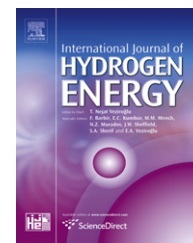


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Technical Communication

Hydrogen storage in rapidly solidified and crystallized Mg–Ni–(Y,La)–Pd alloys

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ABSTRACT

Amorphous-crystalline composite ribbons of quaternary Mg–Ni–(Y,La)–Pd alloys are produced via rapidly solidification and used as precursors for creating nanocrystalline hydrogen storage materials. The resulting materials demonstrate relatively high hydrogen capacity of around 4.5 mass% H and excellent absorption/desorption kinetics at 573 K. Additionally, the alloys demonstrate reversible hydrogen storage at 473 K. A composition of $\text{Mg}_{85}\text{Ni}_{10}\text{Y}_{2.5}\text{Pd}_{2.5}$ fully absorbs and desorbs 4.6 mass% H in 90 min. The cyclability of the quaternary alloys demonstrates good stability, with little loss in maximum capacity through 8–10 cycles. This has been attributed to the improved stability of the nanocrystalline structure attained via the Y and La additions. Thermodynamically, the enthalpy of the hydrogen absorption reaction is reduced by 5 kJ/mol in the quaternary alloys, compared to Mg–MgH₂; while the entropy of reaction is also reduced.

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1. Introduction

Magnesium-based alloys are of great interest for hydrogen storage applications because of their high gravimetric capacity and low cost [1–4]. However, they suffer from significant kinetic and thermodynamic drawbacks. Among these, kinetic issues including surface oxidation of Mg [5], H₂ dissociation into atomic H [3], and diffusion of H in MgH₂ [6], have all been addressed with some success via processing techniques such as high temperature activation (surface oxidation) and ball milling or mechanical alloying (surface oxidation and H diffusion) [1,4,7]; or by adding catalyst materials like Pd or transition metal oxides (H₂ dissociation) [8]. Unfortunately, one of the most significant problems hindering the practical use of Mg-alloys for H-storage, the

high thermodynamic stability of the MgH₂ phase relative to Mg plus H₂ gas, has yet to be overcome. For the equilibrium reaction $\text{MgH}_2 \leftrightarrow \text{Mg} + \text{H}_2$, the enthalpy of reaction, ΔH_r , is –77 kJ/mol of H₂ gas. This results in decomposition temperatures, T_d , of >550 K required for desorption at 1 bar of H₂ pressure; too high for on-board vehicular applications [1,3]. A practical hydrogen storage material should possess a ΔH_r of 20 kJ/mol and 50 kJ/mol, and should be able to release H₂ at or below 373 K near atmospheric pressure [1–4].

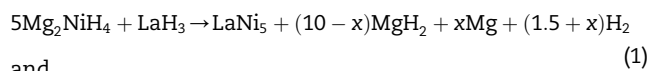
Thermodynamic destabilization of MgH₂ relative to metallic Mg has been attempted through various methods. In theory ball milling can improve the thermodynamics of the hydriding and dehydriding reactions by introducing capillarity effects if particle size is reduced enough. Calculations suggest that a particle radius on the order of 5 nm will reduce

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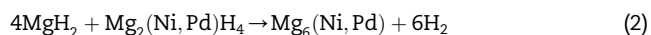
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ΔH , by 10% for pure Mg [4]. The authors have recently demonstrated a decrease in T_d by about 25 K compared to a bulk material, in Mg-Mg₂Ni composites with an average crystallite radius of 15 nm [9]. Alloying Mg with another constituent can also improve the thermodynamics of the hydriding reaction. For example, when Si is mixed with MgH₂, decomposition of the hydride results in the formation of H₂ gas and the intermetallic phase Mg₂Si, instead of metallic Mg. The introduction of this intermediate phase reduces the enthalpy of the hydride decomposition reaction by 40 kJ/mol [10]. Unfortunately, the reaction is not reversible. Additions of Ni to Mg result in the formation of the Mg₂Ni intermetallic phase and a new hydride, Mg₂NiH₄, creating the reaction $\text{Mg}_2\text{NiH}_4 \leftrightarrow \text{Mg}_2\text{Ni} + 2\text{H}_2$. The thermodynamics of this reaction are improved compared to $\text{MgH}_2 \leftrightarrow \text{Mg} + \text{H}_2$, with a ΔH , of –65 kJ/mol. However, this hydride is still too stable, requiring a temperature of 523 K to release the H₂ [11]. Also, the theoretical storage capacity is reduced to only 3.6 mass% H, compared to 7.7 mass% H for pure Mg.

More recently, the present authors have demonstrated improved thermodynamics in ternary Mg–Ni–M alloys, where M is La or Y [12] or Pd [13]. Adding these elements, particularly La and Pd, introduces the equilibrium intermetallic phase LaNi₅ and Mg₆(Ni,Pd). When hydrided, these materials form the same MgH₂ and Mg₂NiH₄ hydrides as Mg and Mg–Ni materials (along with LaH₃). Because the La (in the form of LaH₃) and Pd (likely in Mg₂(Ni,Pd)H₄) participate in the hydriding process, the loss in storage capacity is minimized. Moreover, the LaNi₅ and Mg₆(Ni,Pd) phases provide alternative reaction pathways where two hydrides can form or decompose simultaneously in a single reaction, reducing the overall enthalpy of reaction. Specifically, the reactions



and



have been proposed for La- and Pd-containing alloys, respectively. The recent electron microscopy work of Tanaka et al. [14], showing LaH₃ almost always present in close proximity to Mg₂NiH₄, provides evidence of the validity of Eq. (1); while the work of the present authors support Eq. (2). The reactions ultimately lower the required decomposition temperature and raise the equilibrium pressures. Unfortunately, the improvements in both materials are not sufficient to deem them practical for H-storage applications. The La-containing material rapidly absorbs and desorbs H at 473 K; but the equilibrium pressure is two orders of magnitude below atmospheric pressure [12]. Conversely, the Pd-containing material exhibits an absorption plateau pressure near 1 atm at 473 K, but kinetics, as well as cyclability, are extremely poor [13].

The present study explores the H-storage characteristics of quaternary alloys containing both Y or La and Pd, with a general composition of Mg₈₅Ni₁₀(M_xPd_{5–x}), where M is Y or La. The goal is to create a Mg-based alloy that exhibits rapid, reversible hydrogen storage kinetics at a reduced temperature of 473 K as observed in the Mg–Ni–La alloy; while increasing the equilibrium reaction pressure at 473 K to near atmospheric pressure as observed in Mg–Ni–Pd alloys.

2. Experimental procedure

Ingots with a mass of 50 g and nominal compositions (in mol %) of Mg₈₅Ni₁₀(M_xPd_{5–x}), with Y or La and Pd contents of Y₁Pd₄, La₁Pd₄, Y_{2.5}Pd_{2.5}, or La_{2.5}Pd_{2.5} were prepared using 99.9% pure Mg, Ni, Y, and Pd, and 98% pure La. The above compositions will be referred to hereafter as Y1, La1, Y25, and La25. To accommodate 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 alloy, determined using energy dispersive X-ray spectroscopy, was found to be within 1 mol% of the target composition. Each alloy composition was prepared first by melt spinning into ribbon materials; then ball milling for 30 min to provide fresh unoxidized surfaces. Complete details of the sample preparation methodology can be found elsewhere [9,12,13].

Samples of ball milled material with a mass of 50–60 mg were used for H-storage experiments. The measurements were performed using a custom-made volumetric 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 (<0.005 mass% H). Absorption kinetics measurements were carried out under a H₂ pressure of 2 MPa at temperatures between 473 K and 623 K. Desorption kinetics were measured at a pressure of <1 kPa. To ensure complete activation of the material, hydriding kinetics were measured after at least five absorption/desorption cycles. Pressure-composition isotherm (PCI) measurements were performed at temperatures between 473 K and 623 K. During these 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 temperature of interest.

Crystallization experiments were performed on the melt-spun ribbons by heating the samples at a rate of 10 K/min using a differential scanning calorimeter (DSC) to temperatures of 473 K, 573 K, and 673 K under flowing Ar gas. DSC was also used to heat the hydrided samples to 723 K in order to study the materials after hydride decomposition. Structural characterization of the as-spun, crystallized, and hydrided materials were performed using X-ray diffraction (XRD).

3. Results

3.1. Microstructure

3.1.1. As-spun and heat-treated samples

Fig. 1a shows the XRD results for the four ribbon compositions in the as-spun condition. All four patterns possess a broad diffraction “hump” suggesting a glassy structure. Additionally, the Y1, La1, and La25 samples have a sharper peak near 38° 2 θ superimposed on the amorphous pattern, which corresponds to the (822) peak of the Mg₆(Ni,Pd) intermetallic phase. This indicates that the microstructure of the ribbons consists of primarily an amorphous phase matrix with

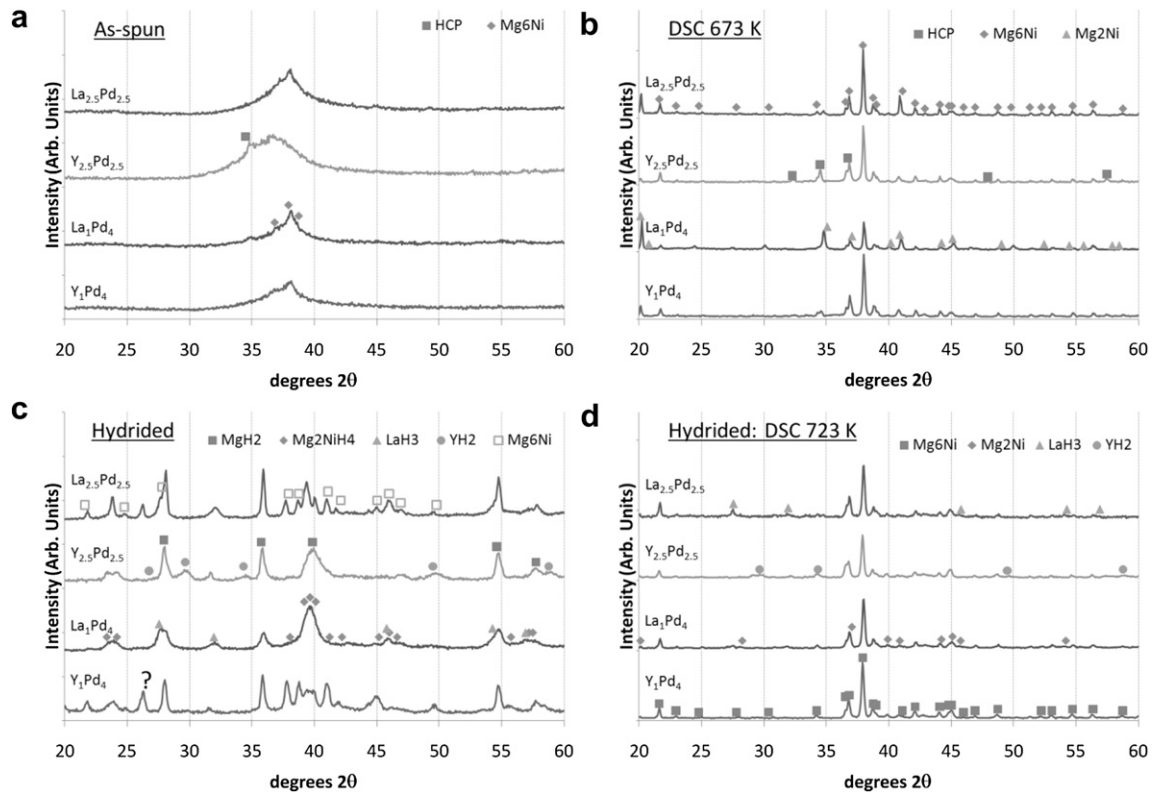


Fig. 1 – XRD patterns of the four melt-spun ribbon compositions a) in the as-spun condition, b) in the crystallized state after being heated to 673 K in the DSC, c) after hydrogenation, and d) after being hydrided and subsequently heated to 723 K.

embedded crystallites of $\text{Mg}_6(\text{Ni},\text{Pd})$ formed during the quenching. The XRD pattern of the Y25 material does not exhibit the $\text{Mg}_6(\text{Ni},\text{Pd})$ peak. Instead, the amorphous peak is broader and shifted to lower 2θ values (larger atomic spacings); and a small peak is present near $35^\circ 2\theta$ corresponding to the (002) peak of hexagonal close-packed (HCP) Mg. When the ribbon surface was removed, the HCP phase disappeared. This suggests it is present only near the ribbon surface, and is formed during the quenching process. These results are consistent with previous studies [12].

When heated to 673 K, the primary crystallization product in all four compositions is the $\text{Mg}_6(\text{Ni},\text{Pd})$ intermetallic, as shown in Fig. 1b. In addition, all the heat-treated materials contained some Mg_2Ni intermetallic; while the ribbons containing Y also have a small amount of HCP Mg. Interestingly, the heat-treated ribbons do not exhibit any peaks corresponding to Y- or La-containing intermetallic phases. This has been previously observed by the authors in the ternary alloy $\text{Mg}_{85}\text{Ni}_{10}\text{Y}_5$ [12], and suggests some solubility of Y and La in the phases that are present in the crystallized samples, i.e. HCP, $\text{Mg}_6(\text{Ni},\text{Pd})$, or Mg_2Ni .

3.1.2. Hydrided/dehydrided materials

The XRD results for the four alloys after being hydrided are presented in Fig. 1c. The samples are in different states of hydrogenation so the results cannot be quantitatively compared. The primary phases in all four materials are MgH_2

and Mg_2NiH_4 , with some YH_2 or LaH_3 present. The Y1 and La25 samples also contain some $\text{Mg}_6(\text{Ni},\text{Pd})$ as a result of incomplete hydriding. These two samples also exhibit a peak near $26^\circ 2\theta$, marked with a question mark in Fig. 1c, which cannot be positively identified as belonging to any known phase. The peak roughly corresponds to a peak in the orthorhombic high pressure allotrope of MgH_2 , and also with a peak corresponding to the Mg_5Pd_2 intermetallic phase. Previous studies of Pd-containing Mg–Ni alloys demonstrate that Mg_5Pd_2 forms during hydriding a temperature of 573 K, and cannot be removed unless the material is heated to 823 K [15–17]. In this study however, Mg_5Pd_2 is not present in the heat-treated materials (Fig. 1b), or after they are dehydrogenated, shown in Fig. 1d.

When dehydrogenated via heating to 723 K in the DSC, Fig. 1d, the four samples exhibit similar XRD patterns. $\text{Mg}_6(\text{Ni},\text{Pd})$ is the majority phase in all four materials, with small amounts of Mg_2Ni and YH_2 or LaH_3 also visible. The unidentified peak near $26^\circ 2\theta$ observed in the hydrided Y1 and La25 samples is not present; suggesting that if Mg_5Pd_2 is present in the hydrided materials, it is much less stable than in ternary Mg–Ni–Pd alloys. Because Mg_5Pd_2 is not present in the alloys for any other conditions, and because the Y1 and La25 samples in Fig. 1c are not fully hydrided, the anomalous peak at $26^\circ 2\theta$ is likely an intermediate phase formed during the hydriding process, possibly the high pressure form of MgH_2 .

3.2. Hydriding characteristics

3.2.1. Kinetics

Once fully activated, all four sample compositions exhibit similar kinetic characteristics during hydrogenation at 573 K, as shown for the fifth absorption/desorption cycle, presented in Fig. 2a and b for absorption and desorption, respectively. The maximum capacities range from 3.9 mass% H in La1, to as high as 4.4 mass% H for the Y1Pd₄ alloy, Full hydrogenation is reached in 20 min or less for all samples. Likewise, desorption at 573 K is rapid in all four materials, requiring less than 5 min. Table 1 summarizes the maximum capacities and times required to absorb/desorb 95% of maximum capacity for the four compositions at 573 K and 473 K.

At 473 K, the hydriding behavior of the four alloys is more varied than for 573 K. As illustrated in Fig. 2c, full absorption during the eighth cycle requires over 120 min in the Y1 and La1 samples, reaching a maximum capacity of 4.4 mass% H and 4.2 mass% H, respectively. This is a dramatic improvement over the ternary Mg₈₅Ni₁₀Pd₅ material, which could not be fully hydrogenated after 1200 min during the second cycle at 473 K [13]; although the maximum capacity is decreased compared to the 5.0 mass% H observed in the ternary alloy. When the Y or La content is increased, i.e. the Y25 and La25 materials, the maximum capacity increases to 4.6 mass% H and 4.5 mass% H, respectively. Additionally, full hydrogenation is reached in only 60 min for both materials. Again, this is after eight hydrogenation cycles; which demonstrates not

Table 1 – Maximum capacities and absorption and desorption times for each of the four alloys at 473 K and 573 K (times are for 95% absorption/desorption of maximum capacity).

Alloy	473 K capacity (mass% H)	$t_{\text{ABS}}^{473 \text{ K}}$ (min)	$t_{\text{DES}}^{473 \text{ K}}$ (min)	573 K capacity (mass% H)	$t_{\text{ABS}}^{573 \text{ K}}$ (min)	$t_{\text{DES}}^{573 \text{ K}}$ (min)
Y1	4.4	66	123	4.4	5	3
La1	4.2	62	149	3.9	4	2
Y25	4.6	32	63	4.3	10	2
La25	4.5	39	94	4.2	12	2

only the improved hydriding kinetics of the quaternary alloys, but also improved cyclability as well, compared to Mg₈₅Ni₁₀Pd₅.

Desorption at 473 K is also much improved in the quaternary samples, compared to the ternary Pd-containing alloy. Fig. 2d shows that most of the hydrogen is desorbed after 150 min in all four alloys. Only about 0.15 mass% H in the Y1 and La1 samples, and no significant H concentration in the Y25 and La25 materials, remains after 150 min. The Y25 sample actually fully desorbs its 4.6 mass% H in <100 min.

3.2.2. Isotherms and thermodynamics

Fig. 3 presents PCI curves for each of the four alloys at temperatures between 473 K and 623 K. The PCI behavior is similar in all four compositions. Each material exhibits two

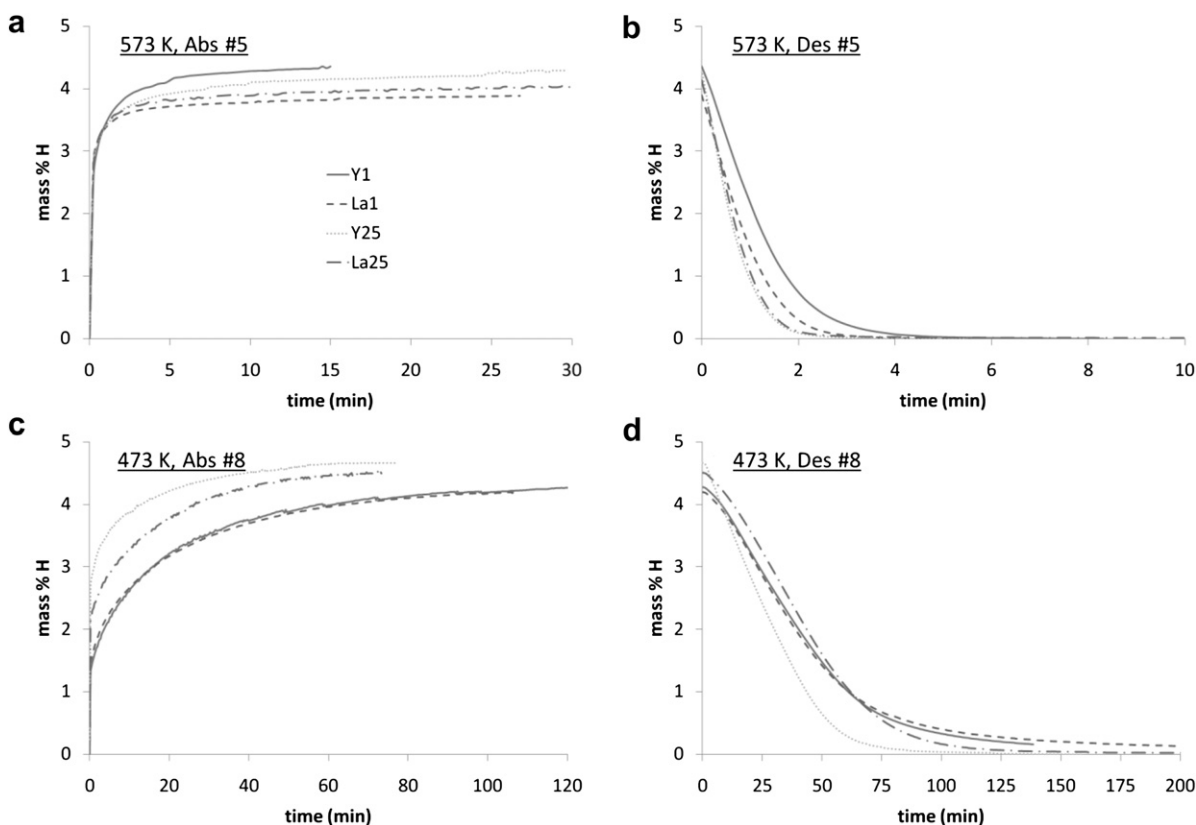


Fig. 2 – Hydriding/dehydriding kinetics for the Y1 (solid), La1 (dash), Y25 (dot), and La25 (dash-dot) materials at a) 573 K for the fifth absorption cycle, b) 573 K for the fifth desorption cycle, c) 473 K for the eighth absorption cycle, d) 473 K for the eighth desorption cycle.

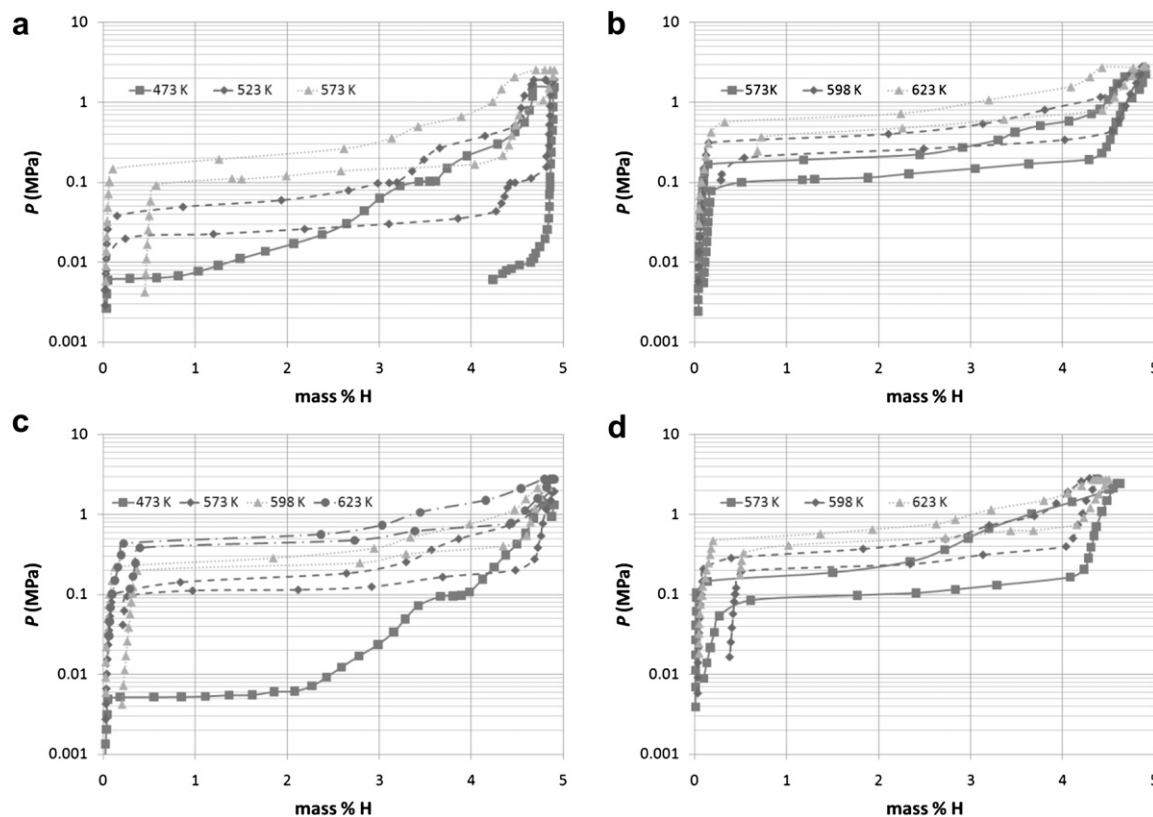


Fig. 3 – Pressure-composition isotherms at different temperatures between 473 K and 623 K for the a) Y1, b) La1, c) Y25, and d) La25 samples.

pressure plateaus corresponding to the formation/decomposition of MgH_2 and Mg_2NiH_4 . The two plateaus partially overlap, and include a sloping region between them. This is partially due to slow reaction kinetics. It is also likely that the thermodynamics of hydride phases are not independent of one another, i.e. MgH_2 and Mg_2NiH_4 can form in a single reaction from the $\text{Mg}_6(\text{Ni},\text{Pd})$ phase; whereas each hydride must form in a separate reaction in binary Mg-Ni materials. Cooperative formation/decomposition of two hydrides has recently been shown to occur in Mg-Ni-La and Mg-Ni-Pd materials as discussed above [12,13]. Because of the addition of a fourth element to the alloy, even more complex reaction pathways are possible; which may be further explored with microscopy and diffraction techniques.

The pressures of the first plateaus observed for the four materials in Fig. 3 are comparable to those expected for pure $\text{Mg} + \text{H}_2 \rightarrow \text{MgH}_2$, although they are slightly higher, particularly at lower temperatures. For instance, the plateau pressure for the Y1 materials at 473 K is roughly 8.0 kPa, compared to 3.8 kPa for pure Mg forming MgH_2 . The increase in plateau pressure is not as dramatic as for $\text{Mg}_{85}\text{Ni}_{10}\text{Pd}_5$ [13], but it does suggest that the thermodynamics of the hydriding reaction are improved. Table 2 summarizes the enthalpy and entropy of reaction, ΔH_r and ΔS_r respectively, for the four alloys, calculated from the van't Hoff relationship between equilibrium plateau pressure, P_{eq} , and temperature, T , i.e. $\ln(P_{eq}/P_0) = \Delta H_r/(RT) - \Delta S_r/R$, where P_0 is 1 atm and R is the ideal gas constant. The uncertainty in the measured values is

Table 2 – Enthalpies and entropies of reaction for each alloy found using the van't Hoff relationship for the first plateaus observed in the PCI curves of Fig. 3, calculated for absorption and desorption. The uncertainties are expressed as plus/minus one standard deviation.

Alloy	ΔH_r^{ABS} (kJ/mol)	ΔS_r^{ABS} (J/mol K)	ΔH_r^{DES} (kJ/mol)	ΔS_r^{DES} (J/mol K)
Y1	-67.7 ± 9.8	121.4 ± 15.6	-77.2 ± 8.0	134.0 ± 10.5
La1	-72.4 ± 5.9	130.6 ± 5.1	-77.6 ± 7.4	135.5 ± 10.4
Y25	-65.7 ± 9.9	117.3 ± 20.0	-77.4 ± 9.5	135.3 ± 7.6
La25	-69.4 ± 8.1	124.4 ± 6.6	-81.3 ± 12.7	140.8 ± 21.7

expressed as plus/minus one standard deviation as calculated from the linear regression analysis. Only the plateau at lower H-content, corresponding to MgH_2 formation and decomposition, is considered because the second plateau pressure cannot be resolved. The calculations are performed for both absorption and desorption. For the absorption process, the magnitudes both of ΔH_r^{ABS} and ΔS_r^{ABS} are lower than the values expected for pure $\text{Mg} + \text{H}_2 \rightarrow \text{MgH}_2$ of -77 kJ/mol and 135 J/mol K , respectively; while on desorption, they are equal to those for pure MgH_2 . The average ΔH_r^{ABS} for all four compositions is about 5 kJ/mol lower than for pure Mg-MgH_2 ; and ΔS_r is reduced by 8 J/mol K . These results demonstrate that decreased enthalpy of reaction is improved is offset to some extent by a decrease in the entropy of reaction.

4. Discussion and conclusions

The quaternary Mg-Ni-(Y,La)-Pd alloys in the present work exhibit some of the same improved H-storage characteristics of previously studied Mg-Ni-La and Mg-Ni-Pd ternary materials. All four compositions demonstrate rapid absorption and desorption kinetics at 573 K , and can reversibly store about $4.5 \text{ mass\% H}$ at 473 K with full absorption/desorption occurring in $<2 \text{ h}$. Additionally, the additions of Y or La dramatically improve the cyclability of the material compared to the ternary composition. This is most likely because they impede phase boundary motion, slowing microstructural coarsening kinetics; allowing the nanocrystalline structure of the devitrified ribbons to persist for longer periods of time at elevated temperatures [12].

The overall thermodynamics of the hydriding reaction are improved in the quaternary alloys compared to pure Mg and binary Mg-Ni alloys; although the increase in plateau pressure at 473 K is not as large as that observed in ternary $\text{Mg}_{85}\text{Ni}_{10}\text{Pd}_5$. The reason for this is likely two-fold. An activation barrier in $\text{Mg}_{85}\text{Ni}_{10}\text{Pd}_5$, arising because of the necessity for medium to long-ranged diffusion of Mg , Ni , and Pd , can introduce hysteresis, increasing the observed absorption pressure and decreasing the desorption pressure. Additions of Y or La may reduce the diffusion-related activation barrier through decreased crystallite size. However, the well-defined MgH_2 plateau followed by a sloping region (indicating a cooperative reaction between two hydrides) observed in the Y25 and La25 alloys, is also present in the ternary material. This suggests that the reactions in the ternary and quaternary materials are the same, but adding Y or La counteracts the improved thermodynamics obtained through alloying with Pd .

The quaternary alloys in this study demonstrate much improved H-storage properties compared to many other Mg -based materials. The reasonable storage capacity of about $4.5 \text{ mass\% H}$, combined with demonstrated reversibility at 473 K and improved cyclability are promising advancements. Additionally, the ability to reversibly store H at decreased temperatures allows a nanocrystalline Mg -based structure to be maintained for longer periods of time during service. Finally, the demonstrated ability to alter hydriding reaction thermodynamics by introducing new metallic phases and opening new reaction pathways may prove useful in other metal-hydride systems.

Acknowledgments

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REFERENCES

- [1] Sakintuna B, Lamari-Darkim F, Hirscher M. Metal hydride materials for solid hydrogen storage: a review. *Int J Hydrogen Energy* 2007;32:1121–40.
- [2] Jain IP, Lal C, Jain A. Hydrogen storage in Mg : a most promising material. *Int J Hydrogen Energy* 2010;35: 5133–44.
- [3] Guo ZX, Shang C, Aguey-Zinsou KF. Materials challenges for hydrogen storage. *J Euro Ceramic Soc* 2008;28:1467–73.
- [4] Berube V, Radtke G, Dresselhaus M, Chen G. Size effects on the hydrogen storage properties of nanostructured metal hydrides: a review. *Int J Energy Res* 2007;3:637–63.
- [5] Zaluska A, Zaluski L. Nanocrystalline magnesium for hydrogen storage. *J Alloy Compds* 1999;288:217–25.
- [6] Freidlmeier G, Groll M. Experimental analysis and modelling of the hydriding kinetics of Ni -doped and pure Mg . *J Alloy Compds* 1997;253–254:550–5.
- [7] Huot J, Liang G, Boily S, Nester AV, Schulz R. Structural study and hydrogen sorption kinetics of ball-milled magnesium hydride. *J Alloy Compds* 1999;293–295:495–500.
- [8] Barkhordarian G, Klaussen T, Bormann R. Kinetic investigation of the effect of milling time on the hydrogen sorption reaction of magnesium catalyzed with different Nb_2O_5 contents. *J Alloy Compds* 2006;407:249–55.
- [9] Lass EA. Improved activation and hydrogen storage properties of a $\text{Mg}_{85}\text{Ni}_{15}$ melt-spun alloy via surface treatment with NH_4^+ solution. *Mater Chem Phys* 2001;130: 937–42.
- [10] Vajo JJ, Mertens F, Ahn CC, Bowman Jr RC, Fultz B. Altering hydrogen storage properties by hydride destabilization through alloy formation: LiH and MgH_2 destabilized with Si . *J Phys Chem B* 2004;108:13977–83.
- [11] Orimo S, Fujii H. Materials science of Mg-Ni -based new hydrides. *Appl Phys A* 2001;72:167–86.
- [12] Lass EA. Hydrogen storage measurements in novel Mg -based nanostructured alloys produced via rapid solidification and devitrification. *Int J Hydrogen Energy* 2011;36:10787–96.
- [13] Lass EA. Reversible hydrogen-storage at reduced temperatures in the intermetallic compound $\text{Mg}_6(\text{Ni}, \text{Pd})$. *Int J Hydrogen Energy* 2011;36:14496–502.
- [14] Tanaka K, Miwa T, Sasaki K, Kuroda K. TEM studies of nanostructure in melt-spun Mg-Ni-La alloy manifesting enhanced hydrogen desorbing kinetics. *J Alloy Compds* 2009; 478:308–16.
- [15] Cuevas F, Fernandez JF, Ares JR, Leardini F, Latroche M. Crystal structure and hydrogenation properties of pseudo-binary $\text{Mg}_6\text{Pd}_{0.5}\text{Ni}_{0.5}$ complex metallic alloy. *J Solid State Chem* 2009;182:2890–6.
- [16] Fernandez JF, Cuevas F, Leardini F, Bodega J, Ares JR, Garces G, et al. A new pseudo-binary $\text{Mg}_6\text{Pd}_{0.5}\text{Ni}_{0.5}$ intermetallic compound stabilized by Pd for hydrogen storage. *J Alloy Compds* 2010;495:663–6.
- [17] Fernandez JF, Ares JR, Cuevas F, Bodega J, Leardini F, Sanchez C. A thermodynamic study of the hydrogenation of the pseudo-binary $\text{Mg}_6\text{Pd}_{0.5}\text{Ni}_{0.5}$ intermetallic compound. *Intermetallics* 2010;18:233–41.