

Article

Improvement in Hydriding and Dehydriding Features of Mg–TaF₅–VCl₃ Alloy by Adding Ni and x wt% MgH₂ (x = 1, 5, and 10) Together with TaF₅ and VCl₃

Young-Jun Kwak  and Myoung-Youp Song *

Division of Advanced Materials Engineering, Jeonbuk National University, 567 Baekje-daero Deokjin-gu, Jeonju 54896, Korea; twistking18@nate.com

* Correspondence: songmy@jbnu.ac.kr; Tel.: +82-10-3260-2379

Abstract: In our previous work, TaF₅ and VCl₃ were added to Mg, leading to the preparation of samples with good hydriding and dehydriding properties. In this work, Ni was added together with TaF₅ and VCl₃ to increase the reaction rates with hydrogen and the hydrogen-storage capacity of Mg. The addition of Ni together with TaF₅ and VCl₃ improved the hydriding and dehydriding properties of the TaF₅ and VCl₃-added Mg. MgH₂ was also added with Ni, TaF₅, and VCl₃ and Mg-x wt% MgH₂-1.25 wt% Ni-1.25 wt% TaF₅-1.25 wt% VCl₃ (x = 0, 1, 5, and 10) were prepared by reactive mechanical milling. The addition of MgH₂ decreased the particle size, lowered the temperature at which hydrogen begins to release rapidly, and increased the hydriding and dehydriding rates for the first 5 min. Adding 1 and 5 wt% MgH₂ increased the quantity of hydrogen absorbed for 60 min, H_a (60 min), and the quantity of hydrogen released for 60 min, H_d (60 min). The addition of MgH₂ improved the hydriding–dehydriding cycling performance. Among the samples, the sample with x = 5 had the highest hydriding and dehydriding rates for the first 5 min and the best cycling performance, with an effective hydrogen-storage capacity of 6.65 wt%.

Keywords: hydrogen-storage materials; magnesium; hydriding and dehydriding rates; cycling performance; microstructure; addition of TaF₅, VCl₃, Ni, and MgH₂



Citation: Kwak, Y.-J.; Song, M.-Y. Improvement in Hydriding and Dehydriding Features of Mg–TaF₅–VCl₃ Alloy by Adding Ni and x wt% MgH₂ (x = 1, 5, and 10) Together with TaF₅ and VCl₃. *Micromachines* **2021**, *12*, 1194. <https://doi.org/10.3390/mi12101194>

Academic Editor: Aiqun Liu

Received: 28 July 2021

Accepted: 27 September 2021

Published: 30 September 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Metal hydride storage has advantages over pressure storage and cryogenic storage, as metal hydrides have higher volumetric capacity and metal hydride storage is safer due to the low pressures involved in hydrogen uptake and release [1].

To increase the hydrogen uptake and release rates of magnesium, magnesium (Mg), or magnesium hydride (MgH₂) was alloyed [2–10] with Ni and Y [11], V [12], and Nb [13]. In addition, Mg or MgH₂ was mixed with compounds such as LaNi₅ [14], FeTi and FeTiMn [15], Nb₂O₅ [16], and La₂O₃ [17]. Mg-containing compounds [18–22] such as La₂Mg₁₆Ni [23], LaMg₁₂ and La₂Mg₁₇ [24], Mg₃Mm (Mm: misch-metal) [25], and Mg₁₇Al₁₂ [26] were synthesized for the same purposes.

Malka et al. [27] reported that certain metal halide additives, especially ZrF₄ and NbF₅ halides, could significantly influence the sorption properties of MgH₂. They reported that the presence of the F anion, which weakened Mg–H bonding, led to the formation of MgF₂ and provided an electron-rich center to trap transition metal atoms. They showed that NbF₅, TaF₅, and particularly TiCl₃, took part in the disproportionation reactions that created a significant number of structural defects. Kumar et al. [28] reported that VCl₃ was reduced to metallic vanadium during ball milling along with MgH₂, and this in situ-formed metallic vanadium doped over the MgH₂ surface and showed an excellent catalytic effect on hydrogenation–dehydrogenation of the Mg–MgH₂ system. They also reported that a microstructural analysis showed an excellent grain refinement property of VCl₃ which

reduced the crystallite size of MgH_2 . Liang et al. [13] improved the hydrogen-storage properties of Mg by adding transition metals such as Ti, V, Mn, Fe, and Ni. In order to find a new route toward improving hydrogen sorption kinetics of Mg nanoparticles, Liu et al. [29] coprecipitated a Mg–Ni nanocomposite from a homogeneous tetrahydrofuran solution containing anhydrous MgCl_2 , NiCl_2 , and lithium naphthalide as the reducing agent.

In the present work, we tried to improve the hydriding and dehydriding properties of Mg by adding halides, transition metal, and metal hydride by preparing alloys via reactive mechanical milling. Selected were TaF_5 and VCl_3 as halides, Ni as a metal, and MgH_2 as a metal hydride. Reactive mechanical milling is milling in an atmosphere in which a reaction can occur during that milling. In the present work, milling was performed in a hydrogen atmosphere. In the hydrogen atmosphere, Mg hydride can form during milling through a reaction of Mg with hydrogen.

In our previous work [30], TaF_5 and VCl_3 were added to Mg. In this work, Ni was added together with TaF_5 and VCl_3 ; Ni, TaF_5 , and VCl_3 were added to Mg at the same time. MgH_2 was also added to Mg together with Ni, TaF_5 , and VCl_3 at the same time, and Mg- x wt% MgH_2 -1.25 wt% Ni-1.25 wt% TaF_5 -1.25 wt% VCl_3 ($x = 0, 1, 5$, and 10) were prepared by reactive mechanical milling. We designated these samples as Mg- $x\text{MgH}_2$ -1.25Ni-1.25 TaF_5 -1.25 VCl_3 ($x = 0, 1, 5$, and 10). The hydriding and dehydriding properties of the prepared samples were then examined. It is thought that the materials developed in our work can be used for motive power fuel and portable appliances as mobile applications, transport and distribution as semi-mobile applications, and industrial off-peak power H_2 -generation, hydrogen-purifying systems, and heat pumps as stationary applications.

2. Materials and Methods

Pure Mg powder (particle size 74–149 μm , purity 99.6%, Alfa Aesar), Ni (APS 2.2–3.0 μm , purity 99.9% metal basis, C typically < 0.1%, Alfa Aesar, Haverhill, MA, USA), TaF_5 (Tantalum (V) fluoride, purity 98%, Aldrich, St. Louis, MI, USA), VCl_3 (Vanadium (III) chloride, purity 97%, Aldrich), and pure MgH_2 powder (hydrogen storage grade, Aldrich) were used as starting materials.

The compositions of mixtures for reactive mechanical grinding were 96.25 wt% Mg + 1.25 wt% Ni + 1.25 wt% TaF_5 + 1.25 wt% VCl_3 and (96.25- x) Mg + x wt% MgH_2 + 1.25 wt% Ni + 1.25 wt% TaF_5 + 1.25 wt% VCl_3 ($x = 0, 1, 5$, and 10). A planetary ball mill (Planetary Mono Mill; Pulverisette 6, Fritsch, Kastl, Germany) with a mill container of 250 mL in volume was used for reactive mechanical grinding. The sample (total weight = 8 g) to ball weight (105 hardened steel balls, total weight = 360 g) ratio was 1:45. All sample handling was performed in an Ar atmosphere. The disc revolution speed was 250 rpm. Reactive mechanical milling was performed in high purity hydrogen gas (≈ 12 bar) for 6 h by repeating the 20 min cycle of 15 min milling and 5 min rest. Hydrogen was refilled every two hours.

The absorbed and released hydrogen quantity were measured as a function of time by the volumetric method using a Sieverts' type hydrogen uptake and release apparatus that was previously described [31]. The hydrogen pressure in the sample-containing reactor was maintained to be nearly constant (under 12 bar for the hydrogen uptake reaction and under 1.0 bar for the hydrogen release reaction) using a back-pressure regulator. The back-pressure regulator enables an appropriate amount of hydrogen to be taken from the standard reservoir (with a known volume) and dosed to the reactor during the hydrogen uptake reaction and an appropriate amount of hydrogen to be removed from the reactor to the standard reservoir during the hydrogen release reaction. From the temperature of the standard reservoir and the variation in hydrogen pressure in the standard reservoir (with a known volume) as a function of time, the variation in the absorbed or released hydrogen quantity was calculated as a function of time. The quantity of the samples used to measure the amount of absorbed or released hydrogen as time passed was 0.5 g. The standard deviations of the amount of absorbed and released hydrogen were ± 0.07 wt% H.

Samples after reactive mechanical milling were characterized via X-ray diffraction (XRD) with Cu K α radiation at a scan speed of 4°/min, using a Rigaku D/MAX 2500 powder diffractometer. The MDI JADE 5.0 program was used to analyze the XRD patterns. Scanning electron microscope (SEM) micrographs of the powders were obtained using a JSM-5900 SEM operated at 20 kV. Particle size distributions of the samples after reactive mechanical milling were analyzed by dynamic light scattering in a particle size analyzer (PSA, ASAP2010 Micrometrics, Norcross, GA, USA).

3. Results

The quantities of absorbed and released hydrogen, H_a and H_d , respectively, were defined using sample weight as a criterion. H_a and H_d were expressed in the unit of wt% H. The quantities of hydrogen absorbed and released from the start for x min are expressed by $H_a(x \text{ min})$ and $H_d(x \text{ min})$, respectively. The hydriding rate for the first 5 min (wt% H/min) was calculated by dividing $H_a(5 \text{ min})$ by 5 and the dehydriding rate for the first 5 min (wt% H/min) was calculated by dividing $H_d(5 \text{ min})$ by 5.

Figure 1 shows the H_a vs. time t curves at 593 K under 12 bar H_2 at the number of cycles, n , of one ($n = 1$) for Mg-1.25TaF₅-1.25VCl₃ and Mg-1.25Ni-1.25TaF₅-1.25VCl₃. Mg-1.25Ni-1.25TaF₅-1.25VCl₃ has a lower hydriding rate for the first 5 min, but a larger quantity of hydrogen absorbed for 60 min than Mg-1.25TaF₅-1.25VCl₃. Mg-1.25Ni-1.25TaF₅-1.25VCl₃ absorbs 2.28 wt% H for 5 min, 3.17 wt% H for 10 min, 5.04 wt% H for 30 min, and 6.12 wt% H for 60 min.

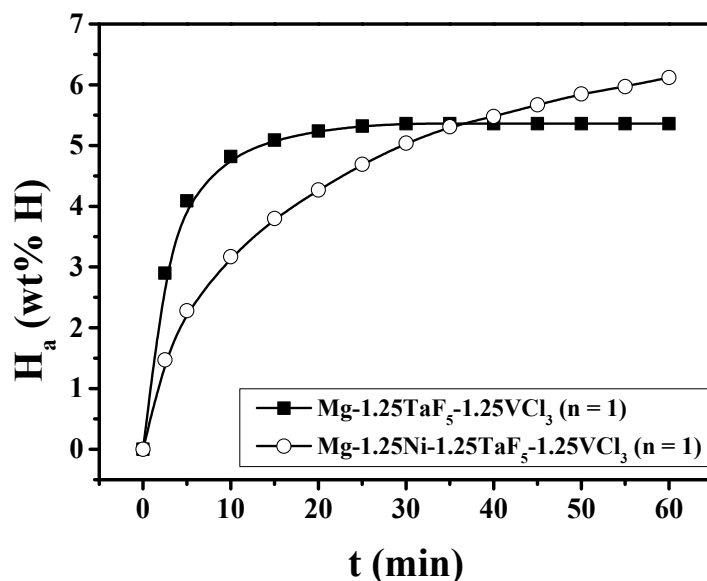


Figure 1. H_a vs. t curves at 593 K under 12 bar H_2 at $n = 1$ for Mg-1.25TaF₅-1.25VCl₃ and Mg-1.25Ni-1.25TaF₅-1.25VCl₃.

The H_d vs. time t curves at 593 K under 1.0 bar H_2 at $n = 1$ for Mg-1.25TaF₅-1.25VCl₃ and Mg-1.25Ni-1.25TaF₅-1.25VCl₃ are shown in Figure 2. Mg-1.25TaF₅-1.25VCl₃ shows a maximum dehydriding rate after about 20 min. On the other hand, Mg-1.25Ni-1.25TaF₅-1.25VCl₃ shows a maximum dehydriding rate after about 15 min. Mg-1.25Ni-1.25TaF₅-1.25VCl₃ has a higher maximum dehydriding rate and a larger quantity of hydrogen released for 60 min than Mg-1.25TaF₅-1.25VCl₃. Mg-1.25Ni-1.25TaF₅-1.25VCl₃ releases 0.11 wt% H for 5 min, 0.53 wt% H for 10 min, 4.11 wt% H for 30 min, and 5.70 wt% H for 60 min.

Figure 1 shows that the addition of Ni together with TaF₅ and VCl₃ increases the quantity of hydrogen absorbed for 60 min of the TaF₅ and VCl₃-added Mg. Figure 2 shows that the addition of Ni together with TaF₅ and VCl₃ increases the maximum dehydriding rate and the quantity of hydrogen released for 60 min of the TaF₅ and VCl₃-added Mg.

X wt% MgH_2 ($x = 1, 5$, and 10) was added together with Ni , TaF_5 , and VCl_3 at the same time with a goal of preparing materials with better hydriding and dehydriding properties.

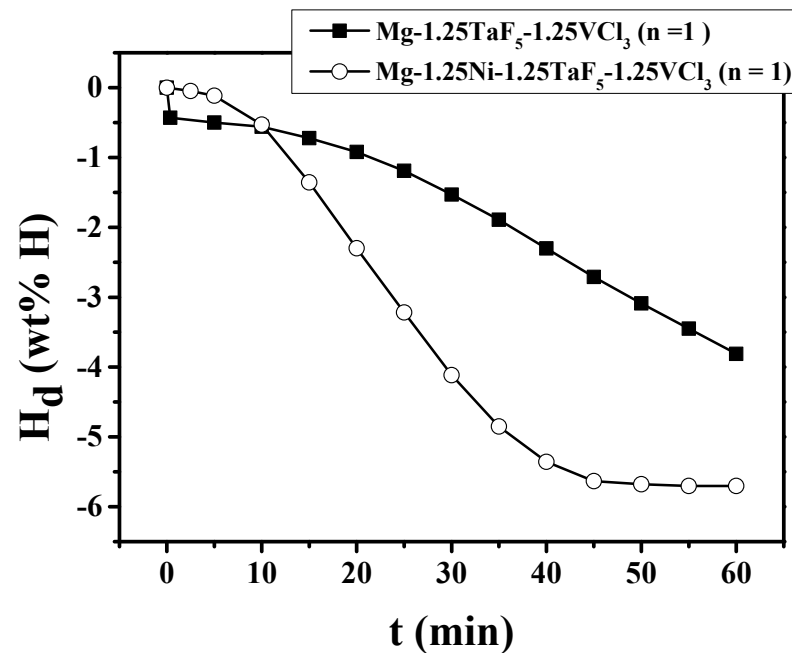


Figure 2. H_d vs. t curves at 593 K under 1.0 bar H_2 at $n = 1$ for $\text{Mg-1.25TaF}_5\text{-1.25VCl}_3$ and $\text{Mg-1.25Ni-1.25TaF}_5\text{-1.25VCl}_3$.

Figure 3 shows the desorbed hydrogen quantity versus time t curves for the as-milled $\text{Mg-xMgH}_2\text{-1.25Ni-1.25TaF}_5\text{-1.25VCl}_3$ ($x = 0, 1, 5$, and 10) when the sample was heated with a heating rate of $5\text{--}6\text{ K/min}$. The ranges of temperature where hydrogen is released rapidly are $648\text{--}688\text{ K}$, $579\text{--}643\text{ K}$, $608\text{--}625\text{ K}$, and $570\text{--}626\text{ K}$, respectively. The addition of MgH_2 lowers the temperature at which hydrogen begins to release rapidly. The curves of the samples with $x = 0$ and $x = 10$ show two stages. The total desorbed hydrogen quantities of the as-milled $\text{Mg-xMgH}_2\text{-1.25Ni-1.25TaF}_5\text{-1.25VCl}_3$ ($x = 0, 1, 5$, and 10) were 2.24, 2.56, 4.24, and 3.50 wt% H, respectively.

The H_a versus t curves at 593 K under 12 bar H_2 at $n = 1$ for $\text{Mg-xMgH}_2\text{-1.25Ni-1.25TaF}_5\text{-1.25VCl}_3$ ($x = 0, 1, 5$, and 10) are shown in Figure 4. The sample with $x = 0$ has a quite high hydriding rate for the first 5 min, and the samples with $x = 1, 5$, and 10 have higher hydriding rates for the first 5 min than the sample with $x = 0$. The addition of MgH_2 increases the hydriding rate for the first 5 min. The sample with $x = 1$ has the highest hydriding rate for the first 5 min, followed in order by the samples with $x = 5, 10$, and 0 . The sample with $x = 1$ has the largest quantity of hydrogen absorbed for 60 min, H_a (60 min), followed in order by the samples with $x = 5, 0$, and 10 . The addition of 1 and 5 wt% MgH_2 increases H_a (60 min) to 6.72 wt% H ($x = 1$) and 6.65 wt% H ($x = 5$) from 6.12 wt% H ($x = 0$). $\text{Mg-1MgH}_2\text{-1.25Ni-1.25TaF}_5\text{-1.25VCl}_3$ absorbs 3.20 wt% H for 2.5 min, 5.69 wt% H for 10 min, and 6.72 wt% H for 60 min. We define the effective hydrogen-storage capacity as the quantity of hydrogen absorbed for 60 min. The sample with $x = 5$ absorbs 5.58 wt% H for 10 min and has an effective hydrogen-storage capacity of 6.65 wt%.

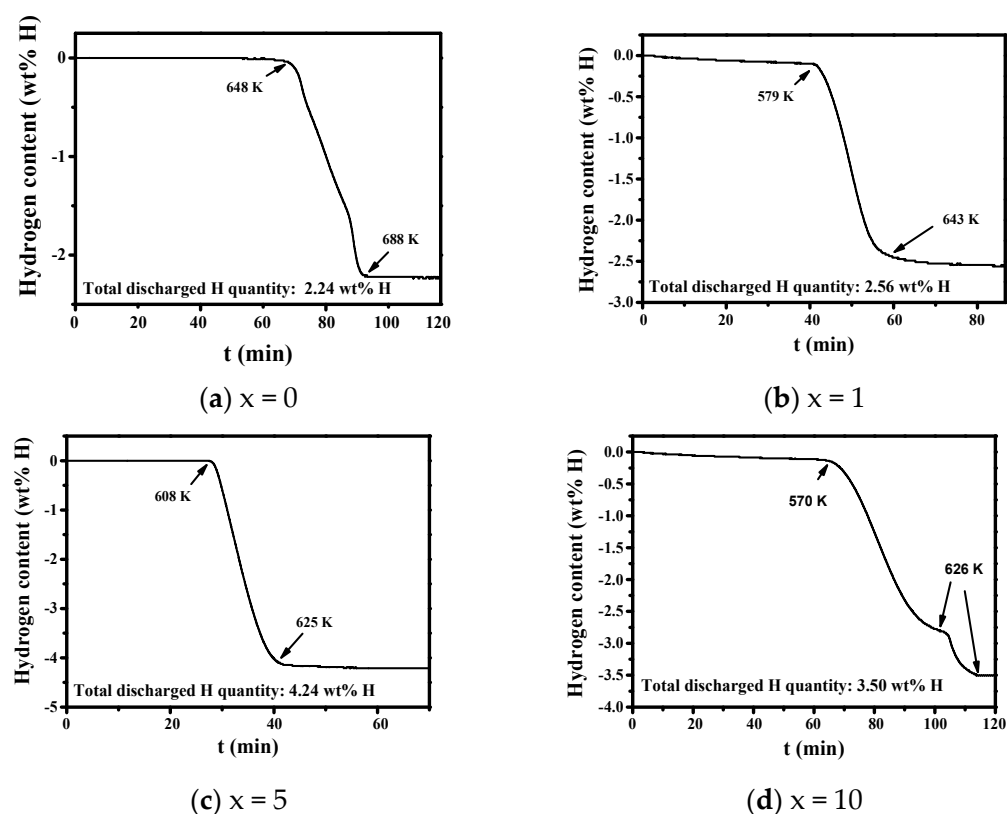


Figure 3. Desorbed hydrogen quantity versus time t curves for the as-milled $\text{Mg-xMgH}_2\text{-1.25Ni-1.25TaF}_5\text{-1.25VCl}_3$; (a) $x = 0$, (b) $x = 1$, (c) $x = 5$, and (d) $x = 10$ when the sample was heated with a heating rate of 5–6 K/min.

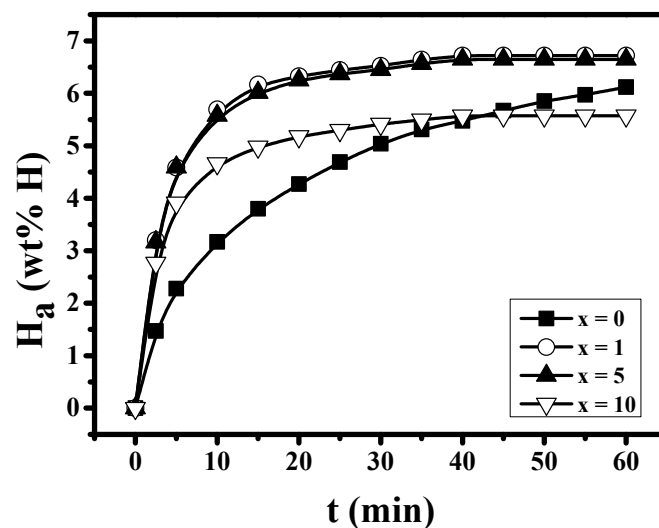


Figure 4. H_a versus t curves at 593 K under 12 bar H_2 at $n = 1$ for $\text{Mg-xMgH}_2\text{-1.25Ni-1.25TaF}_5\text{-1.25VCl}_3$ ($x = 0, 1, 5$, and 10).

Table 1 presents the variations of the H_a with time and hydriding rates for the first 5 min at 593 K under 12 bar H_2 at $n = 1$ for $\text{Mg-xMgH}_2\text{-1.25Ni-1.25TaF}_5\text{-1.25VCl}_3$ ($x = 0, 1, 5$, and 10).

Table 1. Variations of the H_a with time and hydriding rates for the first 5 min at 593 K under 12 bar H_2 at $n = 1$ for $Mg-xMgH_2-1.25Ni-1.25TaF_5-1.25VCl_3$ ($x = 0, 1, 5$, and 10).

Mg- $xMgH_2$ -1.25Ni- 1.25TaF ₅ -1.25VCl ₃ at 593 K	H _a (wt% H)					Hydriding Rate for the First 5 min (wt% H/min)
	2.5 min	5 min	10 min	30 min	60 min	
$x = 0$	1.47	2.28	3.17	5.04	6.12	0.456
$x = 1$	3.2	4.59	5.69	6.52	6.72	0.917
$x = 5$	3.17	4.59	5.58	6.45	6.65	0.917
$x = 10$	2.77	3.91	4.66	5.42	5.57	0.783

The sample with $x = 0$ has quite a high hydriding rate for the first 5 min, and the samples with $x = 1, 5$, and 10 have higher hydriding rates for the first 5 min than the sample with $x = 0$. The addition of MgH_2 increases the hydriding rate for the first 5 min. The samples with $x = 1$ and 5 have the highest hydriding rate for the first 5 min, followed in order by the samples with $x = 10$ and 0 . The sample with $x = 1$ has the largest quantity of hydrogen absorbed for 60 min, H_a (60 min), followed in order by the samples with $x = 5, 0$, and 10 . The addition of 1 and 5 wt% MgH_2 increases H_a (60 min).

The H_d versus t curves at 593 K under 1.0 bar H_2 at $n = 1$ for $Mg-xMgH_2-1.25Ni-1.25TaF_5-1.25VCl_3$ ($x = 0, 1, 5$, and 10) are shown in Figure 5. The sample with $x = 0$ exhibits an incubation period of about 2.5 min, and then the dehydriding rate increases gradually. After 15 min, the dehydriding rate of the sample with $x = 0$ is quite high and becomes very low after 45 min. $Mg-xMgH_2-1.25Ni-1.25TaF_5-1.25VCl_3$ ($x = 1, 5$, and 10) have quite high dehydriding rates from the start. The addition of MgH_2 increases the dehydriding rate for the first 5 min. The sample with $x = 5$ has the highest dehydriding rate for the first 5 min, followed in order by the samples with $x = 10, 1$, and 0 . The sample with $x = 1$ has the largest quantity of hydrogen released for 60 min, H_d (60 min), followed in order by the samples with $x = 5, 0$, and 10 . The addition of 1 and 5 wt% MgH_2 increases H_d (60 min).

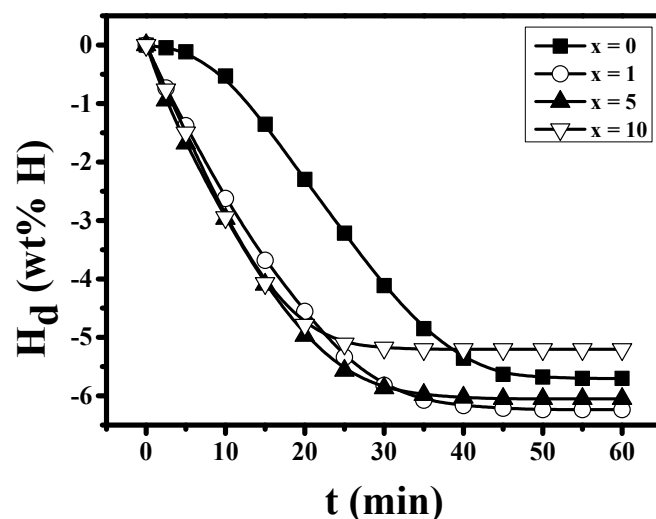
**Figure 5.** H_d versus t curves at 593 K under 1.0 bar H_2 at $n = 1$ for $Mg-xMgH_2-1.25Ni-1.25TaF_5-1.25VCl_3$ ($x = 0, 1, 5$, and 10).

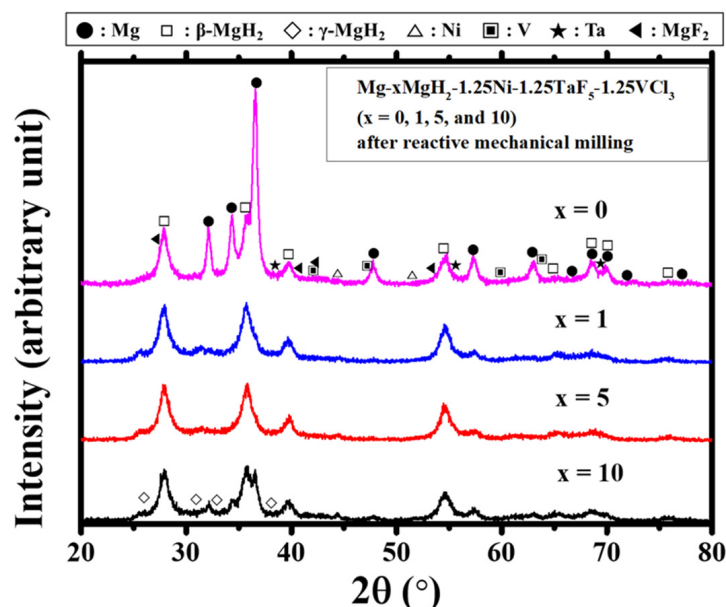
Table 2 presents the variations of H_d with time and the dehydriding rates for the first 5 min at 593 K under 1.0 bar H_2 at $n = 1$ for $Mg-xMgH_2-1.25Ni-1.25TaF_5-1.25VCl_3$ ($x = 0, 1, 5$, and 10).

Table 2. Variations of the H_d with time and the dehydriding rates for the first 5 min at 593 K under 1.0 bar H_2 at $n = 1$ for $Mg-xMgH_2-1.25Ni-1.25TaF_5-1.25VCl_3$ ($x = 0, 1, 5$, and 10).

Mg- $xMgH_2-1.25Ni-1.25TaF_5-1.25VCl_3$ at 593 K	H_d (wt% H)					Dehydriding Rate for the First 5 min (wt% H/min)
	2.5 min	5 min	10 min	30 min	60 min	
$x = 0$	0.05	0.11	0.53	4.11	5.70	0.023
$x = 1$	0.74	1.38	2.62	5.82	6.24	0.276
$x = 5$	0.94	1.68	2.97	5.87	6.05	0.336
$x = 10$	0.76	1.50	2.95	5.18	5.20	0.299

The sample with $x = 0$ has a very low dehydriding rate for the first 5 min, and the samples with $x = 1, 5$, and 10 have much higher dehydriding rates for the first 5 min than the sample with $x = 0$. The sample with $x = 5$ has the highest dehydriding rate for the first 5 min, followed in order by the samples with $x = 10, 1$, and 0. The addition of MgH_2 increases the dehydriding rate for the first 5 min. The sample with $x = 1$ has the largest quantity of hydrogen released for 60 min, H_d (60 min), followed in order by the samples with $x = 5, 0$, and 10. The addition of 1 and 5 wt% MgH_2 increases H_d (60 min).

Figure 6 presents the XRD patterns of $Mg-xMgH_2-1.25Ni-1.25TaF_5-1.25VCl_3$ ($x = 0, 1, 5$, and 10) after reactive mechanical milling. The samples contain Mg, β - MgH_2 , γ - MgH_2 , Ta, V, Ni, and MgF_2 . β - MgH_2 and γ - MgH_2 are formed by a reaction of Mg with hydrogen during reactive mechanical milling. Ta and MgF_2 are formed due to a reaction of TaF_5 with Mg. V is believed to be formed from a reaction of VCl_3 with Mg. The reaction of VCl_3 with Mg is reported to form $MgCl_2$ together with V [32]. Ni remains unreacted after reactive mechanical milling. The intensity of the Mg peaks decrease in the samples containing MgH_2 . This is believed to be due to the decrease in Mg content in MgH_2 -added samples. Larger decrease in particle size due to reactive mechanical milling with the MgH_2 mix is thought to have made the Mg peaks wider.

**Figure 6.** XRD patterns of $Mg-xMgH_2-1.25Ni-1.25TaF_5-1.25VCl_3$ ($x = 0, 1, 5$, and 10) after reactive mechanical milling.

The SEM micrographs of $Mg-xMgH_2-1.25Ni-1.25TaF_5-1.25VCl_3$ ($x = 0, 1, 5$, and 10) after reactive mechanical milling are presented in Figure 7. Particle sizes are not homogeneous, but $Mg-xMgH_2-1.25Ni-1.25TaF_5-1.25VCl_3$ ($x = 1$ and 10) exhibit more homogeneous particle sizes than $Mg-xMgH_2-1.25Ni-1.25TaF_5-1.25VCl_3$ ($x = 0$ and 5). The sample with $x = 5$ has the smallest particle size, followed in order by the samples with $x = 1, 10$, and 0.

The samples with $x = 5$ and 1 have similar particle sizes. The sample with $x = 0$, not containing MgH_2 , has quite large particles, and the particles of this sample form agglomerates. The addition of MgH_2 decreases the particle size.

The variations of H_a values for 5 min and 60 min at 593 K under 12 bar H_2 with the number of cycles for $\text{Mg-}x\text{MgH}_2\text{-}1.25\text{Ni-}1.25\text{TaF}_5\text{-}1.25\text{VCl}_3$ ($x = 0, 1, 5$, and 10) are shown in Figure 8a. The variations of H_d values for 5 min and 60 min at 593 K under 1.0 bar H_2 with the number of cycles for $\text{Mg-}x\text{MgH}_2\text{-}1.25\text{Ni-}1.25\text{TaF}_5\text{-}1.25\text{VCl}_3$ ($x = 0, 1, 5$, and 10) are shown in Figure 8b. The samples with $x = 1, 5$, and 10 have better hydriding and dehydriding cycling performance than the sample with $x = 0$, showing that the addition of MgH_2 improves the cycling performance. The sample with $x = 5$ has the largest value of the quantity of hydrogen absorbed for 5 min, H_a (5 min), at each cycle and the best cycling performance. At $n = 1$, the sample with $x = 1$ has the largest value of the quantity of hydrogen absorbed for 60 min, H_a (60 min), and a slightly larger value of H_a (60 min) than the sample with $x = 5$. At $n = 2-4$, the sample with $x = 5$ has the largest values of H_a (60 min). However, the sample with $x = 5$ has the best cycling performance. The sample with $x = 5$ has the largest value of the quantity of hydrogen released for 5 min, H_d (5 min), at each cycle and the best cycling performance. At $n = 1$, the sample with $x = 1$ has the largest value of the quantity of hydrogen released for 60 min, H_d (60 min), and a slightly larger value of H_d (60 min) than the sample with $x = 5$. However, the sample with $x = 5$ has the best cycling performance.

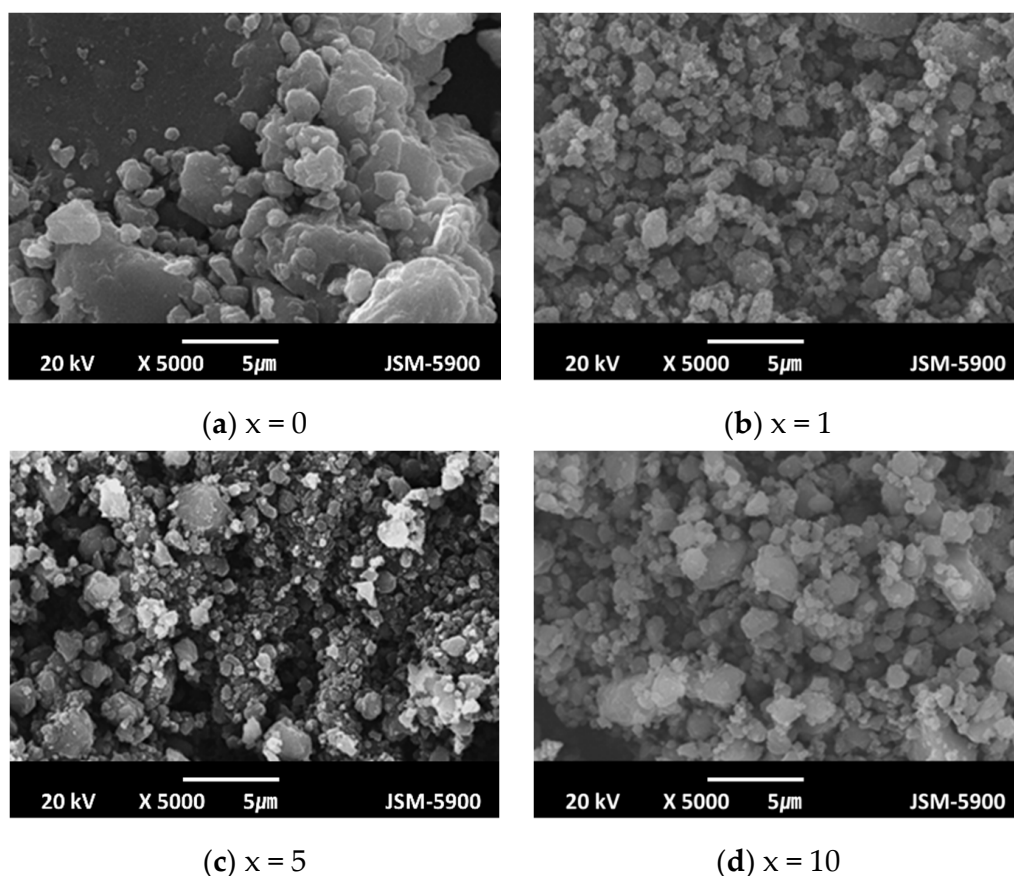


Figure 7. SEM micrographs of $\text{Mg-}x\text{MgH}_2\text{-}1.25\text{Ni-}1.25\text{TaF}_5\text{-}1.25\text{VCl}_3$ ($x = 1, 1, 5$, and 10) after reactive mechanical milling; (a) $x = 0$, (b) $x = 1$, (c) $x = 5$, and (d) $x = 10$.

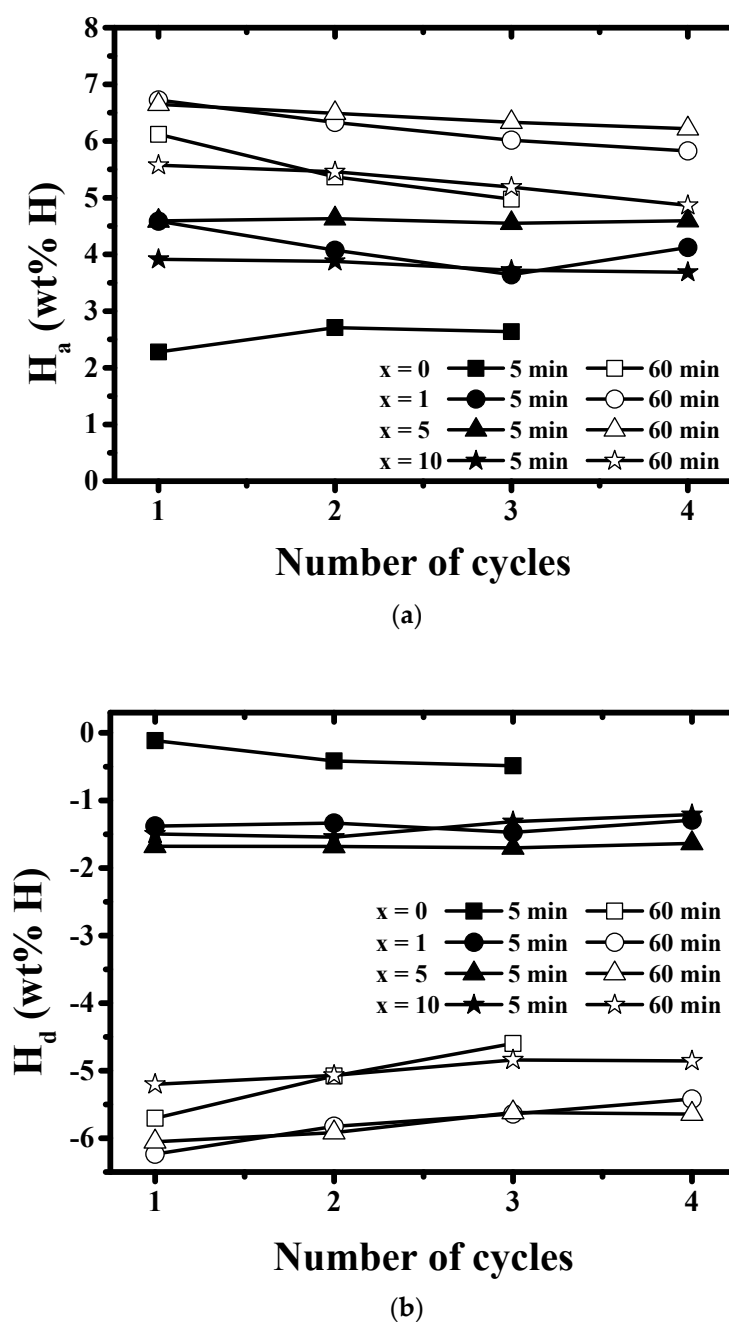


Figure 8. Variations of (a) H_a values for 5 min and 60 min at 593 K under 12 bar H_2 and (b) H_d values for 5 min and 60 min at 593 K under 1.0 bar H_2 with the number of cycles for $Mg-xMgH_2-1.25Ni-1.25TaF_5-1.25VCl_3$ ($x = 0, 1, 5$, and 10).

Figure 9 shows the SEM micrographs of $Mg-xMgH_2-1.25Ni-1.25TaF_5-1.25VCl_3$ ($x = 5$ and 10) after four hydriding and dehydriding cycles. Compared with the particles of these samples after reactive mechanical milling, those of the samples after four hydriding and dehydriding cycles are more agglomerated.

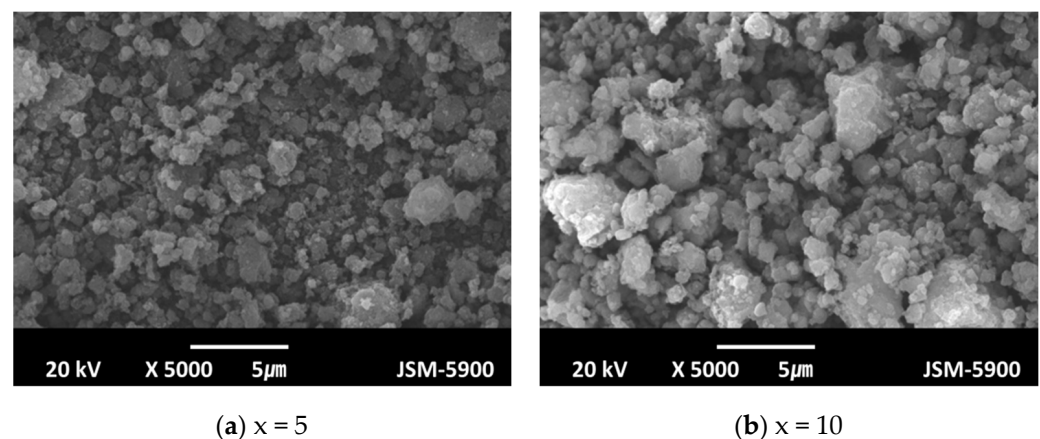


Figure 9. SEM micrographs of $\text{Mg-}x\text{MgH}_2\text{-1.25Ni-1.25TaF}_5\text{-1.25VCl}_3$ ($x = 5$ and 10) after four hydriding and dehydriding cycles; (a) $x = 5$ and (b) $x = 10$.

4. Discussion

The weight percentages of additives were relatively small (2.5 and 3.75 wt%) not to sacrifice the hydrogen-storage capacity of the samples. The addition of Ni together with TaF_5 and VCl_3 increases the quantity of hydrogen absorbed for 60 min of the TaF_5 and VCl_3 -added Mg, as shown in Figure 1. Figure 2 shows that the addition of Ni together with TaF_5 and VCl_3 increases the maximum dehydriding rate and the quantity of hydrogen released for 60 min of the TaF_5 and VCl_3 -added Mg.

Metallic hydrides are more brittle than their parent metals [33]. MgH_2 is brittle [34]. The addition of MgH_2 was expected to increase hydriding and dehydriding rates, as MgH_2 may be pulverized during milling. To prepare materials with better hydriding and dehydriding properties, x wt% MgH_2 ($x = 1, 5$, and 10) was added together with Ni, TaF_5 , and VCl_3 at the same time.

Figure 3 shows that the as-milled $\text{Mg-}x\text{MgH}_2\text{-1.25Ni-1.25TaF}_5\text{-1.25VCl}_3$ ($x = 5$) has the largest total desorbed hydrogen quantity of 4.24 wt%. Figure 4 shows that the samples with $x = 1, 5$, and 10 have higher hydriding rates for the first 5 min than the sample with $x = 0$. The samples with $x = 1$ and 5 have larger quantities of hydrogen absorbed for 60 min, H_a (60 min) than the sample with $x = 0$. Figure 5 shows that the samples with $x = 1, 5$, and 10 have higher dehydriding rates for the first 5 min than the sample with $x = 0$. The samples with $x = 1$ and 5 have larger quantities of hydrogen released for 60 min, H_d (60 min), than the sample with $x = 0$. These results show that the addition of MgH_2 increases the hydriding and dehydriding rates for the first 5 min and the additions of 1 and 5 wt% MgH_2 increase the quantity of hydrogen absorbed and released for 60 min, H_a (60 min) and H_d (60 min). This proves that the addition of MgH_2 made the effects of reactive mechanical milling, which are explained in the following, stronger.

Figure 7 shows that after reactive mechanical milling, the sample with $x = 5$ has the smallest particle size, followed in order by the samples with $x = 1, 10$, and 0 . Figure 7 also shows that the samples with $x = 5$ and 1 have similar particle sizes. A comparison of the results in Figures 4 and 5 with the particle sizes in the SEM micrographs in Figure 7 shows that the smaller the particle size, the higher the hydriding rate for the first 5 min and the dehydriding rate for the first 5 min.

The reactive mechanical milling of Mg with Ni, TaF_5 , and VCl_3 is thought to increase the hydriding and dehydriding rates by forming defects [35–38] (leading to easier nucleation) [39–41], making new clean surfaces (leading to an increase in the reactivity of Mg particles with hydrogen) [30,42], and decreasing the particle size of Mg (leading to a decrease in the diffusion distances of hydrogen atoms) [9,10,36–38,43]. Especially, the added Ni is believed to form the Mg_2Ni phase, which has higher hydriding and dehydriding rates than Mg at the same conditions [36,44], contributing greatly to the increases in the reaction rates. The formed phases ($\beta\text{-MgH}_2$, $\gamma\text{-MgH}_2$, Ta, V, and MgCl_2) are believed to

help the reactive mechanical milling occur more effectively. The result that the addition of MgH_2 increases the hydriding and dehydriding rates for the first 5 min and the result that the additions of 1 and 5 wt% MgH_2 increase H_a (60 min) and H_d (60 min) show that the addition of MgH_2 makes the effects of reactive mechanical milling stronger. Figure 8 shows that H_a (60 min) values decrease as n increases for all the samples. It is believed that the reason of this behavior is that particles coalesce more and more as n increases. The result that the addition of MgH_2 improves the cycling performance, shown in Figure 8, indicates that the added MgH_2 prevents particle from coalescing. The formed phases are also believed to help the sample have better cycling performance. After conducting many studies to improve the reaction kinetics of magnesium with hydrogen, researchers reported as the following. The dissociation rate of hydrogen molecules can be improved by adding catalytic metals, for example, Pd [45] and Co, Ni, or Fe [46]. Nucleation can be facilitated by creating active nucleation sites by mechanical treatment and/or alloying with additives [39]. The diffusion distance of hydrogen can be decreased by the mechanical treatment and/or alloying of Mg with additives, thereby reducing the magnesium particle size [43]. In addition, the hydrogen mobility can be improved by additives that create microscopic paths of hydrogen [43]. A rough surface of magnesium having many cracks and defects is thus considered more advantageous for hydrogen absorption [35].

Compared with the microstructures of these samples after reactive mechanical milling (shown in Figure 7), particles after four hydriding and dehydriding cycles are more agglomerated (shown in Figure 9). Agglomeration is believed to have led to the decreases in the absorbed and released hydrogen quantities of the samples.

Among $\text{Mg-xMgH}_2\text{-1.25Ni-1.25TaF}_5\text{-1.25VCl}_3$ ($x = 0, 1, 5$, and 10), the samples with $x = 1$ and 5 have the highest hydriding rate for 5 min at $n = 1$, but the sample with $x = 5$ has the highest dehydriding rate for 5 min at $n = 1$. Among all the samples, the sample with $x = 5$ has the best cycling performance. The sample with $x = 5$ absorbs 5.58 wt% H for 10 min and has an effective hydrogen storage capacity of 6.65 wt%.

Table 3 presents the hydrogen-storage capacities of several Mg-based alloys. Conditions of sample preparation and reaction are given. The sample $\text{Mg-5MgH}_2\text{-1.25Ni-1.25TaF}_5\text{-1.25VCl}_3$ has quite a high hydrogen-storage capacity. It has a higher hydrogen-storage capacity than Ni and Ti-added Mg alloys.

Table 3. Hydrogen-storage capacities of several Mg-based alloys.

Composition	Ball Milling Time (h)	Reaction Temperature (K)	Reaction Hydrogen Pressure (Bar H_2)	Hydrogen-Storage Capacity (wt% H)	Reference
Mg-2.5TaF ₅ -2.5VCl ₃	6	593	12	5.86 ($n = 1$)	[30]
Mg-1.25TaF ₅ -1.25VCl ₃	6	593	12	5.36 ($n = 1$)	this work
Mg-1.25Ni-1.25TaF ₅ -1.25VCl ₃	6	593	12	6.12 ($n = 1$)	this work
Mg-5MgH ₂ -1.25Ni-1.25TaF ₅ -1.25VCl ₃	6	593	12	6.65 ($n = 1$)	this work
Mg-14Ni-6Ti	6	573	12	4.98	[27]
Mg-1.25Ni-1.25Ti	6	593	12	5.91	[47]

5. Conclusions

The addition of Ni together with TaF₅ and VCl₃ increased the quantity of hydrogen absorbed for 60 min and increased the maximum dehydriding rate and the quantity of hydrogen released for 60 min of the TaF₅ and VCl₃-added Mg. MgH_2 was added together with Ni, TaF₅, and VCl₃, and $\text{Mg-x wt% MgH}_2\text{-1.25 wt% Ni-1.25 wt% TaF}_5\text{-1.25 wt% VCl}_3$ ($x = 0, 1, 5$, and 10) were prepared by reactive mechanical milling. The addition of MgH_2 increased the hydriding and dehydriding rates for the first 5 min, and the additions of 1 and 5 wt% MgH_2 increased the quantities of hydrogen absorbed and released for 60 min, denoted H_a (60 min) and H_d (60 min), respectively. The comparison of H_d versus t and H_a versus t curves with SEM micrographs after reactive mechanical milling showed that

the smaller the particle size, the higher the hydriding rate for the first 5 min, and the dehydriding rate for the first 5 min. The reactive mechanical milling of Mg with Ni, TaF₅, and VCl₃ is thought to increase the hydriding and dehydriding rates by forming defects, making new clean surfaces, and decreasing the particle size of Mg. The addition of MgH₂ made the effects of reactive mechanical milling stronger. The formed phases (β -MgH₂, γ -MgH₂, Ta, V, and MgCl₂) are also believed to have made these effects stronger. The addition of MgH₂ improved cycling performance by preventing particles from coalescing. The formed phases are also believed to have helped the sample have the better cycling performance. Among Mg-xMgH₂-1.25Ni-1.25TaF₅-1.25VCl₃ (x = 0, 1, 5, and 10), the sample with x = 5 had the highest hydriding and dehydriding rates for the first 5 min and the best cycling performance. The sample with x = 5 absorbed 5.58 wt% H for 10 min and had an effective hydrogen-storage capacity of 6.65 wt%.

Author Contributions: Conceptualization, Y.-J.K. and M.-Y.S.; methodology, Y.-J.K. and M.-Y.S.; investigation, Y.-J.K. and M.-Y.S.; data analysis, Y.-J.K. and M.-Y.S.; writing—original draft preparation, Y.-J.K. and M.-Y.S.; writing—review and editing, Y.-J.K. and M.-Y.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Von Colbe, J.B.; Ares, J.-R.; Barale, J.; Baricco, M.; Buckley, C.; Capurso, G.; Gallandat, N.; Grant, D.; Guzik, M.N.; Jacob, I.; et al. Application of hydrides in hydrogen storage and compression: Achievements, outlook and perspectives. *Int. J. Hydrog. Energy* **2019**, *44*, 7780–7808. [[CrossRef](#)]
2. Zhang, X.; Liu, Y.; Ren, Z.; Zhang, X.; Hu, J.; Huang, Z.; Lu, Y.; Gao, M.; Pan, H. Realizing 6.7 wt% reversible storage of hydrogen at ambient temperature with non-confined ultrafine magnesium hydrides. *Energy Environ. Sci.* **2020**, *14*, 2302–2313. [[CrossRef](#)]
3. Liao, W.; Jiang, W.; Yang, X.-S.; Wang, H.; Ouyang, L.; Zhu, M. Enhancing (de)hydrogenation kinetics properties of the Mg/MgH₂ system by adding ANi5 (A = Ce, Nd, Pr, Sm, and Y) alloys via ball milling. *J. Rare Earths* **2020**, *39*, 1010–1016. [[CrossRef](#)]
4. Pukazhselvan, D.; Sandhya, K.; Nasani, N.; Fagg, D.P. Chemical transformation of additive phase in MgH₂/CeO₂ hydrogen storage system and its effect on catalytic performance. *Appl. Surf. Sci.* **2021**, *561*, 150062. [[CrossRef](#)]
5. Paul, D.R.; Sharma, A.; Panchal, P.; Chaudhary, S.; Patidar, D.; Nehra, S. Effect of ball milling and iron mixing on structural and morphological properties of magnesium for hydrogen storage application. *Mater. Today Proc.* **2020**, *42*, 1673–1677. [[CrossRef](#)]
6. Berezovets, V.; Denys, R.; Zavalii, I.; Kosarchyn, Y. Effect of Ti-based nanosized additives on the hydrogen storage properties of MgH₂. *Int. J. Hydrog. Energy* **2021**. [[CrossRef](#)]
7. Yin, Y.; Li, B.; Yuan, Z.; Qi, Y.; Zhang, Y. Enhanced hydrogen storage performance of Mg-Cu-Ni system catalyzed by CeO₂ additive. *J. Rare Earths* **2019**, *38*, 983–993. [[CrossRef](#)]
8. Liu, P.; Chen, H.; Yu, H.; Liu, X.; Jiang, R.; Li, X.; Zhou, S. Oxygen vacancy in magnesium/cerium composite from ball milling for hydrogen storage improvement. *Int. J. Hydrog. Energy* **2019**, *44*, 13606–13612. [[CrossRef](#)]
9. Song, M.Y.; Choi, E.; Kwak, Y.J. Increase in the dehydrogenation rates and hydrogen-storage capacity of Mg-graphene composites by adding nickel via reactive ball milling. *Mater. Res. Bull.* **2020**, *130*, 110938. [[CrossRef](#)]
10. Song, M.Y.; Lee, S.H.; Kwak, Y.J. Improvement in the hydrogenation and dehydrogenation features of Mg by milling in hydrogen with vanadium chloride. *Korean J. Met. Mater.* **2021**, *59*, 721–729. [[CrossRef](#)]
11. Li, Z.; Liu, X.; Jiang, L.; Wang, S. Characterization of Mg-20 wt% Ni-Y hydrogen storage composite prepared by reactive mechanical alloying. *Int. J. Hydrog. Energy* **2007**, *32*, 1869–1874. [[CrossRef](#)]
12. Liang, G.; Huot, J.; Boily, S.; Van Neste, A.; Schulz, R. Hydrogen storage properties of the mechanically milled MgH₂-V nanocomposite. *J. Alloy. Compd.* **1999**, *291*, 295–299. [[CrossRef](#)]
13. Huot, J.; Pelletier, J.; Lurio, L.; Sutton, M.; Schulz, R. Investigation of dehydrogenation mechanism of MgH₂-Nb nanocomposites. *J. Alloy. Compd.* **2003**, *348*, 319–324. [[CrossRef](#)]
14. Fu, Y.; Groll, M.; Mertz, R.; Kulenovic, R. Effect of LaNi₅ and additional catalysts on hydrogen storage properties of Mg. *J. Alloy. Compd.* **2008**, *460*, 607–613. [[CrossRef](#)]
15. Vijay, R.; Sundaresan, R.; Maiya, M.; Murthy, S.S.; Fu, Y.; Klein, H.-P.; Groll, M. Characterisation of Mg-x wt.% FeTi (x = 5–30) and Mg-40 wt.% FeTiMn hydrogen absorbing materials prepared by mechanical alloying. *J. Alloy. Compd.* **2004**, *384*, 283–295. [[CrossRef](#)]
16. Friedrichs, O.; Klassen, T.; Sanchez-Lopez, J.C.; Bormann, R.; Fernandez, A. Hydrogen sorption improvement of nanocrystalline MgH₂ by Nb₂O₅ nanoparticles. *Scr. Mater.* **2006**, *54*, 1293–1297. [[CrossRef](#)]
17. Gupta, R.; Agresti, F.; Russo, S.L.; Maddalena, A.; Palade, P.; Principi, G. Structure and hydrogen storage properties of MgH₂ catalysed with La₂O₃. *J. Alloy. Compd.* **2008**, *450*, 310–313. [[CrossRef](#)]

18. Zhang, Y.; Zhang, W.; Wei, X.; Yuan, Z.; Gao, J.; Guo, S.; Ren, H. Catalytic effects of TiO₂ on hydrogen storage thermodynamics and kinetics of the as-milled Mg-based alloy. *Mater. Charact.* **2021**, *176*, 111118. [CrossRef]
19. Zhang, Y.; Wei, X.; Zhang, W.; Yuan, Z.; Gao, J.; Ren, H. Catalytic effect comparison of TiO₂ and La₂O₃ on hydrogen storage thermodynamics and kinetics of the as-milled La-Sm-Mg-Ni-based alloy. *J. Magnes. Alloy* **2021**. [CrossRef]
20. Zhang, Y.; Wei, X.; Zhang, W.; Yuan, Z.; Gao, J.; Qi, Y.; Ren, H. Effect of milling duration on hydrogen storage thermodynamics and kinetics of Mg-based alloy. *Int. J. Hydrog. Energy* **2020**, *45*, 33832–33845. [CrossRef]
21. Yong, H.; Wei, X.; Zhang, K.; Wang, S.; Zhao, D.; Hu, J.; Zhang, Y. Characterization of microstructure, hydrogen storage kinetics and thermodynamics of ball-milled Mg₉₀Y_{1.5}Ce_{1.5}Ni₇ alloy. *Int. J. Hydrog. Energy* **2021**, *46*, 17802–17813. [CrossRef]
22. Hou, Z.; Wei, X.; Zhang, W.; Yuan, Z.; Ge, Q. Electrochemical hydrogen storage performances of Mg–Ti–Ni–Co–Al-based alloys prepared by mechanical milling. *J. Phys. Chem. Solids* **2021**, *149*, 109788. [CrossRef]
23. Wang, W.; Chen, C.; Chen, L.; Wang, Q. Change in structure and hydrogen storage properties of La₂Mg₁₆Ni alloy after modification by mechanical grinding in tetrahydrofuran. *J. Alloy. Compd.* **2002**, *339*, 175–179. [CrossRef]
24. Sun, D.; Gingsl, F.; Nakamura, Y.; Enoki, H.; Bououdina, M.; Akiba, E. In situ X-ray diffraction study of hydrogen-induced phase decomposition in LaMg₁₂ and La₂Mg₁₇. *J. Alloy. Compd.* **2002**, *333*, 103–108. [CrossRef]
25. Ouyang, L.; Dong, H.; Zhu, M. Mg₃Mn compound based hydrogen storage materials. *J. Alloy. Compd.* **2007**, *446–447*, 124–128. [CrossRef]
26. Yabe, H.; Kuji, T. Thermal stability and hydrogen absorption/desorption properties of Mg₁₇Al₁₂ produced by bulk mechanical alloying. *J. Alloy. Compd.* **2007**, *433*, 241–245. [CrossRef]
27. Malka, I.; Pisarek, M.; Czujko, T.; Bystrzycki, J. A study of the ZrF₄, NbF₅, TaF₅, and TiCl₃ influences on the MgH₂ sorption properties. *Int. J. Hydrog. Energy* **2011**, *36*, 12909–12917. [CrossRef]
28. Kumar, S.; Singh, P.K.; Rao, G.N.; Kojima, Y.; Kain, V. Synergic effect of vanadium trichloride on the reversible hydrogen storage performance of the Mg–MgH₂ system. *Int. J. Hydrog. Energy* **2018**, *43*, 15330–15337. [CrossRef]
29. Liu, Y.; Zou, J.; Zeng, X.; Wu, X.; Li, D.; Ding, W. Hydrogen storage properties of a Mg–Ni nanocomposite coprecipitated from solution. *J. Phys. Chem. C* **2014**, *118*, 18401–18411. [CrossRef]
30. Kwak, Y.J.; Song, M.Y. Enhancement of the hydrogen uptake and release rates of Mg by the addition of TaF₅ and VCl₃ with reactive mechanical grinding. *Nanosci. Nanotechnol. Lett.* **2018**, *10*, 772–778. [CrossRef]
31. Song, M.Y.; Baek, S.H.; Bobet, J.-L.; Hong, S.-H. Hydrogen storage properties of a Mg–Ni–Fe mixture prepared via planetary ball milling in a H₂ atmosphere. *Int. J. Hydrog. Energy* **2010**, *35*, 10366–10372. [CrossRef]
32. da Conceição, M.; Brum, M.; dos Santos, D. The effect of V, VCl₃ and VC catalysts on the MgH₂ hydrogen sorption properties. *J. Alloy. Compd.* **2014**, *586*, S101–S104. [CrossRef]
33. Mandzhukova, T.; Bobet, J.-L.; Khrussanova, M.; Peshev, P. Hydrogen sorption properties of MgH₂–NiCo₂O₄ composites activated mechanically under argon and hydrogen atmospheres. *Mater. Res. Bull.* **2009**, *44*, 1968–1972. [CrossRef]
34. Metallic hydrides. Available online: <https://www.toppr.com/ask/content/story/amp/metallic-hydrides-9178/> (accessed on 14 September 2021).
35. Vigeholm, B.; Kjølner, J.; Larsen, B.; Pedersen, A. Formation and decomposition of magnesium hydride. *J. Less Common Met.* **1983**, *89*, 135–144. [CrossRef]
36. Song, M.; Ivanov, E.; Darriet, B.; Pezat, M.; Hagenmuller, P. Hydriding and dehydriding characteristics of mechanically alloyed mixtures Mg–x wt.% Ni (x = 5, 10, 25 and 55). *J. Less Common Met.* **1987**, *131*, 71–79. [CrossRef]
37. Song, M.Y. Effects of mechanical alloying on the hydrogen storage characteristics of Mg–x wt.% Ni (x = 0, 5, 10, 25 and 55) mixtures. *Int. J. Hydrog. Energy* **1995**, *20*, 221–227. [CrossRef]
38. Song, M.Y. Improvement in hydrogen storage characteristics of magnesium by mechanical alloying with nickel. *J. Mater. Sci.* **1995**, *30*, 1343–1351. [CrossRef]
39. Hjort, P.; Krozer, A.; Kasemo, B. Hydrogen sorption kinetics in partly oxidized Mg films. *J. Alloy. Compd.* **1996**, *237*, 74–80. [CrossRef]
40. Song, M.Y.; Choi, E.; Kwak, Y.J. Preparation of a Mg-based alloy with a high hydrogen-storage capacity by adding a polymer CMC via milling in a hydrogen atmosphere. *Int. J. Hydrog. Energy* **2019**, *44*, 3779–3789. [CrossRef]
41. Song, M.Y.; Choi, E.; Kwak, Y.J. Increase in the dehydrogenation rate of Mg–CMC (Carboxymethylcellulose, Sodium Salt) by adding Ni via hydride-forming milling. *Met. Mater. Int.* **2018**, *25*, 516–527. [CrossRef]
42. Song, M.Y.; Kwak, Y.J. Effects of Zn(BH₄)₂, Ni, and/or Ti doping on the hydrogen-storage features of MgH₂. *Korean J. Met. Mater.* **2019**, *57*, 176–183. [CrossRef]
43. Zaluska, A.; Zaluski, L.; Ström-Olsen, J. Nanocrystalline magnesium for hydrogen storage. *J. Alloy. Compd.* **1999**, *288*, 217–225. [CrossRef]
44. Reilly, J.J.; Wiswall, R.H. Reaction of hydrogen with alloys of magnesium and nickel and the formation of Mg₂NiH₄. *Inorg. Chem.* **1968**, *7*, 2254–2256. [CrossRef]
45. Krozer, A.; Kasemo, B. Equilibrium hydrogen uptake and associated kinetics for the Mg–H₂ system at low pressures. *J. Phys. Condens. Matter* **1989**, *1*, 1533–1538. [CrossRef]
46. Stillesjö, F.; Ólafsson, S.; Hjörvarsson, B.; Karlsson, E. Hydride formation in Mg/Ni-sandwiches studied by hydrogen profiling and volumetric measurements. *Z. Phys. Chem.* **1993**, *181*, 353–358. [CrossRef]
47. Song, M.Y.; Kwak, Y.J. Enhancement of the hydrogenation and dehydrogenation characteristics of Mg by adding small amounts of nickel and titanium. *Mater. Sci.* **2021**. [CrossRef]