 0.5 kPa sensibility) and each time the pressure drops to 0.9 P_i, the system was automatically refilled with H_2, restoring the initial pressure without milling interruption. The mill was stopped well after a steady state with no further H_2 absorption was attained (typically 4–8 h). From the measured H_2 pressure during milling, the reaction progress was monitored and a kinetic curve established in each case.

X ray diffractograms in the interval $20° < 2\theta < 80°$, were obtained in Bragg geometry with a Philips PW1710 diffractometer using Cu K_α radiation, for all the samples. Additionally, the samples containing Fe were also studied by Mössbauer spectrometry (MS) in transmission geometry using a ^{57}Co *Rh* source at constant acceleration. This technique, based on the γ-rays resonant absorption by ^{57}Fe nuclei, allows the investigation of atomic configurations in the neighborhood of Fe atoms and reveals the possible formation of Fe containing compounds or complexes.

Afterwards, each milled sample was dynamically discharged (charged) by increasing (decreasing) the temperature at a given starting H_2 pressure and constant volume. The chamber pressure and sample temperature were measured during the cycle, using strain gauges and a Pt100 thermometer, respectively. The process was repeated several times at varying starting pressures. The resulting P vs T curves were analyzed to extract approximate values of the equilibrium T and P data for H_2 desorption and absorption. The samples were characterized again after their cycling in H_2.

3. Results and discussion

3.1. Hydriding kinetics

For each milling run, the instant number of absorbed hydrogen atoms per metal atom $n_H/n_M = -2V \times \Delta P \times M/R \times T \times m$ was evaluated from the accumulated pressure change ΔP, as a function of milling time t_m. R is the gas constant, M the molar mass of the formula $Mg_{1-x-z}M_xTi_z$ and m the powder mass (see Fig. 1). As previously reported [11], the kinetic curves for Mg–Fe mixtures show complex shapes typical of two stage processes: the prior formation of MgH_2 (fast process) that in turn reacts with Fe to form the complex hydride Mg_2FeH_6 (slow process), while that for Mg–Ni mixtures are simpler and somewhat slower, owing to the existence of the intermetallic Mg_2Ni. On his hand, the milling of pure Ti in H_2 lead to the fast formation of TiH_2 [15] through a mechanically assisted reaction that completes, under similar experimental conditions, in less than 20 min [16,17].

In the present case, the presence of Ti in the starting mixture does not alter greatly the shape of the curves. The main effect being the emergence of a faster initial stage, as compared with that observed in samples without Ti [11], that may be associated with the prompt formation of TiH_2. All the kinetic curves reach a steady state after some hours of milling. In the samples with Fe the nH/nM value attained is, on the average, about 65% of the expected value, 2, for complete reaction. In turn, in the samples with Ni the value reached is 68% of the expected value $2(1 - x)$.

3.2. As milled samples

The as milled samples were characterized by XRD, MS and VSM. As shown in Fig. 2 the main reflections present

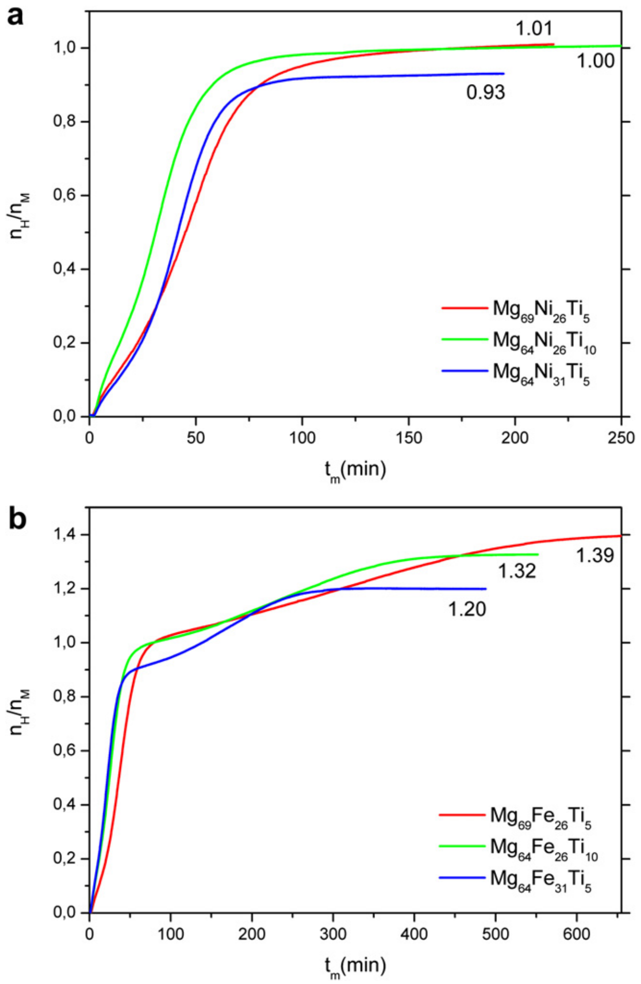

Fig. 1 – The number of absorbed hydrogen atoms per metal atom n_H/n_M as a function of milling time t_m for all the studied samples: (a) MgNiTi, (b) MgFeTi. The stationary values are indicated.

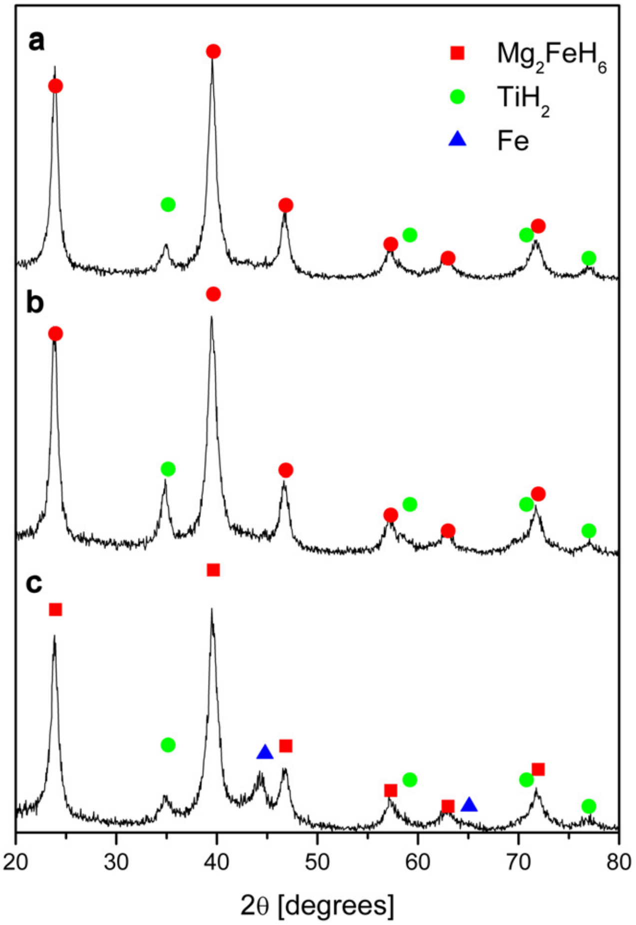

Fig. 2 – X ray diffraction patterns after milling, for samples: (a) $Mg_{69}Fe_{26}Ti_5$, (b) $Mg_{64}Fe_{26}Ti_{10}$ and (c) $Mg_{64}Fe_{31}Ti_5$.

in the diffractograms are those coming from the metallic hydride TiH_2 and from the complex hydrides Mg_2NiH_4 [4] or Mg_2FeH_6 [5] respectively, both with the cubic *Fm3m* structure. The samples with Ni also show traces of $Mg(OH)_2$ and of unreacted Ni. In the samples with Fe, only that with 31 at%Fe show traces of unreacted bcc Fe as confirmed by MS results. No lines coming from the remainder Mg are discernible neither those from Fe–Ti or Ni–Ti intermetallics.

The MS spectra of the Fe containing samples were analyzed by least squares fitting of appropriate theoretical functions. All the measured spectra are similar (see Fig. 3) and could be reasonably well fitted with two or three components: (i) a singlet with isomer shift $\delta \approx -0.1$ mm/s associated with the ternary hydride [5]; (ii) a minority (10%) broad singlet (or an unresolved doublet) centered at $\delta \approx 0.3$ mm/s and assigned to metastable Mg–Fe mixtures [18,19] and (iii) a faint magnetic sextet associated with the unreacted bcc Fe metal, present in the $Mg_{69}Fe_{31}Ti_5$ sample.

3.3. *Desorption – absorption cycles*

Fig. 4 shows the evolution of *P* vs *T* during the thermal H_2-desorption and absorption cycles, for samples $Mg_{64}Ni_{26}Ti_{10}$ and $Mg_{64}Fe_{31}Ti_5$. As may be seen, at certain temperature, the pressure deviates sharply from the empty reactor behavior, indicating the start of the H_2 desorption (absorption) process. Despite the dynamical character of the whole process, we may take these (P,T) values as indicative of the equilibrium values for H_2 sorption. Except for the first desorption, the curves and the associated (P,T) values are repetitive and show the expected $P(T)$ dependence. Indeed they aligned well in a van't Hoff plot, $\ln(P/P_o)$ vs $1/T$ (see Fig. 5). In the case of sample $Mg_{64}Ni_{26}Ti_{10}$ where an ample region was explored, the van't Hoff plot shows practically no hysteresis and values of $\Delta H = 59_1$ kJ/mol and $\Delta S = 120_2$ J/mol K may be fitted for the enthalpy and entropy of hydride formation.

3.4. *Thermally cycled samples*

The cycled samples were again characterized by XRD and MS. As shown in Fig. 6 the main reflections present in the samples with Ni are those coming from the hydrides Mg_2NiH_4, TiH_2 and

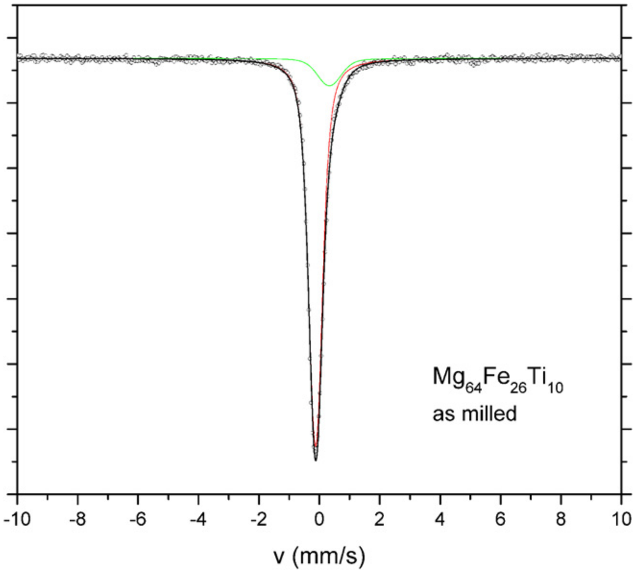

Fig. 3 – **Mössbauer spectra after milling of $Mg_{64}Fe_{26}Ti_{10}$. Also shown the fitted curve and the associated subspectra.**

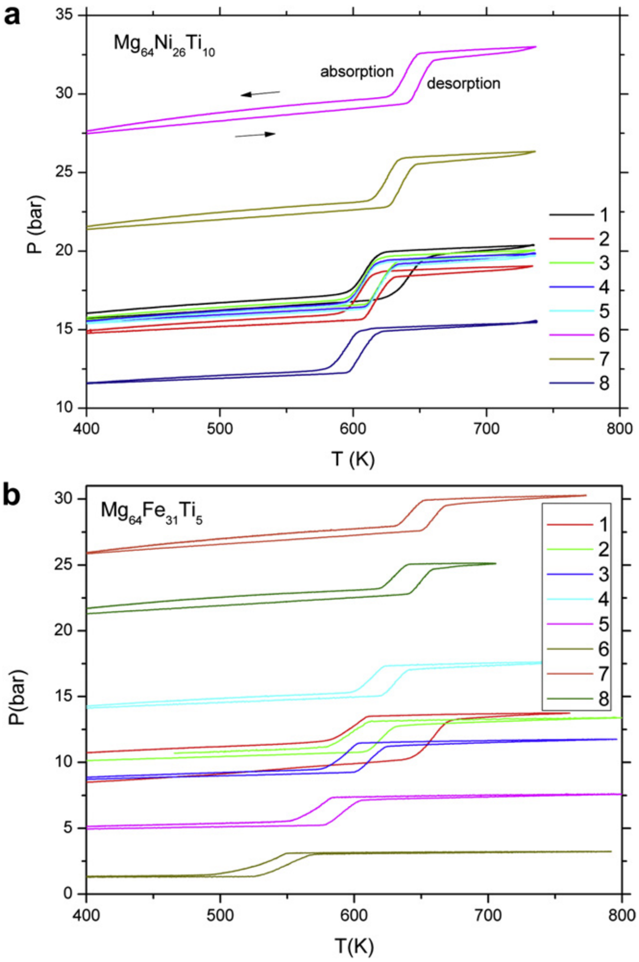

Fig. 4 – **Evolution of P vs T during the thermal H_2 desorption and absorption cycles for (a) $Mg_{64}Ni_{26}Ti_{10}$ and (b) $Mg_{64}Fe_{31}Ti_5$.**

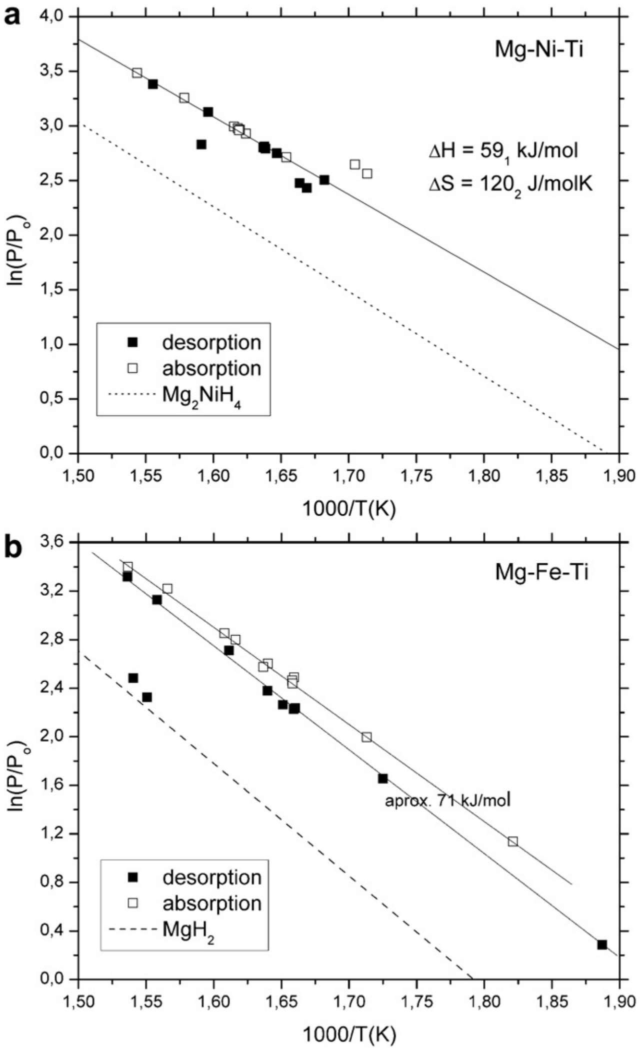

Fig. 5 – **Van't Hoff plots of $\ln P/P_o$ vs 1000/T(K) for (a) MgNiTi samples (a linear fit to the $Mg_{64}Ni_{26}Ti_{10}$ values is shown) and (b) MgFeTi samples (guiding lines for absorption and desorption points are shown). The points that depart from the general behavior correspond to first desorption processes.**

in some cases MgH_2. On the contrary, in the samples with Fe the reflections come mainly from tetragonal MgH_2 consistently with the absence of lines from Mg_2FeH_6. There are also lines coming from bcc Fe or from the intermetallics $TiFe_2$ and TiFe. Generally, the reflection peaks of the cycled samples diffractograms are sharper than those of as milled ones indicating the crystallite mean size growth.

The Mössbauer spectra become rather complex (see Fig. 7) but all of them may be fitted with the same components in varying proportions: (i) a main sextet (Fe) with a secondary one originated in the presence of non magnetic Mg impurities; (ii) two central lines that can be described as a singlet and a doublet, and assigned respectively to TiFe and $TiFe_2$ phases; (iii) a broad central interaction not conclusively interpreted yet. The latter interaction could be attributed to some

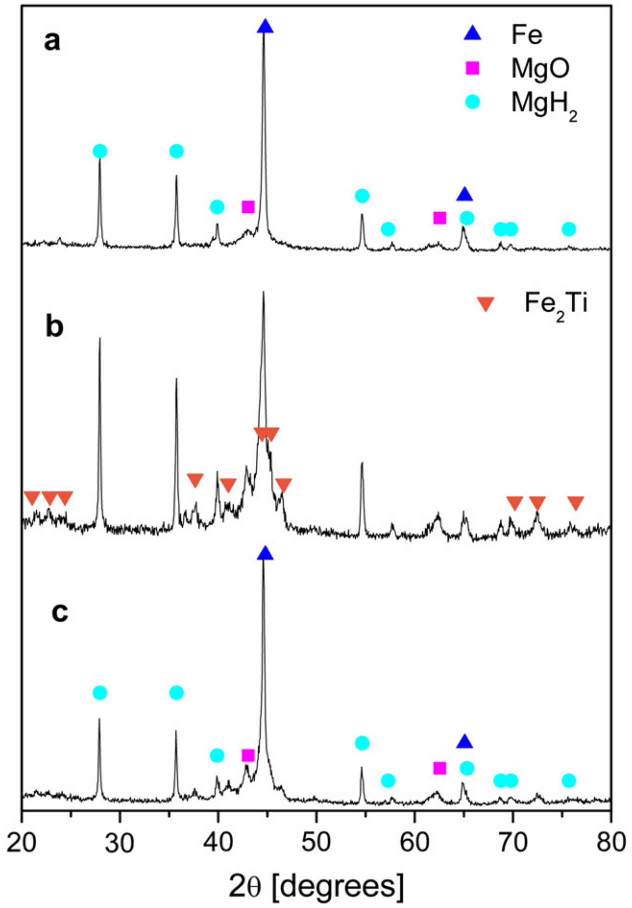

Fig. 6 – X ray diffraction patterns after cycling for samples: (a) $Mg_{69}Fe_{26}Ti_5$, (b) $Mg_{64}Fe_{26}Ti_{10}$ and (c) $Mg_{64}Fe_{31}Ti_5$.

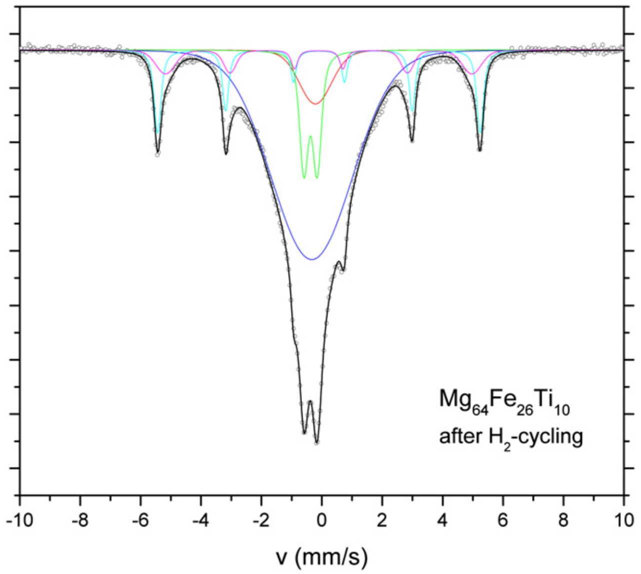

Fig. 7 – Mössbauer spectra after H_2 cycling of $Mg_{64}Fe_{26}Ti_{10}$. Also shown the fitted curve and the associated subspectra.

amorphous or nanocrystalline TiFe complex as those recently observed in films [20].

4. Conclusions

We have explored the properties of mechanically alloyed Mg–Ni–Ti and Mg–Fe–Ti powder mixtures at compositions that had shown remarkable sorption properties under the form of thin films. The main resulting products after milling were the hydrides $MgNi_2H_4$, $MgFe_2H_6$ and TiH_2 without Ni–Ti or Fe–Ti phases. From the kinetic curves we have been able to discern the role of the different additives (Fe, Ni, Ti) during the mechanically activated hydrogen absorption.

For the MgNiTi samples, after their thermally induced desorption, the powders absorbs hydrogen to form mainly Mg_2NiH_4. From the corresponding van't Hoff plots a reduction of about 40 K in the sorption temperature at atmospheric pressure, as compared with normal Mg_2NiH_4, is observed. The sorption properties are thus improved, consistently with the observed reduction in ΔH from 65 to 59 kJ/mol, but they are still far from those reported for thin films (ca. 40 kJ/mol).

In the MgFeTi samples, the first desorption occurs at higher temperature than the following ones. It corresponds to the dissociation of the complex hydride Mg_2FeH_6, which is not formed again after the first desorption, as shown by XRD and MS. From the van't Hoff plots again a reduction of about 40 K in the sorption temperature at atmospheric pressure, as compared with pure MgH_2, is found. MS also suggests the presence of a highly disordered minority phase, probably amorphous or nanocrystalline TiFe. Unfortunately this could not be confirmed by XRD as the expected broad halo would be located at $2\theta \approx 37.5$ where several other reflections superimpose. These amorphous or nanocrystalline phases seem to play an essential role in the reported properties [20].

Given the observed tendency to form separately the hydrides Mg_2TH_y and TiH_2, it would be worth to continue this study, modifying the initial conditions of the added transition metals, mixing or even alloying them, before their incorporation to the Mg powder.

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