Hydrogen storage measurements in novel Mg-based nanostructures produced via rapid solidification and devitrification

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Abstract
Nanostructured materials for hydrogen storage with a composition of Mg$_{85}$Ni$_{15-x}$M$_x$ (M=Y or La, x=0 or 5) are formed by devitrification of amorphous and amorphous-nanocrystalline precursors produced by melt-spinning. All three compositions exhibit a maximum storage capacity of about 5 mass % H at 573 K. When ball-milled for 30 min in hexanes, the binary alloy can be activated (first-cycle hydrogen absorption) at 473 K. Desorption in this sample begins at 525 K, compared to 560 K when the material is activated at 573 K. The decrease in desorption temperature is attributed to a decrease in hydride crystallite size, and is consistent with thermodynamic calculations. Additions of Y and La improve the degradation in storage capacity observed during cycling of the binary alloy by slowing microstructural coarsening. Alloying with La also shows a slight improvement in the thermodynamics of hydride formation and decomposition. The improved thermodynamics are discussed in terms of destabilization of the hydrides relative to new equilibrium phases introduced by alloying additions.
1. Introduction

Mg-based alloys are of great interest in the area of hydrogen storage because of their high gravimetric capacity, low density, and low cost [1-3]. However, they suffer from significant kinetic and thermodynamic drawbacks. Firstly, Mg readily oxidizes forming a diffusion barrier for H reaching the metallic Mg, significantly reducing the kinetics of the hydriding reaction [4]. Once activated, diffusion of H through MgH$_2$ phase is also very sluggish. As a result the H-absorption rate becomes virtually zero once the hydride layer forming on the surface of the Mg particle grows to a thickness of several tens of nanometers [5]. Also affecting the kinetics of hydrogenation is the slow rate of H$_2$ dissociation into atomic H on the Mg surface [2].

The thermodynamic stability of the MgH$_2$ phase is the most significant problem hindering the use of Mg in practical H-storage applications. For the equilibrium reaction MgH$_2$ $\leftrightarrow$ Mg + H$_2$, the enthalpy of formation, $\Delta H_o$, of MgH$_2$ is $\approx$ 76 kJ/mol. This results in decomposition temperatures, $T_d$, of $\approx$ 550 K required for desorption of H$_2$ at atmospheric pressure; too high for on-board vehicular applications [1-2]. For practical vehicular hydrogen storage applications, a hydride material should possess a $\Delta H_o$ of between 20 kJ/mol and 50 kJ/mol, and should be able to release H$_2$ at or below 373 K near atmospheric pressure [1-3].

Much research attention has been focused on alleviating the above problems with the Mg-MgH$_2$ system. In terms of kinetics, Mg-materials are often activated by exposure to high H$_2$ pressures and temperatures of 573 K or greater to remove the surface oxide layer prior to hydrogenation. Additions catalyst materials, such as a surface layer of Pd, or particles of a transition-metal oxide added to a powder, also improve the rate of H-absorption [8]. Ball milling (BM) and mechanical alloying (MA) are two of the most well studied methods for improving the H-storage properties of Mg alloys [1,3]. By BM or MA for several tens to hundreds of hours, a
material is broken down into nanoscale particles. Because of the small dimensions and high surface area to volume ratio of the nanostructured powder, the diffusion distance for H atoms traveling through the hydride is significantly reduced, improving the absorption kinetics by 10 times or greater [9]. Additionally, BM can, in theory, improve the thermodynamics of the hydriding and dehydriding reactions by introducing capillarity effects if particle/grain size is reduced to a small enough size. This critical size, calculated to be on the order of 5 nm in particle radius to reduce $\Delta H_0$ by about 10 % for pure Mg, has not yet been achieved experimentally [3].

Attempts have been made to thermodynamically destabilize the hydride relative to the non-hydride phase via alloying. When Si is mixed with MgH$_2$, decomposition of the hydride results in the formation of H$_2$ gas and the intermetallic phase Mg$_2$Si, instead of metallic Mg. The introduction of this intermediate phase reduces the enthalpy of the decomposition reaction by 40 kJ/mol [6]. Unfortunately, the reaction is not reversible. Additions of Ni promote the formation of an Mg$_2$Ni intermetallic phase and a new hydride, Mg$_2$NiH$_4$, creating the new hydriding reaction $\text{Mg}_2\text{NiH}_4 \leftrightarrow \text{Mg}_2\text{Ni} + 2\text{H}_2$. The thermodynamics of this reaction are improved, with a reduced $\Delta H_0$ of -65 kJ/mol [7]. However, this hydride is still too stable, requiring a temperature of around 523 K to release the H$_2$.

Despite the improvement in H-storage properties in Mg-based materials, their use in practical applications is still hindered by thermodynamic and kinetic limitations. BM and MA, although advantageous, are limited in commercial application due to long required milling times and batch processing [3]. Because of these limitations, it is advantageous to explore alternative methods for producing nanocrystalline materials for hydrogen storage. Interestingly, Mg-based metallic glasses, studied for structural applications, have similar compositions to alloys being
researched for H-storage. By careful selection of alloying elements and processing conditions, Fe-based metallic glasses have been used to create nanocrystalline ferromagnetic alloys with properties superior to those of traditional materials [10]. This raises the question: “Can Mg-based metallic glasses be used as a precursor for creating a nanocrystalline H-storage material?” Research into the H-storage behavior of amorphous Mg-based materials to date shows sluggish absorption kinetics and low capacities [11-14]. Furthermore, very few studies have looked directly at controlling the devitrification process of the glassy phase to create a nanostructured material [15,16]. Only recently has the idea of controlled crystallization of an amorphous metal alloy been suggested as a means of creating nanostructures in other materials [17].

This work focuses on utilizing a similar method to control the crystallization of Mg-based metallic glass precursors to create a nanocrystalline structure; and characterization of the H-storage properties of the resulting materials. The alloy $\text{Mg}_{85}\text{Ni}_{15-x}\text{M}_x$ ($\text{M}=$Y or La, $x=0$ or 5) has been chosen as a base system. Y and La are added as alloying elements to stabilize the glassy phase, and preserve a more refined nanocrystalline structure by slowing crystallization and microstructural coarsening kinetics at elevated temperatures.

2. Experimental procedure

Ingots with a mass of 50 g and nominal compositions of (in mol %) $\text{Mg}_{85}\text{Ni}_{15-x}\text{M}_x$ ($\text{M}=$Y or La, $x=0$ or 5), denoted hereafter as binary ($x=0$), Y5, and La5, were prepared using 99.9 % pure Mg, Ni, and Y, and 98 % pure La. To accommodate for the loss of Mg vapor during melting, as determined by compositional analysis of initial melting attempts, an additional 10 mass % Mg was added to each ingot. The samples were induction melted in an Ar atmosphere and cast into a cooled Cu mold. The composition of each ingot was determined using energy
dispersive X-ray spectroscopy (EDS), and found to be within 1 mol % of the target composition. The surface of each of the as-cast ingots was removed to reduce contamination. The ingots were then cut into pieces for melt spinning (MS). MS was performed under a He environment by ejecting a small amount (1 g to 2 g) of melted alloy onto a 20 cm diameter Cu wheel rotating at a rate of 3000 RPM. The resulting ribbons were 2 mm to 3 mm wide, tens of centimeters in length, and 10 µm to 30 µm in thickness.

Each alloy ribbon was prepared for H-storage measurements via BM, using a ball to powder mass ratio of 20:1, for 30 min in a hexanes medium, providing fresh unoxidized surfaces. Following a method previously reported to prevent oxidation during the processing of Mg-based alloys, hexanes was used as a milling medium [18]. Six 6.4 mm diameter steel balls with a combined mass of 6.2 g and 310 mg of ribbon were used. The powder was recovered from the hexanes and allowed to dry in air. To quantify any contamination from the BM process, the loss in mass of the steel balls during the BM process was monitored. Mass loss was found to be <0.05 %; so, contamination of the powder was considered negligible.

50 mg to 60 mg samples were used for H-storage experiments. The measurements were performed using a Sieverts-type apparatus. The pressure resolution of the device was 10 Pa or 70 Pa, depending on which gauge was used. A resolution of 70 Pa corresponds to a resolution of <0.001 mmol H₂, or <0.005 mass % H. Absorption measurements were carried out under a H₂ pressure of 2 MPa at temperatures between 473 K and 573 K. Desorption kinetics were measured at a pressure of < 1 kPa. The activation cycle, considered the first hydriding cycle, was carried out at 473 K or 573 K. To ensure complete activation of the entire sample, hydriding kinetics were measured using the third absorption/desorption cycle. Pressure-composition isotherms (PCI) were performed at temperatures between 473 K and 673 K. During PCI
measurements, the system was allowed to equilibrate at each pressure for a length of time chosen based on the observed kinetics for each alloy at the isothermal temperature of interest.

Crystallization experiments were performed on the MS ribbons by heating the samples using a differential scanning calorimeter (DSC) to temperatures of 473 K, 573 K, and 673 K under flowing Ar gas. DSC was also utilized to measure $T_d$ for the hydried samples. Structural characterization was performed using X-ray diffraction (XRD). For the calculation of crystallite size using XRD, an alumina standard was used to determine the extent of instrument peak broadening as a function of diffraction angle.

The thermodynamic data used in understanding the hydriding characteristics of the alloys were compiled from a variety of sources. The Mg-Ni-H ternary system has been assessed by Zeng et al. [19]. The Mg-La assessment of Guo and Du was used [20]. The ternary Mg-Ni-Y system has recently been assessed by Mezbahul-Islam and Medraj [21]. Data for the Y-H hydrides are available in the SSUB3 database of the ThermoCalc software [22]. Palumbo et al. have recently performed an assessment of ternary La-Ni-H [23]; however, the stability of the ternary hydride $\text{LaNi}_5\text{H}_x$ ($x=0$ to 7) relative to $\text{LaH}_3$ and face-centered cubic (FCC) Ni is inconsistent with experimental observation. They suggest that $\Delta H_o$ should be approximately 4 kJ/mol lower than the experimentally determined values. Because the stability of the phases relative to each other is of more importance than $\Delta H_o$ in the present work, an additional 4 kJ/mol is added to the calculated free energy of $\text{LaNi}_5\text{H}_x$. 
3. Results and discussion

3.1. Structure of as-spun and annealed ribbons

Figure 1 shows the XRD patterns for the Mg$_{85}$Ni$_{15}$K$_x$ ribbons in the as-spun condition, as well as after being heated to 473 K, 573 K, and 673 K in the DSC. As-spun, the binary and La$_5$ samples are X-ray amorphous, while the Y$_5$ alloy contains a small amount of hexagonal close packing (HCP) phase that has been quenched-in during melt spinning. When annealed to 473 K, the binary alloy, Figure 1a, first crystallizes into the metastable intermetallic phase Mg$_6$Ni. This phase has previously been reported as a crystallization product of binary Mg-Ni glasses and ternary alloys containing Y [11,12]. Upon further heating, this phase begins to decompose. When heated to 673 K, the microstructure contains the expected equilibrium phases of HCP Mg and Mg$_2$Ni intermetallic.

The first phase to form in the Y$_5$ material is HCP, seen in Figure 1b. HCP may be the first crystallization product in this composition because of the small amount present in the as-spun ribbon. At 573 K, peaks corresponding to Mg$_6$Ni are visible, as previously reported [11,12]. Upon further heating to 673 K, the Mg$_6$Ni peaks disappear, and HCP Mg and Mg$_2$Ni form. Only one small peak corresponding to Mg$_{24}$Y$_5$ is seen, indicating there may be some solubility of Y in HCP Mg or Mg$_2$Ni.

Looking at Figure 1c, the first crystallization process undergone by the La$_5$ ribbons at 473 K is the formation of either Mg$_{12}$La or Mg$_{17}$La$_2$. Upon further heating to 573 K and above, HCP Mg and Mg$_2$Ni also appear. There is some confusion as to whether Mg$_{12}$La or Mg$_{17}$La$_2$ is the true crystallization product because they are difficult to distinguish from X-ray data. In similar metallic glasses containing La, Mg$_{17}$La$_2$ is reported as the first phase to form from the glass [11]; while in alloys containing Nd, Mg$_{12}$Nd is the reported devitrification product [15].
Both phases are present in the equilibrium Mg-La phase diagram [24]. However, a search of the ICDD powder diffraction database reveals there is no powder diffraction file for Mg\textsubscript{12}La [25]. The expected crystallization product is Mg\textsubscript{12}La, considering the Mg to La proportions, 0.65 mol Mg to 0.05 mol La (assuming 0.2 mol Mg are used in the formation of Mg\textsubscript{2}Ni). It is likely that Mg\textsubscript{17}La\textsubscript{2} has been reported in previous studies out of convenience; i.e. Mg\textsubscript{12}La was ignored due to the lack of available data. The X-ray peaks for both Mg\textsubscript{17}La\textsubscript{2} and Mg\textsubscript{12}Pr (isomorphic with Mg\textsubscript{12}La, but a slightly different lattice parameter) are shown in Figure 1c. Because Mg\textsubscript{12}La is predicted by the phase diagram, it is used in the thermodynamics calculations for the La5 alloy.

Shown in Table 1 are the average crystallite sizes of the ribbons after being heat treated in the DSC, determined by the peak broadening of the XRD patterns. As expected, increasing temperature results in a larger average crystallite size. Crystallite size increases most dramatically in the binary material. This suggests the nanocrystalline structure formed by devitrification of the glass is destroyed at 573 K, the required temperature for reversible H-storage in Mg-based materials. Y and La additions, on the other hand, hinder microstructural coarsening, and improve the stability of the nanostructure, as evidenced by the smaller average crystallite sizes in the heat treated samples.

DSC scans of the as-spun ribbons (not shown here) indicate that all three compositions crystallize at temperatures between 436 K and 445 K. The binary exhibits a single primary crystallization peak beginning at 436 K. The onset of crystallization in La5 occurs at 445 K. A second, smaller peak is observed at 470 K. Multiple overlapping peaks are seen in the DSC experiment for the Y5 alloy, with an onset of 438 K. The onset temperatures of crystallization are summarized in Table 1. From these data and the XRD scans in Figure 1, the devitrification pathways for each material can be described. The binary glass devitrifies into a single phase
Mg₆Ni microstructure. La5 devitrifies first by the formation of Mg₁₂La, with HCP and Mg₂Ni crystallizing shortly after. Y5 crystallization consists of the formation of multiple phases, with both HCP and Mg₆Ni forming at nearly the same time or temperature. The DSC scans of the binary and Y5 samples also exhibit another broad peak between 523 K and 573 K that corresponds to the decomposition of Mg₆Ni into HCP and Mg₂Ni.

3.2. Hydriding kinetics

The first hydrogenation cycles, or activation, of the binary alloy at 473 K and 573 K, and the Y5 and La5 materials at 573 K are shown in Figure 2a. Activation of Y5 and La5 below 573 K was not possible. The binary alloy could be activated at 473 K, and absorbed H at temperatures as low as 373 K (see [26]). Both Y5 and La5 also exhibit an s-shaped hydriding curve suggesting a two-stage activation process; also observed to a lesser extent in the binary material. This two-stage activation behavior has not been reported previously in BM materials with similar compositions. It is likely a result of the devitrification process of the metallic glass precursor. Because crystallization is slower in the Y5 and La5 materials, it is more pronounced in these samples than in the binary one.

Once fully activated, the absorption process becomes quite rapid at 573 K for all three materials, as demonstrated in Figure 2b by the absorption curves for the third cycle of each of the three materials at 573 K. The third absorption cycle was used to ensure complete activation of each sample. The three alloys absorb nearly 5 mass % H in about 5 min. Desorption curves at 573 K are also similar for the three alloys, represented in Figure 2c. Desorption in the La5 material occurs in about 5 min, while it requires 10 min for full desorption in the Y5 sample. Full dehydrogenation in the binary material requires 7 min.
The maximum capacity of the three alloys varied slightly between samples of the same composition. The capacity of the binary sample decreased significantly as the number of hydriding/dehydriding cycles increased, reaching only 4.3 mass % H by the 8th cycle, as seen in Figure 2d. Capacity degradation in the Y5 and La5 materials is less severe, decreasing from a third cycle maximum of 5.4 mass % H and 5.2 mass % H, respectively, to 4.9 mass % H after 8 cycles. The improvement in cyclability can be attributed to slower coarsening kinetics and stabilized nanostructure brought on by the additions of Y and La. This is confirmed by crystallite sizes given in Table 1. Hydriding the binary material for a single cycle at 573 K results in an average crystallite size of 50 nm, compared to 44 nm and 32 nm for Y5 and La5, respectively. Cycling the material at 573 K further coarsens the microstructure. This coarsening is more dramatic in the binary alloy, resulting in an observed decrease in capacity.

Hydrogen absorption experiments at lower temperatures in the binary, Y5, and La5 materials also revealed absorption kinetics virtually indistinguishable from those at 573 K in Figure 2b, and are not presented here. Figure 3 illustrates the desorption behavior of the three compositions at temperatures between 473 K and 573 K. Desorption was not observed at 473 K in the binary and Y5 materials. All materials show good kinetic behavior at temperatures down to 523 K, with full desorption occurring in 10 min or less. La5 demonstrates desorption of H₂ is possible at a temperature as low as 473 K. Unfortunately, as will be discussed in section 3.4, the equilibrium pressure of the decomposition reaction is well below atmospheric pressure.

### 3.3. Structure of hydrided materials

Figure 4 illustrates the structural characteristics and thermal behavior of the four alloys after being hydrided. In Figure 4a, the XRD patterns for the binary, Y5, and La5 samples are
given after being hydrided at 573 K. In the binary alloy, MgH$_2$ and Mg$_2$NiH$_4$ are present, as anticipated for hydrogenation of Mg$_{85}$Ni$_{15}$. When the binary alloy is hydrided at 573 K, decomposition of the hydrides begins at 560 K, as expected for MgH$_2$, shown in the DSC scan in Figure 4b. When hydrided at a temperature of 473 K, the DSC scan indicates that now decomposition begins around 525 K. This reduced temperature is evidence of the destabilization of the hydride phases by capillarity effects. Thermodynamic calculations agree with this observation, predicting a decrease of about 35 K in the decomposition temperature for MgH$_2$ when crystallite size reaches 38 nm [26]. This corresponds to a decrease in $\Delta H_o$ by about 5 kJ/mol.

When 5 mol % Y and La are added to the alloy, YH$_2$ and LaH$_3$, respectively, are found to form in the hydrided samples (Figure 4a). In the binary Y-H and La-H systems these hydrides are quite stable, requiring temperatures of 1490 K and 1199 K, respectively, at atmospheric pressure for decomposition into Y or La and H$_2$ gas. From the DSC scan in Figure 4c, hydride decomposition begins at 620 K for Y5. In the case of the La5 alloy, decomposition begins at 470 K, well below the decomposition temperature of LaH$_3$, and also below that expected for MgH$_2$ or Mg$_2$NiH$_4$. After heating the La5 sample to 540 K in the DSC, just above the end of the peak, no LaH$_3$ is present in the XRD pattern. Instead, LaNi$_5$H$_x$ and possibly HCP Mg or Mg$_2$Ni are now observed in the XRD pattern. This indicates that LaH$_3$ decomposition is, at least in part, responsible for the heat released at 470 K.
3.4. Thermodynamics

3.4.1. PCI measurements

PCI measurements are plotted in Figure 5 for the three alloys at various temperatures between 473 K and 623 K. Two distinct plateaus are visible in each measurement. The first, at lower pressures, corresponds to the formation and dissociation of MgH₂; while the higher pressure one belongs to Mg₂NiH₄. At 573 K, the plateau pressure of the Mg+H₂↔MgH₂ reaction is slightly above atmospheric pressure in the three materials, about 140 kPa, very near the equilibrium pressure of 160 kPa of pure Mg-MgH₂. As expected, the pressures of both plateaus are proportional to temperature; increasing (decreasing) as temperature is increased (decreased). For the binary and La5 alloys, shown in Figure 5a and c, respectively, the first plateau pressure rapidly decreases to well below atmospheric pressure when temperature is decreased below 573 K. For instance, at 523 K, the Mg+H₂↔MgH₂ plateaus in the binary and La5 samples occur at 25 kPa and 39 kPa, respectively. These plateaus confirm, as mentioned above, that although reversible H-storage is possible at 473 K in the La5 material, the required pressures are too low for practical applications. There is a small increase in plateau pressure with La additions compared to the binary, however, suggesting some improvement in the thermodynamics of the reaction; i.e. the hydrides have been destabilized relative to the non-hydride phases.

From the variation of the equilibrium plateau pressure, \(P_{eq}\), with temperature, the enthalpy, \(\Delta H_o\), and entropy, \(\Delta S_o\), of formation for MgH₂ and Mg₂NiH₄ can be calculated from the van't Hoff relationship, given by the equation

\[
\ln \left( \frac{P_{eq}}{P_o} \right) = \frac{\Delta H_o}{RT} - \frac{\Delta S_o}{R}
\]  

(1)
where $R$ is the ideal gas constant and $P_o$ is one atmosphere, or 100 kPa. Figure 6 plots Eq. (1) for the binary, Y5, and La5 alloys. The calculated $\Delta H_o$ and $\Delta S_o$ values are summarized in Table 2, along with values for pure MgH$_2$ and Mg$_2$NiH$_4$ [19]. The values for the binary and Y5 materials are in agreement with those for pure MgH$_2$ and Mg$_2$NiH$_4$. When La is added to the alloy the magnitudes $\Delta H_o$ and $\Delta S_o$ are reduced for both MgH$_2$ and Mg$_2$NiH$_4$. This suggests, as stated before, that the hydride phases have been destabilized relative to the dehydrided ones.

3.4.2. Destabilization by rare-earth additions

The hydriding/dehydriding behaviors of the Y5 and La5 alloys are difficult to understand because of the multiple intermetallic phases Y and La formed with Mg and Ni, including possible ternary intermetallics [21,27]. The Mg- and Ni-rich phases Mg$_{24}$Y$_5$ or Ni$_{17}$Y$_2$ in the Y5 material and Mg$_{12}$La or LaNi$_5$ are the most likely binary phases to form in alloys of these compositions.

If ternary intermetallic compounds are neglected, the formation of Mg$_{24}$Y$_5$ or Mg$_{17}$La from YH$_2$ and LaH$_3$ and MgH$_2$ or Mg$_2$NiH$_4$ can occur by the reactions

$$24\text{MgH}_2 + 5\text{YH}_2 \leftrightarrow \text{Mg}_{24}\text{Y}_5 + 29\text{H}_2 \quad (2a)$$

$$12\text{MgH}_2 + \text{LaH}_3 \leftrightarrow \text{Mg}_{12}\text{La} + 13.5\text{H}_2 \quad (2b)$$

for the formation of Mg intermetallics, and

$$17\text{Mg}_2\text{NiH}_4 + 2\text{YH}_2 \leftrightarrow \text{Ni}_{17}\text{Y}_2 + 34\text{Mg} + 36\text{H}_2 \quad (3a)$$

$$5\text{Mg}_2\text{NiH}_4 + \text{LaH}_3 \leftrightarrow \text{LaNi}_5 + 10\text{Mg} + 11.5\text{H}_2 \quad (3b)$$

when Ni intermetallics are formed. Equilibriums in Eqs. (2a) and (2b) occur at 683 K and 589 K, respectively. Both of these temperatures are above the decomposition temperature of
MgH₂, however, and the formation of Mg₂₄Y₅ and Mg₁₂La must occur in equilibrium with Mg + H₂. These equilibria occur at 1259 K and 854 K for YH₂ and LaH₃, lower than the decomposition temperatures of binary YH₂ and LaH₃. The decrease in temperature represents a destabilization of the hydrides relative to the Mg intermetallic phases, compared to metallic Mg and Y (or La). However, the decrease in temperature observed experimentally is greater, particularly for the decomposition of LaH₃ at 470 K.

Destabilization of the hydrides may also be achieved by the formation of Ni₁₇Y₂ and LaNi₅ via Eqs. (3a) and (3b), or by the formation of ternary hydrides. There is no known ternary hydride containing Y and Mg or Ni. Hydrides containing Mg and La with H have been previously reported [28], but there is no evidence of their presence in the XRD results of Figure 4a. LaNi₅Hₓ (x=0 to 7), however, is a well known ternary hydride. It is not present in the hydrided La5 material because of the high pressures used in the hydrogenation experiments, where LaH₃ and Ni are more stable. When the La5 sample is heated to 540 K at atmospheric pressure, LaH₃ reacts with Mg₂NiH₄, forming LaNi₅Hₓ and Mg plus H₂ (or MgH₂).

Using the available thermodynamic data, the free energies of possible reaction products that form Ni₁₇Y₂ or LaNi₅ from Mg₂NiH₄ and YH₂ or LaH₃ are plotted as a function of temperature in Figure 7a and b. Also shown in Figure 7b is the free energy when LaNi₅Hₓ is formed. Here, x is chosen to be 3 only because it corresponds to LaNi₅H₃ absorbing the H released by LaH₃ decomposition. The actual value of x is not of significant importance.

From Figure 7a, formation of Ni₁₇Y₂ is shown to be unstable relative to the mixture of Mg₂NiH₄ and YH₂ below 650 K; even if the Mg and H released by decomposition of Mg₂NiH₄ are allowed to form MgH₂. Thus, the hydrides cannot be destabilized by the formation of Mg-Y or Ni-Y intermetallic phases. A similar conclusion can be made for the formation of
intermetallics in the La5 material as well, illustrated in Figure 7b. However, if the
decomposition of Mg$_2$NiH$_4$ and LaH$_3$ results in the formation of LaNi$_5$H$_3$ plus Mg and H$_2$, the
latter phase mixture becomes stable above a temperature of 468 K, in excellent agreement with
470 K experimentally observed to be the decomposition temperature of LaH$_3$ in the La5 alloy.
This reaction gives rise the decrease in $\Delta H_o$ calculated for MgH$_2$ in the La5 PCI experiments.

4. Conclusions

Nanocrystalline hydrogen storage materials were formed by devitrification of melt-spun
Mg-Ni-based metallic glasses. The binary Mg$_{85}$Ni$_{15}$ and ternary Mg$_{85}$Ni$_{10}$Y$_5$ and Mg$_{85}$Ni$_{10}$La$_5$
compositions possessed a maximum capacity of about 5 mass % H at 573 K, and good
absorption/desorption kinetics. When ball-milled for 30 min in a hexanes medium, it was
possible to activate the binary material at 473 K. Comparing binary samples after activation at
473 K and 573 K, average crystallite sizes were found to be 38 nm and 58 nm, respectively. The
decreased crystallite size reduced the onset of H$_2$ desorption from 560 K in the 573 K activated
sample to 525 K in the 473 K activated sample. This decrease was attributed to a destabilization
of the hydride phases through capillarity effects, and was supported by thermodynamic
calculations.

The binary alloy exhibited degradation of storage capacity with increased cycling caused
by microstructural coarsening. This was remedied by the addition of Y or La, which stabilized
the glassy phase and slowed crystallization and growth kinetics. DSC experiments also
demonstrated that by alloying with La, the thermodynamics of the hydriding reaction were
improved because of the introduction of LaNi$_5$H$_x$. This phase provided a reaction pathway for
LaH$_3$ and Mg$_2$NiH$_4$ to decompose simultaneously at a temperature of 468 K, well below the decomposition temperature of either phase alone.

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References


Table 1: Temperature of the onset of crystallization in DSC experiments and average crystallite size (diameter) of the melt-spun samples, determined from XRD peak broadening, after heating to 473 K, 573 K, and 673 K in the DSC, and after being hydrided at 573 K and 473 K (and 373 K for the binary material).

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<th>$T_c$-onset (K)</th>
<th>DSC 473K (nm)</th>
<th>DSC 573K (nm)</th>
<th>DSC 673K (nm)</th>
<th>Hydrided 573K (nm)</th>
<th>Hydrided 473K (nm)</th>
<th>Hydrided 373K (nm)</th>
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<td>Binary</td>
<td>436</td>
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<td>44±14</td>
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<td>445</td>
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Table 2: The $\Delta H_o$ and $\Delta S_o$ values for $\text{MgH}_2 \leftrightarrow \text{Mg} + \text{H}_2$ and $\text{Mg}_2\text{NiH}_4 \leftrightarrow \text{Mg}_2\text{Ni} + 2\text{H}_2$, calculated for the binary, Y5, and La5 alloys using Eq. (1) and the equilibrium pressures in Figure 5.

<table>
<thead>
<tr>
<th>Alloy</th>
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<th>$\Delta S_o$ (J/mol·K)</th>
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<td>-129.8±4.4</td>
<td>-50.8±3.1</td>
<td>-101.6±6.3</td>
</tr>
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Figure 1: XRD patterns of as-spun and DSC heat treated melt-spun ribbons for the (a) binary, (b) Y5, and (c) La5
Figure 2: Hydriding/dehydriding properties of the binary (solid), Y5 (dashed), and La5 (dotted), during (a) activation, or 1st absorption cycle; ($T_{act}$) indicate the activation temperature, (b) 3rd absorption cycle at 573 K, (c) 3rd desorption cycle at 573 K, (d) 8th desorption cycle at 573 K.
Figure 3: Desorption curves at temperatures between 473 K and 573 K for the a) binary, b) Y5, and c) La5 materials. Neither the binary nor Y5 samples showed significant desorption at 473 K.
Figure 4:  

a) XRD patterns for the binary, Y5, and La5 samples after being hydried at 573 K. Also shown is the XRD pattern of the hydried La5 material after being heated to 540 K in the DSC.  
b) DSC scans of the binary alloy after being hydried at 473 K and 573 K.  
c) Comparison of DSC scans for the binary, Y5, and La5 alloys after being hydried at 573 K.
Figure 5: PCI results for (a) binary, (b) Y5, and (c) La5 alloys at different temperatures.
Figure 6: Van't Hoff plots of the a) binary, b) Y5, and c) La5 for MgH\textsubscript{2} and Mg\textsubscript{2}NiH\textsubscript{4} formations. Pressures are normalized to $P_0=100$ kPa.
Figure 7: Free energy as a function of temperature for several mixtures of phases for the a) Y5 and b) La5 materials that could occur as a result of forming the intermetallic phases Ni$_{17}$Y$_2$ and LaNi$_5$ (and LaNi$_5$H$_3$), respectively.