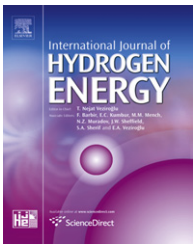
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Complex quaternary hydrides $Mg_2(Fe,Co)H_y$ for hydrogen storage

L. Mendoza-Zélis, M. Meyer, L. Baum*

IFLP, Departamento de Física, Facultad de Ciencias Exactas, UNLP, CC67, 1900 La Plata, Argentina

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ABSTRACT

Complex ternary hydrides based in Mg and transition metals are very attractive materials for hydrogen and energy storage due to their large volumetric capacity, up to 150 kgH_2/m^3 in Mg_2FeH_6 and their high dissociation enthalpies. These compounds may be produced at room temperature by mechanical milling of the constituents in H_2 atmosphere. This technique has also served to explore the synthesis of quaternary hydrides $Mg_2T_{1-z}T'_zH_y$, combining two transition metals to optimize the properties of the resulting hydride. In the present work we analyze the mechanical synthesis of the compounds $Mg_2Fe_{1-z}Co_zH_y$ ($z = 0, ¼, ½, ¾, 1$) by mechanical alloying at room temperature Mg–Fe–Co powder mixtures in adequate proportion, at 0.3 MPa H_2. We follow the mechanosynthesis process trough the analysis of the hydrogen absorption kinetic curves. Samples obtained after a steady state was reached were characterized by X ray diffraction and Mössbauer spectroscopy. The different stages in the mechanosynthesis of these complex hydrides are discussed in terms of the composition and initial state of the powder mixture.

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1. Introduction

There is no need to stress here the importance of hydrogen in the global energy prospects, neither that of solid hydrides as hydrogen reservoirs in fixed and mobile applications. Nanostructured and mechanically alloyed materials play a central role in the present efforts to increase the storage capacity and the rate of hydrogen charge and discharge processes. Mg and its alloys are nominally among the best candidates for hydrogen storage in the form of solid hydrides due to their high volumetric and gravimetric capacity (110 kg H_2/m^3 and 7.66 mass % for MgH_2) but their sorption kinetics should be considerably improved for they become of practical use. The reduction of grain sizes to the nanometer scale and the addition of small quantities of transition metals T as catalysts, have demonstrated to be useful for that purpose [1–3]. However the achieved sorption rates are still far from those required in mobile applications and their potential use might be limited to stationary devices using high temperature fuel cells.

Mg also combines with hydrogen and some transition metals to form complex ternary hydrides Mg_2TH_y ($y = 4$, 5 and 6 respectively for T = Ni, Co and Fe) with very high volumetric hydrogen content, (up to 150 kg H_2/m^3 in Mg_2FeH_6) [2,4,5]. These ternary hydrides contain $[TH_y]^{-4}$ anions with ionic-covalent bonds for H atoms and high dissociation enthalpies (ca. 77 kJ/mol for Mg_2FeH_6) thus becoming good candidates for energy storage also [6]. Except for Ni, in which case the hydride may form reversibly through the reaction $Mg_2Ni + 2H_2 \leftrightarrow Mg_2NiH_4$, none of the other transition metal complex hydrides, including the Co and Fe cases, have the corresponding hydrogen-free intermetallic precursor Mg_2T [7]. A notable case is that of Mg_2FeH_6, since Mg and Fe are practically immiscible (very low terminal solid solubility) and do not form any compound in the absence of a third element. It is worth to note that when

* *Corresponding author*. Tel.: +54 221 423 0122; fax: +54 221 423 6335.
E-mail address: mendoza@fisica.unlp.edu.ar (L. Mendoza-Zélis).
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T-catalyzed Mg samples are cyclically hydrogen charged and discharged, the corresponding ternary hydride could form, affecting not only the net charge capacity but also the system microstructure and thus the sorption kinetics [2,3,8]. At present, MgH_2 and Mg_2TH_y systems are indeed considered among the best candidates for thermal energy storage [6,9] and as hydrogen reservoirs in several applications [10,11].

These complex hydrides have been usually obtained by heat treatments at moderate temperature ($T = 450–520\ ^\circ C$) and high H_2 pressure, yielding incomplete reactions [4,5]. However, improved yields have been achieved recently by mechanical alloying the metallic constituents in H_2 atmosphere at moderate pressure and room temperature [2,8,12–15]. Indeed, when Mg–T mixtures of any composition are milled in H_2 atmosphere the formation of the corresponding ternary compound Mg_2TH_y occurs even for minute T addition [8,16]. This preparation technique has also served to explore the synthesis of quaternary hydrides $Mg_2T_{1-z}T'_zH_y$ combining two transition metals to optimize the properties of the resulting hydride[17,18].

We are carrying on a research program on Mg–T–H systems [3,16,17] with the aim of studying the role of the transition metal T in the sorption kinetics and its effect on the useful storage capacity. In a previous paper we have described the mechanosynthesis of ternary (Mg_2FeH_6, Mg_2CoH_5 and Mg_2NiH_4) as well as quaternary ($Mg_2Fe_{0.5}Co_{0.5}H_y$, $Mg_2Fe_{0.5}Ni_{0.5}H_y$ and $Mg_2Co_{0.5}Ni_{0.5}H_y$) hydrides [17]. All of them were prepared by mechanical milling of the constituent metals in an H_2 ambient. By measuring the H_2 pressure evolution during milling, the reaction progress was monitored and a kinetic curve established in each case. We present in this paper a study on the kinetics of the mechanical synthesis of the system $Mg_2Fe_{1-z}Co_zH_y$, where a varying amount of Co was added together with Fe, fixing the Mg:T ratio in 2:1, corresponding to the complex hydride stoichiometry. We study then the mechanically assisted hydriding process of $Mg_2Fe_{1-z}Co_z$ powder mixtures for z = 0, ¼, ½, ¾ and 1. The hydriding kinetics was followed up to saturation when no further hydrogen consumption was detected. All these steady state samples were characterized by X ray diffraction (XRD) and Mössbauer spectrometry (MS). 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 may reveal the possible formation of Fe containing compounds or complexes. Our main purpose was to characterize the resulting phases and the effect of Co alloying on the hydriding rate.

2. Experimental

The starting pure powders: *Mg* (Sigma–Aldrich, 99.98), *Fe* (Merk, 99.5) and *Co* (Fluka, 99.8) were mixed in molar ratio 2 Mg:(1–z)Fe:zCo, with z = 0, ¼, ½, ¾, 1 and filled in a cylindrical steel milling vial together with one steel ball ($\Phi = 12$ mm). A sample with z = 0.98 was also prepared, using Fe powder (Cambridge Isotope Labs, >99) 95% enriched in the ^{57}Fe isotope, in order to extend the Mössbauer characterization towards the case z = 1. Each sample weighted $m = 500\ mg$, giving a ball to sample mass ratio around 14:1. The milling chamber was connected to a gas reservoir (total volume $V = 165\ cm3$) 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.

The mechanical milling of these powder mixtures was conducted in H_2 atmosphere (N50, $P_o = 0.3$ MPa) using a horizontal mill oscillating at a fixed frequency of 32Hz. The H_2 pressure was measured continuously during the process with a strain gauge (Sensyn SX30) with 0.5 kPa sensibility. To avoid a significant pressure reduction, each time the pressure drops to some prefixed value P_{min}, the system was automatically refilled with H_2, restoring the initial pressure P_o without milling interruption (Fig. 1 displays a typical run). The mill was stopped after a steady state, with no further hydrogen consumption, were achieved, typically after 8 h. The instant number of absorbed hydrogen atoms per formula unit $n = -2V.\Delta P.M/R.T.m$ was evaluated from the pressure change ΔP, as a function of milling time. *R* is the gas constant, *T* the absolute temperature, *m* the powder mass and *M* the molar mass of the formula unit $Mg_2Fe_{1-z}Co_z$.

All the samples were characterized by X ray diffraction in Bragg geometry using a Philips PW1710 diffractometer with Cu K_α radiation. The samples were also analyzed by Mössbauer spectrometry in transmission geometry using a $^{57}Co\ Rh$ source at constant acceleration. The MS spectra were analyzed by least squares fitting of appropriate theoretical functions.

3. Results and discussion

3.1. Hydriding kinetics

Before discussing the observed kinetics we recall some results obtained in simpler systems. The milling of pure metals in H_2 may lead to the formation of metallic hydrides through the mechanically assisted reaction: $M + (y/2)H_2 \rightarrow MH_y$, following a particular kinetics [19]. Although the whole process involves several complex stages, a rather simple kinetic behavior may be observed, the number of absorbed hydrogen atoms per metal atom *n* follows a sigmoidal behavior and tends asymptotically to

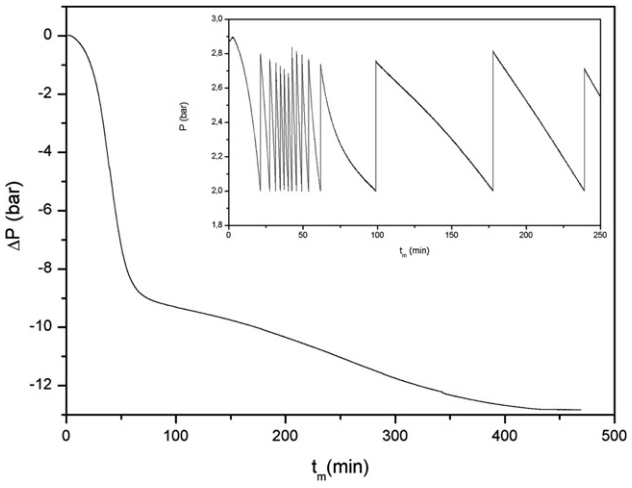


Fig. 1 – Total pressure decrease during milling vs milling time. Inset, original curve showing the hydrogen refilling.

$n_s \leq y$. Furthermore we have found that for a given degree of reaction $x = n/n_s$, the reaction rate dx/dt just depends on the milling intensity I [20]. The associated kinetic constant K depends linearly on the milling intensity I, that comes to play the same role as temperature does in thermally activated processes [21].

In the case of ternary hydrides, based on Mg and a single transition metal (Fe, Co or Ni), we have found [17] that the shape of the kinetic curve strongly depends on the transition metal involved (see Fig. 2). The complex shape observed for Fe arises from a two stage process: the prior formation of MgH_2 (fast process) that in turn reacts with Fe to form the complex hydride (slow process). The curve for Co shows the fastest beginning and then displays a slight shoulder, while that for Ni does not shows such accidents, evidencing a simpler process probably associated with the existence of the hydrogen-free intermetallic precursor Mg_2Ni. None of these systems absorb the total amount of hydrogen expected for a complete reaction (y), approaching by defect the ideal stoichiometry: 6, 5, and 4 for Fe, Co and Ni, respectively.

For the present samples, the instant number of absorbed hydrogen atoms per formula unit, n, has been evaluated from the measured pressure drop and the corresponding kinetic curves traced (see Fig. 3). For all the studied systems the hydriding curves display an acceleration stage with one or more steps, and finally tend smoothly to a steady state corresponding to the maximum value of n reached, n_s. Saturation was always achieved before 8 h of milling; the observed values of n_s are quoted in Table 1 and compared with the nominal stoichiometry, $y = 6-z$.

As already pointed out, the kinetic curve obtained in the pure Fe case ($z = 0$) results from two combined processes: the formation of MgH_2 that in turn reacts with Fe to form the complex hydride. Indeed, our experimental curve could be well fitted (see Fig. 4) by a two-reaction model combining two sigmoidal curves, like:

$$x(t) = pf_1(t) + (1-p)f_2(t) = \frac{p}{1+e^{-k_1(t-\tau_1)}} + \frac{1-p}{1+e^{-k_2(t-\tau_2)}} \quad (1)$$

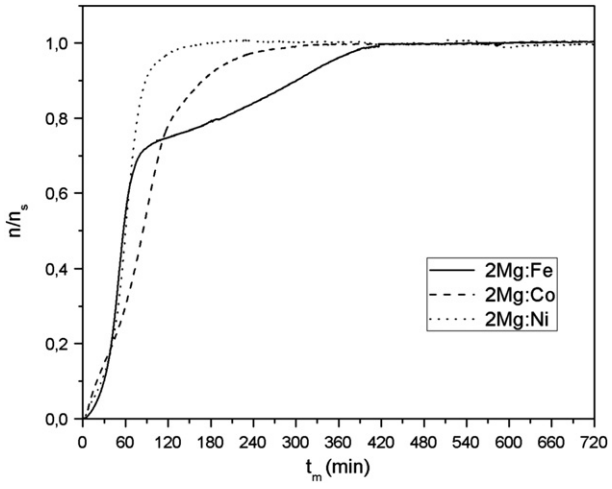


Fig. 2 – Number of absorbed H atoms per formula unit normalized by its stationary state value n_s, vs milling time, during the milling of 2 Mg:T mixtures (T = Fe,Co,Ni) according to reference 17.

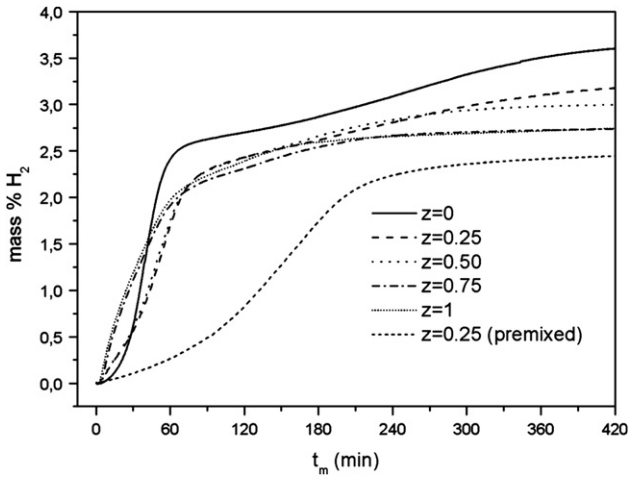


Fig. 3 – Mass percent of absorbed hydrogen, vs milling time, for the studied $Mg_2Fe_{1-z}Co_z$ samples.

where the τ_i are the times for halfreaction, $f(\tau) = 1/2$, when the corresponding reaction rate is maximal and equals $k_i/4$.

Also shown in the figure is the reaction rate (dx/dt) as a function of milling time t_m, where the two processes can be well distinguished with their maxima at 39 and 242 min respectively, as well as in the resulting kinetic curve (dx/dt) vs x shown in the inset.

It is clear from Fig. 3 that the addition of Co, although it reduces the total hydrogen capacity n_s, notably increases the reaction rate in the early stages of absorption. This demonstrates the higher catalyzing power of Co, as compared to that of Fe, for the hydrogenation of Mg.

In order to better understand this process, a $z = ¼$ sample was prepared using an $Fe_{0.75}Co_{0.25}$ powder mixture, previously milled in H_2 for 5h. As verified by X ray diffraction, this premilled powder is a solid solution with the *bcc* structure of *αFe* but with reflection lines about three times broader than in the starting metal powders, indicating smaller crystallite sizes and/or the presence of residual micro-strain. The resulting H absorption kinetics, also displayed in Fig. 3, has a shape similar to that of the $z = 0$ sample, without the rapid initial slope of those with $z \neq 0$, but is about three times slower. This global slowing down of the kinetics was also observed in $z = 0$ and $z = 1$ samples, prepared from Fe or Co powders pre-milled under the same conditions and could then be attributed to the micro-structural changes induced by milling. Instead, the disappearance of the rapid initial slope must be attributed to the alloying of Co, indicating the relevance of the Co structure for its catalytic action.

Table 1 – Number of absorbed H atoms per formula unit at saturation, n_s, in the various samples.

z	composition	ΔP_{max}	n_s	n_s/y	mass%H_2
0	Mg_2Fe	12.899	3.91	0.65	3.64
¼	$Mg_2Fe_{0.75}Co_{0.25}$	11.695	3.50	0.61	3.24
½	$Mg_2Fe_{0.50}Co_{0.50}$	10.836	3.28	0.60	3.02
¾	$Mg_2Fe_{0.25}Co_{0.75}$	10.269	3.09	0.59	2.83
1	$Mg_2Co(^{57}Fe)$	10.285	3.07	0.61	2.80

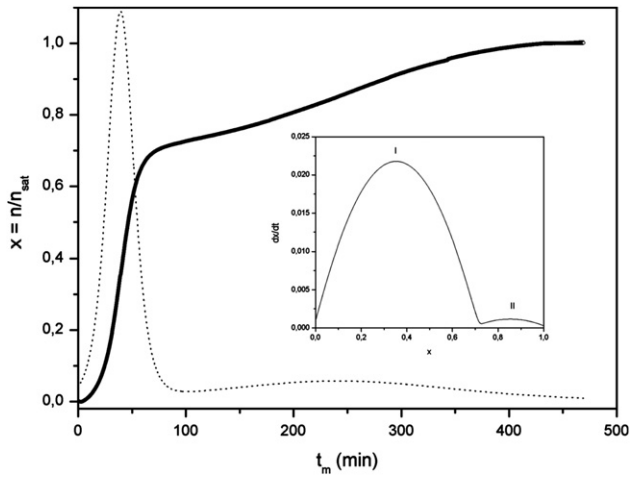


Fig. 4 – Hydrogen absorption kinetic curve: normalized number of absorbed H atoms per formula unit vs milling time for the sample Mg_2Fe. Inset: reaction rate vs reaction degree curve.

3.2. *Hydrides characterization*

The hydrided samples were characterized by X ray diffraction (XRD) and by Mössbauer spectrometry (MS). As shown in Fig. 5 the main reflections present in the diffractograms are those coming from the complex ternary hydrides with the cubic K_2PtCl_6 (*Fm3m*) structure or its tetragonal distortion *P4/nmm* and from metallic bcc Fe. No traces of MgH_2 are observed, but a faint evidence for MgO appears in some cases. It is worth to note that the samples with z = 0, ¼ and ½ display the cubic structure, while those with z = ¾ and 1, the tetragonal one. As already pointed out the reaction is not complete and some reactants are left. For z = 0, ¼, ½, ¾ the lines of *bcc* Fe or Fe–Co solid solutions may be seen, but no lines coming from the remainder Mg are discernible.

All the Mössbauer spectra could be reasonably well fitted with three components: i) a singlet at $\delta \approx -0.1$ *mm/s* associated with the ternary hydride [4]; ii) a magnetic sextet associated with the unreacted transition metal (*bcc* Fe or Fe–Co solid solutions); iii) a broad singlet (or an unresolved doublet) centered at $\delta \approx 0.3$ *mm/s* and assigned to Fe in MgH_2

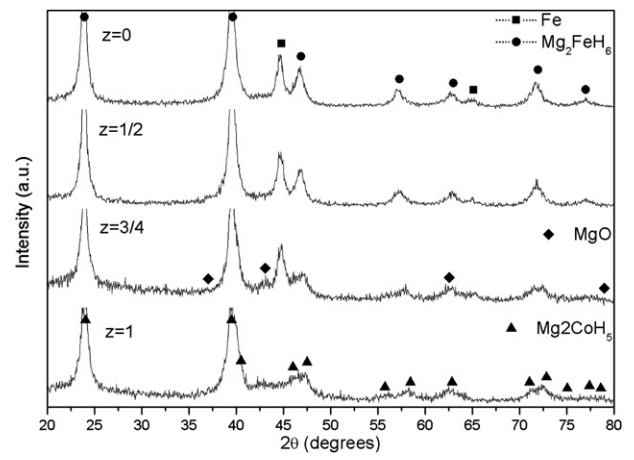


Fig. 5 – X ray diffraction patterns after milling for several studied samples. Also shown are the characteristic reflections from Fe (squares), Mg_2FeH_6 (circles), MgO (rhombi) and Mg_2CoH_5 (triangles).

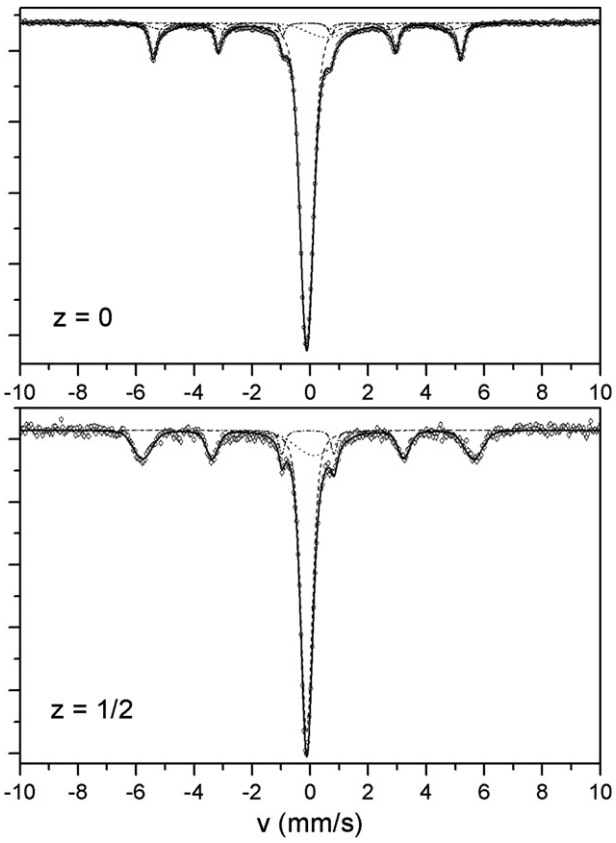


Fig. 6 – Mössbauer spectra for the samples z = 0 and z = 1/2. Also shown, the fitted curve and the associated subspectra.

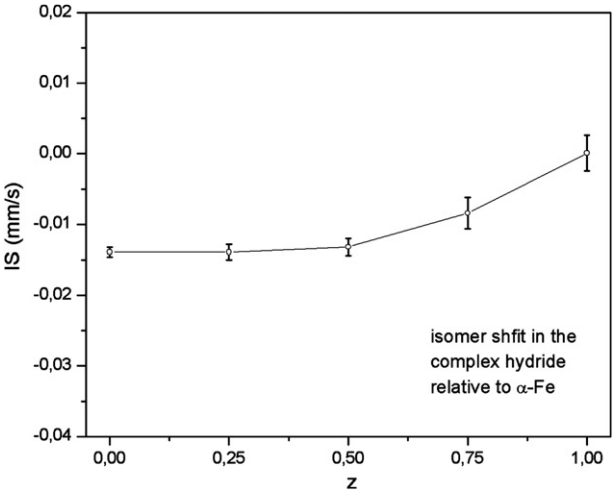


Fig. 7 – Fitted value of the isomer shift, relative to Rh, in the Mössbauer spectra of all the studied samples. The pure Co (z = 1) value corresponds to the sample with 2at% enriched Fe.

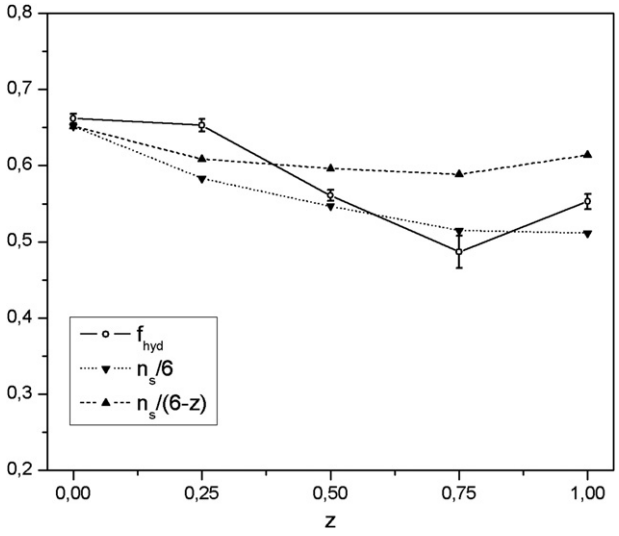


Fig. 8 – Hydride fraction f_{hyd} resulting from the Mössbauer spectra, compared with that obtained from the pressure drop during milling, for all the studied samples.

or metastable Mg–Fe mixtures [22,23]. Fig. 6 shows the spectra for samples with z = 0 and z = 0.5, respectively.

The ternary hydrides, cubic $Mg_2Fe(Co)H_y$ or tetragonal $Mg_2Co(Fe)H_y$, are observed as majority phases with an isomer shift δ practically unaltered with respect to the compound with only Fe, indicating a constancy in the chemical environment of the Fe atoms in these hydrides (see Fig. 7). For Co-rich samples (z = ¾ and 0.98) a slight increase in the corresponding value of δ is observed, indicating a small decrease in the charge density at Fe sites (see Fig. 7). Also a faint quadrupole splitting of this line insinuates, suggesting a breakdown of the cubic symmetry at these sites, consistent with the non cubic lattice structure.

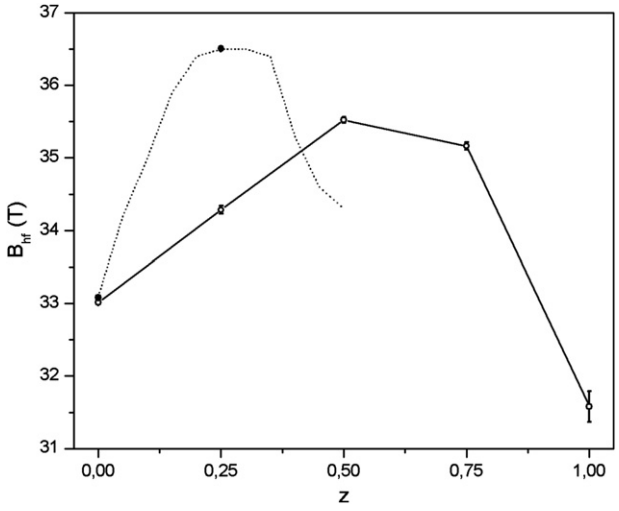


Fig. 9 – Fitted hyperfine magnetic field in Tesla for the remaining bcc FeCo alloy, in the Mössbauer spectra, for normal (open circles) and pre-milled (filled circles) samples. Also shown, as a broken line, are the values reported in reference 25 for FeCo alloys.

Assuming the same Lamb–Mössbauer factors for all the present phases, the fraction of Fe atoms in the complex hydride may be obtained from MS. As shown in Fig. 8, it reaches a minimum for z = ¾. In contrast the corresponding hydride fraction expected from the measured H absorption is almost constant.

Concerning the magnetic phase observed by MS, identified as unreacted transition metal or alloy, the corresponding hyperfine field B_{hf} varies with z as a result of the alloying with Co. According to previous studies, this is due mainly to the variation of the magnetic moment per atom caused by the filling of the 3d shell [24,25]. As shown in Fig. 9 there is a shift between the observed behavior and that reported in Fe–Co alloys, suggesting that the unreacted alloy is poorer in Co than the starting mixture. Conversely the Co content of the hydride should be higher than the nominal composition (z). Finally, it should be noted that in most cases a second, minority, magnetic component of ≈31T is observed and assigned to the presence of non magnetic (Mg) substitutional impurities in the *bcc* lattice.

4. Conclusion

The present work confirms mechanical synthesis as an effective way to produce complex quaternary $Mg_2Fe_{1-z}Co_zH_y$ hydrides. The main resulting products were homogeneous phases with *Fm3m* (z = 0, ¼, ½) or *P4/nmm* (z = ¾, 1) structure, where $[FeH_6]^{-4}$ and $[CoH_5]^{-4}$ anions are randomly mixed. Mössbauer spectroscopy on ^{57}Fe atoms supports this conclusion and shows that the $[FeH_6]^{-4}$ anion symmetry is not altered by the chemical disorder.

The kinetic curves give some additional elements for the interpretation of the competing processes during the mechanically induced hydrogen absorption in the different cases. The formation of the complex hydride occurs always through successive reactions: the prior formation of MgH_2, catalyzed by the transition metals, followed by the formation of the ternary hydride in a slower process. Although the addition of Co reduces the total hydrogen capacity, Co metal has higher catalyzing power than Fe, increasing notably the Mg hydriding rate in the early stages of absorption. This effect is directly related to the Co crystalline structure. Furthermore the overall catalyzing action, of Fe or Co, is greatly affected by their own microstructure.

Finally, the mechanical synthesis produces a shift in the hydride composition towards higher Co content. This could explain why Mössbauer spectroscopy – sensitive only to Fe - underestimates the ternary hydride fraction in the samples.

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