Metal hydride materials for solid hydrogen storage: A review

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Abstract

Hydrogen is an ideal energy carrier which is considered for future transport, such as automotive applications. In this context storage of hydrogen is one of the key challenges in developing hydrogen economy. The relatively advanced storage methods such as high-pressure gas or liquid cannot fulfill future storage goals. Chemical or physically combined storage of hydrogen in other materials has potential advantages over other storage methods. Intensive research has been done on metal hydrides recently for improvement of hydrogenation properties. The present review reports recent developments of metal hydrides on properties including hydrogen-storage capacity, kinetics, cyclic behavior, toxicity, pressure and thermal response. A group of Mg-based hydrides stand as promising candidate for competitive hydrogen storage with reversible hydrogen capacity up to 7.6 wt% for on-board applications. Efforts have been devoted to these materials to decrease their desorption temperature, enhance the kinetics and cycle life. The kinetics has been improved by adding an appropriate catalyst into the system and as well as by ball-milling that introduces defects with improved surface properties. The studies reported promising results, such as improved kinetics and lower decomposition temperatures, however, the state-of-the-art materials are still far from meeting the aimed target for their transport applications. Therefore, further research work is needed to achieve the goal by improving development on hydrogenation, thermal and cyclic behavior of metal hydrides.

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Keywords: Hydrogen storage; Review; Mg-based hydrides; Complex hydrides; Intermetallic compounds; Ball-milling; Kinetics; Storage capacity; Operating temperature and pressure

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1. Introduction

Hydrogen is the ideal candidate as an energy carrier for both mobile and stationary applications while averting adverse effects on the environment, and reducing dependence on imported oil for countries without natural resources.

Hydrogen storage is clearly one of the key challenges in developing hydrogen economy. Hydrogen can be stored as (i) pressurized gas, (ii) cryogenic liquid, (iii) solid fuel as chemical or physical combination with materials, such as metal hydrides, complex hydrides and carbon materials, or produced on-board the vehicle by reforming methanol [1]. Each of these options possesses attractive attributes for hydrogen storage [2].

Available technologies permit directly to store hydrogen by modifying its physical state in gaseous or liquid form in pressurized or in cryogenic tanks. The traditional hydrogen-storage facilities are complicated because of its low boiling point (−252.87°C) and low density in the gaseous state (0.08988 g/L) at 1 atm. Liquid hydrogen requires the addition of a refrigeration unit to maintain a cryogenic state [3] thus adding weight and energy costs, and a resultant 40% loss in energy content [4]. High-pressure storage of hydrogen gas is limited by the weight of the storage canisters and the potential for developing leaks. Moreover, storage of hydrogen in liquid or gaseous form poses important safety problems for on-board transport applications. Designs involving the use of methane as a hydrogen source require the addition of a steam reformer to extract the hydrogen from the carbon which adds weight, additional space requirements, and the need for a device to sequester CO2 [1].

The US Department of Energy (DOE) [5] published a long-term vision for hydrogen-storage applications considering economic and environmental parameters. The predicted minimum hydrogen-storage capacity should be 6.5 wt% and 65 g/L hydrogen available, at the decomposition temperature between 60 and 120°C for commercial viability. It was also predicted low temperature of hydrogen desorption and low pressure of hydrogen absorption (a plateau pressure of the order of a few bars at room temperature) and nonthermal transformation between substrates and products of decomposition as reported by Schulz [6]. Furthermore, the cost of a storage medium and its toxicity properties need to be carefully considered for the realization of the set goals.

Storage by absorption as chemical compounds or by adsorption on carbon materials have definite advantages from the safety perspective such that some form of conversion or energy input is required to release the hydrogen for use. A great deal of effort has been made on new hydrogen-storage systems, including metal, chemical or complex hydrides and carbon nanostructures.

Carbon materials such as activated carbons, carbon nanotubes, and carbon nanofibers have been the subject of intensive research. The research on hydrogen storage in carbon materials was dominated by announcements of high storage capacities in carbon nanostructures. However, the experimental results on hydrogen storage in carbon nanostructures scatter over several orders of magnitude. The hydrogen-storage capacity for carbon materials is reported between 0.2 and 10 wt% [7,8]. The experiments to date claiming very high values could not independently be reproduced in different laboratories. In view of today’s knowledge although they have good reversibility properties, carbon nanostructures cannot store the amount of hydrogen required for automotive applications [9].

Hydrogen forms metal hydrides with some metals and alloys leading to solid-state storage under moderate temperature and pressure that gives them the important safety advantage over the gas and liquid storage methods. Metal hydrides have higher hydrogen-storage density (6.5 H atoms/cm³ for MgH₂) than hydrogen gas (0.99 H atoms/cm³) or liquid hydrogen (4.2 H atoms/cm³) [3]. Hence, metal hydride storage is a safe, volume-efficient storage method for on-board vehicle applications.

There are two possible ways of hydriding a metal, direct dissociative chemisorption and electrochemical splitting of water. These reactions are:

\[ M + \frac{x}{2} H_2 \leftrightarrow MH_x, \]  \hspace{1cm} (1)

\[ M + \frac{x}{2} H_2O + \frac{x}{2} e^- \leftrightarrow MH_x + \frac{x}{2} OH^-, \]  \hspace{1cm} (2)

where M represents the metal.

Metal hydrides compose of metal atoms that constitute a host lattice and hydrogen atoms. Metal and hydrogen usually form two different kinds of hydrides, α-phase at which only some hydrogen is absorbed and β-phase at which hydride is fully formed. Hydrogen storage in metal hydrides depends on different parameters and consists of several mechanistic steps. Metals differ in the ability to dissociate hydrogen, this ability being dependent on surface structure, morphology and purity [10]. An optimum hydrogen-storage material is required to have the

### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCC</td>
<td>body centered cubic</td>
</tr>
<tr>
<td>BM</td>
<td>ball-milling</td>
</tr>
<tr>
<td>Cyc.</td>
<td>cycle</td>
</tr>
<tr>
<td>DOE</td>
<td>US Department of Energy</td>
</tr>
<tr>
<td>H/M</td>
<td>hydrogen atoms per metal atom</td>
</tr>
<tr>
<td>Mm</td>
<td>misch metals</td>
</tr>
<tr>
<td>P-C</td>
<td>pressure-composition</td>
</tr>
<tr>
<td>P_{abs}</td>
<td>hydrogen absorption pressure</td>
</tr>
<tr>
<td>P_{des}</td>
<td>hydrogen desorption pressure</td>
</tr>
<tr>
<td>T_{abs}</td>
<td>hydrogen absorption temperature</td>
</tr>
<tr>
<td>T_{des}</td>
<td>hydrogen desorption temperature</td>
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<td>t_{abs}</td>
<td>hydrogen absorption time</td>
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<tr>
<td>t_{des}</td>
<td>hydrogen desorption time</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
following properties; high hydrogen capacity per unit mass and unit volume which determines the amount of available energy, low dissociation temperature, moderate dissociation pressure, low heat of formation in order to minimize the energy necessary for hydrogen release, low heat dissipation during the exothermic hydride formation, reversibility, limited energy loss during charge and discharge of hydrogen, fast kinetics, high stability against O₂ and moisture for long cycle life, cyclibility, low cost of recycling and charging infrastructures and high safety.

Hydrogen-storage as metal hydride has been the focus of intensive research. The hydrogen-storage systems have been reported in numerous studies [11–17]. The light metals such as Li, Be, Na, Mg, B and Al, form a large variety of metal–hydrogen compounds. They are especially interesting due to their light weight and the number of hydrogen atoms per metal atom, which is in many cases at the order of H/M = 2. Heavier ones may enter the multiple component system only as a low-abundant additive, most likely for alteration of properties or as a catalyst. There is enduring research both on modifying and optimizing the known hydrogen-storage materials, and new resources. The studies are conducted on finding optimum solid hydrogen-storage system [18]. In this review, we briefly mention about hydrogenation properties, advantages and disadvantages of different metal-hydride systems such as Mg-based metal hydrides, complex hydrides, alanates and intermetallic compounds. A brief review of state-of-the art is reported on metal hydrides. This work will serve to evaluate solid fuel hydrogen store for industrial on-board hydrogen storage tank design.

2. Mg-based metal hydrides

There is considerable research on magnesium and its alloys for on-board hydrogen storage due to their high hydrogen-storage capacity by weight and low cost [15]. Besides, the Mg-based hydrides possess good-quality functional properties, such as heat-resistance, vibration absorbing, reversibility and recyclability. In recent years, therefore, much attention has been paid to investigations on specific material properties of Mg alloys for the development of new functional materials.

Magnesium hydride, MgH₂, has the highest energy density (9 MJ/kg Mg) of all reversible hydrides applicable for hydrogen storage. MgH₂ combines a high H₂ capacity of 7.7 wt% with the benefit of the low cost of the abundantly available magnesium [19–22] with good reversibility [23,24].

The main disadvantages of MgH₂ as a hydrogen store are the high temperature of hydrogen discharge, slow desorption kinetics and a high reactivity toward air and oxygen [25,26]. Thermodynamic properties of the magnesium hydride system have been investigated. The results showed high operating temperature which is too high for practical on-board applications [27]. High thermodynamic stability of MgH₂ results in a relatively high desorption enthalpy, which corresponds to an unfavorable desorption temperature of 300 °C at 1 bar H₂ [15,20].

Hydrogen absorption/desorption properties of recently studied Mg-based hydrides are summarized in Table 1. Many efforts have focused on Mg-based hydrides in recent years to reduce the desorption temperature and to fasten the re/dehydrogenation reactions. These can be accomplished to some extent by changing the microstructure of the hydride by ball-milling (mechanical alloying) with elements which reduce the stability of the hydrides and also by using proper catalysts to improve the absorption/desorption kinetics [61].

2.1. Improvement on surface properties and mechanical ball-milling

A critical factor for hydrogen absorption by metals is the metal surface, which activates dissociation of hydrogen molecules and allows easy diffusion of hydrogen into the bulk. Diffusion is not the limiting step initially because no material has been reacted and there are sufficient active sites available [62], but chemisorption is the slowest step for pure Mg at this point [63]. As the reaction progresses, hydrogen diffusion takes place and the hydride layer grows, producing a nearly impermeable layer. Diffusion through this hydride layer becomes the rate-limiting step in the hydride formation process [63].

In addition to formation of a compact hydride layer, exposure to oxygen also lowers absorption rates due to the formation of a highly stable oxide layer [25]. Andreasen et al. [64] have reviewed the kinetics in terms of apparent activation energies and apparent prefactors of Mg-based hydrides. It was suggested that variations in apparent activation energies correlate with the presence of MgO surface layer inhibiting diffusion of hydrogen. Thus, oxidized samples show large apparent activation energies and well activated samples show smaller activation energies.

The ball-milling creating fresh surfaces during processing is an economic process that is widely applied to metal hydrides to achieve good surface properties [15]. The main effects of ball-milling are increased surface area, formation of micro/nanostructures and creation of defects on the surface and in the interior of the material. The induced lattice defects may aid the diffusion of hydrogen in materials by providing many sites with low activation energy of diffusion. The induced microstrain assists diffusion by reducing the hysteresis of hydrogen absorption and desorption [30]. The increased surface contact with catalyst during ball-milling leads to fast kinetics of hydrogen transformations. It is possible to control properties of the store material, according to specific applications. These include changing the alloy composition, surface properties, microstructures and grain size by ball-milling without the additional cost of catalyst and with minimal loss of storage capacity [58]. It is used for production of nanocrystalline magnesium with superior powder morphology that gives remarkable improvement of kinetics and surface activity for hydrogenation [21,25]. The crystalline Mg₅Ni alloy obtained by ball-milling has excellent surface properties compared with those prepared by a conventional metallurgical method [65].

Huot et al. [58] investigated the structural difference between milled and unmilled MgH₂. The specific surface area is decreased by milling 10-fold. Faster hydrogen desorption kinetics, reduction in activation energy and enhanced kinetics observed for the milled MgH₂ compared to the unmilled one are seen in Fig. 1. The activation energies for desorption were measured
<table>
<thead>
<tr>
<th>Material</th>
<th>Method</th>
<th>Temperature (°C)</th>
<th>Pressure (bar)</th>
<th>Kinetics (min)</th>
<th>Cycling stability</th>
<th>Max wt% of H₂</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgH₂–5 mol% Fe₂O₃</td>
<td>BM</td>
<td>T&lt;sub&gt;abs&lt;/sub&gt;: 300</td>
<td>P&lt;sub&gt;abs&lt;/sub&gt;: 2–15</td>
<td>t&lt;sub&gt;abs&lt;/sub&gt;: 20</td>
<td>No data</td>
<td>1.37</td>
<td>[28]</td>
</tr>
<tr>
<td>30 wt% Mg-M mNi₅&lt;sub&gt;1&lt;/sub&gt;–(COAlMn)&lt;sub&gt;x&lt;/sub&gt;</td>
<td>BM</td>
<td>T&lt;sub&gt;abs&lt;/sub&gt;: 15</td>
<td>P&lt;sub&gt;abs&lt;/sub&gt;: 6</td>
<td>t&lt;sub&gt;abs&lt;/sub&gt;: 83</td>
<td>No data</td>
<td>2.30</td>
<td>[22,29]</td>
</tr>
<tr>
<td>Mg–5 wt% Fe₅H₁₂</td>
<td>BM</td>
<td>T&lt;sub&gt;abs&lt;/sub&gt; and T&lt;sub&gt;dec&lt;/sub&gt;: 400</td>
<td>P&lt;sub&gt;dec&lt;/sub&gt;: 30</td>
<td>t&lt;sub&gt;dec&lt;/sub&gt;: 1</td>
<td>No data</td>
<td>2.70</td>
<td>[30]</td>
</tr>
<tr>
<td>MgH₂–5 mol% V₂O₅</td>
<td>BM</td>
<td>T&lt;sub&gt;abs&lt;/sub&gt;: 250</td>
<td>P&lt;sub&gt;abs&lt;/sub&gt;: 15</td>
<td>t&lt;sub&gt;abs&lt;/sub&gt;: 1.6</td>
<td>No data</td>
<td>3.20</td>
<td>[28]</td>
</tr>
<tr>
<td>90 Mg–10 Al</td>
<td>BM</td>
<td>T&lt;sub&gt;abs&lt;/sub&gt; and T&lt;sub&gt;dec&lt;/sub&gt;: 400</td>
<td>P&lt;sub&gt;dec&lt;/sub&gt;: 12</td>
<td>t&lt;sub&gt;dec&lt;/sub&gt;: 5.8</td>
<td>No data</td>
<td>3.30</td>
<td>[31,32]</td>
</tr>
<tr>
<td>Mg–50 wt% ZrFe₄₂Cr₃₀₆</td>
<td>BM</td>
<td>T&lt;sub&gt;abs&lt;/sub&gt;: 250–350</td>
<td>P&lt;sub&gt;abs&lt;/sub&gt;: 20</td>
<td>t&lt;sub&gt;abs&lt;/sub&gt;: 1</td>
<td>2 cyc.: stable</td>
<td>3.40</td>
<td>[33]</td>
</tr>
<tr>
<td>Mg–10 wt% CeO₂</td>
<td>BM</td>
<td>T&lt;sub&gt;abs&lt;/sub&gt; and T&lt;sub&gt;dec&lt;/sub&gt;: 300</td>
<td>P&lt;sub&gt;dec&lt;/sub&gt;: 11</td>
<td>t&lt;sub&gt;dec&lt;/sub&gt;: 5</td>
<td>5 cyc.: not stable</td>
<td>3.43</td>
<td>[34]</td>
</tr>
<tr>
<td>Mg–20 wt% Mn (La, Nd, Ce)</td>
<td>BM (pellet form)</td>
<td>T&lt;sub&gt;abs&lt;/sub&gt;: 300</td>
<td>P&lt;sub&gt;dec&lt;/sub&gt;: 10</td>
<td>t&lt;sub&gt;dec&lt;/sub&gt;: 5</td>
<td>No data</td>
<td>3.50</td>
<td>[35]</td>
</tr>
<tr>
<td>Mg–40 wt% ZrFe₂₄Cr₆₀₆</td>
<td>BM</td>
<td>T&lt;sub&gt;abs&lt;/sub&gt;: 270–280</td>
<td>P&lt;sub&gt;dec&lt;/sub&gt;: 1</td>
<td>t&lt;sub&gt;dec&lt;/sub&gt;: 5</td>
<td>2 cyc.: stable</td>
<td>3.60</td>
<td>[36]</td>
</tr>
<tr>
<td>La₂Mg₁₇–40 wt% LaNi₅</td>
<td>BM</td>
<td>T&lt;sub&gt;abs&lt;/sub&gt; and T&lt;sub&gt;dec&lt;/sub&gt;: 250–303</td>
<td>P&lt;sub&gt;abs&lt;/sub&gt; and P&lt;sub&gt;dec&lt;/sub&gt;: 4–7</td>
<td>t&lt;sub&gt;dec&lt;/sub&gt;: 0.45</td>
<td>Not stable</td>
<td>3.70</td>
<td>[37,38]</td>
</tr>
<tr>
<td>La₀.₅Ni₁₇.₅Mg₁₇</td>
<td>Hydriding combustion synthesis</td>
<td>T&lt;sub&gt;abs&lt;/sub&gt; and T&lt;sub&gt;dec&lt;/sub&gt;: 280–400</td>
<td>P&lt;sub&gt;abs&lt;/sub&gt;: 2.21–11.34</td>
<td>t&lt;sub&gt;abs&lt;/sub&gt;: 15</td>
<td>Not stable</td>
<td>4.03</td>
<td>[39]</td>
</tr>
<tr>
<td>Mg–50 wt% LaNi₄</td>
<td>BM</td>
<td>T&lt;sub&gt;dec&lt;/sub&gt;: 250–300</td>
<td>P&lt;sub&gt;abs&lt;/sub&gt; and P&lt;sub&gt;dec&lt;/sub&gt;: 10–15</td>
<td>t&lt;sub&gt;dec&lt;/sub&gt;: 5</td>
<td>Not stable</td>
<td>4.10</td>
<td>[40]</td>
</tr>
<tr>
<td>MgH₂–2LiNH₂</td>
<td>BM</td>
<td>T&lt;sub&gt;abs&lt;/sub&gt; and T&lt;sub&gt;dec&lt;/sub&gt;: 200</td>
<td>P&lt;sub&gt;abs&lt;/sub&gt;: 50</td>
<td>t&lt;sub&gt;abs&lt;/sub&gt;: 3.33</td>
<td>4 cyc.: stable after 2nd cycle</td>
<td>4.30</td>
<td>[41,42]</td>
</tr>
<tr>
<td>Mg–Co₃H₅</td>
<td>Mixing</td>
<td>T&lt;sub&gt;abs&lt;/sub&gt;: 450–550</td>
<td>P&lt;sub&gt;abs&lt;/sub&gt;: 17–25</td>
<td>t&lt;sub&gt;abs&lt;/sub&gt;: 67</td>
<td>1000 cyc.: stable</td>
<td>4.48</td>
<td>[43]</td>
</tr>
<tr>
<td>MgH₂–5 mol% Al₂O₃</td>
<td>BM</td>
<td>T&lt;sub&gt;abs&lt;/sub&gt;: 300</td>
<td>P&lt;sub&gt;dec&lt;/sub&gt;: 15</td>
<td>t&lt;sub&gt;dec&lt;/sub&gt;: 5</td>
<td>No data</td>
<td>4.49</td>
<td>[28]</td>
</tr>
<tr>
<td>1.1MgH₂–2LiNH₂</td>
<td>BM</td>
<td>T&lt;sub&gt;abs&lt;/sub&gt;: 200</td>
<td>P&lt;sub&gt;dec&lt;/sub&gt;: 30</td>
<td>t&lt;sub&gt;abs&lt;/sub&gt;: 30</td>
<td>9 cyc.: stable</td>
<td>4.50</td>
<td>[44,45]</td>
</tr>
<tr>
<td>Mg–20 wt% TiO₂</td>
<td>BM</td>
<td>T&lt;sub&gt;dec&lt;/sub&gt;: 350</td>
<td>P&lt;sub&gt;dec&lt;/sub&gt;: 20 bar</td>
<td>t&lt;sub&gt;dec&lt;/sub&gt;: 2</td>
<td>Not stable</td>
<td>4.70</td>
<td>[46]</td>
</tr>
<tr>
<td>Mg–30 wt% MnNi₄₆Fe₃O₄</td>
<td>BM (hexane medium)</td>
<td>T&lt;sub&gt;dec&lt;/sub&gt;: 300–550</td>
<td>P&lt;sub&gt;dec&lt;/sub&gt;: 2</td>
<td>t&lt;sub&gt;dec&lt;/sub&gt;: 30</td>
<td>No data</td>
<td>5.00</td>
<td>[47]</td>
</tr>
<tr>
<td>MgH₂–5 wt% V</td>
<td>BM</td>
<td>T&lt;sub&gt;abs&lt;/sub&gt; and T&lt;sub&gt;dec&lt;/sub&gt;: 300</td>
<td>P&lt;sub&gt;abs&lt;/sub&gt; and P&lt;sub&gt;dec&lt;/sub&gt;: 1–3</td>
<td>t&lt;sub&gt;abs&lt;/sub&gt;: 2</td>
<td>2000 cyc.: stable</td>
<td>5.00</td>
<td>[48]</td>
</tr>
<tr>
<td>Mg–Fe–Mg₂Fe₆H₈</td>
<td>Mixing</td>
<td>T&lt;sub&gt;abs&lt;/sub&gt;: 473–552</td>
<td>P&lt;sub&gt;abs&lt;/sub&gt;: 77–85</td>
<td>t&lt;sub&gt;abs&lt;/sub&gt;: 90</td>
<td>600 cyc.: stable</td>
<td>5.00</td>
<td>[43]</td>
</tr>
<tr>
<td>MgH₂–Mg₂Fe₆H₈</td>
<td>Mixing</td>
<td>T&lt;sub&gt;abs&lt;/sub&gt; and T&lt;sub&gt;dec&lt;/sub&gt;: 350–525</td>
<td>P&lt;sub&gt;abs&lt;/sub&gt; and P&lt;sub&gt;dec&lt;/sub&gt;: 3.6–93.7</td>
<td>t&lt;sub&gt;abs&lt;/sub&gt;: 90–1440</td>
<td>600 cyc.: stable</td>
<td>5.00</td>
<td>[49]</td>
</tr>
<tr>
<td>MgH₂–5 at% Ti</td>
<td>BM</td>
<td>T&lt;sub&gt;abs&lt;/sub&gt;: 200</td>
<td>P&lt;sub&gt;dec&lt;/sub&gt;: 10</td>
<td>t&lt;sub&gt;dec&lt;/sub&gt;: 3.33</td>
<td>No data</td>
<td>5.00</td>
<td>[50]</td>
</tr>
<tr>
<td>MgH₂–5 at% Ni</td>
<td>BM</td>
<td>T&lt;sub&gt;abs&lt;/sub&gt;: 300</td>
<td>P&lt;sub&gt;abs&lt;/sub&gt;: 0.15</td>
<td>t&lt;sub&gt;abs&lt;/sub&gt;: 0.83</td>
<td>No data</td>
<td>5.00</td>
<td>[50]</td>
</tr>
<tr>
<td>Mg–30 wt% LaNi₂₂₈</td>
<td>BM</td>
<td>T&lt;sub&gt;abs&lt;/sub&gt;: 280</td>
<td>P&lt;sub&gt;abs&lt;/sub&gt;: 10</td>
<td>t&lt;sub&gt;abs&lt;/sub&gt;: 5</td>
<td>3 cyc.: stable</td>
<td>5.40</td>
<td>[51]</td>
</tr>
<tr>
<td>MgH₂–5 at% V</td>
<td>BM</td>
<td>T&lt;sub&gt;abs&lt;/sub&gt;: 300</td>
<td>P&lt;sub&gt;abs&lt;/sub&gt;: 10</td>
<td>t&lt;sub&gt;abs&lt;/sub&gt;: 1.6</td>
<td>3 cyc.: stable</td>
<td>5.50</td>
<td>[50]</td>
</tr>
<tr>
<td>Mg–10 wt% Fe₂O₃</td>
<td>BM</td>
<td>T&lt;sub&gt;abs&lt;/sub&gt;: 300</td>
<td>P&lt;sub&gt;dec&lt;/sub&gt;: 10</td>
<td>t&lt;sub&gt;dec&lt;/sub&gt;: 1.66</td>
<td>No data</td>
<td>5.56</td>
<td>[52]</td>
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<tr>
<td>Mg–30 wt% CFMnNi₅</td>
<td>Mixing and encapsulation</td>
<td>T&lt;sub&gt;abs&lt;/sub&gt; and T&lt;sub&gt;dec&lt;/sub&gt;: 500</td>
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MgH$_2$–5 wt% V BM

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<th>$P_{\text{des}}$</th>
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Mg–10 wt% Cr$_2$O$_3$ BM

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<th>$t_{\text{abs}}$</th>
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<th>$P_{\text{des}}$</th>
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Mg–10 wt% Mn BM

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<th>$t_{\text{abs}}$</th>
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Mg–0.2 mol% Cr$_2$O$_3$ BM

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<th>$t_{\text{abs}}$</th>
<th>$T_{\text{des}}$</th>
<th>$P_{\text{des}}$</th>
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MgH$_2$–5 at% Ge BM

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<th>$t_{\text{abs}}$</th>
<th>$T_{\text{des}}$</th>
<th>$P_{\text{des}}$</th>
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Mg–0.5 wt% Nb$_2$O$_5$ Mixing

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<th>$t_{\text{abs}}$</th>
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<th>$P_{\text{des}}$</th>
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<th>$\text{cyc.}:$ stable</th>
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MgH$_2$–5 mol% Ni BM (benzene and cyclohexane medium)

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<th>$t_{\text{abs}}$</th>
<th>$T_{\text{des}}$</th>
<th>$P_{\text{des}}$</th>
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MgH$_2$–0.2 mol% Ni BM

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<th>$P_{\text{abs}}$</th>
<th>$t_{\text{abs}}$</th>
<th>$T_{\text{des}}$</th>
<th>$P_{\text{des}}$</th>
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<td>3–10</td>
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3Mg(NH$_2$)$_2$–8LiH BM

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<th>$T_{\text{abs}}$</th>
<th>$P_{\text{abs}}$</th>
<th>$t_{\text{abs}}$</th>
<th>$T_{\text{des}}$</th>
<th>$P_{\text{des}}$</th>
<th>$t_{\text{des}}$</th>
<th>$\text{cyc.}:$ stable</th>
<th>$\text{cyc.}$: not stable</th>
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<tbody>
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<td>1</td>
<td>7.0</td>
<td>No data</td>
<td>No data</td>
<td>No data</td>
<td>140–190</td>
<td>7.0</td>
</tr>
</tbody>
</table>

Hydrogenation properties are very sensitive to these surface modifications. The ball-milled powders do not require activation compared to the conventional methods. For all nanocrystalline hydrides investigated, the grain boundary does not dramatically affect the pressure–composition (P–C) isotherms. This describes the thermodynamic aspects of hydride formation which is more visible in the Van’t Hoff plots that illustrate the relationship between equilibrium pressure and changes in enthalpy and entropy. The pressure for hydrogen desorption of the unmilled MgH$_2$ is lower than that of the milled one, as seen in Fig. 2.

Aoyagi et al. [67] proposed that ball-milling of the alloys under inert environment leads to reduction in powder size and creation of new surfaces, which are effective for the improvement of the hydrogen absorption rate. Hydrogen absorption rate of Mg-based alloys also increases with the milling time. Liang et al. [30] proposed that ball-milling of Mg–5 wt% FeTi$_{1.2}$ produces fine powder with nanometer-sized grains and large microstrain, which results in an increase in the hydriding and dehydriding rates. The high absorption rate is due to the large quantity of phase boundaries and the porous surface structure [40]. Nanocrystalline hydrides enhanced the hydrogenation kinetics, even at relatively low temperatures. These

![Fig. 1. Hydrogen desorption curves of unmilled MgH$_2$ (solid symbols) and ball-milled (hollow symbols) MgH$_2$ under a hydrogen pressure of 0.15 bar [58].](image-url)
structures can be obtained by means of local change in the stable atomic positions into the metastable configuration. Ball-milling of LiNH2/MgH2 results in low dehydrogenation temperature (200 °C) but with markedly slow kinetics and lowered hydrogen uptake capacity [41]. Wagemans et al. [68] investigated the quantum chemical perspective of MgH2. Small MgH2 clusters have much lower desorption energy than bulk MgH2, hence enabling hydrogen desorption at lower temperatures. The hydrogen desorption energy decreases significantly when the crystal grain size becomes smaller than 1.3 nm. A MgH2 crystallite size of 0.9 nm corresponds to a desorption temperature of only 200 °C [68]. Particles with nanocrystalline structure with grain size of 10 nm or less, increase the density of grain boundaries, resulting in easier activation [69].

In another approach, a hydrogen-absorbing material can be hydrogenated during ball-milling [70]. It was shown that ball-milling under hydrogen atmosphere is a convenient method for the formation of metal hydrides which causes simultaneous hydrogen uptake and mechanical deformation resulting from ball-milling. Huot et al. [71] produced MgH2 under H2 atmosphere by ball-milling. This method improved the hydride formation kinetics. Chen et al. [72] studied also the formation of metal hydrides under H2 atmosphere. The results indicated that pulverization and deformation processes occurring during high-energy ball-milling play a major role in the hydriding reaction. It is concluded that ball-milling is a simple and inexpensive method of producing high hydrogen content metal hydrides.

Mg–10 wt% Fe2O3 is synthesized by mechanical grinding under H2 atmosphere [52]. It increases the H2-sorption rates with 5.56 wt% H2 absorption, by facilitating nucleation by creating defects on the surface of Mg particles and reducing the particle size of Mg and thus by shortening the diffusion distances of hydrogen atoms. By using the same method, it was proposed recently that the presence of nickel lowered the onset temperature of MgH2 desorption to 225 °C by ball-milling under hydrogen atmosphere [71]. Tessier et al. [70] synthesized Mg2Ni with the same method. Furthermore, Orimo et al. [73] found that ball-milling of Mg2Ni under hydrogen resulted in a significant facilitation of hydrogen desorption. Alloying time has a significant effect on hydride properties of Mg2Ni. Abdellaoui et al. [74] proposed that absorption capacity changes with alloying duration. Barkhordarian et al. [75] investigated the effect of milling time on the magnesium hydrogen sorption reaction. Reaction kinetics is enhanced by increasing the milling time, as shown in Fig. 3. Ball-milling is generally used to produce powders in the range of 60–100 μm [25,76] to create more active sights for hydrogen penetration. Smaller particle sizes also eliminate the formation of hydride layers greater than 50 μm [25].

Although extensive work has been done on hydrogen storage in bulk materials as thin film hydride is an emerging field of research. Research performed on thin films of pure magnesium concluded that the thinner the magnesium sheet, the faster it achieved complete formation of MgH2. It was found that hydrogen penetrated to an average depth of 30 μm and stopped [77]. Mg portions of the film have converted totally into MgH2 at temperatures not higher than 200 °C [78]. Hydrogen-storage properties of nanocomposite three-layered Pd/Mg/Pd films have been previously investigated. After hydrogenation under a hydrogen gas pressure of 1 bar at 100 °C, Pd layers contain only 0.15–0.30 wt% H2, whereas the Mg film contains 5.0 wt% hydrogen [79]. Pd/Mg films with different degree of crystallization in the Mg layer are prepared in different sputtering conditions [77]. The dehydriding temperature decreases with decreasing the degree of crystallization in the Mg layer in
Table 2. Hydrogen absorption/desorption properties of Mg–Ni-based hydrides

<table>
<thead>
<tr>
<th>Material</th>
<th>Method</th>
<th>Temperature (°C)</th>
<th>Pressure (bar)</th>
<th>Kinetics (min)</th>
<th>Cycling stability</th>
<th>Max wt% of H₂</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg₂Ni–1 wt% Pd</td>
<td>BM</td>
<td>T_abs: 200</td>
<td>P_abs: 15</td>
<td>t_abs: 27</td>
<td>4 cyc.: stable</td>
<td>2.50</td>
<td>[86]</td>
</tr>
<tr>
<td>Mg₂Ni</td>
<td>BM</td>
<td>T_abs: 300</td>
<td>P_abs: 11.6</td>
<td>t_abs: 10</td>
<td>4 cyc.: stable</td>
<td>3.50</td>
<td>[86]</td>
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<td>BM</td>
<td>T_abs: 300</td>
<td>P_abs: 12</td>
<td>t_abs: 83</td>
<td>2 cyc.: not stable</td>
<td>3.60</td>
<td>[89]</td>
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<td>No data</td>
<td>3.53</td>
<td>[74,88]</td>
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<td>BM</td>
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<td>P_abs: 1–15</td>
<td>t_abs: 1</td>
<td>No data</td>
<td>4.10</td>
<td>[82]</td>
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<td>BM</td>
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<td>P_abs: 1–2</td>
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<td>BM</td>
<td>T_abs and T_des: 350</td>
<td>P_abs: 10</td>
<td>t_abs: 30</td>
<td>10 cyc.: stable</td>
<td>4.66</td>
<td>[91]</td>
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<tr>
<td>65 wt% Mg₂H₂–35 wt% Mg₂NiH₄</td>
<td>BM</td>
<td>T_abs: 220–240</td>
<td>P_abs: 0.5</td>
<td>t_abs: 10</td>
<td>20 cyc.: stable</td>
<td>5.00</td>
<td>[66]</td>
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</table>

Pd/Mg films. The lowest crystallization of films absorb 5.6 wt% of hydrogen and all hydrogen desorbed at a temperature lower than 190 °C in a vacuum [77].

Mechanical alloying can be preferred in the presence of organic solvents such as benzene, cyclohexane or carbon materials [80,81]. Nanosized MgH₂ ball-milled with benzene showed reversible hydriding/dehydriding with high capacity under 1 bar hydrogen pressure. It was proposed that the organic additives of benzene or cyclohexane are essential for decisive characteristics of the resulting magnesium to sustain nanosized magnesium with high-degree of dispersion [20]. Wet milling in the presence of toluene leads to hydrogen and carbon pick up in the powder, and also require much longer milling times [82]. Hydriding properties of Mg-based composites which are prepared by mechanical milling of magnesium powder and graphite or graphite supporting 5 wt% Pd in the presence of various additives (tetrahydrofuran, benzene or cyclohexane) have been studied [80]. In particular, the presence of tetrahydrofuran in the milling process strongly affected the hydriding and dehydriding kinetics of the resulting composites [80]. There is a synergetic interaction between Mg and aromatic carbon atoms of graphite containing charge transfer to some extent.

It has been found that the hydrogenation properties of Mg, such as hydrogenation/dehydrogenation temperature and hydriding rate, can be more or less improved by forming composite structures. Zhu et al. [22,29] reported that the hydrogen sorption properties of Mg and Mg–Ni-based alloys can significantly be improved by forming composites having proper microstructural feature.

Mg₂NiH₄ attracts wide interest for being a promising hydrogen storage material due to its relatively high capacity, low cost, light weight and low-toxicity [83] and for its unusual structural and bonding properties [84,85]. The hydrogen absorption and desorption properties of Mg–Ni-based alloys are listed in Table 2. Mg₂NiH₄ forms eagerly by hydrogenating the alloy Mg₂Ni [92]:

\[ \text{Mg}_2\text{Ni} + 2\text{H}_2 \rightarrow \text{Mg}_2\text{NiH}_4. \] (3)

Upon hydrogenation, Mg₂Ni reacts with 3.6 wt% of hydrogen and transforms into the hydride phase, Mg₂NiH₄, and the dehydriding temperature is 250–300 °C at desorption pressure of 2.1–3.0 bar [22,66,74,84,88]. High hydrogen capacity of four hydrogen atoms per Mg₂Ni, combined with the small specific weight of the alloy is the most important advantage of Mg₂Ni over other magnesium hydrides [93].

There are numerous publications regarding the upgrade of hydrogenation properties of Mg₂NiH₄. Their hydriding properties are thought to be strongly affected by their nanometer-scale structures by means of thermodynamic and kinetic aspects. MgNi₂ prepared by ball-milling is found to react with hydrogen even at room temperature, whereas polycrystalline material needs hydrogenation temperature of 250–350 °C and pressure of 15–50 bar [84]. Haussermann et al. [92] investigated the structural stability and bonding properties of the Mg₂NiH₄ using ab initio density functional calculations. Particular changes of the hydriding properties of the nanostructured Mg₂NiH₄ have been also reported [19,22,25,73,94].

The nanocrystalline Mg₂Ni intermetallic compound formed by mechanical alloying of Mg and Mg₂Ni can absorb hydrogen rapidly without activation. The Mg + Mg₂Ni composites need activation, but once activated, they absorb hydrogen more rapidly than Mg₂Ni at low temperature of 150 °C under 12 bar with high capacity of 4.2 wt% [89]. Nanoparticles of Mg₂Ni leads to superior hydrogenation behavior including easy activation and hydrogen uptake in the first cycle itself compared to the conventional crystal phase [86,87]. Nanocrystalline Mg₂Ni with Pd exhibits much faster absorption kinetics at 200 °C than the as-ball-milled samples (reaction halftime of 2 and 33 min, respectively) [86].

2.2. Cyclic stability

Cyclic stability is one of the major criteria for applicability of metal/metal hydride systems for reversible hydrogen storage. Depending on the nature of the additives, cycling temperatures and starting microstructures, various structures and intermediate phases can be obtained. Song et al. [34] synthesized magnesium hydrides with additives of Cr₂O₃, Al₂O₃ and CeO₂. All the samples absorb and desorb less hydrogen at the fifth cycle than at the first cycle due to the agglomeration of the particles.
during hydrogenation/dehydrogenation cycling. Misch metals (Mm) such as Ce, La, Nd and Pr, are used to increase the cyclic stability [95,35]. However, the increased concentration of Mm in the samples has an adverse effect on hydrogen-storage capacity and their reaction rate [35]. Gross et al. [37] have reported formation phase changes, segregation and disintegration of La$_2$Mg$_{17}$ + 40 wt% LaNi$_5$ during cycling at temperatures up to 350°C. It was also reported that hydrogen capacity of La$_{0.5}$Ni$_{5}$Mg$_{17}$ decreases with cycling [39].

There are few publications regarding high number of cyclic tests. Reiser et al. [43] investigated the behavior of Ni-doped Mg and Mg$_2$CoH$_5$. They indicated that they are almost stable even after 800 cycles with small fluctuations in the hydrogen capacity, as shown in Fig. 4. The cyclic stability of MgH$_2$–5 wt% V is studied by Dehouche et al. [48] up to 2000 cycles. They concluded that there is no change in isotherms and no disintegration of the materials even when hydrogen content reached 5 wt%. Also the cyclic stability of MgH$_2$ + 0.2 mol% Cr$_2$O$_3$ is previously examined at 1000 cycles. Although desorption time is increased, an increase of H$_2$ storage capacity is reported by about 8% between the first and the 500 or 1000 cycle due to structural relaxations and crystallite growth [55]. Friedelmeier et al. [96] observed a decrease in the kinetics of hydrogen absorption after 4300 cycles, but no loss in the hydrogen capacity of Mg–2 at% Ni alloy. However, to achieve the same storage capacity, the system temperature had to be increased. Nevertheless, Dehouche et al. [97] showed 15% decrease in hydrogen capacity after 2100 cycles with a starting material of nanocrystalline Mg$_2$Ni. This was attributed to the formation of the non-hydride forming MgNi$_2$ phase, during the cycling process.

The resistance of metal hydrides to impurities is one of the critical issues for on-board applications in order to maintain performance over the lifetime of the material. The effects of N$_2$, O$_2$, CO$_2$ and CO on a pure magnesium powder have been studied [98]. Both O$_2$ and N$_2$ slowed the rate of hydrogen absorption, while CO and CO$_2$ entirely prevented the uptake of hydrogen [98,99]. The performance of MgH$_2$–V–Ti was evaluated after 1000 cycles under a H$_2$ atmosphere containing 101 ppm moisture. Hydrogen-storage capacity increased 5% but desorption properties deteriorated due to surface modification of the particles [100].

2.3. Catalyst effect

Catalysis is one of the critical factors in the improvement of hydrogen sorption kinetics in metal hydride systems that enables fast and effective dissociation of hydrogen molecules [21]. Effective catalysts, even added in small amounts enhance the formation of a hydride in reasonable extent. There is intensive research about finding a proper catalyst to enhance the hydriding properties. It was reported that the rate of absorption is controlled by the following factors: the rate of hydrogen dissociation at the surface, the capability of hydrogen to penetrate from the surface which is typically covered by an oxide layer into metal, the rate of hydrogen diffusion into the bulk metal and through the hydride already formed.

Palladium is a good catalyst for hydrogen dissociation reaction. The hydriding properties are enhanced by catalysis through nanoparticles of Pd located on magnesium surface [25]. The reactivity of palladium after exposure to oxygen is recovered during exposure to hydrogen because of the easy decomposition of palladium oxide [93]. However, high cost of palladium is the main disadvantage for the industrial applications [15]. Zaluski et al. [86] have also reported on the presence of Pd as a catalyst in nanocrystalline Mg$_2$Ni, LaNi$_5$ and FeTi systems, enhance the absorption rates even at lower temperatures and maintain less sensitivity to air exposures.

Hydrogen molecules have a strong affinity for nickel and readily dissociate and adsorb onto surface-layer nickel clusters [101,102]. Through the addition of 1 at% of nickel to magnesium, Holtz and Imam [76] achieved a 50% increase in hydrogen capacity, a decrease in the temperature for the onset of hydrogenation from 275 to 175°C, and a lowering of the dehydrogenation onset temperature from 350 to 275°C.

In addition to Pd and Ni, Ge can be used for the catalysis of hydrogenation kinetics [60]. The presence of Ge decreases the hydride decomposition temperature in a range from 50 to 150°C, depending on the catalyst amount. But the catalytic effect of Ge disappears after few hydrogen absorption/desorption cycles [60]. Vanadium also acts as a catalyst for the dissociation of hydrogen molecules. It was also reported using V as a catalyst, hydrogen capacity can be increased up to 5.8 wt% while the thermodynamic parameters of MgH$_2$ were not altered [54], as shown in Fig. 5.

Titanium and vanadium block the oxidation of the alloy surface, and therefore, increase the discharge capacity over multiple cycles [103]. A nanocrystalline Mg$_{1.9}$Ti$_{0.1}$Ni alloy shows good absorption kinetics at room temperature [104]. The Ti decreases the kinetic barriers of absorption while the Ni protects the alloy from deactivation due to oxide layer formation.

The poor kinetics of MgH$_2$ are greatly improved by addition of different oxide catalysts that enhance hydriding properties at relatively low temperature, such as V$_2$O$_5$ [28] and Cr$_2$O$_3$ [34,55]. The oxide particles may operate as a milling ball during high-energy ball-milling that creates many defects in the Mg powder. Defects provide hydrogen an easy path to Mg [28]. It was also proposed that Cr$_2$O$_3$ yields fast hydrogen absorption, whereas V$_2$O$_5$ and Fe$_3$O$_4$ cause the most rapid desorption of hydrogen [57]. The addition of TiO$_2$ also resulted in...
a markedly improved hydrogenation performance of Mg, rapid kinetics, low working temperature and excellent oxidation resistance [46]. Liang et al. [40] suggested that La showed a catalytic effect on Mg–50 wt% LaNi5 nanocomposite.

In addition to catalyst type, the amount of catalysts used has a significant effect on hydrogen absorption behavior. Oelerich et al. [57] investigated different amounts of oxides for catalysis but it is shown that only 0.2 mol% of the catalyst is sufficient to provide fast sorption kinetics. The effect of Nb2O5 concentration on the kinetics of magnesium hydrogen sorption reaction at 300°C is studied. Fastest kinetics are obtained using 0.5 mol% Nb2O5 with a 7.0 wt% of hydrogen capacity [26].

In the search for efficient and inexpensive catalysts for hydrogen sorption reactions, a new type of catalytic compounds is developed [105]. These catalytic complexes demonstrated remarkable enhancement in sodium alanates and magnesium, as well as in hydrogen generation through hydrolysis [105].

2.4. Chemical composition

The type and the chemical composition of the metal alloy is one of the most important factors in the metal–hydrogen system [21]. Bouraricha et al. [31] prepared Mg/Al alloys by high-energy ball-milling. The measured hydrogen capacity of the material decreases with Al content, from H/M = 1.74 for pure unmilled Mg, to 1.38 for Mg:Al (90:10), and then to 1.05 for Mg:Al (75:25). But it improves the kinetics. Ball-milling has a possibility to combine two or more phases having different hydrogenation characteristics [21]. Wang et al. [33,36] combined both the catalytic and milling effect in a system of fine ZrFe1.4Cr0.6 particles covering Mg particles that resulted in an enhancement in absorption/desorption rates. ZrFe1.4Cr0.6 dispersing homogeneously on the particle surfaces and in the interior of the material played an important role in promoting the decomposition of MgH2. That probably could account for the decrease in activation energy. In another study [51], mechanically alloyed Mg–30 wt% LaNi2.28 reported to have good hydriding properties with 5.40 wt% hydrogen storage under 30 bar hydrogen pressure.

With energetic ball-milling, the solubility limit of magnesium in lithium slightly increased [106]. Luo [44] developed LiNH2/MgH2 system by partial substitution of Li by Mg which has a storage capacity of 4.5 wt% at 200°C and 30 bar. Mechanical alloying of Mg with some elements such as Zn, Al, Ag, Ga, In or Cd resulted in reducing the stability of magnesium hydride. Indium and cadmium gave the best results [107].

Bogdanovic et al. [49] and Reiser et al. [43] considered the Mg2FeH6–MgH2 systems. The maximum amount of stored hydrogen is 5.0 wt% which is one third less than magnesium difhydride with 7.7 wt%, but the Mg2FeH6–MgH2 system possesses numerous advantages including the low price of starting materials, the free choice and constancy of the heat delivery temperature by controlling the applied hydrogen pressure and absence of heat losses with time. The intermetallic hydride Mg2FeH6 shows the high volumetric hydrogen density of 150 kgH2/m3, which is more than double of liquid hydrogen [108].

Nanocomposites of MgH2 and 3d transition metals, Ti, V, Mn, Fe and Ni, have been investigated intensively [48,50,109]. The composites containing Mg–Ti and Mg–V exhibited the rapid absorption kinetics such as absorption time of 2–5 min. Formation enthalpy and entropy of magnesium hydride is distorted by milling with transition metals. Furthermore, the activation energy of desorption for magnesium hydride is reduced at 200°C.

3. Complex hydrides

Another class of light-weight storage materials is complex hydrides. Complex hydrides are known as “one-pass” hydrogen-storage systems which mean that H2 evolves upon contact with water. Sodium, lithium and beryllium are the only elements lighter than magnesium that can also form solid-state compounds with hydrogen. The hydrogen content reaches the value of 18 wt% for LiBH4. Use of complex hydrides for hydrogen storage is challenging because of both kinetic and thermodynamic limitations.

Intense interest has developed in low weight complex hydrides such as alanates [AlH4]−, amides [NH2]−, imides and borohydrides [BH4]−. In such systems, the hydrogen is often located at the corners of a tetrahedron. The alanates and borates are especially interesting because of their light weight and the capacity for large number of hydrogen atoms per metal atom. Borates are known to be stable and decompose only at elevated temperatures. Alanates are remarkable due to their high storage capacities; however, they decompose in two steps upon dehydriding.
3.1. Sodium alanates

Sodium alanates are complex hydrides of aluminum and sodium. Sodium tetrahydroaluminate–NaAlH4 and trisodium hexahydroaluminate–Na3AlH6 have been known for decades. Sodium aluminum hydride, NaAlH4, would seem to be a possible candidate for application as a practical on-board hydrogen-storage material due to the theoretically reversible hydrogen-storage capacity of 5.6 wt%, low cost and its availability in bulk.

Although they have good hydrogen-storage capacity, complex aluminum hydrides are not considered as rechargeable hydrogen carriers due to irreversibility and poor kinetics. However, by using appropriate transition or rare-earth metals as catalysts, the complex hydrides can be made reversible. Bogdanovic and Schwickardi [110,111] demonstrated upon doping with proper titanium compounds, the dehydrogenation of aluminum hydrides could be kinetically enhanced and maintain reversibility under moderate conditions in the solid state. Unlike intermetallic hydrides, these complex-based hydrides release hydrogen through a series of decomposition reactions as described in two equations below, for the dehydrogenation reactions of NaAlH4:

\[
\text{NaAlH}_4 \leftrightarrow \frac{1}{3} \text{Na}_3\text{AlH}_6 + \frac{2}{3} \text{Al} + \text{H}_2, \tag{4a}
\]

\[
\text{Na}_3\text{AlH}_6 \leftrightarrow 3\text{NaH} + \text{Al} + \frac{3}{2} \text{H}_2. \tag{4b}
\]

Theoretically, NaAlH4 and Na3AlH6 contain large amounts of hydrogen, 7.4 and 5.9 wt%, respectively. However, the release of hydrogen does not occur in a single-step reaction. NaAlH4 first decomposes evolving molecular hydrogen and form an intermediate compound, Na3AlH6 and metallic Al. This intermediate phase then decomposes to NaH with additional metallic Al formation and hydrogen evolution. The reversibility of these two reactions is a critical factor for the practical applications.

Stoichiometrically, the first step consists of 3.7 wt% H2 release and the second step 1.9 wt%, for a theoretical net reaction of 5.6 wt% reversible gravimetric hydrogen storage [111,112]. The process is characterized by slow kinetics and reversibility only under severe conditions. The operating temperatures are between 185 and 230°C, and 260°C for the first and the second reaction, respectively. Finally, the decomposition of NaH occurs at a much higher temperature, with the total hydrogen release of 7.40 wt%. For hydrogen storage, only the first two reactions need to be considered, because the decomposition of NaH occurs at too high temperature of 425°C for practical storage systems.

Previously Jensen et al. [113] reviewed the catalytically enhanced sodium aluminum hydrides. Recently, numerous studies are being carried out to enhance the hydriding properties of NaAlH4 as listed in Table 3.

The effects of liquid alkoxides Ti(Obu')4 + Zr(OPr')4 on hydriding properties of sodium alanates were investigated by Sandrock et al. [116]. The liquid alkoxides contribute to hydrocarbon contamination of the released hydrogen. Moreover the surface of sodium alanate is damaged by the catalyst which causes decreasing the cyclic capacity.

The dry-doping TiCl3 catalyst is investigated by the same group [123]. It largely eliminates the high catalyst weight, low capacity and contamination problems noted above for the alkoxide catalysts [116]. Both the hydriding and dehydrogenation rates increases by doping [123]. Under the same rehydrogenation conditions, the amount of evolved hydrogen from the Ti-doped NaAlH4 is about 50 times as much as that of the undoped NaAlH4. This clearly indicates that the addition of titanium species enhances kinetically not only the dehydrogenation, but also the rehydrogenation reaction of NaAlH4 [118]. With 2 mol% TiN as a doping agent, cyclic storage capacity of 5 wt% H2 is achieved after 17 cycles. However, decrease in hydrogenation rate with number of cycles is observed [122]. Zirconium doping is also used for the same purpose. The dehydrogenation kinetics of NaAlH4 is significantly improved. Although effects of zirconium are poorer than titanium as a catalyst for the dehydrogenation of NaAlH4 to Na3AlH6 and Al, it is a superior catalyst for the dehydrogening of Na3AlH6 to NaH and Al [119].

Sun et al. [124] examined the details of the doping role of titanium and zirconium on NaAlH4 with XRD. Significant changes occur in the lattice parameters of sodium alanates upon doping. Hence the enhancement of dehydrogenation kinetics is associated with dopant induced lattice distortions rather than the catalytic effect [124]. Phase transitions and crystal structure modifications of doped-NaAlH4 were also observed by Gross et al. [125]. Contrary to Sun et al. [124], they proposed the catalytic effects of doping materials in the enhancement of kinetics of NaAlH4. It was earlier reported that the presence of Ti is not enough rather a particular local arrangement is required for the dehydrogenation reaction [126]. Ti-cluster-doped NaAlH4 is investigated [122,127]. The hydrogenation and dehydrogenation measurements indicate that the state of the precursor is of even greater importance than the simple amount of Ti in the material. The small size of the Ti clusters seem to be responsible for the increase of the reaction rate [127].

Although titanium has positive effects as a catalyst, kinetics is not fully enhanced. The hydrogen desorption can last up to 4200 min in some cases [123]. To improve the kinetics Thomas et al. [128] investigated the effects of mechanical ball-milling on the microstructural character of NaAlH4 in the presence of catalyst. Fracture and fragmentation of particles are observed in particle morphology. The direct synthesis of Na3AlH6 and Na2LiAlH6 by energetic mechanical alloying was also investigated earlier [129]. The milled NaAlH4 or Na3AlH6 exhibited great improvement of the kinetics of absorption and desorption. The addition of carbon in the milling process improved their performance as well [120]. Mechanically alloyed Na3AlH6 exhibits faster kinetics than Na3AlH6 obtained from the decomposition of NaAlH4 [130]. Moreover, the hydrogen-storage performance of NaAlH4 was found to be highly dependent on the milling time which increases with time [117]. Consequently mechano-chemical synthesis method which involves simply ball-milling of the appropriate reagents at high energy, is applied to prepare Na3AlH6 [114]. It can desorb the same amount of hydrogen at 200°C within only 150 min and
without a catalyst, giving reaction rate about 10 times faster than conventionally produced, non-catalyzed hydrides [114].

3.2. Lithium and potassium alanates

A survey of important studies on lithium-based hydrogen-storage compounds are summarized in Table 4. It shows clearly high capacities of stored hydrogen as weight percent material.

In theory, lithium alanates are very attractive for hydrogen storage, because of their high hydrogen content. The total hydrogen content is 10.5 and 11.2 wt% for LiAlH4 and Li3AlH6, respectively. Unfortunately, LiAlH4 has an extremely high equilibrium pressure of hydrogen, even at room temperature. LiAlH4 is in fact an example of an unstable hydride, which decomposes easily, but which cannot be re-hydrogenated [114]. The desorption of LiAlH4 occurs in two steps:

\[ 3\text{LiAlH}_4 \rightarrow \text{Li}_3\text{AlH}_6 + 2\text{Al} + 3\text{H}_2, \quad (5a) \]

\[ \text{Li}_3\text{AlH}_6 \rightarrow 3\text{LiH} + \text{Al} + \frac{3}{2}\text{H}_2. \quad (5b) \]

The hydrogen released in the two reactions shown, corresponds to 5.3 wt% from the decomposition of LiAlH4 and 2.65 wt% from the decomposition of Li3AlH6 at temperatures between 160 and 200 °C. After completion of the reactions, 2.65 wt% of the total hydrogen content in LiAlH4 remains unreleased in form of LiH which can be desorbed only at very high temperatures of above 680 °C [114]. Therefore, the commercialization of lithium-based compounds is hindered by their slow kinetics and high temperature absorption and desorption.

The reversible hydrogen decomposition of KAlH4 has been studied previously [138]. The hydrogen capacity was above 3.5 wt% under 10 bar of hydrogen in a temperature range of 250–330 °C, the reversible reaction smoothly proceeds without any catalyst, which is different from the reactions of NaAlH4 and LiAlH4 [138].

3.3. Lithium nitrides

Lithium nitride is usually employed as an electrode, or as a starting material for the synthesis of binary or ternary nitrides. Although the temperature required to release the hydrogen at usable pressures is too high for hydrogen-storage applications it was suggested that the metal–N–H system could prove to be a promising route for reversible solid hydrogen storage [45].

The idea of hydrogen storage in lithium compounds goes back to 1910, when Dafert and Miklauz [139] reported the reaction between Li3N and H2 to Li3NH4. In fact Li3NH4 has been proved to be the product of the following reaction, which was proposed by Ruff and Georges [140]:

\[ \text{Li}_3\text{N} + 2\text{H}_2 \rightarrow \text{LiNH}_2 + 2\text{LiH}. \quad (6) \]
Consequently, Li3N can theoretically store 10.4 wt% hydrogen. Li3N has two plateaus in the P–C isotherm. Desorption isotherms cannot return to the origin. Under P–C isotherm conditions, about 55% of hydrogen can be desorbed at temperatures above 230 °C. More important for hydrogen storage, is that this mixture could decompose to release hydrogen gas upon heating, according to the following reaction:

\[
\text{LiNH}_2 + 2\text{LiH} \rightarrow \text{Li}_2\text{NH} + \text{LiH} + \text{H}_2.
\] (7)

Hydrogen storage leads to the formation of LiNH2 and LiH. Theoretically 7 wt% of hydrogen can be reversibly stored in Li2NH [45].

A critical potential issue regarding this N-based storage material is the generation of NH3, which consumes some H2 and also poisons the downstream processes. Hu et al. [141] demonstrated that NH3 produced via the decomposition of LiNH2 is irreversibility stands as an important problem for use of these materials to be utilized as storage medium. Authors reported their attempts to rehydride the decomposition product by heating at 8 MPa but without success.

A proposed way for lowering the hydrogen desorption temperatures of Li-based complex hydrides is partial cation substitutions using different valence cations with larger electronegativities. It was predicted that the dehydridding reactions of LiNH2 with partial Mg substitutions are useful as hydrogen-storage materials for fuel–cell applications [142]. The starting and ending temperatures for the hydrogen desorption reaction from LiNH2 are lowered about 50 K by the partial cation substitution of Li by Mg [143,144].

### 3.4. Lithium boro- and beryllium hydrides

The importance of boron for hydrogen-storage technologies have been reported [145]. LiBH4 has a gravimetric hydrogen density of 18 wt%. The compound was first synthesized by Schlesinger and Brown [146] in an organic solvent. According to the work of Stasinevich and Egorenko [147] hydrogen desorbs from LiBH4 at temperatures greater than 470 °C. Despite its great storage capacity, all attempts to synthesize LiBH4 from the elements at elevated temperatures up to 650 °C and pressure of 150 bar failed to date [108,148]. Moreover, LiBH4 is an expensive compound [15].

It was found that the compound releases hydrogen in different reaction steps and temperature regimes. The low temperature desorption releases only a small amount (0.3 wt%) of hydrogen. The high temperature phase releases up to 13.5 wt% of hydrogen. A total of 4.5 wt% of the hydrogen remains as LiH in the decomposition product.

Vajo et al. [137] show that LiBH4 can be reversibly store 8–10 wt% hydrogen at temperatures of 315–400 °C by addition of MgH2 including 2–3 mol% TiCl3. Formation of MgB2 storage capacity of about 10 wt%, however, reversibility is lacking. Although desorption conditions seem to be advantageous, irreversibility stands as an important problem for use of these materials to be utilized as storage medium. Authors reported their attempts to rehydride the decomposition product by heating at 8 MPa but without success.
stabilizes the dehydrogenated state and destabilizes the LiBH₄ [137]. However, the kinetics is too slow with the absorption time up to 6000 min hinder practical applications.

Besides alanates, nitrides and borohydrides, lithium–beryllium hydrides are a new group of metal hydrides for hydrogen storage. They show high reversible hydrogen capacity with more than 8 wt% at 150 °C. The reaction of hydride formation is fully reversible. Since lithium and beryllium are the lightest hydride-forming metals, reversible hydrogen capacity in these complex compounds is higher than in any other known hydrides [149]. On the other hand, the Li₅Be₂H₇ is a highly toxic material [15].

4. Intermetallic compounds

Research on intermetallic compounds for hydrogen storage was already attempted more than 20 years ago. The discovery of hydrogen absorption by LaNi₅ [150] and FeTi [151], opened new possibilities for industrial developments. However, for onboard storage, they remained at the stage of prototypes due their weight penalty and low hydrogen-storage capacity [152].

The different families of intermetallic compounds classified on the basis of their crystal structures, such as AB₂ type (Laves phase), AB₅ type phases and Ti-based body centered cubic, BCC, alloys are well known as hydrogen-storage materials. Intermetallic compounds are often obtained by combining an element forming a stable hydride with an element forming a nonstable hydride. As for the metallic hydrides, the dissociative chemisorption of hydrogen is followed by hydrogen diffusion into the interstitial sites.

The hydriding properties of these compounds are summarized in Tables 5 and 6. For practical applications at ambient temperature and pressure, their low energy density per unit weight is an important critical disadvantage. For instance, the hydrogen capacity of the most popular LaNi₅-based alloys operating at moderate temperature does not exceed 1.4 wt%.

Among the AB₅ type alloys, due to their low working temperature and pressure, metal alloys containing high amounts of LaNi₅ have been studied as hydrogen-storage materials by various research groups around the world [176–180]. Some of the studies were carried with pure compounds, while others studied blending of the material with various metals through melt- or mechanical alloying techniques. Important results from these studies are represented below.

The parent compound LaNi₅ absorbs about 1.0 H/LaNi₅ (1.5 wt%), however, its cost is relatively high and the plateau pressure is low. The P–C diagram shows a flat plateau, low hysteresis, but unfortunately the hydrogen capacity is degraded after a few cycles. Therefore, these materials are still far from meeting the US DOE goal of 6.5 wt% reversible hydrogen capacity. Due to their potential for commercial applications, researchers have been studying the effects of milling, mechanical alloying or melting with other metals and surface treatment techniques such as carbon monoxide treatment. Table 6 presents the major outputs from a number of studies on AB₅ type compounds for hydrogen storage.

The early studies on LaNi₅ as hydrogen-storage material has been reported by Aoyagi et al. [67]. The effect of ball-milling on hydrogen absorption properties has been investigated, and maximum hydrogen content has been reported as 0.25 wt%. It is concluded that activation treatment is necessary for LaNi₅ to be useful for hydrogen-storage applications. Kaplan et al. [181] have investigated the hydrogen absorption in pure LaNi₅ both theoretically and experimentally. The group reported that LaNi₅ has 1.28 wt% hydrogen-storage capacity for 8.3 min hydriding process. They characterized the hydriding process by exothermic reaction between LaNi₅ and H₂ that leads to rapid temperature increase. These supported the results from theoretical calculations.

With different stoichiometric addition of other metals, LaNi₅ compounds were shown to be enhanced for hydrogen-storage by the works of Chen et al. [182], Corre et al. [175], and Lu et al. [174]. They achieved hydrogen-storage capacities with different stoichiometric LaNi₅ samples such as 1, 1.44 and 1.32 wt%, respectively. Chen et al. [182] applied chemical coating by copper and achieved kinetics and cycling behavior during hydrogenation /dehydrogenation process. By CO surface treatment, 1.44 wt% hydrogen capacity is achieved in LaNi₅. Lu et al. [174] processed the LaNi₅ using a twin roll process in order to achieve uniform nanocrystalline structure with 1.32 wt% storage capacity.

Apart from the above reported works, a few important studies in the literature are worth mentioning. Liu et al. [183], Wang et al. [184], and Suda et al. [185] reported on the fluorination of hydriding alloys and its effects on properties. The aim of these experiments was to form a Ni-rich layer in order to improve the initial activation and impurity tolerance. There are also theoretical studies found in the literature, on LaNi₅ utilization for hydrogen storage, tank design and optimization. Kikkinides et al. [186] showed the direct relation between hydrogen-storage performance and optimization in LaNi₅ systems. Storage time could be improved by 60% through optimization.

The mechanism of hydrogen diffusion in LaNi₅BH₅ is investigated. The results suggested that hydrogen occupies sites coordinated by lanthanum and nickel only, while the basal La–B planes act as barriers to hydrogen diffusion along the hexagonal axis. Boron has an adverse effect on the hydrogen sorption properties of intermetallic compounds because it acts as a barrier for hydrogen diffusion and favors localization of the hydrogen atoms in the metal matrix away from the boron atom sites [131].

The AB₂ type compounds are derived from the Laves phases crystal structures. The potential AB₂ types are obtained with Ti and Zr on the A site. The B elements are represented mainly by different combinations of 3d atoms, V, Cr, Mn and Fe. The hydrogen-storage capacity can reach up to 2 wt% in Laves phase V–7.4%Zr–7.4%Ti–7.4%Ni [166]. The Laves phase series of compounds has attracted large attention in the last decade due to their good hydrogen-storage capacity. Most of Laves phases show relatively high capacities faster kinetics, longer life and a relatively low cost in comparison to the LaNi₅-related systems [155]. However, their hydrides are too stable at room temperature [187]. In general the AB₂ type compounds seem to be
<table>
<thead>
<tr>
<th>Material</th>
<th>Method</th>
<th>Temperature (°C)</th>
<th>Pressure (bar)</th>
<th>Kinetics (min)</th>
<th>Cycling stability</th>
<th>Max wt% of H₂</th>
<th>Ref.</th>
</tr>
</thead>
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<td>T&lt;sub&gt;abs&lt;/sub&gt; and T&lt;sub&gt;des&lt;/sub&gt;: 100, 25</td>
<td>P&lt;sub&gt;abs&lt;/sub&gt;: 5−10</td>
<td>t&lt;sub&gt;abs&lt;/sub&gt; and t&lt;sub&gt;des&lt;/sub&gt;: 6.6</td>
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<td>[154]</td>
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<td>P&lt;sub&gt;abs&lt;/sub&gt;: 30</td>
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<td>0.99</td>
<td>[155]</td>
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<td>T&lt;sub&gt;abs&lt;/sub&gt;: 120</td>
<td>P&lt;sub&gt;abs&lt;/sub&gt;: 47</td>
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<td>No data</td>
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<td>[156]</td>
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<td>No data</td>
<td>1.00</td>
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<td>P&lt;sub&gt;abs&lt;/sub&gt;: 4</td>
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<td>No data</td>
<td>1.10</td>
<td>[159]</td>
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<td>[160]</td>
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<td>[161]</td>
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<td>[162]</td>
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<td>P&lt;sub&gt;abs&lt;/sub&gt;: 100</td>
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<td>No data</td>
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<td>[163]</td>
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<td>[164]</td>
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<td>[165]</td>
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<td>P&lt;sub&gt;abs&lt;/sub&gt;: 100</td>
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<td>1.20</td>
<td>[166]</td>
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<td>1.20</td>
<td>[167]</td>
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<td>1.20</td>
<td>[168]</td>
</tr>
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<td>RF levitation melting + BM</td>
<td>T&lt;sub&gt;abs&lt;/sub&gt;: 120</td>
<td>P&lt;sub&gt;abs&lt;/sub&gt;: 100</td>
<td>No data</td>
<td>No data</td>
<td>1.20</td>
<td>[169]</td>
</tr>
<tr>
<td>Ti&lt;sub&gt;0.9&lt;/sub&gt;CrMn</td>
<td>RF levitation melting + BM</td>
<td>T&lt;sub&gt;abs&lt;/sub&gt;: 120</td>
<td>P&lt;sub&gt;abs&lt;/sub&gt;: 100</td>
<td>No data</td>
<td>No data</td>
<td>1.20</td>
<td>[170]</td>
</tr>
<tr>
<td>Ti&lt;sub&gt;0.9&lt;/sub&gt;CrMn</td>
<td>RF levitation melting + BM</td>
<td>T&lt;sub&gt;abs&lt;/sub&gt;: 120</td>
<td>P&lt;sub&gt;abs&lt;/sub&gt;: 100</td>
<td>No data</td>
<td>No data</td>
<td>1.20</td>
<td>[171]</td>
</tr>
<tr>
<td>Ti&lt;sub&gt;0.9&lt;/sub&gt;CrMn</td>
<td>RF levitation melting + BM</td>
<td>T&lt;sub&gt;abs&lt;/sub&gt;: 120</td>
<td>P&lt;sub&gt;abs&lt;/sub&gt;: 100</td>
<td>No data</td>
<td>No data</td>
<td>1.20</td>
<td>[172]</td>
</tr>
<tr>
<td>TiCr&lt;sub&gt;1.1&lt;/sub&gt;V&lt;sub&gt;0.9&lt;/sub&gt; + BM</td>
<td>RF melting</td>
<td>T&lt;sub&gt;abs&lt;/sub&gt;: 120</td>
<td>P&lt;sub&gt;abs&lt;/sub&gt;: 100</td>
<td>No data</td>
<td>No data</td>
<td>1.20</td>
<td>[173]</td>
</tr>
</tbody>
</table>
more sensitive to gaseous impurities than the AB$_5$ type compounds. Thus, a small amount of oxygen can be a poison for the AB$_5$s, while, for the AB$_2$s, it acts as a reactant, reducing the storage capacity slightly. CO is a poison for both types of compounds, although capacity recovery is possible by recycling in pure hydrogen [188].

Hydrogen absorption of FeTi powders has previously been extensively studied. FeTi is a well-known hydrogen-storage compound with a total hydrogen capacity of around 1.90 wt% with inexpensive elements. Hydrogen capacity of FeTi can be accomplished to 1.90 wt% by the catalytic effect of 1 wt% Pd addition [165]. However, the activation process of FeTi is troublesome due to the formation of titanium oxide layer. Both high-pressure and high temperature are required to achieve a reproducible absorption/desorption of the maximum amount of hydrogen in the compound [151,187].

New BCC solid solution alloys have been reported to absorb more hydrogen than the conventional intermetallic compounds. In recent years, study of Ti-based BCC phase alloys has been studied in several laboratories because of their remarkable hydrogen capacities. However, the high cost is one of the critical drawbacks limiting their successful practical applications. Ti–10Cr–18Mn–27V–5Fe and Ti–10Cr–18Mn–32V has hydrogen-storage capacities of 3.01 and 3.36 wt%, respectively [170]. Increasing the V content is effective in accelerating hydrogen desorption plateau pressure. The maximum and effective hydrogen absorption, enhancing the hydrogen absorption capacity and flattening the hydrogen desorption plateau, while decreasing hydrogen desorption plateau pressure. The maximum and effective hydrogen-storage capacities of Ti–V–Cr–Mn alloys are 3.98 and 2.51 wt%, respectively [172].

It is well known that vanadium is expensive; therefore, decreasing of the vanadium content is another goal of the investigations. In Ti–V–Cr–Mn compounds, increasing the Cr content and the addition of Mn is necessary to increase the effective hydrogen capacity by increasing the plateau pressure, but also to decrease costs by decreasing the vanadium content. The BCC phase solid solution of V$_{0.375}$Ti$_{0.25}$Cr$_{0.30}$Mn$_{0.075}$ exhibited an effective hydrogen capacity of 2.20 wt% [167].

In order to improve the hydrogen-storage properties and reduce the cost of Ti–V-based BCC alloys, the effect of Fe substitution in Ti–10Cr–18Mn–32V alloy is also investigated [170]. It was reported that Fe addition increases the activation performance, hydrogen absorption–desorption plateau pressure, hydrogen desorption capacity and reduce the hysteresis of hydrogen absorption–desorption plateau, and the cost of alloy [170].

The quasicrystals have a new type of translational long-range order, display non-crystallographic rotational symmetry. They contain high amounts of interstitial sites. The quasicrystalline Ti$_{45}$Zr$_{38}$Ni$_{17}$ has 2.23 wt% storage capacity [168]. The sorption of hydrogen between the layers of the multilayered wall of nanotubular TiO$_2$ was studied in the temperature range of 195–200 $^\circ$C and at pressures of up to 6 bars. Hydrogen can intercalate between layers in the walls of TiO$_2$ nanotube [189].

### 5. Conclusion

Hydrogen storage is a key issue in the success and realization of hydrogen technology and economy. According to US DOE, the hydrogen-storage capacity target for commercialization is 6.5 wt% at the decomposition temperature between 60 and 120 $^\circ$C with high cycle life. Although pure water contains 11.1 wt% of hydrogen, its decomposition requires much thermal, electric, or chemical energy [15].

Since the conventional hydrogen fuel storage methods of pressurized H$_2$ gas and cryogenic liquid H$_2$ pose safety and permeation problems along with high cost, they do not meet future on-board applications goals set for hydrogen economy. Solid state hydrogen fuel storage either absorption in the interstices of metals and metallic alloys or adsorption on high surface area materials such as activated carbons gain the attention for possible future hydrogen applications. The present article reviews the hydrogen-storage materials for transport applications which require research into further aspects of tank technology, heat management and solid fuel recycling. The work is carried out in an attempt to facilitate prospectus material choice for further tank design aiming at on-board vehicle applications.

Hydrogen can be stored in metal hydrides under moderate temperature and pressure. Metal hydrides are the promising candidates due to their safety advantage with high volume-efficiency storage capacity for on-board applications. Intensive research has been recently conducted on the metal hydrides for improving adsorption/desorption properties based on hydrogen-storage capacity, kinetics, thermal properties, toxicity, cycling behavior and cost.

### Table 6
Hydrogen absorption/desorption properties of LaNi$_5$ compounds

<table>
<thead>
<tr>
<th>Material</th>
<th>Method</th>
<th>Temperature ($^\circ$C)</th>
<th>Pressure (bar)</th>
<th>Kinetics (min)</th>
<th>Cycling stability</th>
<th>Max wt% of H$_2$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaNi$_5$</td>
<td>Twin-rolling</td>
<td>$T_{abs}$: 20 $T_{abs}$: 60</td>
<td>$P_{abs}$: 20 $P_{abs}$: 10</td>
<td>$t_{abs}$: 1.6 No data</td>
<td>8 cyc.: not stable No data</td>
<td>0.25</td>
<td>1.27</td>
</tr>
<tr>
<td>La$<em>{0.95}$Ce$</em>{0.05}$Ni$<em>{4}$Co$</em>{0.15}$Mn$<em>{0.65}$Al$</em>{0.3}$</td>
<td>CO surface treatment</td>
<td>$T_{abs}$: 0–100</td>
<td>$P_{abs}$: 50 $P_{abs}$: 0.6</td>
<td>$t_{abs}$: 1.8</td>
<td>20 cyc.: stable after fifth cycle</td>
<td>1.40</td>
<td></td>
</tr>
<tr>
<td>LaNi$_5$</td>
<td>CO surface treatment</td>
<td>$T_{abs}$: 25 $T_{abs}$: 0–100</td>
<td>$P_{abs}$: 50 $P_{abs}$: 25</td>
<td>$t_{abs}$: 13.6</td>
<td>20 cyc.: stable after fifth cycle</td>
<td>1.44</td>
<td></td>
</tr>
</tbody>
</table>
Group of Mg-based hydrides is a promising candidate for competitive mobile hydride storage with the reversible hydrogen capacity of up to 7.6 wt%. However, slow kinetics and high hydrogen desorption temperatures up to about 300°C reduce the efficiency and applicability in vehicles. Although much effort has been devoted to those materials in order to decrease their decomposition temperature, enhance the kinetics and cycle life by using appropriate catalysts and production method of ball-milling, further research is needed.

The complex hydrides released hydrogen by the step reactions unlike the metallic hydrides. Although the storage capacities of complex hydrides are theoretically high, there is a big difference between the theoretical and the presently practical attainable hydrogen capacities. Repeated hydrogenation cycles need to be applied for the potential applications to ensure the reversibility of these materials. Moreover, the slow kinetics problem is a significant obstacle for practical on-board applications. The intermetallic compounds do not satisfy the requirements for mobile storage for the reason that their low storage capacities up to 2 wt% for available use and along with high costs. An alternative application may be seen in effective use as thermodynamic devices [188].

There is no perfect choice of hydrogen store material to meet the set US DOE goals for transport applications. Although some results are encouraging, such as improved kinetics and lower decomposition temperatures for metal hydrides, further research is needed to develop materials satisfying the needs for technical applications. In the light of the achievements, there is high potential in developing better hydride materials with high reversible hydrogen capacity at ambient temperatures. In addition, technological improvements in vehicle design and system integration along with cost efficiency will determine the on-board applicability of the selected material [2]. The success and realization of hydrogen economy using hydrogen stored solid fuel technology will be dependent on the meeting of above goals.

Acknowledgments

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References


[53] Holtz RL. Basic user’s guide for NRL 6323 hydrogen storage system, 1996.


[137] Santos DS dos, Bououdina M, Fruchart D. Structural and hydrogenation properties of an 80 wt% TiC1-xVx0.9–20 wt% NiLa composite material. Int J Hydrogen Energy 2003;28:1237–41.

[138] Liu Y, Pan H, Gao M, Li G, Sun X, Lei Y. Investigation on the characteristics of La0.75Ti0.25Ni2.65La2.65Co0.75(1< x<0.85) metal hydride electrode alloys for Ni/MH batteries. Part I: phase structures and hydrogen storage. J Alloys Compds 2005;387:147–53.


