



Metal Hydride Composite Structures for Improved Heat Transfer and Stability for Hydrogen Storage and Compression Applications

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Abstract: Metal alloys and intermetallic compounds offer an attractive method for safely storing hydrogen (H₂). The metal alloys absorb H₂ into their structure, often swelling and fracturing as a result of phase transformation during hydride formation/decomposition cycles. The absorption of H₂ is an exothermic process, requiring the effective and efficient removal of heat. This can be challenging as heat transfer to/from powdered beds is notoriously difficult, and often limited by poor thermal conductivity. Hence, the observed reaction kinetics for absorption and desorption of H₂ is dominated by heat flow. The most common method for improving the thermal conductivity of the alloy powders is to prepare them into composite structures with other high thermal conductivity materials, such as carbons and expanded natural graphite. Such composite structures, some also combined with polymers/resins, can also mitigate safety issues related to swelling and improve cyclic durability. This paper reviews the methods that have been used to prepare such composite structures and evaluates the observed impact on thermal conductivity.

Keywords: metal hydride; composite; thermal conductivity; expanded natural graphite

1. Introduction

Metal hydrides (MH) are attractive for hydrogen (H₂) storage and compression applications, particularly where waste heat is available. Metal hydride-based compressors have the advantages of no moving parts, simplicity in design, compactness, and safety and reliability [1]. Metal hydrides have higher volumetric hydrogen storage density (e.g., 150 kgH₂/m³ in Mg₂FeH₆) than compressed hydrogen gas (<40 kgH₂/m³ at 800 bar) or liquid hydrogen (70.8 kgH₂/m³ at -252 °C and 1 bar) [2].

Metal hydrides are formed via the reversible reaction of a hydride-forming metal/alloy or intermetallic compound with H_2 gas:

$$M(s) + \frac{x}{2}H_2(g) \leftrightarrow MH_x(s) + Q$$
 (1)

where M is a metal/alloy, (s) and (g) relate to the solid and gas phases, respectively, and Q is the energy released [1]. This leads to the potential for solid-state storage of H_2 under moderate temperatures and pressures. H_2 absorption is an exothermic process, as outlined in Equation (1). Heat released during hydride formation must be continuously removed to prevent the hydride/alloy system from heating up. If the temperature is allowed to increase, the corresponding equilibrium pressure will also increase, which will result in no further H_2 sorption taking place. Conversely, when H_2 is recovered, heat must be added to release hydrogen.



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To improve kinetics, metal alloys used for H₂ storage/compression are often in powdered form. These alloy powders swell as they absorb H_2 as the crystalline cell volume increases with H₂ entering the interstitial positions in the crystalline structure of the metal alloy. This, in turn, creates internal stresses which are sufficient to fracture the metal hydride with continued cycling, resulting in the creation of submicron particles [3]. A smaller particle size increases the surface area of the powders, promoting a faster diffusion of hydrogen into the alloy powders. For example, it has been demonstrated that Mg nanoparticles with smaller size (i.e., 25 nm) had much faster H₂ sorption kinetics [4]. Mg colloids with a particle size of 5 nm began to dehydrogenate at 85 °C, which was much lower than that of commercial micrometer-size MgH₂ (400 °C) [5]. Moreover, morphologies can also play a vital role in the materials' performance [6–9]. Although nanostructured metal hydrides show improved performance in sorption/desorption kinetics, they tend to aggregate, resulting in decreased sorption capacity with multiple cycles. Other challenges faced when using powdered metal hydride materials include effective removal of the surface oxide layer of the powders (needed to allow the hydrogen absorption reaction to proceed), higher heat flow (due to increased reaction kinetics), and limited heat transfer to/from powdered beds. The heat transfer is limited as the thermal conductivity of MH powdered beds is poor, owing to their porosity and inter-particle contact resistance. For example, thermal conductivities of packed LaNi₅ powders are very low, in the range of $0.1-1 \text{ W/m} \cdot \text{K}$, compared with a bulk thermal conductivity at $12.5 \text{ W/m} \cdot \text{K}$ [10,11]. As a result of the poor thermal conductivity, the observed charging/discharging rate for absorption and desorption of hydrogen is dominated by heat flow [12].

For a commercial system, the practicalities of filling and long-term operation of MHfilled vessels needs to be improved, particularly at the scale required for H₂ fuel cell electric vehicles (FCEV). In order to fill a MH vessel quickly, heat must be removed efficiently and effectively from the system (and reversely quickly added for discharge of H_2). The poor heat transfer capability of a powdered metal hydride bed is a considerable restriction on the design and construction of hydrogen storage and compression systems [13]. Various modifications to MH vessels such as introducing metal fins, cooling tubes, and phase change materials (PCMs) have been suggested to improve heat transfer characteristics [14]. These modifications, however, significantly increase the cost and complexity of MH storage vessels. Potentially more economical alternatives involve mixing the MH with conductive materials and forming composite structures. These thermally conductive additions could be metals (e.g., Al powder) or carbon-based materials such as expanded natural graphite (ENG) [15–18], activated carbon [19], carbon nanotube [20], and carbon fiber [21]. With the addition of 20 wt% carbon fiber, the thermal conductivity of TiFe_{0.9}Ni_{0.1} composite was increased from about 0.5 to 2 W/m·K using aramid pulp as a binder [21]. A solid compact combining LaNi₅ powder with 20 wt% Al powder was found to dramatically increase the thermal conductivity of the LaNi₅ hydride from around $1 \text{ W/m} \cdot \text{K}$ to $32.5 \text{ W/m} \cdot \text{K}$ [13].

To improve the handling capability of the hydride, contain its expansion, and improve durability, composites with polymers/resins have also been suggested [22,23]. Polymers can also be used as a binder to bind fine MH powders onto surfaces of microporous carbon scaffolds or substrates [24]. Tokiwa et al. [22] measured the distortion imparted on an MH storage vessel as a result of H₂ sorption. While the addition of the resin to the composite was effective in reducing the distortion of the storage vessel, the performance varied depending on the polymer used.

To solve the stability issue of the nanostructured metal hydrides, nanoconfinement provides a feasible solution to prevent particle aggregation by limiting its mobility in a nanoporous support [25]. Combining MH powders in structures with components of high thermal conductivity can also help overcome the challenges associated with heat transfer. As a result, MH composite materials have attracted great interest [26,27]. This paper provides a review of methods that have been explored to generate MH composite structures for improved heat transfer for H₂ storage and compression applications. For a practical reactor, it is desirable to maximize its gravimetric and volumetric sorption capacities. Therefore, it is best to minimize the amount of support material to achieve a high hydrogen storage capacity and avoid the need for excessive heating/cooling of inert material. The MH mass fraction in the composite is expected to be as high as possible. This review focuses on MH composite materials with a relatively high MH mass fraction.

2. Composite Materials

The "ideal" composite material for hydrogen storage and compression should satisfy several requirements:

- High hydrogen permeability.
- High thermal conductivity.
- Certain degree of elasticity to accommodate metal particles expansion/contraction during hydride formation/decomposition.
- Certain degree of mechanical strength to be resistant to mechanical degradation though charging cycles.
- Thermal stability to work within desired temperature interval.
- Absence of chemical interactions with metal/alloy.

To accommodate the expansion during hydrogenation, MH in pellet/granule form could be compacted with other flexible materials. In earlier studies, several different metal matrix materials and fabrication techniques were tested for practical fabrication of the composites containing the hydrogenated metal alloy and aluminium, nickel, and copper as matrix [3,28]. Using an aluminium matrix was abandoned due to the difficulty of sintering aluminium [3]. The compacts with nickel powder had a very low green strength, could not form stable pellets under cold compaction, and had to be vacuum sintered at temperatures from 1200 °C to 1300 °C, while the compacts made with copper powders demonstrated relatively high green strengths and the unsintered pellets could survive 138 sorption/desorption cycles with minor degradation on the edges [3]. Moreover, compacts with metal additions such as nickel and copper have a substantially increased reactor bed parasitic thermal mass due to their relatively high densities ($\sim 8.9 \text{ g/cm}^3$) and require complex chemical processes (e.g., solution coating, sintering under 300 bar H_2) [15]. More recently, porous graphite was suggested as a matrix material which provides a simple, economic, and effective way to increase the thermal conductivity of MH compacts. For example, it has been reported that compacts with 2.28 wt% ENG had a higher effective thermal conductivity of about 19.45 W/m·K compared with 8 W/m·K for compacts with 6.14 wt% Al-foams [17].

Compacts with polymers as a binder between the metal alloy powders have also been explored to accommodate metal hydride expansion and/or provide a support for the powdered alloy material. Although a polymer has relatively low thermal conductivity, it can prevent the metal alloy from forming more porous structures between the metal powders during sorption/desorption cycles, which can limit the reduction in thermal conductivity. When the amount of polymer addition is controlled at a low level, the polymer is only present on limited areas of the powder surfaces. It acts as a binder to hold the powder together, improving the quality of the direct contact between the powder particles, which prevents excessive loss of thermal conductivity during thermal cycles. Additives such as ENG can also be incorporated to further improve the thermal conductivity of MH composites. The key factor that influences the thermal conductivity of the composite is the quality of the direct contact between the powders during the sorption and desorption cycles.

Mixtures of polymer/resin with hydrides and conductivity enhancers have also been suggested [22]. In polymer-bonded composites, hydrogen transport to or from the MH particles occurs through pre-existing cracks and porosity and/or by molecular diffusion through the polymer binders. Factors that can increase the diffusion coefficient of hydrogen through the polymer binders include chemistries of polymers free of Cl, O, N, and S that reduce polarization of the polymer, a larger free volume due to molecular-scale gaps or pores between the chains of polymers, lower-density molecular structures, and complex-

ities of the side-branch groups. For semi-crystalline polymers, there are crystalline and amorphous regions in the polymer, and the crystalline region has less permeability due to the lack of molecular-scale gaps or pores. Consequently, a higher fraction of crystalline regions could hinder hydrogen transport [29–34].

Polyethylene (PE) is the most common and cost-effective nonpolar semicrystalline polymer used including low-density PE (LDPE) and high-density PE (HDPE). These polymers have different densities varying between 0.88–0.96 g/cm³ and melting temperatures in the range of 115–135 °C [34]. LDPE has demonstrated a hydrogen permeability of ~2.0–3.0 × 10⁻¹⁵ mol·m/(m²·s·Pa), which is 2–3 times higher than HDPE (p < 5 bar and 50 °C, [35]), due to its lower crystallinity and greater free volume. Temperatures above 50 °C will increase the free volume in polymeric materials [36], leading to a greater hydrogen permeability in either LDPE or HDPE. Hydrogen diffusion through the PE polymers at this permeability is considered faster than the reaction kinetics of MHs, and thus not the factor limiting hydrogen transport in a polymer matrix MH composite [37]. Since the melting point of PE is low, low-temperature metal hydrides (e.g., LaNi₅ with a reaction temperature < 100 °C) are commonly selected for manufacturing PE-based metal hydride composites [38].

Polypropylene (PP) is another nonpolar semicrystalline polymer utilized as either matrix or binder for low-temperature metal hydride composites. The melting point of the PP is between 130 °C and 171 °C, with densities in the range of 0.855 (amorphous) to 0.946 (crystalline) g/cm³. Due to its similar characteristics to PE polymers, H₂ permeability is almost identical to the PE polymer [39]. The use of the PP in polymer MH composites, therefore, is exchangeable with PE [40–44], in terms of permeability, working temperature, and weight.

A higher working temperature polymer becomes essential when high-temperature metal hydrides are involved, such as MgH₂ (working temperature > 300 °C). One example of a high-temperature polymer is high-temperature-vulcanized polysiloxanes, especially polydimethylsiloxanes (PDMS). The glass transition temperature of PDMS is –149 °C [45] and it can operate under extreme environments and temperature from –55 to 300 °C [46]. The hydrogen permeability of PDMS is measured as ~3 × 10⁻¹³ mol·m/(m²·s·Pa) at 35 °C and up to 16 bar [47,48], which is significantly higher than ~3 × 10⁻¹⁵ mol·m/(m²·s·Pa) determined for LDPE [49]. The PDMS polymer is often deployed to form a porous scaffold system, rather than a continuous matrix, in the metal hydride composites that contain either high-temperature non-Pd hydrides (e.g., MgH₂) or volatile/liquid complex metal hydrides [50].

Polymethylpentene (PMP) is a semicrystalline polymer with the chemical formula $(C_6H_{12})_n$ and is commonly called TPXTM. It has a side branch at the molecular level, which makes it a promising candidate for gas transport. It has a melting temperature of around 230 °C, suitable for most of H₂ and MH reactions. PMP is also used to form the scaffold system for polymer metal hydride composites [37,40,51,52].

As high-temperature polymers typically have a poor hydrogen permeability, the role of the polymers in the high-temperature metal hydride composites has been changed to hold MH particles onto a scaffold or substrate that are based on carbon or ceramic materials or bind the particles together [53,54]. The polymers are often coated onto the surfaces of the powders, rather than as a continuous matrix. While the polymer coating on the MH particles is thin, it is still desirable for the polymer to provide surface protection for the MH powders from oxidation and other contaminates [44,55]. A wide range of other high-temperature polymers has been explored as the scaffold system for MH composites. These polymers include polyvinyl chloride (PVC, $(C_2H_3Cl)_n$, melting point < 260 °C) [56], Phenol formaldehyde resins (PF) that decompose at >220 °C [53,54], thermoplastic polyesters, e.g., NylonTM, melting point of heating 210–260 °C and of cooling 180–210 °C [57], and thermoplastic fluoropolymers (e.g., polyvinylidene difluoride (PVDF), melting point of 177 °C) [41,44].

2.1. Composites with Expanded Natural Graphite (ENG)

MH composite compacts with ENG as the binder were suggested as an alternative and efficient solution for MH reaction beds instead of commercially available Al-foams [17]. The effective thermal conductivity is reduced by increasing the MH to ENG mass ratio. It was concluded that the MH to ENG ratio should be higher than 20 and the effective thermal conductivity should be >8 W/m·K in order to be competitive to Al-foams, which can be achieved in composites with relatively low porosities [58].

Various materials compacted at different pressures with different proportions of ENG (in range of 2.5–34 wt%) were prepared and tested [16–18,58–60]. Melt-spun magnesium alloy flakes and ENG compacts prepared as cylindrical pellets have demonstrated good effective thermal conductivity [18]. Later, this research group demonstrated that Hydralloy C5 (AB₂ type metal hydride)/ENG composite pellets can be used for hydrogen storage applications [59]. Hydrogenation performance and the pellet evolution (composites with 5 wt% ENG compacted at 75 MPa were tested) during the observed hydrogenation cycles was found to be promising for use in tubular storage tanks.

Another composite of a mixture of Mg(NH₂)₂, LiH, and KOH (molar ratio of 1:2:0.07) with 9 wt% ENG addition were prepared at a compaction pressure of 156 MPa [60]. The increase in the compaction pressure led to the reduction in the desorption kinetics for the 1st sorption cycle but had a minor effect for the following cycles. The composite of La_{1-x}Ce_xNi₅ and ENG was fabricated by compaction at 30 MPa, and the thermo-physical properties of the composite were measured [16]. The thermal conductivity was increased from 2 to 8 W/m·K.

Figure 1 shows the influence of ENG content on the thermal conductivity of $Mg_{90}Ni_{10}$ -ENG compacts and their approximate hydrogenation states (i.e., MgH_2 -ENG compacts) [18]. The thermal conductivity of all composites showed a high degree of anisotropy. It was much higher in the radial direction, which is perpendicular to the compaction direction. The compaction pressure had a significant impact on the radial thermal conductivity for $Mg_{90}Ni_{10}$ -ENG compacts. On the other hand, it had little impact for MgH_2 -ENG compacts. For lower ENG content compacts, there was a decrease in thermal conductivity when it was in a hydrogenated state. It is suggested that the heat transfer characteristics can be tuned in a wide range depending on ENG content and compaction pressure.

2.2. Composites with Polymers

The Japan Steel Works have developed composites of MmNi_{4.4}Mn_{0.1}Co_{0.5} powder with two resins (i.e., LASTOSIL[®] M4648 and WACKER SilGel[®] 612). Pressure-composition-temperature (PCT) isotherms of the raw alloy and resin composites were found to be similar, however, the H₂ reaction rate was noted to be slower for the composite compared to the alloy powder [61]. Strain measurements performed on the MH containers confirmed lower strain recorded for the containers containing the resin composites. This lower strain was thought to be due to the immobilization and uniform distribution of the MH powder [61]. A 1000 Nm³-class hydrogen storage system was fabricated, filled with 7.2 tons of MH composite materials. This system could work at maximum hydrogen charging/discharging rates of 70 Nm³/h at a medium flow rate of 30 NL/min at temperatures in the range of 25–35 °C [61]. Resin composites prepared by Watanabe et al. [62] similarly showed no signs of damage after five absorption/desorption cycles. Even though disintegration of the MH powders took place, they were found to be firmly fixed in the resin matrix.



Figure 1. (a) Radial (solid line) and axial (dashed line) thermal conductivities of the $Mg_{90}Ni_{10}$ -ENG compacts at different compaction pressures as a function of ENG content. (b) Radial (solid line) and axial (dashed line) thermal conductivities of the MgH₂-ENG compacts at different compaction pressures as a function of ENG content (0 wt% black, 5 wt% orange, 10 wt% blue, 25.5 wt% green). Note: MgH₂ is treated as the approximate hydrogenated state of $Mg_{90}Ni_{10}$. Figure adapted from Pohlmann et al., International Journal of Hydrogen Energy; published by Elsevier, 2010 [18].

Checcetto et al. [38] prepared composites of LaNi₅ powders distributed in a H₂ permeable elastomer (polysiloxane), with MH contents of 50 and 83 wt%. The composite with 50 wt% alloy exhibited a low H₂ storage capacity, thought to be due to the MH particles being separated and the chemistry at the MH–polymer interface, limiting H₂ absorption by the metal particles. When the MH content was increased to 83 wt%, H₂ sorption was noted to increase; however, this was still lower than anticipated. It was suggested that H₂ disassociation needed to occur at a metal surface, which was hindered in the polymer composites.

In further work, Checcetto et al. [43] showed that surface chemistries in metal–polymer composites were important and can impede the activation of the metal alloy surface. It was speculated that this is the underlying mechanism as to why some polymer–metal composites showed reduced H₂ storage capacity. LaNi₅ particles (<30 μ m) dispersed in polysiloxane showed negligible H₂ storage capacity while LaNi₅ particles dispersed in polyethylene were completely hydrogenated. Conversely, Pd powders (average size 1 μ m) dispersed in polysiloxane were found to completely hydrogenate. For complete hydrogenation of a metal–polymer composite, weak chemical interactions between the polymeric chain and the metal surface are required (i.e., nonpolar polymers). H₂ desorption rates were noted to be slower for all composite materials, thought to be due to slow H₂ diffusion into the polymeric part of the composite.

This work shows that combining polymers with metal alloys can be effective in accommodating the expansion that occurs as the hydride phase is formed. However, care needs to be taken in the selection of the polymer to ensure that it not only maintains suitable properties at the operating temperatures of H_2 charging and discharging, but also does not impede the activation and subsequent sorption of H_2 by the composite. There is also potential to explore the possibility that permeative polymers could play a role in protecting the metal powders during prolonged operation.

3. Liquid-State Fabrication Methods to Produce Metal Hydride Composites

3.1. High-Temperature Melt Infiltration to Form Supported Composites

For some metallic-bonded metal hydrides, melt infiltration can load their metals into certain supports by melting the metal alloys under appropriate conditions [63]. Loading is determined by the wettability of the melt on the support [64]. If the contact angle is smaller than 90°, the pores of the support can be filled by capillary force. On the other hand, if the contact angle is larger than 90° (non-wetting), external pressure is needed to fill the pores of the support [65]. This method can achieve relatively high loadings in a single step. However, this is only applicable to metal hydrides with melting temperatures where the support materials are stable. Therefore, the maximum temperature that can be applied is also limited by the nature of the support materials. Magnesium nanoparticles were prepared by infiltration of nanoporous carbon with molten magnesium [66]. The size of the Mg crystallites was affected by the pore size of the carbon and can be less than 2 nm. The maximum loading without bulk magnesium aggregation was up to 13 wt%.

3.2. Low-Temperature Solution Impregnation to Form Supported Composites

For the ionic- or covalent-bond metal hydrides that can form complex metal hydrides in a solution, the supported composites can be fabricated at low temperature using a solution method. Solution impregnation is widely used for catalyst preparation. A solution of the MH is allowed to infiltrate the porous support materials, and then the solvent can be removed by a drying process. This method relies on the solubility of the hydride in an organic solvent. The most common solvents are ethers, diethyl ether, and tetrahydrofuran (THF). A main disadvantage is that high loadings can only be obtained by repeated processes as the metal hydride solubility is often low. Cahen et al. [67] incorporated LiBH₄ into a mesoporous carbon by room temperature impregnation using 0.029 wt% LiBH₄ in methyl tert-butyl ether (MTBE). The composite with a 33:67 weight ratio (LiBH₄/carbon) showed excellent desorption kinetics with a hydrogen release of 3.4 wt% in 90 min at 300 °C, whereas the decomposition of neat LiBH₄ was not significant at the same temperature.

3.3. Low-Temperature In-Situ Solution Synthesis to Form Supported Composites

In-situ solution synthesis uses MH precursors instead of as-prepared metal or MH. The MH nanoparticles are formed in the pores of the support. It can achieve relatively high loadings in a single step. However, it highly relies on the nature of the MH and the properties of the support. For example, Mg(Bu)2 has been widely investigated as a precursor to synthesis of MgH₂ [68]. MgH₂ nanoparticles with a size less than 3 nm were formed inside the pores of a carbon scaffold and a significant reduction in reaction enthalpy and entropy was found for the composite. A $MgH_2/graphene$ composite with MgH_2 loading of 75 wt% (MHGH-75) was synthesized via the hydrogenation of $Mg(Bu)_2$ in cyclohexane [69]. Nickel was further introduced as a catalyst to enhance hydrogen storage performance of MgH₂. The MHGH-75 composite showed H₂ sorption capacity of 4.3 wt% in 60 min at $200 \,^{\circ}$ C under 30 bar H₂ pressure. Moreover, the sorption capacity of the composite with nickel catalyst (Ni-MHGH-75) was 5.4 wt%. Conversely, there was no sorption observed from ball-milled MgH_2 and MgH_2 /graphene under the same conditions. Figure 2 shows the cyclic performance and the thermal conductivity of the composites [69]. Overall, the Ni-MHGH-75 composite demonstrated stable cycling performance up to 100 cycles. Compared with MgH₂ nanoparticles (NPs) and ball-milled MgH₂/graphene composite, the thermal conductivity of MHGH-75 composite was increased by \approx 93.5-fold and 5.6-fold, respectively, at both room temperature and 200 °C. It is suggested that graphene acts not only as a structural support, but also as a space barrier to prevent the growth of MgH_2 nanoparticles and as a thermally conductive pathway. Similar results have been reported for a NaBH $_4$ /graphene composite [70].





Figure 2. (a) Reversible H₂ absorption (under 30 atm hydrogen pressure) and desorption (under 0.01 atm hydrogen pressure) of Ni-MHGH-75 (circles) and MHGH-75 (triangles) at 200 °C. (b) Thermal conductivity of MHGH-75 in comparison with MgH₂ NPs and ball-milled MgH₂ containing 25 wt% graphene (BM MgH₂/GR) at room temperature and 200 °C, respectively. Figure adapted from Xia et al., Advanced Materials; published by Wiley, 2015 [69].

4. Powder-Based Fabrication Methods

Most literature reports investigated MH/composite in the powder form. For the metallic metal hydrides, e.g., based on Mg, V, Ti, La, and Al metals, combing the powders of these alloys with support materials without melting the metal is a popular method as they are simple, low cost, and consume less energy in comparison with the liquid fabrication route.

However, the powder composite has some disadvantages, especially for large-scale systems. First, the breakdown of metal particles into fine powders after hydrogenation cycles is well-known. This will limit the loading of the material in the reactor and can introduce internal stress to the reactor wall [71]. Second, it will reduce the thermal conductivity of the material, increasing heat transfer resistance, which may adversely impact sorption/desorption kinetics. Fine MH powders are found to have a typical thermal conductivity of ~0.1 W/m·K [15]. As a result, additional heat management measures such as fins, Al-foams, and phase change materials must be considered [14], which will increase the system cost and further reduce the packing density of the reactor. Although most pilot and industrial hydride tanks are using MH/composite powder, it is important to explore properties of composite materials in other forms such as pellet/disc and film/sheet. These composites can be synthesized by applying additional molding steps. It is expected that

they have a much higher thermal conductivity and better structural integrity, which is beneficial to the overall performance of the reactor.

4.1. Powder Preparation by Ball Milling

Ball milling is one of the most-common techniques to reduce the particle size of MH [72] as either standalone (unsupported) hydrogen storage materials or as the constituents to be incorporated into a supported composite. It can readily reduce the particle size of MH down to a few nanometers and introduce many defects that can enhance hydrogen diffusion processes. Carbon material in this case is used as an additive rather than a support. Hydrogen or solvents can be introduced during the milling process [73,74]. It is a convenient method for the activation and formation of MH. Moreover, it can prevent or minimize the formation of a metal oxide layer when an inert atmosphere is applied. It has been reported that the hydrogen sorption rate increased significantly as a result of reactive ball milling of magnesium with different carbon allotropes (e.g., graphite, ultrafine diamonds, carbon nanotubes, and amorphous carbon powder) [75]. Figure 3 shows the impact of activated carbon (AC) on the hydrogen sorption capacity of ball-milled MgH₂-AC composites. Overall, the addition of AC can improve H₂ sorption kinetics, particularly at low temperature conditions, compared with ball-milled MgH₂ nanoparticles. The MgH₂-5 wt% AC composite shows H₂ sorption capacities of 6.5, 6.7, and 6 wt% in 10, 120, and 600 min at 300, 200, and 150 °C, respectively.



Figure 3. Hydrogen sorption isotherms of the as-prepared MgH₂-xAC composites (x represents the weight percentage of AC) at (**a**) 300 °C, (**b**) 200 °C, and (**c**) 150 °C with an initial hydrogen pressure of 2 MPa, and (**d**) the comparison of the capacities of hydrogenation within 2 h at 300 °C and relevant activation energies for hydrogenation. Figure adapted from Jia et al., International Journal of Hydrogen Energy; published by Elsevier, 2012 [76].

The hydrogenation process can also be accelerated by the addition of catalysts [72,77]. Meng et al. [78] reported an improvement in the hydrogen storage properties of MgH₂ by introducing electrospun carbon fiber-encapsulated nickel catalyst. For instance, the MgH₂-10 wt% Ni/Carbon fiber composite demonstrated dehydrogenation capacities of 5.79 wt% and 6.12 wt% at 280 °C and 300 °C, respectively, whereas the as-milled MgH₂ hardly decomposed at the same temperature.

Ball milling has also been used to coat alloy particles, e.g., with polymer materials. Rafatnejad et al. [55] used ball milling to coat MgH₂ powders with poly(methyl methacrylate) (PMMA). The aim here was to apply a protective coating to the alloy particles to protect them from oxidation.

If the operating temperature is moderate but above the polymer melting point, the solid-state metal powders can be utilized to form the composites without melting.

4.2. Polymer Solution Forming (Casting)

A composite of polyethylene (PE) and LaNi₅ alloy was prepared by dissolving pellets of low-density PE in boiling heptane [43]. A fine powder of LaNi₅ was added to the solution, and heptane was removed via evaporation. A final homogenous composite was prepared by melting and then shaping the resulting material into disks by hot-pressing. Checchetto et al. [43] also achieved a dispersion of Pd powder into poly(N-vinyl pyrrolidone) by dissolving the polymer into a small amount of ethanol at room temperature. The Pd powder was added to the resulting viscous mixture, and ultrasound was used to increase homogeneity. The ethanol was then evaporated under vacuum over three days.

Japan Steel Works have applied this method to produce composites with $MmNi_{4.4}Mn_{0.1}Co_{0.5}$ powder and resins [61]. The powder and resins were mixed sufficiently to uniformly distribute the alloy particles (1 mm), before being poured into a low-strength aluminium container. Microstructural analysis confirmed the alloy powder to be uniformly distributed in the composite. Watanabe et al. [62] developed cylindrical composites by solidifying a mixture of polyvinyl alcohol, starch, and CaNi₅ powder in a cylindrical vessel at 120–180 °C. The composite was then washed to remove starch after solidification. This resulted in a porous composite with the CaNi₅ bound by the resin. A thin film composite was also prepared by pouring the mixture onto a plate and solidifying at 100 °C. They noted a slight decrease in the H₂ absorption capacity of the composite materials compared to the raw alloy, but little damage to the resin was observed.

To avoid settling and/or segregation of alloy particles as the polymer cures, the polymer/alloy composite mixtures are often quite viscous. This can make filling tanks difficult, particularly through narrow openings. Japan steel works have a patented process using vibrations to assist filling MH storage tanks with a resin/alloy/carbon fiber composite that has a pre-cured consistency similar to wet sand [23]. Vibrating the tank during filling is noted to result in more even distribution of the composite within the MH tank.

4.3. Solid State Compacting

Compaction is commonly used to prepare MH composites in a pellet form. Cold compaction was found as the most practical method of forming the composite. Acceptable microstructures were fabricated using uniaxial pressing, while isostatic pressing could be used if more uniform matrix density is required or if it is able to decrease residual matrix stresses [3].

The properties of the composite such as density, porosity, and thermal conductivity [79] can be affected by the applied compaction pressure [60]. In general, the porosity will decrease when the compaction pressure increases, but it could limit the mass transfer of hydrogen [80]. There are currently commercially available MHs developed for storage applications that are supplied in the form of compacted pellets (e.g., GKN [81]).

4.4. Solid-State Cold Rolling

Cold rolling is another method for MH composite preparation and molding [82–84]. Mg-Mg₂Ni-carbon soot/graphite composites were prepared by cold rolling and their sorption/desorption kinetics are shown in Figure 4 [85]. The graphite composite delivered the fastest absorption kinetics (4.5 wt% in 80 s), while it was only 0.7 wt% for the Mg-Mg₂Ni alloy.



Figure 4. Hydrogenation (20 bar H₂ pressure, filled markers) and dehydrogenation (0.1 bar vacuum, empty markers) capacity as a function time for Mg–Mg₂Ni and Mg–Mg₂Ni–soot/graphite hybrids at 300 °C. Figure adapted from Gupta et al., International Journal of Alloys and Compounds; published by Elsevier, 2015 [85].

4.5. Hot Pressing

Hot pressing uses high pressure and temperature to form powder compacts. Pentimalli et al. [86] used a ball mill to develop a MH–polymer composite resulting in the metal particles being coated in the polymer material. The composite was consolidated by hot pressing into pellets (6 kN force for 30 min, 150–175 °C). The composite materials showed no losses in loading capacity or kinetic properties compared to the raw alloy powder. Micro cracks and channels were noted to form in the polymer matrix after cycling, allowing the easy passage of H₂ to the embedded alloy particles.

Selection of hot-pressing process parameters, such as temperature and pressure, is influenced by the melting or glass transition temperatures of the polymer and the desired porosity level in the formed composites. One hot-forming example conducted at 100 MPa and 165 °C [41] aimed to fabricate composites consisting of LaNi₅, polymer, and graphitic flakes with about 25–30% porosity, 55–60% LaNi₅, and 10–15% polymers and graphite.

4.6. Extrusion

Extrusion is a deformation-based manufacturing process and can produce MH composites of various forms. Watanabe et al. [62] developed a CaNi₅ composite with resin by extrusion. A mixture of a fine granular phenol resin, a liquid-state phenol resin, and CaNi₅ was extruded into a cylindrical form and solidified at 147–157 °C. It was confirmed that the metal hydride powders were well fixed in the resin matrix although the breakdown of the powders was observed after a few cycles. Pentimalli et al. [87] combined high-energy ball milling with extrusion as a low-cost method to generate polymeric composites with LaNi₅-type MH. Acrylonitrile butadiene styrene (ABS) copolymer was selected due to its rheological and thermal properties that make it suitable for extrusion, its wide availability, and low cost. It does not exhibit significant gas barrier behavior and the presence of a rubber component is able to compensate for the volumetric expansion/contraction resulting from hydrogen absorption/desorption by the hydride particles. The polymer was supplied as spherical pellets and reduced to powder by centrifugal milling after embrittlement in liquid nitrogen. Graphite powder was also added to the final composite to increase thermal conductivity. The three components were blended using high-energy ball milling. The blends obtained were then extruded using a bench top compounder (110–220 °C) and cut to form pellets. This resulted in a composite with a homogeneous porous microstructure. Thermal conductivity increased from 0.2 W/m·K for the raw polymer to 2 W/m·K for the composite. PCT isotherms showed little difference between the composite and raw alloy.

5. Cyclic Stability and Composite Evolution

Cyclic stability is an important parameter for composite materials. It is imperative that the composite maintains its structural integrity during cycling. Otherwise, its properties can change significantly, and the composite may eventually break down into fine powders.

It was reported that the unsintered composites of $LaNi_{4.25}Al_{0.75}$ with copper could be handled and survived a 138-cycle absorption/desorption test with only minor degradation on the edges [3]. Additional vacuum sintering treatment was suggested for strengthening the copper matrix without affecting the ability of the composite to absorb hydrogen.

Figure 5 shows the hydrogen storage capacity and mass decrease in two MH sheets (70 wt% MH, 10 wt% aramid pulp, 20 wt% carbon fiber) as a function of cycle number [21]. There were prepared by wet papermaking method. For the $La_{0.6}Y_{0.4}Ni_{4.9}Al_{0.1}$ (LYNA) composite, the hydrogen uptake increased slowly in the first 20 cycles and a decreasing trend was observed up to 100 cycles, while the TiFe_{0.9}Ni_{0.1} (TFN) composite maintained its sorption capacity. The mass losses were less than 1 wt% after 100 cycles for both samples, indicating the composites had a good mechanical stability.



Figure 5. Hydrogen storage capacity and mass decrease in MH sheets (TFN: TiFe_{0.9}Ni_{0.1}; LYNA: La_{0.6}Y_{0.4}Ni_{4.9}Al_{0.1}) during hydrogenation cycle test at 3.8 MPa of hydrogen and was vacuumed for 1 h. Figure adapted from Yasuda et al., International Journal of Hydrogen Energy; published by Elsevier, 2013 [21].

Regarding MH/ENG composites, it was observed that lower activation temperatures require more cycles to reach full performance [58]. It was also found that the grain size of Hydralloy C5 used in the composites decreased during cyclic hydrogenation (from 108 nm to 15 nm), which is believed to be beneficial for the sorption kinetics [59].

Figure 6 shows the radial thermal conductivity of Hydralloy C5-10 wt% ENG composite throughout 1000 cycles [88]. The composite had a diameter of 13.5 mm and thickness of 6.7 mm and was compacted at 75 bar. The thermal conductivity of the composite decreased from 40 W/m·K to 12.7 W/m·K after 250 cycles. Then, it was in the range of 10–15 W/m·K up to 1000 cycles. This is much higher than that of loose powder beds [89]. The good thermal conductivity of the composite was supported by the temperature profile during the sorption process. The bed temperature increased from 50 °C to nearly 78 °C when sorption occurred, before dropping down to 50 °C in 3 min.



Figure 6. The radial thermal conductivity of Hydralloy C5-10 wt% ENG composite throughout 1000 cycles. Cycling temperature: 50 °C; absorption pressure: 40 bar; desorption pressure: 1 bar. Figure adapted from Dieterich et al., International Journal of Hydrogen Energy; published by Elsevier, 2015 [88].

The Japan Steel Works reported the cycling performance of $MmNi_{4.4}Mn_{0.1}Co_{0.5}$ composites with two resin materials [61]. No shape collapse of the composite materials was observed after 100 absorption and desorption cycles. As the MH powder was immobilized in high elasticity resin, cracks were also not observed in the composites after cycling.

6. Summary and Concluding Remarks

Metal alloys and intermetallic compounds are a promising option for the safe storage of H_2 . Challenges relating to cyclic stability and heat transfer to/from particle beds can be improved by forming composites of the alloy powders with high thermal conductivity materials, such as ENG. Such composites can be prepared by a number of methods, often dependent on the properties of the storage alloy. It is worth noting that high MH content is favorable for the composite as additives can cause the loss of H_2 storage capacity. In general, liquid-based methods can achieve better dispersion of metal alloy, which is beneficial to the reaction kinetics, while its loading can be limited. On the other hand, powder-based methods are versatile and can be easily scaled up. However, the dispersion of metal alloy may not be as good as those produced from liquid-based methods.

Challenges related to the expansion of metal particles as they absorb H_2 and form a hydride phase can be mitigated by incorporating the metal particles into composite structures with polymers. Care needs to be taken in the selection of the polymer, however, to ensure polymer–metal surface chemistries do not impede performance. For example, if the polymer can form strong bonds with the metal surface, this bonding will decrease the contact of the hydrogen with the active metal surfaces, leading to a decrease in hydrogen absorption. With ENG additive, the applied compaction pressure should be optimized. A higher thermal conductivity can be achieved by applying a higher pressure (i.e., reduced porosity). Conversely, a denser structure may hinder H_2 Transport.

With suitable selection of conductivity enhancers and polymers, composite structures can be prepared with improved heat transfer, cycling performance, and durability.

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