Improvement in Hydriding and Dehydriding Features of Mg–TaF$_5$–VCl$_3$ Alloy by Adding Ni and x wt% MgH$_2$ (x = 1, 5, and 10) Together with TaF$_5$ and VCl$_3$

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Abstract: In our previous work, TaF$_5$ and VCl$_3$ were added to Mg, leading to the preparation of samples with good hydriding and dehydriding properties. In this work, Ni was added together with TaF$_5$ and VCl$_3$ to increase the reaction rates with hydrogen and the hydrogen-storage capacity of Mg. The addition of Ni together with TaF$_5$ and VCl$_3$ improved the hydriding and dehydriding properties of the TaF$_5$ and VCl$_3$-added Mg. MgH$_2$ was also added with Ni, TaF$_5$, and VCl$_3$ 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. The addition of MgH$_2$ 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% MgH$_2$ increased the quantity of hydrogen absorbed for 60 min, $H_d$ (60 min), and the quantity of hydrogen released for 60 min, $H_a$ (60 min). The addition of MgH$_2$ 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 TaF$_5$, VCl$_3$, Ni, and MgH$_2$

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 (MgH$_2$) was alloyed [2–10] with Ni and Y [11], V [12], and Nb [13]. In addition, Mg or MgH$_2$ was mixed with compounds such as LaNi$_5$ [14], FeTi and FeTiMn [15], Nb$_2$O$_5$ [16], and La$_2$O$_3$ [17]. Mg-containing compounds [18–22] such as La$_2$Mg$_{16}$Ni [23], LaMg$_{12}$ and La$_2$Mg$_{17}$ [24], Mg$_3$Mm (Mm: misch-metal) [25], and Mg$_{17}$Al$_{12}$ [26] were synthesized for the same purposes.

Malka et al. [27] reported that certain metal halide additives, especially ZrF$_4$ and NbF$_5$ halides, could significantly influence the sorption properties of MgH$_2$. They reported that the presence of the F anion, which weakened Mg–H bonding, led to the formation of MgF$_2$ and provided an electron-rich center to trap transition metal atoms. They showed that NbF$_5$, TaF$_5$, and particularly TiCl$_3$, took part in the disproportionation reactions that created a significant number of structural defects. Kumar et al. [28] reported that VCl$_3$ was reduced to metallic vanadium during ball milling along with MgH$_2$, and this in situ-formed metallic vanadium doped over the MgH$_2$ surface and showed an excellent catalytic effect on hydrogenation–dehydrogenation of the Mg–MgH$_2$ system. They also reported that a microstructural analysis showed an excellent grain refinement property of VCl$_3$ 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-xMgH$_2$-1.25Ni-1.25TaF$_5$-1.25VCl$_3$ (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 Ka 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-1.25TaF\(_3\)-1.25VCl\(_3\) and Mg-1.25Ni-1.25TaF\(_3\)-1.25VCl\(_3\). Mg-1.25Ni-1.25TaF\(_3\)-1.25VCl\(_3\) has a lower hydriding rate for the first 5 min, but a larger quantity of hydrogen absorbed for 60 min than Mg-1.25TaF\(_3\)-1.25VCl\(_3\). Mg-1.25Ni-1.25TaF\(_3\)-1.25VCl\(_3\) 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-1.25TaF\(_3\)-1.25VCl\(_3\) and Mg-1.25Ni-1.25TaF\(_3\)-1.25VCl\(_3\).

The \( H_d \) vs. time t curves at 593 K under 1.0 bar \( H_2 \) at \( n = 1 \) for Mg-1.25TaF\(_3\)-1.25VCl\(_3\) and Mg-1.25Ni-1.25TaF\(_3\)-1.25VCl\(_3\) are shown in Figure 2. Mg-1.25TaF\(_3\)-1.25VCl\(_3\) shows a maximum dehydriding rate after about 20 min. On the other hand, Mg-1.25Ni-1.25TaF\(_3\)-1.25VCl\(_3\) shows a maximum dehydriding rate after about 15 min. Mg-1.25Ni-1.25TaF\(_3\)-1.25VCl\(_3\) has a higher maximum dehydriding rate and a larger quantity of hydrogen released for 60 min than Mg-1.25TaF\(_3\)-1.25VCl\(_3\). Mg-1.25Ni-1.25TaF\(_3\)-1.25VCl\(_3\) 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 TaF\(_3\) and VCl\(_3\) increases the quantity of hydrogen absorbed for 60 min of the TaF\(_3\) and VCl\(_3\)-added Mg. Figure 2 shows that the addition of Ni together with TaF\(_3\) and VCl\(_3\) increases the maximum dehydriding rate and the quantity of hydrogen released for 60 min of the TaF\(_3\) and VCl\(_3\)-added Mg.
X wt% MgH₂ (x = 1, 5, and 10) was added together with Ni, TaF₅, and VCl₃ at the same time with a goal of preparing materials with better hydriding and dehydriding properties.

Figure 2. Hd vs. t curves at 593 K under 1.0 bar H₂ at n = 1 for Mg-1.25TaF₅-1.25VCl₃ and Mg-1.25Ni-1.25TaF₅-1.25VCl₃.

Figure 3 shows the desorbed hydrogen quantity versus time t curves for the as-milled Mg-xMgH₂-1.25Ni-1.25TaF₅-1.25VCl₃ (x = 0, 1, 5, and 10) when the sample was heated with a heating rate of 5–6 K/min. The ranges of temperature where hydrogen is released rapidly are 648–688 K, 579–643 K, 608–625 K, and 570–626 K, respectively. The addition of MgH₂ 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 Mg-xMgH₂-1.25Ni-1.25TaF₅-1.25VCl₃ (x = 0, 1, 5, and 10) were 2.24, 2.56, 4.24, and 3.50 wt% H, respectively.

The Hd versus t curves at 593 K under 12 bar H₂ at n = 1 for Mg-xMgH₂-1.25Ni-1.25TaF₅-1.25VCl₃ (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 MgH₂ 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, H₆ₐ (60 min), followed in order by the samples with x = 5, 0, and 10. The addition of 1 and 5 wt% MgH₂ increases H₆ₐ (60 min) to 6.72 wt% H (x = 1) and 6.65 wt% H (x = 5) from 6.12 wt% H (x = 0). Mg-1MgH₂-1.25Ni-1.25TaF₅-1.25VCl₃ 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%.
The addition of MgH₂ increases the hydriding rate for the first 5 min. The sample with x = 1, 5, and 10 have higher hydriding rates for the first 5 min than the sample with x = 0. 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 Ni together with TaF₅ and VCl₃ increases the maximum desorption temperature of H₂. The Hₐ versus t curves at 593 K under 12 bar H₂ at n = 1 for Mg-xMgH₂-1.25Ni-1.25TaF₅-1.25VCl₃ (x = 0, 1, 5, and 10) are shown in Figure 4. The Hₐ versus t curves at 593 K under 12 bar H₂ at n = 1 for Mg-xMgH₂-1.25Ni-1.25TaF₅-1.25VCl₃ (x = 0, 1, 5, and 10) were 2.24, 2.56, 4.24, and 3.50 wt% H, respectively. The released hydrogen quantity versus time t curves for the as-milled Mg-xMgH₂-1.25Ni-1.25TaF₅-1.25VCl₃ (n = 1) were 2.24, 2.56, 4.24, and 3.50 wt% H, respectively. The H_d versus t curves at 593 K under 12 bar H₂ at n = 1 for Mg-xMgH₂-1.25Ni-1.25TaF₅-1.25VCl₃ (n =1 ) were 2.24, 2.56, 4.24, and 3.50 wt% H, respectively. The H_d versus t curves at 593 K under 12 bar H₂ at n = 1 for Mg-xMgH₂-1.25Ni-1.25TaF₅-1.25VCl₃ (x = 0) were 2.24, 2.56, 4.24, and 3.50 wt% H, respectively.

Table 1 presents the variations of the Hₐ with time and hydriding rates for the first 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 = 1 has the highest hydriding rate for the first 5 min, followed in order by the samples with x = 5, 0, and 10. The addition of MgH₂ increases the hydriding rate for the first 5 min. The sample with x = 1, 5, and 10 have higher hydriding rates for the first 5 min than the sample with x = 0. 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 Ni together with TaF₅ and VCl₃ increases the maximum desorption temperature of H₂. The Hₐ versus t curves at 593 K under 12 bar H₂ at n = 1 for Mg-xMgH₂-1.25Ni-1.25TaF₅-1.25VCl₃ (x = 0, 1, 5, and 10) were 2.24, 2.56, 4.24, and 3.50 wt% H, respectively. The released hydrogen quantity versus time t curves for the as-milled Mg-xMgH₂-1.25Ni-1.25TaF₅-1.25VCl₃ (n = 1) were 2.24, 2.56, 4.24, and 3.50 wt% H, respectively. The H_d versus t curves at 593 K under 12 bar H₂ at n = 1 for Mg-xMgH₂-1.25Ni-1.25TaF₅-1.25VCl₃ (n =1 ) were 2.24, 2.56, 4.24, and 3.50 wt% H, respectively. The H_d versus t curves at 593 K under 12 bar H₂ at n = 1 for Mg-xMgH₂-1.25Ni-1.25TaF₅-1.25VCl₃ (x = 0) were 2.24, 2.56, 4.24, and 3.50 wt% H, respectively.

Figure 3. Desorbed hydrogen quantity versus time t curves for the as-milled Mg-xMgH₂-1.25Ni-1.25TaF₅-1.25VCl₃; (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. Hₐ versus t curves at 593 K under 12 bar H₂ at n = 1 for Mg-xMgH₂-1.25Ni-1.25TaF₅-1.25VCl₃ (x = 0, 1, 5, and 10).

Table 1 presents the variations of the Hₐ with time and hydriding rates for the first 5 min at 593 K under 12 bar H₂ at n = 1 for Mg-xMgH₂-1.25Ni-1.25TaF₅-1.25VCl₃ (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) |
|-----------------------------------------------------|---------------|-----------------------------------------------|
| x = 0                                               | 2.5 min       | 5 min                                        |
|                                                     | 1.47          | 2.82                                         |
| x = 1                                               | 3.2           | 4.59                                         | 6.52 |
| x = 5                                               | 3.17          | 4.59                                         | 6.45 |
| x = 10                                              | 2.77          | 3.91                                         | 5.42 |

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 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).

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).

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).

![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).](image-url)
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) |
|------------------------------------------------------------|-------------------|-----------------------------------------------|
| 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 0.336 |
| 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, \( \beta \)-MgH\(_2\), \( \gamma \)-MgH\(_2\), Ta, V, Ni, and MgF\(_2\). \( \beta \)-MgH\(_2\) and \( \gamma \)-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.

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 Mg-xMgH$_2$-1.25Ni-1.25TaF$_5$-1.25VCl$_3$ ($x = 0, 1, 5,$ 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 Mg-xMgH$_2$-1.25Ni-1.25TaF$_5$-1.25VCl$_3$ ($x = 0, 1, 5,$ 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 Mg-xMgH$_2$-1.25Ni-1.25TaF$_5$-1.25VCl$_3$ (x = 1, 1, 5, and 10) after reactive mechanical milling; (a) x = 0, (b) x = 1, (c) x = 5, and (d) x = 10.](image-url)
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.
Metallic hydrides are more brittle than their parent metals [33]. MgH₂ is brittle [34]. The addition of MgH₂ was expected to increase hydriding and dehydriding rates, as MgH₂ may be pulverized during milling. To prepare materials with better hydriding and dehydriding properties, x wt% MgH₂ (x = 1, 5, and 10) was added together with Ni, TaF₅, and VCl₃ at the same time.

Figure 3 shows that the as-milled Mg-xMgH₂-1.25Ni-1.25TaF₅-1.25VCl₃ (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, Hₐ (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, Hₐ (60 min), than the sample with x = 0. These results show that the addition of MgH₂ increases the hydriding and dehydriding rates for the first 5 min and the additions of 1 and 5 wt% MgH₂ increase the quantity of hydrogen absorbed and released for 60 min, Hₐ (60 min) and Hₐ (60 min). This proves that the addition of MgH₂ 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, TaF₅, and VCl₃ 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 Mg₂Ni 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 (β-MgH₂, γ-MgH₂, Ta, V, and MgCl₂) are believed to

Figure 9. SEM micrographs of Mg-xMgH₂-1.25Ni-1.25TaF₅-1.25VCl₃ (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 TaF₅ and VCl₃ increases the quantity of hydrogen absorbed for 60 min of the TaF₅ and VCl₃-added Mg, as shown in Figure 1. 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.

Metallic hydrides are more brittle than their parent metals [33]. MgH₂ is brittle [34]. The addition of MgH₂ was expected to increase hydriding and dehydriding rates, as MgH₂ may be pulverized during milling. To prepare materials with better hydriding and dehydriding properties, x wt% MgH₂ (x = 1, 5, and 10) was added together with Ni, TaF₅, and VCl₃ at the same time.

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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.

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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$_d$ (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 Mg-xMgH$_2$-1.25Ni-1.25TaF$_5$-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 Mg-5MgH$_2$-1.25Ni-1.25TaF$_5$-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 TaF$_5$ and VCl$_3$ 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 TaF$_5$ and VCl$_3$-added Mg. MgH$_2$ was added together with Ni, TaF$_5$, and VCl$_3$, 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. 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, TaF₃,
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-1.25TaF₃-1.25VCl₃ (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
cert 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%.

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