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Synthesis, Characterisation and Hydrogen Sorption Properties of Mechanically Alloyed $\text{Mg}(\text{Ni}_{1-x}\text{Mn}_x)_2$

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Abstract

Hydrogen storage materials based on the stoichiometry $\text{Mg}(\text{Ni}_{1-x}\text{Mn}_x)_2$ have been synthesized by High Energy Ball Milling (HEBM) and studied as potential candidate materials for solid state hydrogen storage. The microstructures of the as-cast and the milled alloys were characterized by means of X-ray Powder Diffraction (XRD) and Scanning Electron Microscopy (SEM) both prior and after the hydrogenation process. The storage characteristics (Pressure-Composition-Temperature isotherms) and the sorption kinetics obtained by a commercial and automatically controlled Sievert-type apparatus. The X-ray results showed that the substitution of Mn over Ni could eliminate and inhibit the MgNi_2 phase. The calculation of the average crystallite size showed that the increase of the amount of Mn can reduce the size at the early stages, but for Mn content higher than 0.25 the crystallite size increases, while the microstrain levels decreased monotonically. The hydrogenation and dehydrogenation measurements took place at several temperatures (150-200-250-300 °C). The results showed that the kinetics for both the hydrogenation and dehydrogenation can be fast for operation at temperatures between 250 and 300 °C, but for temperatures below 200 °C the hydrogenation process is very slow, and the dehydrogenation process cannot be achieved.

Keywords: Hydrogen Storage; Metal Hydrides; Mechanical Alloying; Mg-based intermetallics;

1. Introduction

Hydrogen is a potential energy carrier considered for both stationary and mobile applications [1, 2]. The utilisation of hydrogen also allows the energy storage resulting from renewable sources; this could potentially be the route to overcome the production of hydrogen from fossil fuels, which causes CO₂ release [3, 4]. While the introduction of hydrogen seems to be an ideal solution for stationary and mobile applications, there are various drawbacks preventing the massive application of a hydrogen-based economy. Those issues are mostly related to hydrogen production, storage, compression and safety [5].

Metal hydrides (MH) which can reversibly store and release hydrogen via chemisorption have been studied as potential materials for solid-state hydrogen storage [6, 7]. Many intermetallic compounds have attracted attention for solid-state storage applications due to their capability of storing and release hydrogen under moderate temperature and pressure conditions. These intermetallic alloys are normally symbolised as AB_n , where $n=0.5, 1, 2, 5$. The A part usually involves rare earths (such as La), an alkaline metal (Mg) or transition metals (Ti, Zr) to form a stable hydride at moderate temperature and pressure [8-10]. On the contrary, the B side part is normally a latter transition metal (Ni, Fe) and doesn't form stable hydrides [11]

In recent years, there have been serious and solid research endeavours towards the development of potential materials for solid-state hydrogen storage and the understanding of the nature of the sorption mechanisms [12, 13]. Magnesium-based alloys have attracted much attention due to the large theoretical hydrogen storage capacity, high abundance and relatively low cost [14]. It has been reported that pure Mg can store up to 7.6 wt% [15-17]. Despite the large hydrogen storage/release capacity, there are some drawbacks in the use of Mg alloys for practical on-board applications such as slow kinetics, high operation temperatures related to the high stability of the Mg-H bonds (expressed to the large enthalpy of the hydride formation/deformation) and high reactivity with oxygen [18, 19].

Considerable research has been conducted on magnesium alloys for the establishment of novel synthetic routes for new high-performance materials. These studies are mainly focus on the element substitution [20], new production methods by using different hydrogen environments [21, 22], preparation of composite materials through the addition of dopants to improve microstructure/microchemistry [23] and thermal

techniques [24] to improve hydrogen storage characteristics. Several studies have reported that the partial substitution of Mn over Ni in MgNi_2 intermetallics could potentially lead to lower storage/release temperature ranges [25, 26].

Amongst the most efficient ways to improve the hydrogen storage performance of Mg-based materials is the application of stresses during the synthesis, by High-Energy Ball Milling (HEBM) [27, 28], resulting on the formation of an amorphous/nanocrystalline state of the material. By HEBM synthesis of new compounds and formation of composites with catalytic additions of other elements is achieved. When applying such techniques, due to the large stresses generated, the microstructure of the materials is continuously refined until a chemically and microstructure homogeneous material is obtained. This method is suitable for the synthesis of Mg-based alloys comparing to conventional metallurgical techniques, due to the low miscibility of Mg with most of transition metals, the high vapor pressure of Mg and the difference between the melting points [29]. Several other novel techniques have been proposed and introduced in order to synthesize high performance materials for hydrogen storage such as hybrid microwave heating [30], laser ablation techniques [31] and hydriding combustion synthesis (HCS) [32].

In the current work, alloys based on the $\text{Mg}(\text{Ni}_{1-x}\text{Mn}_x)_2$ stoichiometry have been prepared by High Energy Ball Milling and studied for their hydrogen storage/release capability. Five different stoichiometries of the $\text{Mg}(\text{Ni}_{1-x}\text{Mn}_x)_2$ nominal composition were synthesized by High Energy Ball Milling (HEBM) under Argon atmosphere at room temperature using a planetary high-energy ball mill. The samples milled for 10h and 20h at 350 rpm under Argon environment. The microstructures characterized by means of XRD and Scanning Electron Microscopy (SEM) whereas the phases identified by Rietveld refinement analysis. The Pressure-Composition-Temperature (P-c-T) properties of the studied materials obtained by using a commercial Sievert-type apparatus at several temperatures (200–250–300 °C) for both the hydrogenation and dehydrogenation process.

2. Experimental Procedure

Starting element powders of Mg (99.8%, 325 mesh), Ni (99.8%, 325 mesh) (Alfa Aesar) and Mn (99.95%, 325 mesh) (ProChem Inc) were stoichiometrically mixed and poured into the stainless-steel vials under argon atmosphere (inside a MBRAUN

UNIlab Pro Glove Box). The milling process held in high-purity Argon environment within sealed vials using a commercial Fritsch “Pulverisette-7” miller. Each stoichiometry milled for 10 and 20h respectively at 350 rpm. Thus, for each stoichiometry, two samples extracted. After one hour of milling, the process was paused for 30 min to prevent the temperature increase to high levels within the vials. After 5h of milling, the process was paused again. Then the vials transferred in the glove box. The powder stacked on the walls and the bottom of the vial removed by using a spatula and returned to the sample. In this way, the homogeneity of the prepared samples ensured. The microstructure of both the as-milled and the hydrogenated samples was characterized by means of X-ray diffraction (XRD) using a BRUKER AXS D8-Advance Diffractometer (CuK α radiation with $\lambda=1.5418 \text{ \AA}$ operating at 40 kV/100 mA with a scanning speed of 8°/min in the 2θ range from 10 to 80°). The phase identification was achieved by Rietveld refinement using the commercial software Match!3 coupled with FullProf Suite. The morphology of the samples analyzed by Scanning Electron Microscopy (SEM) using a Zeiss NEON 40 EsB Microscope. A Multi-Pin Specimen Mount used to introduce the samples in the microscope cabin. Carbon Conductive Tabs purchased from *Ted Pella, Inc.* used. Pressure–composition–temperature (P – c – T) relationships obtained by the Sieverts’ method using a commercial apparatus (PCTPro 2000-HyEnergy). Almost 0.85 g of each sample placed in the sample holder and transferred to the apparatus. Several cycles of activation took place at 300 °C for both the hydrogenation and dehydrogenation. The pressure kept at 20 bar for the uptake, while for the release it was 0.5 bar. The purity grade of hydrogen gas used was 99.999%. Five different stoichiometries of the nominal composition Mg(Ni $_{1-x}$ Mn $_x$) $_2$ were selected and they are presented in Table 1. The hydrogenation process took place at 200-250-300 °C with a hydrogen pressure of 20 bar and the dehydrogenation process was performed at the same temperatures under vacuum. The activation process consisted of four cycles of hydrogen uptake (20 bar) and release (0.5 bar) at 300°C. The crystallite size and microstrain calculated from Eq.1 [33]

$$B(2\theta) = 4 \cdot \varepsilon \cdot \frac{\sin \theta}{\cos \theta} + \frac{K \cdot \lambda}{L \cdot \cos \theta} \quad (1)$$

Where λ is the wavelength of the X-ray radiation (1.54060 Å for the case of CuK α 1), B is the peak width, K is the Scherrer constant and in the current study, it was assumed as 0.94 for the Full Width of Half Maximum (FWHM) of spherical crystals with cubic symmetry and L is the FWHM of the peak (rad).

Table 1. List of the synthesized Mg(Ni_{1-x}Mn_x)₂ samples

3. Results and Discussion

3.1. Microstructural Characteristics

Fig. 1 presents the X-ray diffraction patterns for the as-synthesised samples of Mg(Ni_{1-x}Mn_x)₂ ($x=0.1, 0.25, 0.5, 0.75, 0.9$) milled for 10 h (Fig. 1a) and 20 h (Fig. 1b). For the phase identification, Rietveld refinement was performed by using the commercial software Match!3 in combination with FullProf Suite. The details of the identified phases are presented in *Appendix A*. Figure 2 presents the refinement (calculated pattern vs the experimental) for the sample Mg(Ni_{0.5}Mn_{0.5})₂ milled for 20h. The phase abundance identified from the refinement analysis is available on Table 2 for all the synthesised samples.

Fig. 1. X-ray diffraction patterns of the starting elemental powder mixtures milled for 10 h (Fig. 1a) and the mixtures milled for 20 h (Fig. 1b)

Table 2. Phase abundance for all the synthesised samples as identified from the Rietveld refinement analysis.

It is observed that all the synthesised alloys exhibit several diffraction peaks for phases corresponding to Mg_2Ni , $MgNi_2$, MgO , $MnNi$, Mg , Mn and MnO . The $MgNi_2$ phase is intensively represented for the samples with low amount of Mn ($x=0.1, 0.25$) but for larger amounts ($x=0.5, 0.75$) the abundance is lower and when the amount of Mn reaches $x=0.9$ the phase disappears. On the other hand, the Mg_2Ni phase exists in all compositions; this behaviour shows that the substitution of Mn over Ni tends to inhibit the formation of the $MgNi_2$ phase and this is justified from the atom ratio changes between Mg and Ni [29]. Since Mg is soft and easy to adhere to the walls of the vials and the stainless-steel milling balls, during the high energy mechanical alloying the real amount of Ni is higher than 33 at.% for low Mn content which

corresponds to the $[Mg_2Ni+MgNi_2]$ region in the Mg-Ni phase diagram [35]. In such case, for low amounts of Mn, the Mg_2Ni and $MgNi_2$ phases coexist. For larger quantities of Mn, the real Ni content drops below 33 at.% which now belongs to the $[Mg_2Ni+Mg]$ region of the phase diagram and as a result the amount of the $MgNi_2$ phase decreases and gradually disappears

Fig. 2. Rietveld refinement for the phase identification for the sample $Mg(Ni_{0.5}Mn_{0.5})_2$ milled for 20 h.

For hydrogen storage applications, it is very important to note that the $MgNi_2$ phase does not react with hydrogen; and subsequently does not store/release hydrogen in contrast to the Mg_2Ni phase, which theoretically can store hydrogen up to 3.6 wt.% [36]. Thus, the substitution of Mn over Ni tends to improve the hydrogen storage properties of the alloys. Furthermore, from Fig. 1a and 1b, it is extracted that the peaks corresponding to the Mn phase exist in all cases (the main peak is in the region of $2\theta\sim 43^\circ$) and as the amount of Mn increases, the peak intensity increases as well. This is possibly related to the electronegativity differences of the elements Mg (1.31) < Mn (1.55) < Ni (1.91). Due to the larger difference between Mg and Ni, compared to the difference between Mg and Mn, the formation of the bonding between Mg and Ni is promoted and as a result, it is difficult for Mn to substitute the site of Ni in the Mg_2Ni lattice.

Fig. 3 presents the X-ray diffraction patterns for the sample $Mg(Ni_{0.75}Mn_{0.25})_2$ milled for 10 h (down) and 20 h (up). No significant change on the intensities of the diffraction peaks was observed for Mg and Mn phases. An increase in the intensity of the peaks and width decrease for the Ni phase was observed at 44.24° (10 h)- 44.66° (20 h), 51.56° (10 h) - 52.17° (20 h) and 76.21° (10 h) - 76.68° (20 h) indicating an increase on the crystallite size and/or the accumulation of microstrains during the alloying process. It was also observed that for all the samples, Mn showed high intensity peaks, which is explained from the poor solubility of Mn to the Mg_2Ni phase.

Fig. 3. X-ray diffraction patterns for the sample $Mg(Ni_{0.75}Mn_{0.25})_2$ milled for 10 h (down) and 20 h (up).

Fig. 4 presents the evolution of the crystallite size and microstrains for all the prepared samples milled for 10 h. Initially, when substituting Mn over Ni at low quantities (from $x=0.1$ to $x=0.25$) the average crystallite size decreases from 17.65 nm to 15.99 nm. By further increasing the amount of Mn over Ni, the average crystallite size increase to 23.53 nm ($x=0.5$), 25.52 nm ($x=0.75$) and 28.72 nm ($x=0.9$), with the minimum size obtained for $x=0.25$. The microstrain decreases on a monotonically-based manner from 1.35% to 1.06%.

Fig. 4. Evolution of the average crystallite size and macrostrain for the sample $Mg(Ni_{1-x}Mn_x)_2$ milled for 10 h for all the substitutions of Mn for Ni.

Mn is brittle and hard, whereas Mg and Ni are ductile and malleable. When the amount of the substituted Mn over Ni increases, the alloy becomes harder and more brittle. This phenomenon can cause collisions that are more intensive during the milling process and a corresponding formation of fracture crystal grains. Thus, the average crystal size decreases initially as presented in Fig. 4. The decrease of the crystallite size lead to the increase of the grain boundaries. As a result, the defects migrate out of the crystallites and promote the microstrain release. When the amount of the substituted Mn increases more than $x=0.25$, the resulting temperature from the intense collisions begins to dominate. The growth of crystal grains is then promoted and lattice strain release, which can potentially explain the increase of the crystallite size and the further reduction of the microstrain.

Fig. 5 presents the SEM micrographs for the sample $Mg(Ni_{0.5}Mn_{0.5})_2$ milled for 10 h (Fig. 5a) and 20 h (Fig. 5b). The particles (in fact, clusters of smaller particles agglomerated) are flaky and present inhomogeneous size distribution. The agglomeration possibly arises from the substantial amounts of energy that is transferred to the powder during the milling process. From the micrographs, it is extracted that the increase of the milling time over 10 h does not significantly decrease the particle size of the synthesized materials. This phenomenon indicates that a steady equilibrium between fracturing (tend to decrease the particle size) and welding (tend to increase the particle size) is attended.

Fig. 5. SEM micrographs of the sample $Mg(Ni_{0.5}Mn_{0.5})_2$ milled for 10 h (5a) and 20 h (5b).

Fig. 6 shows the X-ray diffraction patterns for the sample $\text{Mg}(\text{Ni}_{0.25}\text{Mn}_{0.75})_2$ milled for 10 h, before (down) and after (up) the hydrogenation process. After the hydrogenation, the formation of a new phase observed. The new phase is the monoclinic Mg_2NiH_4 ($I 1c1$) which stores hydrogen up to 3.6 wt% at more moderate temperature and pressures compared to MgH_2 . The main peaks of that phase were observed at $2\theta=36.36^\circ - 36.66^\circ - 38.16^\circ - 39.48^\circ - 40.02^\circ - 40.96^\circ$ and 42.20° .

Fig. 6. Comparison of the XRD of the sample $\text{Mg}(\text{Ni}_{0.25}\text{Mn}_{0.75})_2$ milled for 10 h before and after the hydrogenation process. The lower spectrum corresponds to the sample as milled, before the hydrogenation and the upper spectrum represents the sample after the hydrogenation process.

Fig. 7 illustrates the SEM micrographs for the sample $\text{Mg}(\text{Ni}_{0.25}\text{Mn}_{0.75})_2$ milled for 10 h, before (7a) and after (7b) the hydrogenation process. The presence of the new Mg_2NiH_4 phase is also present in the micrographs.

Fig. 7. SEM micrographs of the sample $\text{Mg}(\text{Ni}_{0.25}\text{Mn}_{0.75})_2$ milled for 10 h (a) and after the hydrogenation process (b)

Finally, Table 3 presents the lattice parameters for the obtained crystal phases for all the synthesized samples as extracted from the Rietveld refinement process.

Table 3. Lattice parameters for the obtained phases for all the synthesized samples as identified from the Rietveld refinement analysis.

3.2. Activation Process for the Synthesized Samples

The activation process used for all the synthesized samples consisted of several cycles of hydrogen uptake at an elevated temperature (300 °C) under hydrogen pressure of 20 bar, followed by a hydrogen release process at the same temperature under 0.5 bar. Table 4 summarizes the uptake/release capacities during the activation and the duration of an activation cycle for all the synthesized samples. The samples with the lowest amount of Mn, $\text{Mg}(\text{Ni}_{0.9}\text{Mn}_{0.1})_2$ milled both for 10h and 20h store the minimum amount of hydrogen (0.25 wt%) after leaving the samples at 20 bar for 20h. The samples could release the stored hydrogen in 60 min. As the Mn content increases the samples can store larger amounts of hydrogen; the sample

Mg(Ni_{0.75}Mn_{0.25})₂ milled for 10h could store 0.5 wt% after 20 h and release the same amount of hydrogen after the first minute of the dehydrogenation process. When the amount of Mn increases more ($x=0.5$) the sample milled for 10 h could store 1 wt% after 2 h and the release time was less than 0.5 min. The sample milled for 20h showed a storage capacity of 0.8 wt% after 5h and a release time of 1 min. The sample Mg(Ni_{0.25}Mn_{0.75})₂ milled for 10 h showed a capacity of 1.1 wt% after leaving under 20 bar for 5 h and a release time of 2.5 min, while the sample milled for 20 h showed 1.25 wt% at the end of 2.5 h and release time 3 min. Finally, for the highest amount of Mn in the stoichiometry ($x=0.9$) milled for 10 h, the amount of hydrogen stored was 0.95 wt% after 5 h of hydrogenation. The dehydrogenation process was fast and able to release the amount of hydrogen stored at the first minute. Similar behavior observed with the sample milled for 20 h, with a slightly less amount of hydrogen stored (0.85 wt%).

Table 4. Hydrogen sorption characteristics and the duration for an activation cycle of the synthesized samples for both the hydrogenation and dehydrogenation process

3.3. Hydrogenation and Dehydrogenation Characteristics

The hydrogenation kinetic curves for the synthesized intermetallics are presented in Fig. 8a (for 10 h milling) and Fig. 8b (for 20 h milling). The temperature during the hydrogenation process was 300 °C under 20 bar. As extracted, for both milling times, the sample with Mn content of $x=0.1$ (lower amount of Mn) stores a negligible amount of hydrogen after 30 min. When the amount of the substituted Mn increases ($x=0.25$) the storage ability of the sample milled for 10 h increases (stores up to 0.4 wt% in the first five min.). On the contrary, the sample milled for 20 h with the same stoichiometry, presents a significantly lower storage capacity (less than 0.1 wt%). A possible explanation for this behavior is the high abundancy of the MgNi₂ phase in the sample milled for 20 h; in combination with the fact that the MgO phase is also present in large quantities, leading to the creation of oxide layers in the surface of the powder blocking the hydrogen diffusion towards the metallic lattice.

By increasing the amount of the substituted Mn ($x=0.5$ and $x=0.75$) the hydrogenation capacity increases for both cases of milling time (10 and 20 h). Further

addition of Mn (higher than $x=0.75$) leads to a decrease on the amount of hydrogen that can be stored in the samples for both milling times. The positive impact of the Mn substitution over Ni at the $\text{Mg}(\text{Ni}_{1-x}\text{Mn}_x)_2$ samples is attributed with the fact that the unit cell volume increases and refines the grains. An increase in the cell volume is beneficial to the hydrogenation capacity [37]. At the same time, as the amount of Mn increases, the formation of the MnNi and Mg phases is promoted. This is confirmed from the XRD analysis, as presented in Table 2. The formation of those two phases eliminate the presence of the Mg_2Ni phase; thus, when the amount of Mn over Ni reaches a limit (in such materials substitution over $x=0.75$) will cause a decrease on the hydrogenation/dehydrogenation capacity of the samples.

During the hydrogenation process, the main phase Mg_2Ni transforms into the hydride phase as explained from the microstructural analysis. It is important to note that between 245 °C and 210 °C the hydride $\text{Mg}_2\text{Ni-H}$ phase transforms from a high-temperature cubic structure to a low temperature monoclinic phase [38]. When hydrogen is absorbed by the Mg_2Ni phase beyond 0.3 H per formula unit, the system undergoes a structural rearrangement to the stoichiometric complex $\text{Mg}_2\text{Ni-H}$ hydride with a 32% increase in the volume.

Fig. 8. Hydrogenation kinetic curves for the samples synthesised for 10 h (8a) and 20h (8b). The measurements took place at 300 °C under hydrogen pressure of 20 bar.

3.4 Temperature Effect on the Hydrogenation and Dehydrogenation Process

The temperature effect on the hydrogenation and dehydrogenation studied for all the synthesized samples. Isothermal curves for the hydrogenation and dehydrogenation recorded at various temperatures (200 °C – 250 °C and 300 °C). Fig. 9 presents the isothermal curves for the sample $\text{Mg}(\text{Ni}_{0.5}\text{Mn}_{0.5})_2$ milled for 10 h (Fig. 9a) and 20 h (Fig. 9b) respectively. For both cases, an almost flat plateau appears at all isotherms. The plateau slope is one of the main factors that affect the process of solid-state hydrogen storage. It arises from compositional fluctuations due to the presence of impurities or due to the fluctuations of the stoichiometry AB_{n+x} [39]. In addition, the plateau slope can also result from the different the lattice expansions at various equilibrium pressures and the relaxation of residual forces to relieve the stress in the metal matrix [40]. As a result, the real stoichiometry of the samples does not present any fluctuations. In addition, the width of the plateau region, where the co-existence

of the α - and β - phase of the hydride takes places, determines the amount of hydrogen that can be reversibly stored within the hydride. Thus, the synthesised intermetallics can store more than 95% of the amount of hydrogen on a reversible manner. The different operation temperatures affect in a negligible way the hydrogenation capacity but at the same time, the plateau pressure increases with the temperature increase. For the isotherm curve recorded at 300 °C the plateau pressure is 6.8 bar for the sample milled for 10 h, whereas for the sample milled for 20 h is 7.1 bar.

Fig. 9. Isothermal curves for the sample $Mg(Ni_{0.5}Mn_{0.5})_2$ milled for 10 h (9a) and 20 h (9b). The isotherms were obtained at 200 °C – 250 °C and 300 °C

Fig. 10 presents the dehydrogenation behavior for the sample $Mg(Ni_{0.5}Mn_{0.5})_2$ milled for 10 h (Fig. 10a) and for 20 h (Fig. 10b). The dehydrogenation behavior recorded also at the same temperatures as the hydrogenation (200 °C – 250 °C and 300 °C) at a pressure of 0.5 bar. During the dehydrogenation at 300 °C, for both samples (milled for 10 and 20 h), the hydrogen release is very fast, and the samples can release the stored hydrogen during the first minute of the process. The release process at a lower temperature (250 °C) is slower and the full discharge of the sample takes place after 8 min (10 h milling) and 5 min (20 h milling). When the dehydrogenation temperature drops to 200 °C, the hydrogen release is very slow and practically no hydrogen is desorbed from the hydride. This phenomenon is explained from the endothermic nature of the dehydrogenation process, where large amounts of heat are necessary to recover the stored hydrogen.

Fig. 10. Temperature effect on the dehydrogenation process for the sample $Mg(Ni_{0.5}Mn_{0.5})_2$ milled for 10 h (10a) and 20 h (10b). The dehydrogenation process obtained at 200 °C – 250 °C and 300 °C.

4. Conclusions

Hydrogen storage materials based on the stoichiometry $Mg(Ni_{1-x}Mn_x)_2$ have been synthesised by High Energy Ball Milling and studied as potential materials for solid-state hydrogen storage. X-ray diffraction analysis applied in combination with Rietveld refinement for the phase identification; the microstructure of the synthesised samples studied with Scanning Electron Microscopy (SEM). The effect of the substitution of Mn over Ni investigated. It has been found that when the content of

Mn is low, the Mg_2Ni and MgNi_2 phases co-exist; when the amount of Mn increases, the abundance of the MgNi_2 phase decreases. For a content of Mn higher than 0.75, the MgNi_2 phase disappears. On the contrary, the Mg_2Ni phase is present in all stoichiometries, indicating that the substitution of Mn over Ni eliminates the MgNi_2 phase. The average crystallite size for Mn content $x=0.1$ was calculated 17.65 nm; When the amount of Mn increases ($x=0.25$) the crystallite size decreases to 15.99 nm. Further increase in the Mn content results in the increase of the crystallite size, while the microstrain decreases almost monotonically. The hydrogenation/dehydrogenation capacity increases with the increase of Mn as the MgNi_2 phase is eliminated. When the Mn content reaches and exceeds $x=0.75$, the capacity drops due to the formation of the MnNi phase. The time for hydrogen release at 300°C was at some cases less than 1 min, but on the other hand no hydrogen release observed at 200°C .

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Appendix A.

Details of the identified phases

Phase	Entry System	Space Group	Crystal System	Unit Cell	Calculated Density
Mn-a	96-901-1069	I – 43m	Cubic	$\alpha=8.9121 \text{ \AA}$	7.474 g/cm ³
Mg₂Ni	96-100-8172	P 62 22	Hexagonal	$\alpha=5.2050 \text{ \AA}$ $c=13.2360 \text{ \AA}$	3.442 g/cm ³
Ni	96-210-0662	F m -3 m	Cubic	$\alpha=3.5210 \text{ \AA}$	8.929 g/cm ³
MnO	96-900-6661	F m -3 m	Cubic	$\alpha=4.4397 \text{ \AA}$	5.384 g/cm ³
MgNi₂	96-210-6101	P 63/m m c	Hexagonal	$\alpha=4.8240 \text{ \AA}$ $c=15.8260 \text{ \AA}$	5.900 g/cm ³
MgO	96-900-6484	F m -3 m	Cubic	$\alpha=4.4453 \text{ \AA}$	3.048g/cm ³
Mg	96-901-3059	P 63/m m c	Hexagonal	$\alpha=3.2147 \text{ \AA}$ $c=5.2203 \text{ \AA}$	1.727 g/cm ³
MnNi	96-152-3338	I 4/m mm	Tetragonal	$\alpha=2.6390 \text{ \AA}$ $c=3.5200 \text{ \AA}$	7.695 g/cm ³
Mg₂NiH₄	96-153-0510	I 1c1	Monoclinic	$\alpha=13.2012 \text{ \AA}$ $b=6.4067 \text{ \AA}$ $c=6.4913 \text{ \AA}$ $\beta=93.21^\circ$	2.600 g/cm ³

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