



REVIEW

Hydrogen Storage Materials for Metal Hydride Heat Pump Systems: A Review on Selection, Classification, and Performance Improvement

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Received: 15 July 2026; Accepted: 16 September 2026; Published: 27 October 2026

ABSTRACT: Metal hydride heat pumps (MHHPs) are promising for utilizing low-grade renewable thermal energy and waste heat in building heating, cooling, and temperature-upgrading applications. System performance and reliability depend heavily on hydrogen storage materials, particularly on their thermodynamics, kinetics, capacity, thermal conductivity, and resistance to cyclic pulverization. This review systematically examines these materials thermodynamically and kinetically across MHHP cycles: thermodynamics define the pressure-temperature equilibrium and reaction direction, while kinetics govern absorption/desorption rates, ultimately determining thermal power output and system responsiveness. Based on these requirements, selection guidelines are summarized, emphasizing optimal operating pressures, high enthalpy, sufficient capacity, low hysteresis, rapid kinetics, good reversibility, and long cycle life. Four major alloy families (i.e., AB₅, AB₂, AB, and A₂B) are critically analyzed alongside emerging alternatives such as A₂B₇-type La-Y-Ni alloys. To overcome performance bottlenecks, two complementary enhancement strategies are discussed: (i) thermal management via conductive additives and reactor design, and (ii) pulverization mitigation through compositional tuning, coatings, porous frameworks, and specialized forms (i.e., slurries, thin films, and amorphous alloys). Meanwhile, their economic feasibility, scalability challenges, and pilot-scale validation are discussed. Finally, future research directions are highlighted, including establishing comprehensive databases, developing high-precision kinetic models, evaluating real-world performance, and exploring novel alloys, all of which are essential for scaling MHHP technology toward sustainable energy deployment.

KEYWORDS: Metal hydride heat pump (MHHP); hydrogen storage materials; reaction kinetics; heat and mass transfer; thermal management

1 Introduction

Global energy demand continues to rise with population growth and rapid global economic development [1,2]. However, the extensive and unsustainable use of fossil fuels has led to the emission of a large number of greenhouse gases, such as carbon dioxide and methane, and the resulting climate change has become an important environmental problem, which has aroused wide concern. Globally, the building

sector is a major consumer of energy [3,4]. Building operation accounts for 30% of global final energy consumption and 26% of global energy-related emissions, of which 8% are direct emissions from buildings and 18% are indirect emissions from electricity and heat production used by buildings [5]. Therefore, integrating renewable and sustainable energy into the built environment and improving building energy efficiency are important measures to limit carbon dioxide emissions and mitigate climate change [6,7].

A heat pump (HP) is a device for thermal upgrading and energy saving, which can upgrade low-temperature heat from renewable and sustainable energy to a higher temperature level (i.e., temperature lift), enabling low-carbon heating and cooling in buildings [8,9]. There are many kinds of HP technologies [10–13], among which metal hydride (MH) based chemical HP systems, namely metal hydride heat pumps (MHHPs), offer unique and often irreplaceable advantages [14–18]. Since the Argonne National Laboratory in the United States built the first MHHP prototype in the mid-1970s using $\text{LaNi}_5\text{-CaNi}_5$ and $\text{MmNi}_{4.15}\text{Fe}_{0.85}\text{-LaNiAl}_{0.3}$ pairs for cooling and heating, MHHPs have been recognized as promising alternatives to conventional HP systems [19–21]. MHHPs can be driven by low-grade heat sources (typically less than 50°C [18,20,22]), such as industrial waste heat, solar energy, geothermal energy, and ocean thermal energy. Furthermore, owing to the flexibility in selecting MH pairs, MHHPs can operate over a wide temperature range (e.g., from -50°C up to 700°C , with the upper limit determined by the reversible hydrogen storage capability of the material [13,20,23]) for various applications [24].

MHHPs can be classified from multiple perspectives (e.g., function, operating temperature, driving force, system configuration, and working medium), as shown in Fig. 1. Based on the function, they include heating, temperature upgrading, refrigeration, dual-effect, and multi-effect types [21,25,26]. According to the operating temperature, they are commonly divided into typical ranges, such as low temperature (-50°C – 20°C), room temperature (25°C – 45°C), medium temperature (100°C – 150°C), and high temperature (higher than 200°C) systems [13,14,17]. By the driving force of hydrogen flow, they are divided into thermally driven or compressor-driven closed MHHPs [27–30] and potential energy driven open MHHPs [31,32]. According to the system configuration (i.e., number of metal alloys), they are grouped into single-stage, double-stage, and multi-stage MHHPs [33–35]. By the working medium, they include pure alloy hydride systems and hybrid systems combining organic hydrides and metal hydrides [17,36,37]. Among these, the dual-effect, multi-stage, and hybrid MHHPs are derivative cycles based on the fundamental heating, cooling, and temperature-upgrading configurations, and they are the main focus of this field.

Before examining these derived systems, it is instructive to recall the basic operating principle common to all MHHPs. Any MHHP cycle is fundamentally based on a pair of MHs with different hydrogen equilibrium pressures at the same temperature [15]. One MH undergoes hydrogenation (exothermic) while the other undergoes dehydrogenation (endothermic). Through the significant thermal effects of these reactions, temperature upgrading, heating, or cooling can be achieved. However, a single MH pair operates intermittently and cannot provide continuous heating or cooling [38]. Hence, to achieve quasi-continuous or fully continuous operation for a single-stage MHHP system, at least two pairs of MHs (i.e., four reactors) are required theoretically, as illustrated in Fig. 2 (reactors MH1a/MH2a and MH1b/MH2b). In such a configuration, typically two distinct MH alloys are used, each loaded into two reactors. More importantly, according to the literature [21,35,39], to realize truly continuous cooling or heating without interruption for dual-effect, multi-stage, and hybrid MHHPs, three or more distinct types of hydrogen storage alloys are needed. This requirement directly links the system architecture to the selection of hydrogen storage materials, which is the central theme of this review.

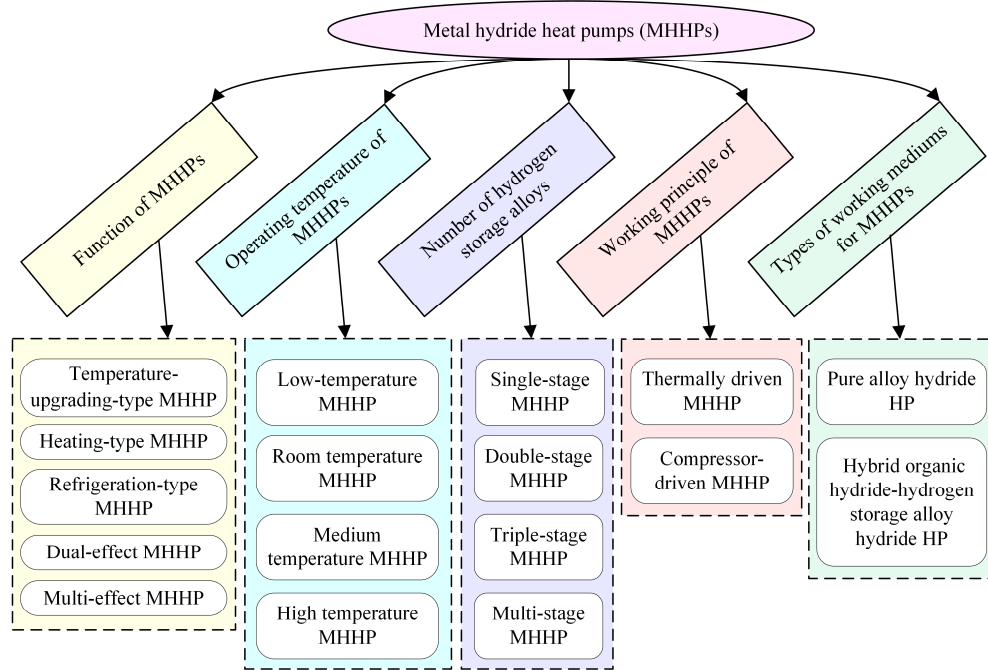


Figure 1: Classification of MHHP systems.

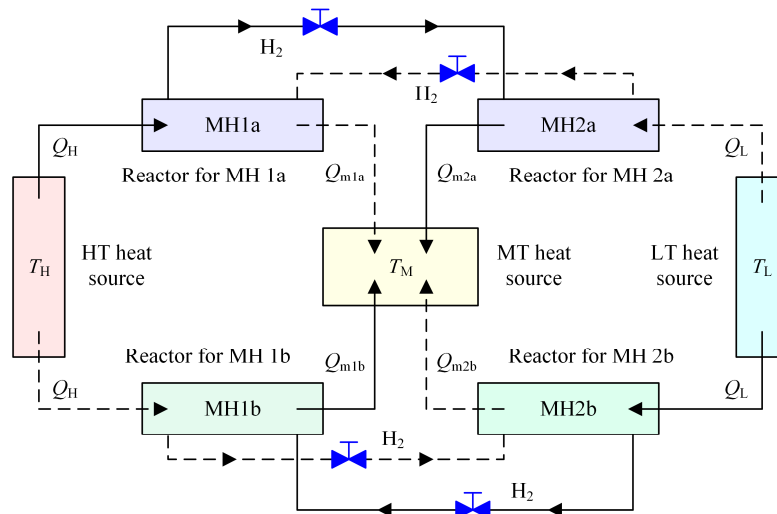


Figure 2: A continuous operating hydrogen absorption-desorption cycle of a single-stage MHHP system [17].

Research on MHHPs has spanned various aspects, including system development and performance [20, 33,40,41], hydrogen storage materials [42–46], heat transfer within MH beds [47–50], and heat exchange between hydrides and heat sources [27,51]. However, as observed by the authors, the annual publication output on MHHP technology has not grown steadily in recent years, suggesting that key technical bottlenecks remain unaddressed [52–54]. To identify these bottlenecks and advance MHHP technology, this review comprehensively examines hydrogen storage materials for MHHPs. To ensure the efficient and stable heat pump operation, hydrogen storage materials need to be purposefully selected and paired. Based on the operation characteristics of MHHPs, this review discusses the selection and classification of hydrogen storage materials from both thermodynamic and kinetic perspectives. Thermodynamic properties

determine the direction of the hydrogen reaction, and kinetic properties determine the rate of hydrogen absorption and desorption. Furthermore, the classification of hydrogen storage materials and methods to improve the properties of hydrogen storage materials are reviewed in detail. Finally, the material cost, system economic feasibility, industrial scalability challenges, and current status of engineering applications were analyzed and discussed, thereby providing future research directions.

2 Description of Hydrogen Storage Materials

2.1 Thermodynamic Properties

A metal hydride (MH) is a compound formed by the reversible reaction of hydrogen with one or more metallic elements (or intermetallic compounds). The process of hydrogen absorption and desorption is a reversible reaction, which can be expressed by Eq. (1) [53,55].



where M represents the hydrogen storage material, which is normally a metal alloy for low-, room-, and medium-temperature applications, though high-temperature alloys also exist, and MH_n stands for the corresponding metal hydride; n is the hydrogen atom number. The reaction enthalpy ΔH_{MH} kJ/mol H_2 is a measure of the heat exchanged during the reaction: a negative ΔH_{MH} corresponds to exothermic absorption, while a positive ΔH_{MH} corresponds to endothermic desorption.

Hydrogen is the working medium of MHHP in the reaction process. The heat pump uses hydrogen storage materials as energy carriers, converting them during the cycle into substances needed for the next reaction. For each reaction process, the equilibrium pressure-temperature relationship of selected hydrogen storage materials is governed by the van't Hoff law (see Eq. (2)) [56,57], which forms the thermodynamic basis for MHHPs.

$$\ln P_{eq} = -\frac{1000 \times \Delta H_{MH}}{RT} + \frac{\Delta S_{MH}}{R} \quad (2)$$

where P_{eq} is the equilibrium pressure of hydrogen under the temperature T, Pa; ΔS_{MH} is the entropy change of the hydride reaction, J/(mol·K); R is the ideal gas constant, which is 8.134 J/(mol·K).

The thermodynamic properties of MHs determine a specific correlation among equilibrium hydrogen pressure (P_{eq}), hydrogen concentration (C), and temperature (T) during hydrogen absorption/desorption reactions. Fig. 3a,b presents the ideal pressure-concentration-temperature (P-C-T) curve of an MH alongside its corresponding van't Hoff diagram [58–61], illustrating the qualitative pressure-temperature (P-C) relationship under isothermal conditions (i.e., constant T). The transitions between the solid solution phase (α phase) and hydride phase (β phase) correspond to the hydrogen absorption and desorption processes in MH alloys. At the beginning of the absorption reaction, hydrogen atoms dissolve in the metal to form a solid solution (α phase). With increasing hydrogen pressure and hydrogen concentration in the α phase, the local interactions between hydrogen atoms and the host lattice atoms leads to the nucleation and growth of the hydride (β phase) [61]. When the two phases coexist, the P-C-T curve exhibits a plateau, where the ordinate represents the hydrogen equilibrium pressure, and the length of the plateau corresponds to the hydrogen absorption capacity. By substituting the temperature and equilibrium pressure into the van't Hoff equation, thermodynamic properties such as the reaction enthalpy and entropy can be obtained, as shown

in Fig. 3b. Specifically, the reaction enthalpy change (ΔH_{MH}) and entropy change (ΔS_{MH}) can be derived from the slope and intercept of the linear fit, respectively [59,60].

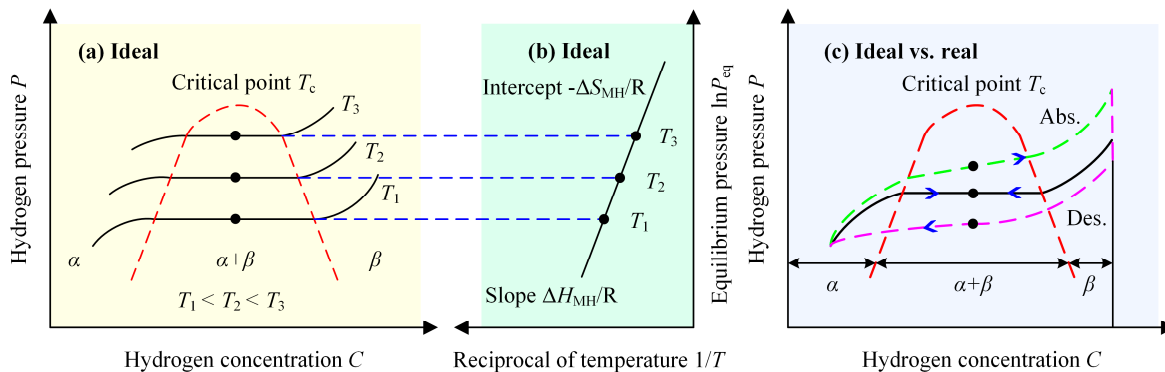


Figure 3: The P-C-T schematic diagram and corresponding van't Hoff plot [58,60,62]. (a) Ideal P-C-T schematic diagram [58,60]; (b) Ideal van't Hoff plot [58,60]; (c) Ideal versus real P-C-T schematic diagram [62].

However, in practice, pressure-composition isotherms of metal hydrides deviate from the ideal flat plateau in Fig. 3c. Two key non-ideal features are plateau slope and hysteresis [59]. The plateau slope refers to the gradual pressure change with hydrogen concentration during the $\alpha \leftrightarrow \beta$ transformation, primarily due to compositional inhomogeneities [63]. The hysteresis is the pressure difference between absorption and desorption plateaus, quantified as $\ln(P_{ab}/P_{de})$ [64], primarily resulting from lattice strain caused by volumetric mismatch (typically 10%–30% expansion [65]) between phases. Both characteristics degrade MHHP performance [62,66,67]: under limited driving temperature differences, even modest slope or hysteresis reduces system efficiency. Fortunately, alloy composition tuning can mitigate these effects. For instance, Sn or Co substitution in AB_5 (e.g., $LaNi_5$ -based) reduces hysteresis [68], V and Cu substituting in AB_2 (e.g., $TiMn_2$ -based) improve sloping properties [69], whereas Mn and Co modifications in AB_2 (e.g., $TiCr_2$ -based) enhance both slope and hysteresis performance [70]. Therefore, the plateau slope and hysteresis should be explicitly considered alongside capacity and kinetics when selecting MH alloys for HP applications.

2.2 Reaction Kinetics

The reaction kinetics of hydrogen absorption and desorption in MH alloys directly determines the rate of the hydrogenation/dehydrogenation reaction, and thus affects the rates of heat absorption and release. For a heat pump system, improving the reaction kinetics of hydrogen storage alloys is one of the important ways to enhance the energy conversion efficiency of the system. To date, a large body of literature has reported on the relevant mechanisms and theoretical studies concerning the kinetics of these reactions in hydrogen storage alloys [71–76].

The hydrogen absorption kinetics of the alloys is governed by a number of different microscopic processes, including gas phase transport of hydrogen molecules, surface physical adsorption, chemisorption, and the nucleation and growth of the α and β hydride phases. The kinetic models used for hydrogen absorption reactions of MHs are mainly divided into two categories [77]: the geometrical contraction model and the nucleation-growth-impingement model. The geometrical contraction model includes the Contracting Volume model [78,79], the Jander model [80,81], the Ginstling-Brounshtein model [82], the Valensi-Carter model [83,84], and the Chou model [85,86]. The nucleation-growth-impingement model includes the classical JMAK (Johnson Mehl Avrami Kolomogorov) model [87,88] and the nucleation index

incorporated JMAK model [89,90]. However, these models are not universal, as different models tend to apply to different MH alloys. Analysis methods based on these models mainly include the isothermal fitting method [91,92], the non-isothermal calculation method [93], and their simultaneous fitting approach [90]. Moreover, the assumptions and derivation steps of these models are often not readily available, and the selection of corresponding analysis methods is sometimes confusing. In response to the above issues, Pang et al. [77] systematically summarized the analysis methods based on these kinetic models of MH alloys, and proposed a relatively novel analysis method, as shown in Fig. 4. For the geometrical contraction models, interface-controlled equations govern steps (A1–A3 and A5), while diffusion-controlled ones govern step (A4). For the nucleation-growth-impingement models, diffusion-controlled equations govern step (B1 or D2), while interface-controlled ones govern step (B2 or D1) [77]. This indicates that both model categories can involve either diffusion or interface control, depending on the specific rate-controlling step.

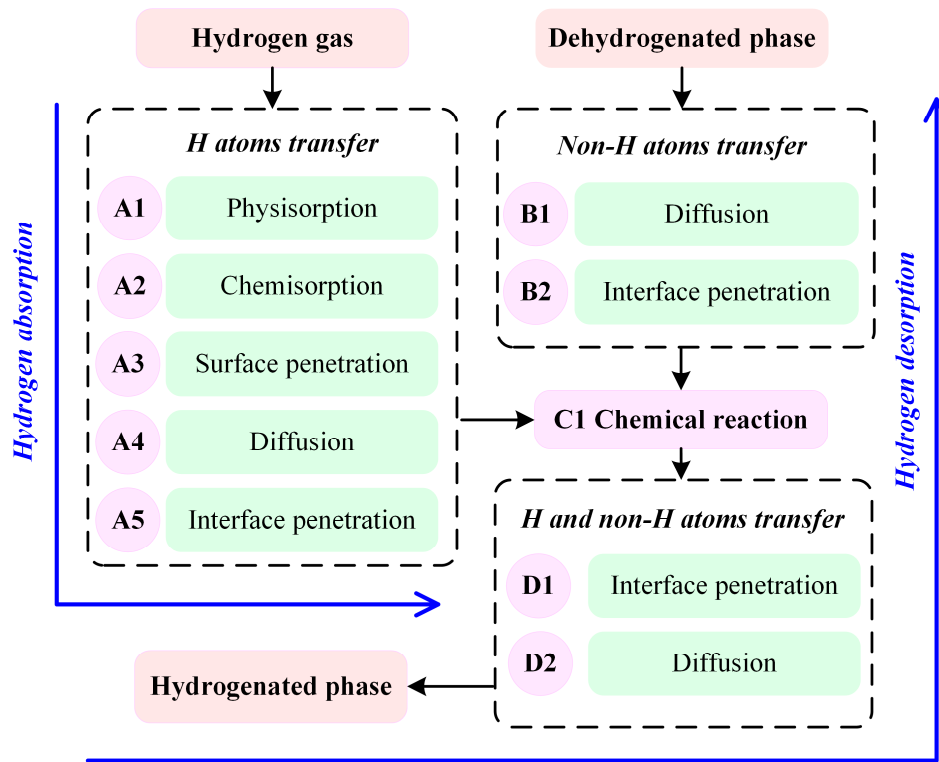


Figure 4: The schematic diagram of kinetic steps of hydrogenation and dehydrogenation [77].

The thermal conductivity of MH is usually one of the key factors determining the hydrogenation and dehydrogenation reaction rates. When the hydrogenation reaction rate is high, accompanied by a large amount of reaction heat release, the MH alloy has an obvious self-heating effect, resulting in an instantaneous temperature increase of 10°C during the hydrogenation process [94]. However, the thermal conductivity of MHs is typically significantly lower than that of their constituent alloys, with values generally ranging from 0.1 to 2 W/(m·K) [95,96], which means that for alloys with faster reaction kinetics, this low thermal conductivity becomes the limiting factor [55,96–98]. Consequently, the absorption and desorption rates of hydrogen in the hydride reaction are determined by the hydrogenation kinetics and the overall heat transfer performance of the reactor, and thus the heat transfer of MH alloys should be taken into particular consideration when designing MHHP systems.

In addition to classical models, data-driven approaches offer new routes for predicting hydrogen storage kinetics. For instance, the U.S. Department of Energy's publicly available hydride database, covering intermetallic compounds (AB , A_2B , AB_2 , and AB_5), Mg-based alloys, solid solutions, and complex hydrides, has been analyzed using supervised machine learning (ML) methods, where decision tree regression models achieved a coefficient of determination of 0.93 in predicting hydrogen storage capacity based on charging pressure and temperature [99], demonstrating that ML can help determine optimal operating conditions for MH reactors without relying on detailed mechanistic assumptions. Such methods complement mechanistic models and enable rapid screening of alloy candidates for MHHP applications.

2.3 Selection Criteria of Hydrogen Storage Alloys

The heat required for MHHP operation is provided by the thermal effects of the hydrogen absorption and desorption processes of the MH alloys. Therefore, the rate of heat absorption and release per unit mass plays a critical role in the performance of the MHHP system. As mentioned above, the continuous operation of the MHHP unit requires at least one pair of hydrogen storage alloys. This means that the factors that affect the performance of the MHHP system are not only the hydrogen storage properties of each individual alloy, but also the compatibility between the paired alloys.

The selection of hydrogen storage alloys for MHHP systems should consider multiple criteria, which can be categorized into three groups:

(1) Thermodynamic and kinetic criteria

Each alloy should possess suitable operating temperatures and pressures [21], high enthalpy values (with $\Delta H_{MH,A}$ and $\Delta H_{MH,B}$ for the paired alloys in the range of -9 to -7 kcal/mol H_2 , approximately -37.7 to -29.3 kJ/mol [100]), a significant equilibrium pressure difference between the high- and low-temperature ends (particularly for thermally driven systems, where this difference serves as the driving force for hydrogen circulation [100]), good reversibility, rapid kinetics, and high hydrogen diffusivity [21].

(2) Capacity and plateau characteristics

Each alloy should exhibit a large hydrogen absorption capacity under standard conditions, typically requiring either a gravimetric capacity of 1.8 wt% (equivalent to 200 L (STP) per kg of alloy) or an H/M ratio exceeding 1.5 wt% [100]. Additionally, a small hysteresis coefficient [$\ln(P_{ab}/P_{de}) < 0.25$] and a flat P-C-T plateau [$d(\ln P_{de})/d(H/M) < 1.0$] are desirable to ensure efficient and stable operation [100].

(3) Engineering practicality and reliability

The alloys should have excellent heat transfer performance, with thermal conductivity generally required to exceed $0.5 \text{ W/(m}\cdot\text{K)}$ [100]. Beyond these performance-oriented criteria, practical considerations such as stability in air, safety, environmental friendliness, long service life, and low cost are also essential. For example, life cycle assessment of large-scale metal hydride systems identifies the metal hydride alloy itself, particularly titanium in TiFe-based systems, as the largest environmental burden [101]. Energy consumption during operation accounts for less than 7% of most impact categories, underscoring that material production dominates the environmental footprint [101]. Substituting primary with recycled feedstock can substantially reduce emissions: for AB_2 -type alloys, using 100% recycled material yields up to an 80% reduction in global warming potential [102].

Meanwhile, different alloy families present distinct safety profiles. $LaNi_5$ is classified as water-reactive (releasing flammable gases), skin sensitizer, and suspected carcinogen [43]. Mg-based hydrides exhibit pyrophoricity and significant dust explosion hazards, with the lower explosion concentration limit ranging

from 25 to 60 g/m³ [103] and the maximum explosion pressure reaching 1.17 MPa [104]. In contrast, TiFe-based alloys offer a lower-toxicity alternative but require high-temperature activation [105,106]. During cyclic operation, hydrogen flammability (4%–75% in air) [107] and the volumetric expansion ratio (10%–30%) that may exert pressure equivalent to several times the hydrogen pressure on reactor walls constitute additional safety concerns [108]. Mitigation strategies include increasing recycled feedstock content, applying protective surface coatings against oxidation and poisoning, and using appropriate operating pressure, implementing proper thermal management and pressure relief devices, and establishing end-of-life recycling protocols for rare earth elements [43]. These factors should be weighed alongside thermodynamic and kinetic criteria in alloy selection for MHHP systems.

The above criteria, based on the early screening guidelines proposed by Xiao [100] and Ni et al. [21], provide useful benchmarks. However, they should be interpreted with consideration of specific application requirements and advances in alloy development over the past decades. Based on the criteria discussed above and the specific temperature requirements of different heat sources, Fig. 5 provides a systematic decision flowchart to guide the preliminary selection of appropriate alloy families, balancing thermodynamics, kinetics, and practical engineering constraints.

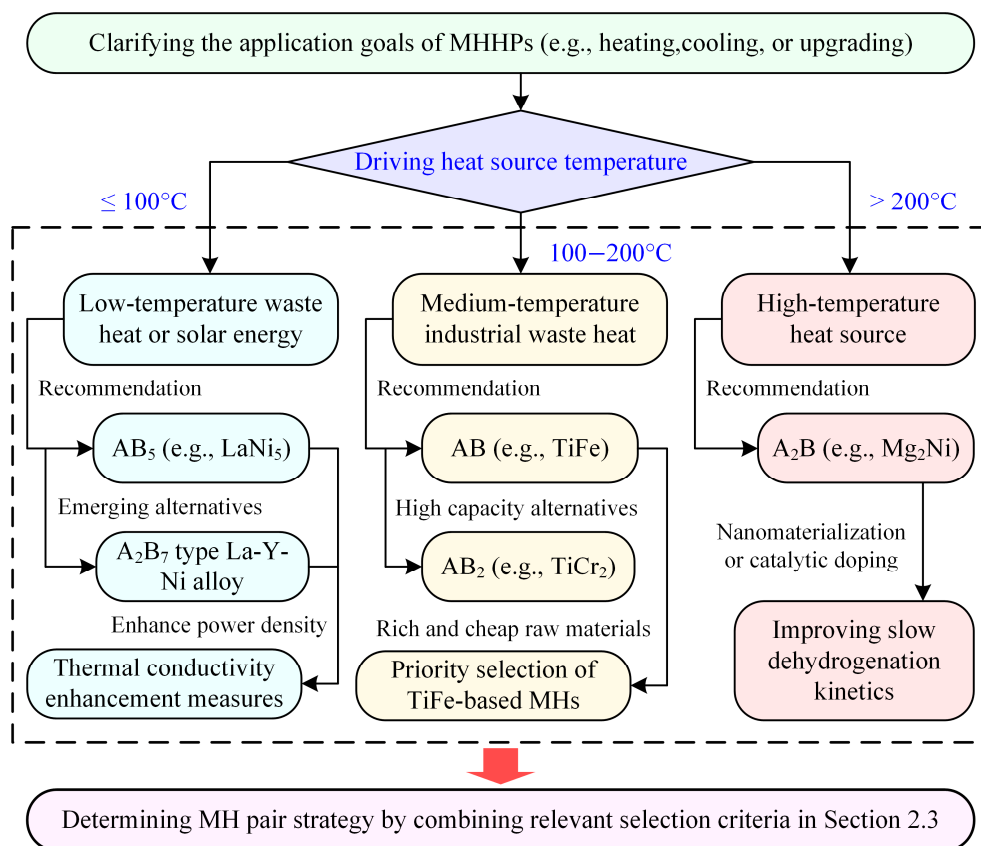


Figure 5: Schematic diagram of hydrogen storage alloy selection process in MHHP system.

In addition, a key factor limiting the service life of MH alloys is the volumetric expansion (10%–30% [100]) and contraction (10%–25% [21]) that occur during repeated hydrogen absorption and desorption cycles. Long-term cyclic expansion and contraction lead to cracking and pulverization of the metal particles [109–111], which increase hydrogen flow resistance and reduce heat and mass transfer efficiency [112,113]. Such

repeated expansion also induces significant local pressure buildup within the reactor, potentially causing mechanical damage and hydrogen leakage. Therefore, the number of working cycles of MHs is generally required to exceed 10,000 [100].

2.4 Metal Hydrides for Thermochemical Energy Storage Applications

Besides their role in MHHPs, MHs also serve as promising thermochemical energy storage (TCES) materials for high-temperature applications such as concentrated solar power generation and industrial waste heat recovery [114]. Among these, NaMgH₃ has attracted increasing attention due to its high thermal storage density (2881 kJ/kg) [115] and considerable hydrogen capacity (6.0 wt% or 88.0 g/L), with dehydrogenation occurring at approximately 673 K under 0.2 MPa H₂ [116]. However, its practical application is hindered by sluggish kinetics and thermal management challenges, which can be mitigated by nanosized catalyst doping [115]. System-level techno-economic studies have further indicated that NaMgH₃-based storage can be among the lower-cost MH options relative to some other hydrides [117], and coupling MH-based TCES with heat pump cycles offers a promising pathway to enhance overall energy utilization efficiency [12,118].

In recent years, the TCES field has progressively advanced to pilot-scale investigation, where system performance under transient thermal inputs and long-term cyclic conditions has been evaluated [114,119]. These experiences, particularly in reactor thermal management, cycle stability requirements, and techno-economic validation, offer valuable reference for MHHP scale-up, as both technologies share common challenges in managing coupled heat and mass transfer within hydride beds.

3 Classification of Hydrogen Storage Alloys

Ga, Mg, Ti, Zr, V, Nb, Pd, and rare-earth elements are all pure metals that can form metal hydrides. However, a single pure metal usually requires high hydrogen absorption pressure and operating temperature, so it is mainly used for high temperature heat storage [30]. When these metals are alloyed with other metals, the hydrogen absorption and desorption processes can be carried out at lower temperatures and pressures, which facilitates the application of MHHPs in the field of low-temperature waste heat recovery. Hydrogen storage alloys exist in various forms, such as powder, slurry, glassy state, thin films, and microparticles. In terms of chemical composition, however, typical hydrogen storage alloys are classified into four main types (as shown in Fig. 6): AB₅ [120], AB₂ [121], AB [106] and A₂B [122].

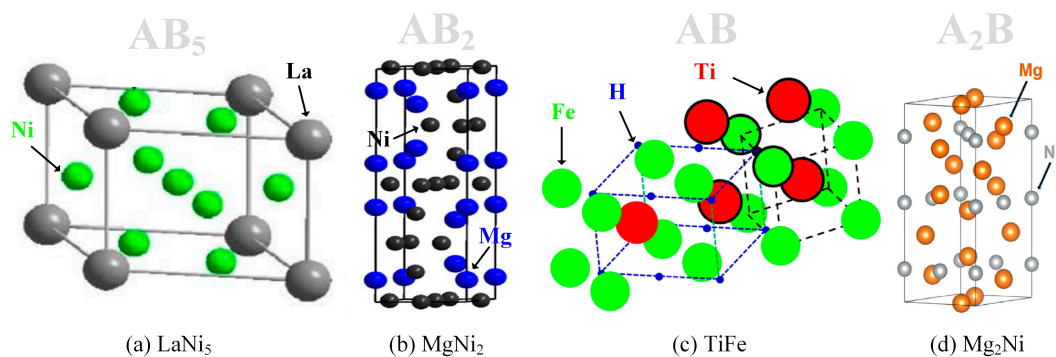


Figure 6: Comparison of crystal structures of four main hydrogen storage alloy families. (a) LaNi₅ as a representative of AB₅-type alloy [123]; (b) MgNi₂ Laves phase as a representative of AB₂-type alloy [124]; (c) TiFe as a representative of AB-type alloy [125]; (d) Mg₂Ni as a representative of A₂B-type alloy [126,127].

The designation of hydrogen storage alloys as A_xB_y is based on the distinct hydrogen affinities of their constituent elements [128]. A-site elements are those with strong affinity for hydrogen, capable of forming thermodynamically stable hydrides; this category includes alkaline-earth metals, rare-earth (lanthanide) elements, and early transition metals such as Ti, Zr, and Hf [17,128,129]. In contrast, B-site elements have weak affinity for hydrogen and do not form stable hydrides themselves; they are typically late transition metals (e.g., Ni, Co, Mn, Cr, Fe, Cu) and p-type elements (e.g., Al, Sn) [128,130]. The association of A- and B-type metals to form A_xB_y intermetallics enables reversible hydrogen storage under practical conditions of temperature and pressure.

Importantly, the site occupancy of a given element is not strictly intrinsic but depends on the specific alloy stoichiometry and crystal structure [131]. For example, Ti occupies the A-site in TiFe (AB-type) and TiMn₂ (AB₂-type) alloys [105,128], yet it can act as a B-site substituent in certain multicomponent rare-earth-based AB₅-type alloys [129,132]. Similarly, Zr predominantly occupies A-sites in C14/C15 Laves phase structures (e.g., ZrMn₂, ZrCr₂) [133], but can also be incorporated into B-sites in modified AB₅-type alloys [134,135]. Substitutional doping at either A or B sites (i.e., partial replacement of the original A- or B-site elements with other metals) is a key strategy for tuning hydrogen storage properties, including plateau pressure, hysteresis, capacity, and cycling stability [128]. By adjusting the stoichiometric ratio x and y , as well as the elemental composition at each site, the properties of A_xB_y alloys can be tailored to meet the specific requirements of MHHP applications [17].

3.1 AB₅-Type Hydrogen Storage Alloy

LaNi₅ is the most typical representative of AB₅-type (rare-earth-based) alloys and is also the earliest developed MH alloy, exhibiting excellent overall properties [136,137]. It offers advantages such as moderate equilibrium pressure, low hysteresis, easy activation, and strong poisoning resistance. However, its main drawbacks include severe pulverization and capacity degradation during long-term cycling, as well as relatively high material cost [136–138]. To reduce costs, researchers have developed a series of alloys, such as CeNi₅, PrNi₅, NdNi₅, ZrNi₅, YNi₅, CaNi₅, TiNi₅, MmNi₅, and MnNi₅, by using single rare-earth elements (e.g., Ce, Pr, Nd, Sm, and Y), single alkaline-earth elements (e.g., Ca), mixed rare-earth metals (e.g., cerium-rich mischmetal (Mm) and lanthanum-rich mischmetal (Ml)), or by substituting Zr or Ti for La [139–143]. Subsequently, many scholars attempted to substitute Cu, Mn, Fe, Cr, Zr, and Al for Ni to prepare rare-earth-based multi-element hydrogen storage alloys and improved the hysteresis and activation properties by adjusting the plateau pressure. In particular, the addition of Zr can not only increase the ΔH value of the hydride but also inhibit the pulverization of the alloy [144].

In addition, to improve the performance and cycle life of mixed rare-earth-based hydrogen storage materials, it is usually necessary to add Co and Al. By adjusting the composition of different elements in the alloy, a series of rare-earth hydrogen storage alloys suitable for various applications can be obtained. The typical compositions of multi-element hydrogen storage alloys include LaNi_{5-x}M_x (M = Al, Co, Mn, Cu, Ga, Sn, In, Cr, and Fe) [145,146], LaNi_{5-x-y-z}Al_xSn_yFe_z, La_{0.78}Ce_{0.22}Ni_{3.73}Co_{0.30}Mn_{0.30}Al_{0.17}Fe_{0.5-x}Si_x, and LaNi_{5-x-y-z}Al_xCo_yMn_z [120].

3.2 AB₂-Type Hydrogen Storage Alloy

There are three main series of AB₂-type alloys (Laves phase structure based on Ti and Zr) [133,147,148]: Zr-V, Zr-Cr, and Zr-Mn series, with typical representatives being ZrM₂, TiM₂ (M = Mn, Ni, V, etc.), and other common examples including Zr(V_xNi_{1-x})₂, ZrMn_{0.8-x}Cr_xNi_{1.2}, and TiMn_{1.5}. The composition of these alloys varies greatly due to the characteristics of their lattice structures; therefore, good comprehensive

properties can be achieved through doping substitution [147,149]. Furthermore, Ti, Zr, Ta, and Hf can be used to replace the A-site in AB_2 , while transition metals (such as Fe, Co, Ni, Mn, Cr, and V) can be used to replace the B-site [150]. Accordingly, various multi-element alloys Ti-Zr-Ni-M (M represents one or more elements among Mn, V, Al, Co, Mo, and Cr) with different properties have been developed [150,151].

However, these alloys typically suffer from difficult initial activation, i.e., slow hydrogen absorption kinetics. To address this issue, researchers have found that adding rare-earth metals (including mischmetal) to AB_2 alloys can effectively improve their activation behavior, as demonstrated in the $M_{0.93}Mg_{0.07}Ni_{2.96}Co_{0.60}Mn_{0.37}Al_{0.17}$ (M = rare-earth elements, Ce, Y, etc.) [152] and the $La_{1-x}Ce_xMgNi_{3.5}Mn_{0.5}$ [153] series. In fact, the constituent elements in these multi-element alloys contribute uniquely to hydrogen storage performance: Ti, Zr, and V serve as the basic hydride-forming elements; Ni provides rapid catalytic activity; Co and Mn offer surface activity related to improving hydrogen exchange; and Cr, Al, and Fe enhance the stability of the alloys in hydrogen storage applications [121]. According to the literature [144], multi-element alloying products based on $ZrMn_2$ and $TiCr_2$ with $MgZn_2$ -type laves structures show the greatest application potential.

3.3 AB-Type Hydrogen Storage Alloy

The earliest developed AB-type alloy (Ti-based) is TiFe [154], which is cheap and resource-abundant [106], and can be hydrogenated and dehydrogenated at room temperature and atmospheric pressure after proper activation [155]. The alloy has a large theoretical hydrogen storage capacity of up to 1.9 wt% [106]. However, its main drawbacks are its susceptibility to oxidation and poor poisoning resistance. Its activation requires high temperatures and pressures ($T = 400\text{--}450^\circ\text{C}$, $P = 65$ bar [106]), which greatly limits its large-scale industrial application.

At present, the most common method to activate TiFe is alloying with single or multiple elemental substitutions, such as $TiFe_{1-x}M_x$ (M = V, Cr, Mn, Sn, Mo, Ni, Ta, and Al), $TiFe_{0.8-x}Ni_{0.2}Co_x$, $TiFe_{0.8}Mn_{0.1}V_x$, and $Ti_{1.1-x}M_xFe_{0.8}Mn_{0.2}$ (M = Pr, Sm, and Nd) [156–159]. Although alloying can improve the initial hydrogen absorption kinetics of TiFe, adding other elements may lead to a decrease in hydrogen storage capacity and desorption plateau pressure. More importantly, elemental substitution can also induce hysteresis, namely, the separation between absorption and desorption plateau pressures. Hysteresis primarily arises from lattice strain caused by volumetric expansion [65,160] and reduces the effective pressure difference in MHHPs, degrading system efficiency [62,66,67]. In this regard, Shang et al. [161] found that the addition of Pr can promote the TiFe phase, generate a Pr segregation phase, increase the lattice unit cell volume, and refine the grains of TiFe, thus significantly improving the hydrogen storage performance of Pr-containing alloys. The increase in Pr content leads to an increase in the enthalpy change (ΔH) of the $Ti_{1.1-x}Fe_{0.7}Ni_{0.1}Zr_{0.1}Mn_{0.1}Pr_x$ alloy, and the hydrogenation capacity and kinetics of the alloy with $x = 0.02$ reach their maximum values within 1000 s. Zhai et al. [162] found that partially substituting Ti with La not only significantly improved the hydrogen absorption kinetics of $Ti_{1-x}La_xFe_{0.8}Mn_{0.2}$ alloy but also increased the equilibrium plateau pressure of the alloy hydride. Key research directions for achieving large-scale application of TiFe-based alloys include reducing the surface density, providing fast diffusion channels for hydrogen atoms, increasing the diffusion rate of hydrogen atoms via crystal defects, and increasing the phase interface [163].

3.4 A₂B-Type Hydrogen Storage Alloy

The typical representative of A_2B -type alloys is Mg_2Ni , which has a large theoretical hydrogen storage capacity of up to 3.67 wt% [164]. The raw materials are abundant and inexpensive. However, its main drawback is poor hydrogen desorption kinetics [165], which typically requires higher operating temperatures (above 250°C [164,166]). The kinetic properties of hydrogen absorption and desorption of

Mg-based alloys can be effectively improved via mechanochemical methods [122] or by adding a certain amount of TiFe and TiNi via ball milling [167]. In recent years, improving Mg-based hydrogen storage alloys has attracted extensive research interest [168–174]. Yong et al. [174] prepared $\text{Mg}_{90}\text{Ce}_5\text{Y}_5$ alloy with high capacity and stability by the vacuum induction melting method. This multi-phase alloy exhibited enhanced kinetic properties.

Zhong et al. [168] prepared $\text{Mg}_2\text{Ni}_{0.7}\text{M}_{0.3}$ ($\text{M} = \text{Al}, \text{Mn}, \text{and Ti}$) alloys by the solid-state sintering method. The results showed that the hydrogen absorption and desorption properties of the $\text{Mg}_2\text{Ni}_{0.7}\text{M}_{0.3}$ alloys were significantly improved. The apparent dehydrogenation activation energies of the $\text{Mg}_2\text{Ni}_{0.7}\text{Al}_{0.3}$, $\text{Mg}_2\text{Ni}_{0.7}\text{Mn}_{0.3}$, and $\text{Mg}_2\text{Ni}_{0.7}\text{Ti}_{0.3}$ alloys decreased significantly by 46.12, 59.16, and 73.15 kJ/mol, respectively. Matheus et al. [122] obtained a highly active Mg_2Ni hydrogen storage alloy through high-energy reactive ball milling, annealing heat treatment, and pre-absorption and desorption cycling treatment, which can adsorb and desorb hydrogen below 300°C. The desorption kinetics of the alloy is similar to that of alloys obtained by nanoparticle synthesis or hydrogenation combustion synthesis, and it exhibits even better absorption capacity.

3.5 Other Types of Alloys

AB_5 alloy is the most widely used hydrogen storage material in MHHPs, and most of the prototypes developed to date employ this alloy. However, due to its inherent structural limitations (CaCu_5 -type), the optimized maximum theoretical hydrogen storage capacity of this alloy type usually makes it difficult to meet the required targets [175]. In addition, the activation of AB_2 - and AB -type alloys is difficult, while the cyclic stability of A_2B -type alloys is poor. Despite considerable efforts to enhance these properties, further improvements remain desirable.

M-Mg-Ni hydrogen storage alloys, as a substitute for traditional AB_5 alloy, are widely studied in metal hydride materials. Active Mg is one of their main components. Owing to the high vapor pressure of Mg, the chemical composition of M-Mg-Ni alloys is difficult to control during high-temperature melting processing. The ultrafine Mg powder formed by the volatilization of Mg also poses safety risks [175,176]. Although new manufacturing techniques, such as helium/argon melting protection [177–180], sintering [181–184], suppression of Mg volatilization via additives or alloying [185,186], and high-energy ball milling [167,187,188] have been investigated, these approaches still suffer from high costs or complex procedures.

To address the above issues, scholars have developed Mg-free hydrogen storage alloys with high capacities, such as A_2B_7 -type La-Y-Ni alloys with various La/Y ratios [189–192], as well as AB_3 -, A_2B_7 -, and A_5B_{19} -type La-Y-Ni and La-Y-Ni-Mn-Al series alloys [175]. Xiong et al. [192] prepared A_2B_7 -type $\text{LaY}_2\text{Ni}_{10.5-x}\text{Mn}_x$ ($x = 0.0, 0.5, 1.0, \text{ and } 2.0$) alloys by vacuum induction melting, quenching, and annealing, replacing part of Ni with Mn. The results showed that the hydrogen storage capacity was the highest at $x = 0.5$, but the cycle stability was inferior to that of the other alloys. Wang et al. [190] pointed out that the effect of Al on improving the cyclic stability of A_2B_7 -type $\text{LaY}_{1.9}\text{Ni}_{10.2-x}\text{Al}_x\text{Mn}_{0.5}$ ($x = 0\text{--}0.6$) alloy was limited.

Liu et al. [191] prepared A_2B_7 -type $\text{La}_{3-x}\text{Y}_x\text{Ni}_{9.7}\text{Mn}_{0.5}\text{Al}_{0.3}$ ($x = 1, 1.5, 1.75, 2, 2.25, \text{ and } 2.5$) alloy via the magnetic levitation induction melting method. They found that with increasing Y content, the structural stability of the alloys was improved, but the corrosion, pulverization, and dissolution of Al were also intensified. Li et al. [189] found that as the Y content increased, the hydrogen storage capacity of A_2B_7 -type La-Y-Ni alloys gradually rose from 1.309 wt% (La:Y = 1:1) to 1.713 wt% (La:Y = 1:5), which was closely related to the increase in the hydrogen diffusion rate. Therefore, the determination of Y content needs to take into account both alloy stability and hydrogen storage capacity. Yan et al. [175] prepared $\text{LaY}_2\text{Ni}_{8.2}\text{Mn}_{0.5}\text{Al}_{0.3}$

(AB₃-type), LaY₂Ni_{9.7}Mn_{0.5}Al_{0.3} (A₂B₇-type), and LaY₂Ni_{10.6}Mn_{0.5}Al_{0.3} (A₅B₁₉-type) hydrogen storage alloys by the induction melting and rapid quenching method. The results showed that all three alloys had stable multi-phase microstructures, and the activation properties and cycle stability of the A₂B₇ and A₅B₁₉ alloys were superior to those of AB₅.

In addition to the above classification based on alloy composition, hydrogen storage materials for MHHPs are also categorized by operating temperature into high-temperature (above 500°C, e.g., TiH₂ and NaH) [30,193], medium-temperature (200–500°C, e.g., Mg-based MH) [193,194], and low-temperature (room temperature, e.g., TiFe and LaNi₅) groups [30,195], each serving distinct heat pump cycles.

3.6 Summary of Alloy Performance Metrics

Based on the detailed discussions in Sections 3.1–3.5, it is evident that each alloy family exhibits distinct advantages and drawbacks when considered for MHHP applications. To provide a clear and rapid reference for material selection, Table 1 summarizes the quantitative and qualitative performance metrics of the five major alloy families, including their hydrogen storage capacity, reaction kinetics, cycle stability, anti-pulverization capability, relative cost, and operating temperature range. This comparison highlights that no single alloy universally satisfies all MHHP requirements. On the contrary, the optimal choice depends on the specific operating temperature, power density, and economic constraints of the target application.

For low-temperature building heating/cooling applications, AB₅-type alloys remain the first choice due to their mature technology and fast kinetics, despite their limited capacity. For high-temperature thermal upgrading (>150°C), A₂B-type alloys are more suitable, provided that kinetic enhancement measures are applied. AB₂ and AB-type alloys offer a compromise between cost and performance but require careful activation and anti-pulverization design.

4 Thermal Performance Improvement of Hydrogen Storage Alloys

The heat and mass transfer mechanisms in hydrogen storage alloys are extremely complex, involving heat conduction through metal particles, contact heat transfer between particles, hydrogen flow, as well as radiative and convective heat transfer in the voids [207]. The effective thermal conductivity of these alloys is generally small, typically in the range of 0.1–1 W/(m·K), particularly when the inter-particle contact thermal resistance is high [208]. Moreover, during cyclic operation, the repeated expansion and contraction of the alloy due to heat uptake and release lead to cracking and pulverization. These effects not only further reduce the effective thermal conductivity but also increase the resistance to hydrogen flow within the reactor, thereby degrading the absorption/desorption kinetics and the overall heat pump performance [21,209].

When the thermal conductivity is low, the heat released during absorption cannot be dissipated promptly and thus accumulates in the reactor, raising both the system temperature and the equilibrium pressure. This, in turn, suppresses the hydrogen absorption capacity and rate, and may even halt the absorption reaction in severe cases. Therefore, enhancing the heat and mass transfer characteristics of metal hydride alloys is critical for improving the performance of MHHP systems.

To systematically address the inherent limitations of hydrogen storage alloys, Fig. 7 illustrates a comprehensive logic diagram linking the two primary performance bottlenecks (i.e., low effective thermal conductivity and cyclic pulverization) to their corresponding enhancement strategies. This framework serves as a roadmap for the detailed discussions presented in Sections 4.1 and 4.2.

Table 1: Comparisons of key performance metrics for major alloy families in MHHP applications.

Alloy Family	Hydrogen Storage Capacity	Ab/Desorption Kinetics	Cycle Life (Stability)	Anti-Pulverization	Relative Cost	Temperature Range	References
AB ₅ (LaNi ₅ -based)	1.0–1.5 wt%	Fast/fast	Moderate (<1000 cycles decay)	Poor	High	~100°C	[57,138,196]
AB ₂ (Laves phase)	1.6–2.1 wt%	Moderate/moderate	Good (up to 5000 cycles)	Moderate	Medium	~150°C	[197,198]
AB (TiFe-based)	1.8–1.9 wt%	Slow (needs activation)/moderate	Moderate	Moderate	Low	~100°C	[126,196,199,200]
A ₂ B (Mg ₂ Ni-based)	3.3–3.7 wt%	Slow (unless modified)/slow	Poor (rapid decay)	Moderate	Low	>250°C	[201–204]
A ₂ B ₇ (La-Y-Ni-based)	1.3–1.8 wt%	Fast/fast	Improved (better than AB ₅)	Improved	Lower than AB ₅	~60°C	[189,205,206]

Note: Capacity values represent typical ranges for representative compositions; actual values vary with specific stoichiometry and operating conditions. Cost estimates are qualitative rankings based on raw material abundance and processing complexity.

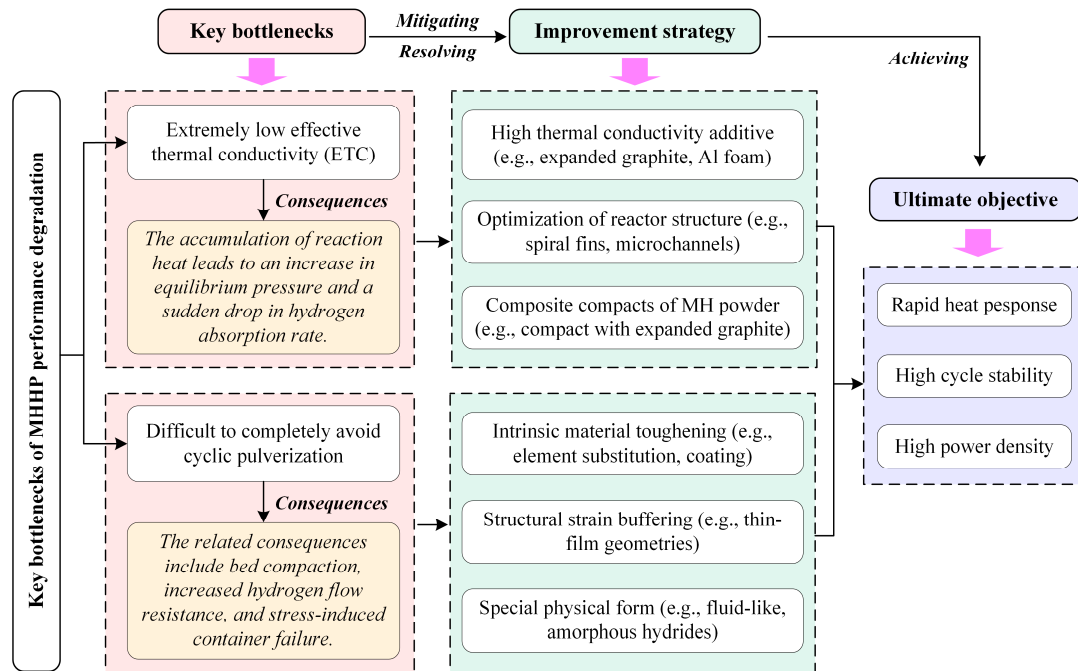


Figure 7: Schematic diagram of performance bottlenecks and improvement strategies.

4.1 Enhancement of the Effective Thermal Conductivity

It has been well established that the effective thermal conductivity (ETC) of hydrogen storage alloys is significantly influenced by both hydrogen pressure and hydrogen concentration [47,208,209]. Additionally, several other factors, including the porosity of the hydride bed [209], the structural shape of the MHs [210–212], and the thickness of the hydride layer [14,213–216], have been identified as critical determinants of thermal transport and hydrogen flow behavior.

Hahne et al. [208] demonstrated that the ETC of metal hydride alloys depends primarily on hydrogen pressure, with temperature exerting only an indirect effect. They further noted that the ETC increases with the rising concentration of hydrogen atoms participating in the reaction. In a systematic study using $\text{LaNi}_{4.7}\text{Al}_{0.3}$ as the hydrogen storage alloy, Raju et al. [217] investigated the dependence of hydrogenation and dehydrogenation performance on key parameters such as hydrogen pressure, operating temperature, and heat transfer fluid flow rate. Their results confirmed the influence of these parameters and provided a basis for recommending favorable operating conditions.

To enhance the ETC from the material perspective, various high-conductivity additives or structural components have been incorporated into the hydride bed, including copper wire [218], aluminum foam [219], carbon nanotubes [220], phase change material [221], and naturally expanded graphite [211]. Table 2 summarizes some studies on ETC of enhanced hydrogen storage alloys. Overall, these additives and structural modifications have been shown to considerably increase the effective thermal conductivity of metal hydrides.

However, the introduction of metals such as aluminum and copper, while beneficial for thermal conductivity, inevitably reduces the gravimetric hydrogen storage capacity and increases the sensible heat loss of the hydride bed. Furthermore, Chaise et al. [229] observed that when solid-state diffusion occurs between the magnesium hydride and the metal matrix, a significant degradation in storage capacity is also evident at elevated temperatures. Kim et al. [210] proposed a novel method to fabricate dense

composite materials by mixing light expanded natural graphite (ENG) with MHs, effectively mitigating the issue of bed porosity. Nevertheless, this approach still suffers from high energy consumption during the high-pressure compaction process. Gkanas et al. [216] determined that the optimal heat transfer coefficient of 2000 W/(m²·K) could be achieved when the compact thickness was controlled at 10.39 mm. Additionally, Yasuda et al. [110] incorporated aramid pulp and carbon fiber into TiFe_{0.9}Ni_{0.1} and La_{0.6}Y_{0.4}Ni_{4.9}Al_{0.1} alloys, reporting that the in-plane thermal conductivity increased to 3.20 W/(m·K) with higher carbon fiber fractions.

Table 2: Studies on ETC of enhanced hydrogen storage alloys.

References	Alloys	Augmentation Technique	ETC (W/(m·K))
Kapischke et al. [222]	Mg	Adding 2% Ni	4–9
Ghafir et al. [218]	MmNi _{4.46} Al _{0.54}	Copper wire net matrix	0.5–2.75
Lloyd et al. [223]	LaNi ₅	Powder plated with copper and cold pressed with tin binder	2.9–6.2
Wang et al. [219]	LaNi ₅	Compact with expanded graphite	3–6
Ron et al. [224]	LaNi ₅	Aluminum matrix of the composite	8–23
Suda et al. [225]	MmNi _{4.51} Al _{0.47}	Multilayer waved sheet of copper	Up to 14
Yasuda et al. [110]	TiFe _{0.9} Ni _{0.1} ; La _{0.6} Y _{0.4} Ni _{4.9} Al _{0.1}	Aramid pulp and carbon fiber	Up to 3.2
Sánchez et al. [211]	LmNi _{0.485} Sn _{0.15}	Compact with expanded graphite	19.45
Atalmis et al. [226]	LaNi ₅	Copper coating and/or expanded natural graphite (ENG)	~6 times with copper coating; ~12 times with ENG
Dieterich et al. [227]	Hydralloy® C5	Expanded natural graphite	10–15
Madaria and Kumar [228]	La _{0.8} Ce _{0.2} Ni ₅	Graphite flakes (CMPGF); Graphite flakes with copper wire mesh structure (CMPGFCu)	CMPGF: 4.7; CMPGFCu: 6.8

It is worth noting that the relationship between thermal conductivity and absorption performance is not strictly monotonic. Raju and Kumar [230] reported that increasing the hydride thermal conductivity from 2 to 8.5 W/(m·K) enhanced the hydrogen absorption capacity in the reaction bed; however, a further increase from 8.5 to 24 W/(m·K) led to a continuous decrease in absorbed hydrogen mass. Similarly, Freni et al. [231] pointed out that raising the thermal conductivity from 10 to 15 W/(m·K) produced no significant improvement in absorption reaction time. These findings show that thermal conductivity is not the sole factor governing heat and mass transfer rates in metal hydride systems.

Despite the effectiveness of these enhancement strategies in improving ETC, alleviating porosity issues, and accelerating kinetics, they often introduce supplementary drawbacks. For instance, Madaria et al. [209] showed that filling the bed with metallic structures increased ETC but simultaneously added substantial weight to the reactor. Wang et al. [219] proposed that the aluminum foam content in the packed bed should remain below 10%, as higher fractions compromise the hydrogen absorption/desorption capacity. Kim et al. [232] demonstrated that ENG mixing significantly boosted ETC with negligible negative impact

on permeability. However, the fabrication of composite blocks requires high-pressure equipment, leading to considerable electrical energy consumption and stringent processing requirements.

In addition to material modifications, reactor geometric design has emerged as another effective route to enhance the heat and mass transfer performance of hydrogen storage alloys. Various reactor configurations, including tubular, annular-disc, micro-channel, and finned-tube designs [233–237], have been developed to optimize thermal management and hydrogen reaction kinetics. Among these, fin optimization has received particular attention. Keshari et al. [238] demonstrated that increasing fin diameter and array density effectively improves absorption efficiency, while variable cross-section annular fins and corrugated fins substantially reduce absorption time compared to conventional designs [239,240]. Spiral fin and spiral microchannel reactors have also shown superior heat transfer rates and reaction kinetics due to enhanced turbulence intensity [241,242].

More recently, the integration of fins with metal foam or phase change materials (PCMs) has demonstrated synergistic effects. For instance, reactors combining fins and metal foam achieved thermal resistance as low as 0.0099 K/W, with a 38% improvement in hydrogen absorption efficiency over fin-only reactors [243]. Similarly, PCM-integrated reactors, particularly those embedded with metal foam, have shown significant improvements in both heat release and heat recovery during cyclic operation [244,245]. Despite these advances, systematic comparisons of different reactor configurations under identical operating conditions remain limited, and the compatibility between various reactor designs and specific MHHP cycles warrants further investigation.

4.2 Enhancement of Pulverization Resistance

In addition to thermal conductivity, the severe pulverization of metal hydride particles during repeated hydriding/dehydriding cycles poses a critical obstacle to long-term durability. As summarized in Fig. 8, current anti-pulverization strategies can be classified into three categories according to their underlying mechanisms: (i) intrinsic material toughening (e.g., alloy composition modification [190,191,246,247] and surface coatings [248–251]), which reduces lattice expansion strain or provides a ductile shell to inhibit crack propagation; (ii) structural strain buffering (e.g., porous frameworks [110,211,219,252] and thin-film geometries [253–255]), which accommodates volumetric changes via internal void spaces or dimensional confinement; and (iii) physical state engineering (e.g., fluid-like [256–259] and amorphous [260–263] hydrides), which eliminates particle-to-particle stress transfer or suppresses grain-boundary fracture. The following subsections will examine these strategies in detail, with particular emphasis on their specific implementations, performance trade-offs, and remaining challenges.

4.2.1 Compositional Modification for Anti-Pulverization

To address the severe pulverization of hydrogen storage alloys during cyclic operation, compositional modification, either by introducing a third element or substituting a constituent element, has been widely adopted to enhance the intrinsic cracking resistance of the material. However, extrinsic approaches, such as the fabrication of composite particles, have proven insufficient. For instance, Wang et al. [266] reported that while Al powder/hydride compressed composites exhibited high crack resistance, slight cracks still emerged after 1000 cycles, and similar polymer-based composites (e.g., MnNi_5 -polyurethane) failed to withstand temperatures exceeding 393 K. Regarding elemental additives, Wang et al. [190] pointed out that the beneficial role of Al in improving long-term cycling stability is quite limited, as severe powdering persisted during extended tests. Liu et al. [191] prepared $\text{La}_{3-x}\text{Y}_x\text{Ni}_{9.7}\text{Mn}_{0.5}\text{Al}_{0.3}$ ($x = 1, 1.5, 1.75, 2.25, \text{ and } 2.5$) alloys via magnetic levitation induction melting and found that raising Y content enhanced the structural

stability of the host lattice. Nevertheless, the overall cyclic stability deteriorated due to the concurrent corrosion, pulverization, and Al dissolution.

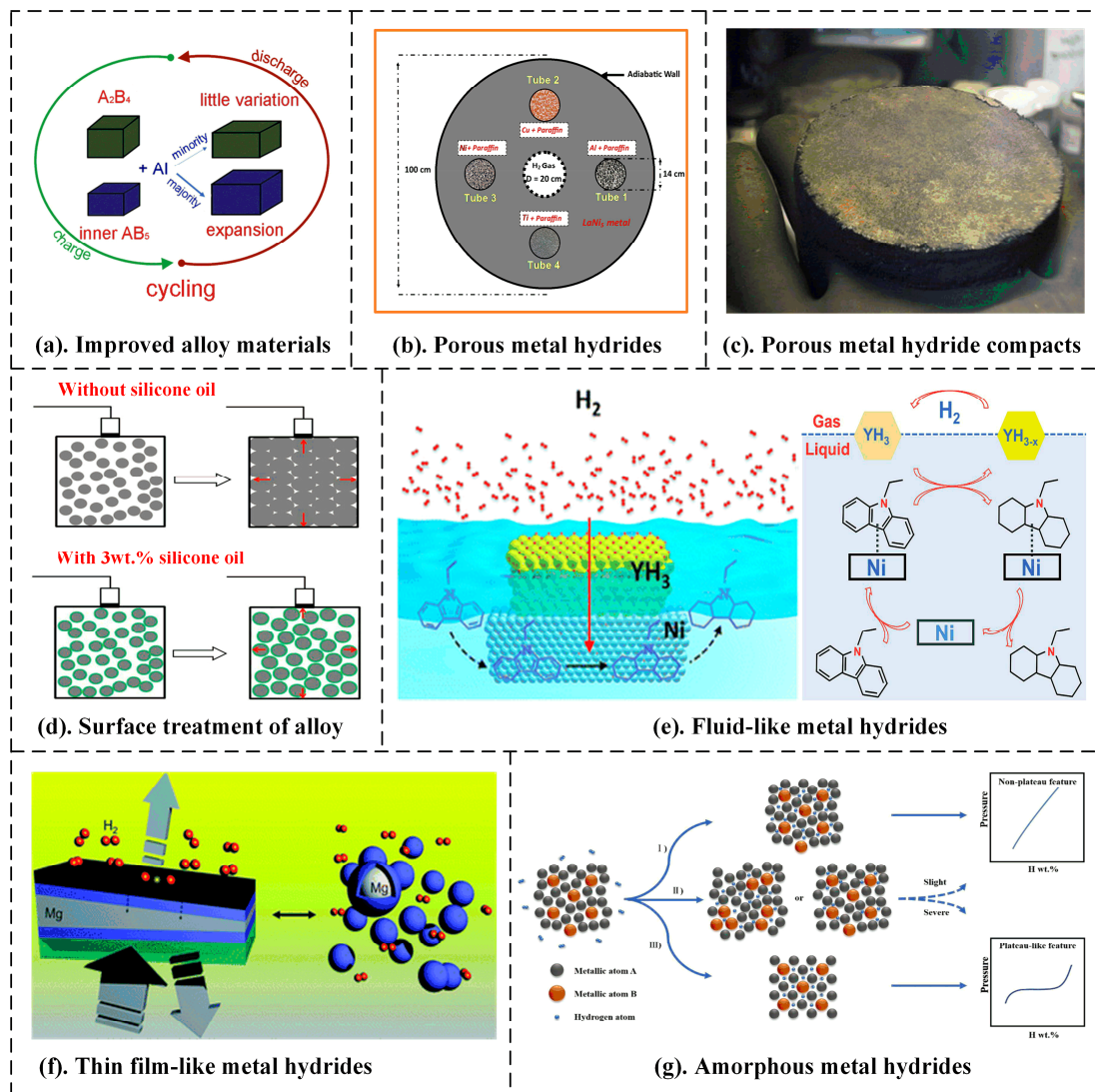


Figure 8: Schematic diagram of different metal hydride structures. (a) Compositional modification of hydrogen storage alloy [190], (b) porous metal hydrides [264], (c) porous metal hydride compacts [229], (d) surface treatment of hydrogen storage alloy [248], (e) fluid-like metal hydrides [256], (f) thin film-like metal hydrides [265], and (g) amorphous metal hydrides [260].

In contrast, Wan et al. [246] demonstrated that in $\text{Zr}_{0.8}\text{Ti}_{0.2}\text{Co}_{1-x}\text{Ni}_x$ ($x = 0, 0.1, 0.2$, and 0.3) alloys prepared by vacuum arc melting method, partial substitution of Co by Ni notably strengthened the anti-pulverization ability. At 573 K, the hydrogen storage capacity retention increased from 58.7% ($x = 0$) to 76.3% ($x = 0.3$), although a higher temperature of 673 K led to hydrogen-induced disproportionation, which severely degraded the performance. More recently, He et al. [247] revealed that tuning the $[\text{AB}_5]/[\text{A}_2\text{B}_4]$ subunit ratio effectively alleviates lattice strain accumulation, reducing pulverization and enhancing cyclic stability, providing theoretical guidance for La-Y-Ni-based alloys. Despite these efforts, no single hydrogen

storage alloy has yet been developed that can undergo multiple absorption/desorption cycles without encountering significant pulverization issues.

4.2.2 Porous Metal Hydrides and Compacts

To simultaneously address the pulverization and poor thermal conductivity of loose alloy powders, porous metal hydrides have been developed by mixing hydride powders with highly ductile metals (e.g., Cu, Al) or high-conductivity materials (e.g., expanded graphite) to form a rigid porous skeleton that anchors the hydride particles. Based on the fabrication routes, these structures can be broadly divided into two categories: sintered/porous frameworks and compressed compacts.

For sintered or bonded porous frameworks, Kim et al. [210] prepared LaNi_5 composites with re-compressed expanded graphite (REG), which increased the effective thermal conductivity from 0.1 to 3–6 W/(m·K) while effectively suppressing powdering. Rodríguez et al. [211] reported that the expanded natural graphite (ENG)/hydride compacts achieved a much higher thermal conductivity of up to 19 W/(m·K), but this came at the cost of a reduced hydrogen absorption rate. Yasuda et al. [110] developed hydride sheets using aramid pulp and carbon fiber, whose porosity was twice that of conventional packed beds, significantly mitigating the pulverization caused by repeated volumetric expansion/contraction. Pohlmann et al. [252] demonstrated that, compared with loose $\text{Mg}_{90}\text{Ni}_{10}$ sheets, the dense melt spinning hydride-graphite composite cylindrical particles exhibited superior thermal conductivity and anti-pulverization performance. Furthermore, to reduce reactor weight, Wang et al. [219] analyzed the relationship between Al foam addition and thermal conductivity, finding that the required Al foam amount for forced-convection cooling was 20% less than that for natural convection under maximum hydrogen storage conditions.

Regarding compressed compacts (i.e., pressing hydride powder with Al, Cu, or graphite powders into blocks), the primary goal is to prevent the loss of effective thermal conductivity caused by powdering. Ron et al. [224] found that when the Al mass fraction ranged from 0.075 to 0.3, the thermal conductivity of LaNi_5 -Al matrix compacts was 16 to 46 times higher than that of pristine LaNi_5 powder. Notably, Ron et al. [267] also pointed out that LaNi_5 and $\text{MmNi}_{4.15}\text{Fe}_{0.85}$ compacts with an Al matrix could operate stably without pulverization even after 30,000 hydrogenation/dehydrogenation cycles. However, Klein et al. [268] noted that the effective thermal conductivity of REG/ LaNi_5 compacts decreases with increasing mass ratio of hydride to graphite, although REG is significantly more cost-effective than Al foam. In addition, the incorporation of expanded natural graphite has little influence on thermodynamic properties but reduces hydrogen permeability, particularly along the direction parallel to the compression axis, which imposes specific requirements on the thickness of the compacted block [229]. Despite these extensive efforts, reports on porous metal hydrides with comprehensively optimized performance remain scarce.

4.2.3 Surface Treatment of Hydrogen Storage Alloys

Surface treatment of hydrogen storage alloys involves forming a protective coating or film on the material surface via specific techniques to mitigate the pulverization problem. For instance, Kim et al. [232] coated metal hydride powder with copper and compressed it into porous compacts, which effectively suppressed pulverization while also improving thermal conductivity. Considering that pulverization originates from excessive expansion stress during cycling, Wang et al. [266] mixed MnNi_5 powder with 6 wt% silicone oil and found that the expansion stress of alloy particles was significantly reduced, thereby suppressing hydride fragmentation. Subsequently, Li et al. [248] demonstrated that adding 3 wt% silicone oil could effectively alleviate expansion stress; they also noted that the maximum expansion stress increased with rising charging pressure during the cycling process. The underlying mechanism for stress reduction is attributed

to the silicone oil film formed on the particle surfaces, which acts as a “buffer pad” between particles. This film reduces particle aggregation and enhances particle mobility during hydrogen absorption/desorption cycles [248]. To sum up, silicone oil surface treatment proves to be an effective strategy for tackling the pulverization of hydrogen storage alloy materials. However, the inert oil phase contributes extra mass without participating in hydrogen storage, thereby reducing the gravimetric hydrogen storage capacity of the alloy. For instance, Zheng et al. [269] reported that the addition of 5 wt% silicone oil slightly reduced the initial hydrogen storage capacity of a $V_{40}Ti_{26}Cr_{26}Fe_8$ alloy, although it simultaneously improved the absorption reversibility. Therefore, the dosage of silicone oil must be carefully optimized to balance stress mitigation against capacity retention in practical MHHP applications.

4.2.4 Metal Hydrides with Special Structures

Beyond conventional powder modifications, fabricating metal hydrides into special physical forms, such as fluid-like slurries, thin films, and amorphous alloys, has emerged as an effective strategy to circumvent pulverization while tailoring reaction kinetics and thermal management.

(1) Slurry-phase hydrogen storage materials

Slurries refer to fluid-like suspensions formed by dispersing hydride powders in carrier liquids (e.g., n-undecane, ammonium fluoride solution, benzene, ethanol, isooctane, cyclohexane, benzyltoluene, n-ethylcarbazole, and silicone oil [257,270–272]). Reilly et al. [273] investigated the isothermal absorption kinetics of $LaNi_5H_x$ suspended in n-undecane and identified that the rate-limiting step was hydrogen dissolution in the solvent. Further, Reilly et al. [274] reported that dissolved CH_4 in n-decane reduced the surface tension of the suspension, thereby lowering both the activation energy (E_a) and the pre-exponential factor. Gamo et al. [275] found that the hydrogen absorption rate in a 0.1% surfactant solution was markedly higher than that in pure water. Regarding catalytic applications, Chen et al. [36] demonstrated that a $Mg_2Ni-C_6H_6$ slurry treated with NH_4F first absorbed hydrogen to form hydrides, which then catalytically hydrogenated benzene to cyclohexane. Chen et al. [37] further confirmed that $La_{1.8}Ca_{0.2}Mg_{14}Ni_3$ suspended in C_6H_6 exhibited hydrogenation performance similar to that of gas-solid reactions, with a strong catalytic effect on benzene hydrogenation. Notably, Chen et al. [258] showed that NH_4F/C_6H_6 -treated cast alloys yielded a much higher hydrogenation rate than untreated cast-alloy slurries. An et al. [276] found that suspending MNi_5 in C_6H_6 not only improved thermal conductivity but also alleviated pulverization. Cai et al. [277] further revealed that the standard entropy values for slurry-phase hydrogenation were comparable to those of gas-solid systems. As summarized by Wu et al. [256], solid hydride and liquid organic carrier slurries offer highly complementary advantages.

Despite the promising features of hydride slurries, several intrinsic limitations hinder their practical deployment in MHHP systems. First, the hydrogen dissolution in organic liquid carriers is typically rate-limiting, particularly when the solubility of H_2 in the carrier is low (e.g., approximately 0.035 mol/L at 30°C and 1013 kPa), which severely restricts the overall hydrogen transfer rate [273]. Second, although the metal hydride slurries can accommodate volumetric expansion, mitigate pulverization, and prevent irreversible capacity degradation commonly observed in dry packed beds, the long-term cycling induces particle agglomeration and sedimentation, which necessitates periodic re-dispersion interventions to maintain stable slurry flowability and hydrogenation performance [257]. Third, the chemical compatibility between hydride particles and organic carriers, especially at high temperatures, can induce undesirable side reactions, carrier hydrogenation, or surface poisoning of the hydride particles [278].

To overcome these barriers, future breakthroughs are expected in three directions: (i) development of high-H₂-solubility carriers with enhanced thermal stability (e.g., modified benzyltoluene), (ii) surface treatment of hydride particles using thin catalytic coatings (e.g., Pd, Ni) to accelerate interfacial H₂ dissociation without compromising suspension stability, and (iii) incorporation of modifying additives or nanostructured stabilizers to prevent particle settling and aggregation over extended cycle life [257,270].

In terms of application scenarios, slurries are particularly attractive for compact, mobile, or modular MHHP systems where continuous pumping and flow-through reactor designs are advantageous. Unlike fixed packed beds, slurry-based reactors eliminate the need for complex internal heat exchangers, as the convective heat transfer within the flowing slurry can be significantly higher than the effective thermal conductivity of packed beds [279]. However, for large-scale stationary MHHP applications where simplicity and maintenance are prioritized, the added complexity of slurry circulation and separation systems may exceed the benefits. Therefore, the most promising application for slurry-based MHHPs is likely in transportation waste heat recovery (e.g., marine vessels) and distributed solar-thermal cooling systems, where compactness, rapid response, and modularity are key performance drivers.

(2) Thin-film metal hydrides

Thin-film metal hydrides, typically fabricated via reactive plasma sputtering [253], direct current (DC) magnetron sputtering [254], radio frequency sputtering [280], flash evaporation [281], or vacuum thermal evaporation [282], exhibit unique anti-pulverization properties due to dimensional constraints. Adachi et al. [281] found that LaNi₅ and MnNi_{4.5}Mn_{0.5} films with thicknesses below 1.0×10^5 nm did not suffer pulverization even after 150 cycles. However, substrate effects are critical. For instance, Huy et al. [253] prepared 1.8- μ m-thick MgH₂ films by one-step reactive plasma-assisted sputtering and observed that films deposited on graphite substrates maintained fully reversible capacity over 28 cycles, whereas those on polyimide foils delaminated and transformed into loose powder. Platzner et al. [280] noted that porous, easily oxidized films could be produced by increasing pressure, H₂/Ar ratio, or reducing power. Matsuda et al. [283] reported that after 200 cycles, hydrogenated 6Mg-Ni films contained Mg₂NiH₄, MgH₂, and Mg nanocrystals, with Mg crystallization degrading desorption kinetics and cycling ability. Jangid et al. [254] prepared Mg/Ti/Ni multilayer films via DC magnetron sputtering and through comprehensive surface/structural/optical/electrical characterization, concluded that such multilayers are promising for solid-state storage. Importantly, Le et al. [284] found that, compared with less-reactive SiO₂ substrates, the interfacial formation of Mg₂Si on Si substrates significantly enhanced desorption kinetics.

The primary advantage of thin-film metal hydrides lies in their size restriction: when the film thickness is below a critical thickness (experimentally identified to be on the order of 1.0×10^5 nm for LaNi₅-based systems [281]), the mechanical strain can be effectively accommodated without catastrophic pulverization. This size-dependent anti-pulverization behavior offers a potential path to ultra-long cycle life. However, several critical limitations must be addressed before thin films can be considered for practical MHHP applications. As demonstrated by Le et al. [284], films deposited on Si substrates form irreversible Mg₂Si interfacial layers, causing irreversible capacity decay, whereas inert substrates (e.g., SiO₂) maintain better reversibility but at much slower desorption kinetics. Furthermore, the gravimetric and volumetric hydrogen storage density of the entire film-substrate assembly is substantially lower than that of bulk hydrides because the active hydride layer typically accounts for less than 10% of the total mass/volume [285]. This low active-material fraction fundamentally limits the practical energy density of film-based systems. Additionally, although the scalability and manufacturing cost of physical vapor deposition techniques (e.g., sputtering, thermal evaporation) has made significant progress [286], its economic feasibility still needs to

be evaluated in detail when applied to prepare thin-film metal hydrides for large-scale MHHP reactors that require loading kilograms to tons of hydrogen storage material.

To address the aforementioned constraints, future research should focus on the following three aspects: (i) development of roll-to-roll deposition processes on flexible, low-cost substrates (e.g., polymer foils or metal sheets [253]) to reduce manufacturing costs and increase throughput, (ii) exploration of self-supported nanoporous hydride films or 3D thin-film structures that decouple the mechanical robustness from the substrate constraint, and (iii) integration of thin-film hydrides into micro-scale MHHP devices [287] or on-chip thermal management systems [288], where the amount of hydrogen stored is small but the cycle speed and reliability are crucial.

Thin-film hydrides are unlikely to compete with bulk hydrides in large-scale heating or cooling applications due to their low active-material fraction and high cost. Instead, their application scenarios lies in micro-scale MHHP devices for localized cooling/heating of electronic components, sensor systems, and hydrogen purification membranes where rapid kinetics, pulverization-free operation, and precise control of hydrogen flow are more critical than capacity. The cycle stability observed in thin films (e.g., 150 cycles without pulverization [281]) makes them particularly suitable for high-frequency switching applications where conventional HM beds would rapidly fail due to pulverization.

(3) Amorphous metal hydrides

Amorphous alloys can absorb large amounts of hydrogen while offering superior resistance to pulverization. Zhang et al. [289] reported that amorphous $\text{Mg}_{11}\text{Y}_2\text{Ni}_2$ transforms into amorphous, metastable, and stable phases at different temperatures, all of which can be hydrogenated to MgH_2 , Mg_2NiH_4 , and YH_2/YH_3 . Han et al. [262] identified nano-amorphous alloys as promising candidates for reversible storage at moderate temperatures. Compositionally, Bu et al. [290] found that increasing Nd content in $(\text{Mg}_{24}\text{Ni}_{10}\text{Cu}_2)_{100-x}\text{Nd}_x$ ($x = 0-20$) alloys significantly enhanced the degree of amorphization, while Żywczak et al. [291] obtained amorphous $\text{Ti}_{45}\text{Zr}_{38}\text{Co}_{17}$ compounds by substituting Co for Ni. Han et al. [261] pointed out that hydrogenation of amorphous Zr_2Co produces highly stable ZrH_2 , Zr_2CoH_5 , and ZrCoH_3 . Zhou et al. [263] demonstrated that amorphous $\text{Mg}_{85}\text{Ni}_5\text{Y}_{10}$ alloy exhibited much higher hydrogen storage capacity, absorption/desorption kinetics, and stability than its crystalline counterpart. Therefore, amorphous alloys represent another effective route to mitigate pulverization in hydrogen storage materials.

Amorphous metal hydrides offer a fundamentally distinct hydrogenation behavior compared to their crystalline counterparts. The absence of long-range order, combined with a high density of chemically disordered environments, creates a broad distribution of interstitial sites with varying hydrogen binding energies [292]. This generally results in absence of a distinct P-C-T plateau, broader hydrogen absorption/desorption pressure ranges, and in some cases, higher hydrogen storage capacities due to the accommodation of hydrogen in both tetrahedral and octahedral sites [260]. Furthermore, the amorphous alloy exhibits multiple cracks after cycling, which are beneficial for hydrogen storage kinetics by providing additional diffusion pathways and exposing uniformly distributed catalytic particles [263].

However, the practical application of amorphous hydrides in MHHPs faces three main bottlenecks. First, amorphous alloys are thermodynamically metastable; after heating (typically above 150–300°C, depending on composition), they undergo irreversible crystallization, which drastically alters the hydrogenation properties and often leads to slightly slower kinetics [289]. For MHHP systems that involve temperature fluctuations during cycling, this crystallization risk imposes severe constraints on the allowable operating temperature condition. Second, while Mg-based amorphous alloys can achieve capacities exceeding 3 wt% [263], certain amorphous systems (e.g., Zr-based) exhibit reversible capacities lower than

their crystalline forms due to the hydrogen-induced disproportionation and slow kinetics [261]. Third, the broader application of amorphous alloys is constrained by the limited critical size and poor room-temperature workability compared with conventional crystalline alloys [293]. Potential future directions to overcome these limitations include: (i) development of nanostructured amorphous alloys that retain the high anti-pulverization capability of amorphous phases while exhibiting excellent cycling stability due to the fully recoverable amorphous structure and reduced particle aggregation at lower operating temperatures [262], (ii) exploration of high-entropy amorphous alloys where the sluggish diffusion kinetics and high configurational entropy characteristics at high temperatures [294], and (iii) Alloying strategies (e.g., addition of Zr or Y) can effectively increase the hydrogen solubility [295] or significantly refine the nanocrystalline microstructure and stabilize it against grain growth [296].

Due to their generally superior anti-pulverization performance compared to crystalline counterparts, amorphous alloys are suitable for medium-temperature MHHP systems (up to 150°C), provided that operating temperatures remain below the crystallization threshold of the specific optimized composition. However, for high-temperature applications (>300°C) where crystallization becomes inevitable, crystalline Mg-based or high-temperature hydrides remain more appropriate. Additionally, the absence of a distinct pressure plateau in amorphous alloys can be advantageous in temperature-upgrading systems requiring smooth, continuous output rather than stepwise pressure changes, although the potential impact of pressure-composition hysteresis on system efficiency would require careful evaluation for specific material and system.

In summary, while slurries, thin films, and amorphous alloys each offer unique advantages in mitigating pulverization and tailoring reaction kinetics, they also introduce distinct trade-offs in terms of stability, scalability, and cost. The selection among these special structures should be guided by the specific operating temperature, power density requirements, and economic constraints of the target MHHP application, and future research should prioritize cost-effective fabrication methods and comprehensive long-term stability assessments under realistic cyclic conditions.

4.3 Economic Feasibility and Scalability Challenges

In addition to the technical performance metrics discussed above, the economic viability and scalability of MHHP systems are critical factors determining their industrial adoption. Although hydrogen storage alloys offer unique advantages in thermal upgrading applications, their high material costs, manufacturing complexity, and system-level integration challenges remain substantial barriers to large-scale deployment.

4.3.1 Material Cost Analysis

The cost of hydrogen storage alloys varies significantly across different families. According to market reports, the global solid-state hydrogen storage alloy market reached a production volume of 19,400 t in 2024, with an average selling price of USD 14,285/t [297]. Active material costs for metal hydrides generally range from USD 12–25/kg, translating to USD 8–15/(kW·h) of hydrogen stored, depending on alloy composition and rare-earth content [298]. For AB₂-type alloys, which generally have lower raw material costs and higher hydrogen storage capacity than AB₅-type alloys, the global market for metal hydride alloys was estimated at USD 423 million in 2031, with an average global market price of approximately USD 133/kg [299].

Recent techno-economic analyses have provided quantitative comparisons of different hydride systems on a levelized cost basis. Wang et al. [300] demonstrated that metal hydride systems can be cost-competitive with 35 MPa compressed gas systems, with TiFe_{0.85}Mn_{0.05} achieving USD 0.45/(kW·h) and complex metal hydride Mg(NH₂)₂·2.1LiH·0.1KH achieving USD 0.38/(kW·h). Extending hydrogen absorption times and

increasing operating cycles significantly reduce the levelized cost of storage, especially for complex metal hydrides [300]. Key strategies to further enhance competitiveness include using waste heat, reducing the use of valuable minerals, and achieving metal hydride production costs of USD 10/kg [300].

For Mg-based hydrides specifically, the cycle life of the storage material is a key determinant of levelized cost. After 3000 cycles, the levelized cost of storage for Mg-based hydrides has been estimated to reduce to USD 0.44/kg H₂ [301]. This highlights the economic benefit of developing alloys with extended cycle life, as longer-lasting materials amortize their initial cost over more operating cycles.

4.3.2 System-Level Economic Analysis

Although material costs offer a useful economic indicator, the overall economic feasibility of MHHP systems depends on multiple system-level factors, including reactor design, heat exchanger complexity, manufacturing scale, and operational parameters.

The DLR (German Aerospace Center) has provided a first estimation of system mass, volume, and investment cost for a 15 kW MHHP cooling system. The system would contain approximately 24 kg or 20 L of metal hydride material, corresponding to a total system mass of 50 kg and a system volume of 100 L [302]. The estimated investment cost for small-series production is USD 9254.4 [302]. Under typical operating conditions (electricity price: USD 0.23/(kW·h), 3750 operating hours/year), such a system could achieve annual energy cost savings of approximately USD 6478, suggesting a rapid return on investment in continuous hydrogen flow applications (e.g., dual-effect, multi-stage, and hybrid MHHPs) [302].

For hydrogen infrastructure integration, a comprehensive thermodynamic assessment of MHHPs has quantified fuel savings of approximately 10%–20% and additional heat supply of 10%–30% in open-loop industrial process-heating applications [13]. The study further examined scaling behavior, integration challenges, and economic feasibility, assuming an MH unit price of USD 57.84/kg and a total system cost of four times the MH material cost [13].

In residential applications, integrating metal hydride storage with heat pump systems and photovoltaics has demonstrated a 7.1-year payback period and 83% energy self-sufficiency, with annual energy cost savings of USD 294.98 [303]. However, other studies have reported that the payback period can exceed 35 years under less favorable conditions, primarily owing to the high initial cost of metal hydrides [304]. This wide variation underscores the importance of application specific economic assessments. A techno-economic analysis of metal hydride energy storage system for residential heat pumps similarly concluded that long payback periods are primarily due to high initial cost and hydrogen compression costs [304].

4.3.3 Scalability Challenges for Industrial Adoption

Despite promising techno-economic indicators, several challenges must be addressed before MHHP technology can achieve widespread industrial deployment.

Engineering and manufacturing scalability. The transition from laboratory-scale (g to kg) to industrial-scale (t) production of hydrogen storage alloys presents significant challenges in composition control, phase homogeneity, and cost management. A case study on a 1.25 t batch of AB₂ alloy for large-scale stationary systems demonstrated the need for systematic experimental characterization, modeling, and life cycle-cost assessment at this industrial scale [102]. Such large-batch evaluations are essential for validating material properties and establishing reliable manufacturing protocols. The life cycle assessment of this scale-up case revealed that scaling from 10 kW to 10 MW reduces storage costs by nearly 85%, driven by economies of scale [102].

Reactor design and thermal management. As reactor size increases, the ratio of heat exchange surface area to hydride volume decreases, exacerbating the thermal management challenges discussed in Section 4.1. For large-scale MHHP systems, system design strategies such as coil optimization, exploitation of material thermal inertia, and heat pump selection are critical factors to further enhance performance [118]. The increasing complexity of heat exchangers with scale directly impacts manufacturing costs and reliability.

Material cost and supply chain constraints. The global solid-state hydrogen storage alloy market is forecast to reach USD 1802 million by 2032, with a CAGR (Compound Annual Growth Rate) of 26.7% [305]. Despite this growing market, the high production and processing costs remain a major restraint. Rare-earth price volatility poses significant cost pressure. For example, in late 2025, the price of praseodymium-neodymium oxide fluctuated around USD 74,907–75,352/t (data from Domestic Bulk Commodity Data Platform), while dysprosium oxide remained stable at USD 241,779–244,746/t (data from China Tungsten Industry Online). The availability and cost of critical minerals (particularly Co in AB₅ alloys) represent ongoing supply chain risks. For large-scale stationary applications, using waste heat and reducing the use of critical minerals are key strategies to enhance the competitiveness of MHHP systems [300].

Standardization and performance validation. Most reported performance data are obtained under idealized laboratory conditions, and there is a lack of standardized testing protocols and performance metrics for MHHP systems. Current prototypes are typically at TRL (Technology Readiness Level) 3–5, indicating that significant engineering development remains before commercial deployment [306]. This impedes fair comparison across different materials and system configurations, as well as the development of industry-wide design guidelines.

In summary, while MHHP technology offers unique advantages for low-grade thermal upgrading, its economic feasibility and scalability depend on a combination of material cost reduction, manufacturing process optimization, reactor design innovation, and strategic integration with available waste heat sources. Continued advances in these areas will be essential for transitioning MHHP technology from laboratory prototypes to commercially viable systems.

4.4 Field Demonstration and Pilot-Scale Validation

Despite the abundance of laboratory-scale material characterizations, documented field demonstrations and pilot-scale validations of MHHP systems are still remarkably scarce. The few existing installations have revealed that real-world performance is strongly influenced by dynamic thermal conditions, impurity buildup, and long-term cyclic degradation which are often mitigated or overlooked under ideal benchtop testing [67,307]. These site-specific challenges, rather than material thermodynamics alone, represent the primary bottleneck for system scale-up and necessitate dedicated pilot campaigns prior to commercial deployment.

One of the earliest and most thoroughly documented demonstration efforts is the HYCSOS chemical heat pump developed at Argonne National Laboratory in the late 1970s. The demonstration test facility employed four stainless steel tanks, each holding about 5 kg of either LaNi₅ or CaNi₅ hydride, with internal heat transfer tubing and three fluid heat transfer loops [308,309]. Initial operation demonstrated that approximately 5 mol of hydrogen could be transferred from CaNi₅ at 106°C to LaNi₅ at 8°C, with half-cycle times of less than 1 min for 50% hydrogen transfer [308]. However, the system's thermal losses were found to be non-negligible despite the use of thermal insulation, and the experimentally measured heat transfer rates deviated from predictions based on idealized laboratory-scale material property data [309]. The HYCSOS experience revealed that reactor-scale heat transfer limitations, particularly the low effective

thermal conductivity of hydride beds (typically 0.1–1 W/(m·K)), could not be fully captured by small-sample measurements, necessitating iterative design refinements.

More recent compressor-driven metal hydride heat pump (CDMHHP) demonstrations have provided quantitative performance benchmarks under near-practical conditions. Park et al. [40] built a CDMHHP using a commercial oil-type compressor and demonstrated a maximum cooling power of 353 kcal/(kg·h) and an energy efficiency (COP) of 1.8 with a half-cycle time of 3 min, achieving a minimum cooling temperature of 6°C at an airflow rate of 7 Nm³/min. In a separate CDMHHP configuration employing porous metal hydride compacts, a cold output of approximately 0.25 kW/kg of LaNi₅ was achieved with a cycle time of one minute [310]. While these values compare favorably with laboratory-scale expectations, the demonstrations also highlighted that compressor efficiency (only 31%) and additional thermal losses significantly degrade the overall system COP relative to thermodynamic predictions [310]. The discrepancy between ideal cycle analysis and measured performance underscores the critical role of system-level inefficiencies that are often overlooked in material-focused laboratory studies.

The DLR has recently advanced MHHP demonstration toward integrated system applications. Their HP project targets the integration of metal hydride heat pumps into hydrogen infrastructure, with a 15 kW cooling system containing approximately 24 kg of metal hydride material [302]. Experimental validation has demonstrated a specific cooling power of 585 W per kilogram of metal hydride mass in reactors with total weight under 30 kg and volume below 20 dm³ [311]. However, even this advanced prototype operates under controlled laboratory conditions rather than true field environments; issues such as long-term cyclic degradation, hydrogen impurity effects, and transient heat source variability remain insufficiently characterized. These demonstration experiences collectively indicate that while MHHP technology has proven its fundamental feasibility, the path to commercial deployment requires systematic attention to reactor-scale heat transfer enhancement, long-term material stability under realistic operating cycles, and the development of standardized testing protocols that bridge the gap between laboratory characterizations and field performance.

5 Recommendations for Future Research

The preceding sections have surveyed the state of the art in hydrogen storage materials for MHHPs, covering thermodynamic and kinetic fundamentals, alloy classification, and performance enhancement strategies. Despite the considerable progress reviewed above, several critical gaps remain in the development and deployment of hydrogen storage materials for MHHP systems. Addressing these gaps will require efforts across fundamental materials science, engineering characterization, and system-level integration.

5.1 Establishment of a Comprehensive Database and High-Precision Kinetic Models

Accurate prediction of hydrogenation and dehydrogenation reaction rates is essential for determining the exothermic and endothermic heat flows in MHHPs, which directly govern system performance. However, current kinetic models often rely on empirical parameters that lack extrapolation capability, limiting their applicability to alloy compositions and operating conditions beyond those experimentally tested. To overcome this bottleneck, systematic experimental studies covering a broad range of alloy compositions, temperatures, and pressures are urgently needed. A database integrating reaction rates, activation energies, enthalpy-entropy pairs, density, and full P-C-T curves for representative MH alloys would provide a solid foundation for developing universally applicable kinetic models. In parallel, advanced modeling approaches, such as ML-assisted kinetic prediction, hold promise for accelerating the discovery of optimal alloy pairs without exhaustive trial-and-error approaches. Recent work based on the U.S. Department

of Energy's publicly available hydride database has preliminarily demonstrated the feasibility of using ML for rapid hydrogen storage capacity prediction and material classification, offering a pathway to reduce experimental screening efforts [99]. Future efforts should focus on extending such ML models to incorporate kinetic rate parameters (rather than just equilibrium capacity), thereby enabling direct prediction of absorption/desorption rates under dynamic MHHP operating conditions.

5.2 Performance Evaluation under Realistic Cyclic Operating Conditions

Most reported performance data for MH hydrogen storage materials are obtained under idealized laboratory conditions (e.g., pure hydrogen, constant-temperature baths, and fresh alloys). However, practical MHHP operation involves hydrogen sources containing impurities, fluctuating heat source temperatures, and inevitable material degradation over thousands of cycles. Therefore, future research should place greater emphasis on: (i) long-term cycling tests under simulated real operating conditions, particularly variable and intermittent heat-source temperatures and realistic hydrogen purity levels, to quantify degradation mechanisms such as impurity poisoning and thermal-conductivity loss; (ii) optimized reactor thermal management strategies that mitigate the coupled effects of pulverization-induced conductivity degradation on overall system efficiency; and (iii) the development of standardized testing specifications and performance metrics to enable fair cross-comparison across different materials and system configurations. In this context, the established engineering practices from pilot-scale TCES systems, such as those based on Mg- and NaMgH₃-based hydrides for concentrated solar power applications, offer valuable and directly transferable insights, particularly in reactor design, thermal buffering, and cyclic stress management, to accelerate MHHP scale-up.

5.3 Development of Integrated Material-System Design Strategies

As discussed in Sections 3 and 4, the selection of MH alloys for heat pump applications involves multiple, often conflicting, criteria: thermodynamic compatibility, fast kinetics, high capacity, thermal conductivity, pulverization resistance, and cost. Currently, most studies focus on optimizing individual material properties in isolation, which rarely translates into optimal system-level performance. A paradigm shift toward integrated material-system co-design is recommended, wherein material selection is guided by system-level simulation that incorporates reactor configuration, heat exchanger design, and operating strategies from the outset.

5.4 Exploration of Novel Alloy Systems beyond Conventional Types

While AB₅-type alloys remain the workhorse of current MHHPs due to their well-established properties, their limited hydrogen capacity fundamentally constrains system performance. Emerging alloy systems, such as Mg-free high-capacity A₂B₇-type La-Y-Ni alloys, show promise but require further optimization in terms of cycle stability and cost reduction. Future research should also explore high-entropy alloys, which may offer tailorable thermodynamic properties and enhanced resistance to pulverization through multi-principal-element effects, as well as systematically evaluate the feasibility of replacing expensive rare-earth components with low-cost abundant elements (e.g., Fe, Mn, and Ti), particularly for large-scale applications where material cost is a major barrier. Beyond compositional exploration, alternative material forms (e.g., slurries, thin films, and amorphous alloys) also warrant further investigation. While these configurations offer distinct advantages in mitigating pulverization through size confinement and the suppression of grain-boundary fracture, their scalability and cost-effectiveness remain open questions that require targeted attention before they can be considered for practical MHHP applications.

6 Conclusion

Metal hydride heat pumps (MHHPs) represent a promising thermal upgrading technology capable of utilizing low-grade renewable thermal energy and waste heat for building heating, cooling, and temperature-upgrading applications. The performance and reliability of MHHPs are fundamentally governed by the hydrogen storage materials employed, particularly their thermodynamic properties, hydrogenation/dehydrogenation kinetics, reversible hydrogen capacity, thermal conductivity, and resistance to pulverization during cyclic operation.

This review has systematically examined hydrogen storage materials for MHHPs from both thermodynamic and kinetic perspectives, following the operational characteristics across various cycle configurations. The thermodynamic properties determine the equilibrium pressure-temperature relationship and the direction of the hydrogenation reaction, while the kinetic properties govern the rates of hydrogen absorption and desorption, which in turn dictate the heating/cooling power and system responsiveness.

The selection criteria for MH alloys in heat pump applications are summarized, emphasizing the need for appropriate operating pressures, high enthalpy values, a large hydrogen capacity, low hysteresis, fast kinetics, good reversibility, and long cycle life. Four major alloy families, i.e., AB₅ (rare-earth based), AB₂ (Laves phases), AB (TiFe-based), and A₂B (Mg₂Ni-based), have been critically reviewed, highlighting their respective advantages, limitations, and recent compositional optimization strategies. Emerging high-capacity alternatives, such as A₂B₇-type La-Y-Ni alloys, have also been discussed as potential successors to conventional AB₅ alloys.

To address the inherent performance bottlenecks of MH materials, this review has further summarized two complementary enhancement approaches: (i) improving thermal conductivity through the addition of high-conductivity materials (e.g., expanded graphite, aluminum foam, and copper matrices) and advanced reactor designs; and (ii) enhancing pulverization resistance via compositional modification, surface coatings, porous framework fabrication, and special physical forms (e.g., slurries, thin films, and amorphous alloys). Their economic feasibility, scalability challenges, and pilot-scale validation are discussed. Each approach involves inherent trade-offs among thermal conductivity improvement, hydrogen capacity retention, fabrication complexity, and cost, which must be balanced according to specific applications.

Despite significant progress, several critical challenges remain. They span multiple scales from the lack of fundamental property data and predictive kinetic models at the material level, to insufficient performance validation under realistic operating conditions, and finally to the need for integrated material-system co-design and cost-effective manufacturing of novel alloy systems. Addressing these multiscale challenges through the research directions outlined in Section 5 is essential for advancing MHHP technology toward practical, large-scale deployment in the renewable and sustainable energy landscape.

Acknowledgement: This work was supported by the Natural Science Foundation of Shandong Province, China. The authors also acknowledge Shandong University of Technology for providing the research facilities and administrative support.

Funding Statement: The authors gratefully acknowledge the financial supports provided by the Shandong Excellent Young Scientists Fund Program (Overseas), China (Grant No. 2023HWYQ-080), and the Natural Science Foundation of Shandong Province, China (Grant No. ZR2023QE171 and ZR2022ME003).

Author Contributions: The authors confirm contribution to the paper as follows: conceptualization, Yi Zhang; investigation, Yi Zhang, Haibo Li, Haigang Xu and Weijing Ding; resources, Yi Zhang, Dan Zhou and Guanmin Zhang; project administration, Yi Zhang; methodology, Yi Zhang, Bing Luo, Haibo Li, Haigang Xu and Shuaijie Ding; visualization, Yi Zhang, Haigang Xu, Dan Zhou and Weijing Ding; supervision, Guanmin Zhang; formal analysis,

Bing Luo, Haigang Xu, Dan Zhou and Shuaijie Ding; writing-original draft: Yi Zhang; writing—review & editing, Yi Zhang, Bing Luo, Haibo Li, Haigang Xu, Dan Zhou, Weijing Ding, Shuaijie Ding and Guanmin Zhang. All authors reviewed and approved the final version of the manuscript.

Availability of Data and Materials: Not applicable.

Ethics Approval: Not applicable.

Conflicts of Interest: Given his role as Guest Editor of this journal, Yi Zhang had no involvement in the peer review of this article and had no access to information regarding its peer review. Full responsibility for the editorial process for this article was delegated to another journal editor. The authors declare no other conflicts of interest.

References

1. Emmanuel JK, Ngabala FJ. Global energy demand and the role of technological innovation towards renewable energy generation for economic growth and a cleaner environment: A review. *Sustain Environ.* 2026;12(1):2633481. [CrossRef].
2. van Ruijven BJ, De Cian E, Sue Wing I. Amplification of future energy demand growth due to climate change. *Nat Commun.* 2019;10(1):2762. [CrossRef].
3. Parvin K, Hossain MJ, Arsad AZ, Ker PJ, Hannan MA. Building energy technologies towards achieving net-zero pathway: A comprehensive review, challenges and future directions. *J Build Eng.* 2025;100:111795. [CrossRef].
4. González-Torres M, Pérez-Lombard L, Coronel JF, Maestre IR, Yan D. A review on buildings energy information: Trends, end-uses, fuels and drivers. *Energy Rep.* 2022;8:626–37. [CrossRef].
5. International Energy Agency. Tracking clean energy progress 2023: Assessing critical energy technologies for global clean energy transitions. 2023 [cited 2026 Sep 15]. Available from: <https://www.iea.org/reports/tracking-clean-energy-progress-2023>.
6. Luo XJ. Retrofitting existing office buildings towards life-cycle net-zero energy and carbon. *Sustain Cities Soc.* 2022;83:103956. [CrossRef].
7. Raslavičius L, Striūgas N, Felneris M. New insights into algae factories of the future. *Renew Sustain Energy Rev.* 2018;81:643–54. [CrossRef].
8. Zhai Z, Xiong T, Hu L, Liu Y, Liu G, Yan G. Experimental investigation on performance enhancement of an air source heat pump by using a novel vapor bypass approach. *Energy.* 2026;344:139909. [CrossRef].
9. Pan T, Zhang S, Chang C, Van Fan Y, Yang Z, Wang B, et al. Equation-oriented thermodynamic optimisation of heat pump integration in industrial heat recovery systems: A system-level pathway to cost and emission reduction. *Energy.* 2025;335:137936. [CrossRef].
10. Sadeghi H, Ijaz A, Singh RM. Current status of heat pumps in Norway and analysis of their performance and payback time. *Sustain Energy Technol Assess.* 2022;54:102829. [CrossRef].
11. Zhou C, Ye S, Ni L, Yao Y. A review of heat pump research in China using bibliometric methods. *J Renew Sustain Energy.* 2022;14:012701. [CrossRef].
12. Zhang S, Hu S, Wang J, Yang X, Wang R, Zhang S, et al. Performance investigation on heat pump with thermal storage for metal hydride hydrogen storage. *Appl Therm Eng.* 2026;295:130620. [CrossRef].
13. Malleswararao K, Klockow E, Wimmer A, Linder M, Bürger I. Hydrogen based heat pumps using metal hydrides: Synergies between H₂ infrastructure and industrial heat supply. *Int J Hydrogen Energy.* 2026;230:154794. [CrossRef].
14. Malleswararao K, Dutta P, Murthy SS. Applications of metal hydride based thermal systems: A review. *Appl Therm Eng.* 2022;215:118816. [CrossRef].
15. Shafiee S. Operational principles and effect of operating parameters on performance of metal hydride heat pumps. *Int J Refrig.* 2020;120:22–30. [CrossRef].
16. Muthukumar P, Kumar A, Raju NN, Malleswararao K, Rahman MM. A critical review on design aspects and developmental status of metal hydride based thermal machines. *Int J Hydrogen Energy.* 2018;43(37):17753–79. [CrossRef].

17. Ge YT, Lang PY. Alloy selections in high-temperature metal hydride heat pump systems for industrial waste heat recovery. *Energy Rep.* 2022;8:3649–60. [[CrossRef](#)].
18. Zhang XY, Ge YT. Performance analysis of metal hydride heat pump system with CFD modelling development and actual reactor designs. *Int J Hydrogen Energy.* 2024;94:1146–59. [[CrossRef](#)].
19. Gruen DM, Mendelsohn MH, Sheft I. Metal hydrides as chemical heat pumps. *Sol Energy.* 1978;21(2):153–6. [[CrossRef](#)].
20. Li G, Liu H, Li L, Yang K, Du P, Lv M. Research progress of metal hydride heat pump and airconditioner. *J Refrig.* 2005;2:1–7. (In Chinese). [[CrossRef](#)].
21. Ni J, Yang T, Chen J, Chen Z, Qin F, Lv M, et al. Metal hydride heat pump and air-conditioning. *Acta Energiæ Solaris Sin.* 2006;27(3):314–20. (In Chinese). [[CrossRef](#)].
22. Yang FS, Zhang ZX, Bao ZW. An extensive parametric analysis on the performance of a single-stage metal hydride heat transformer. *Int J Hydrogen Energy.* 2012;37(3):2623–34. [[CrossRef](#)].
23. Rönnebro ECE, Whyatt G, Powell M, Westman M, Zheng FR, Fang ZZ. Metal hydrides for high-temperature power generation. *Energies.* 2015;8(8):1–25. [[CrossRef](#)].
24. Wu Y, Wang Q, Chen C, Wu J. Research progress of metal hydride heat pumps. *Low Temp Spec Gases.* 1990;4:1–8. (In Chinese).
25. Kumar S, Dutta P, Srinivasa Murthy S, Aristov YI, Gordeeva L, Li TX, et al. Studies on a metal hydride based year-round comfort heating and cooling system for extreme climates. *Energy Build.* 2021;244:111042. [[CrossRef](#)].
26. Liang B, Zhang Z, Wang Y. Performance Analysis to Metal Hydride Heat Pumps for Temperature Upgrading. *J Xi'an Jiaotong Univ.* 2004;38(1):89–92. (In Chinese). [[CrossRef](#)].
27. Yang FS, Wang GX, Zhang ZX, Rudolph V. Investigation on the influences of heat transfer enhancement measures in a thermally driven metal hydride heat pump. *Int J Hydrogen Energy.* 2010;35(18):9725–35. [[CrossRef](#)].
28. Park J-G, Jang K-J, Lee P-S, Lee J-Y. The operating characteristics of the compressor-driven metal hydride heat pump system. *Int J Hydrogen Energy.* 2001;26(7):701–6. [[CrossRef](#)].
29. Kim KJ, Feldman KT Jr, Lloyd G, Razani A. Compressor-driven metal-hydride heat pumps. *Appl Therm Eng.* 1997;17(6):551–60. [[CrossRef](#)].
30. Li X, Feng R, Li Z, Cui H, Kang Q, Zhao X, et al. Research progress on metal hydride heat pump technology. *Mod Chem Ind.* 2022;42(11):27–32. (In Chinese). [[CrossRef](#)].
31. Wimmer A, Linder M, Bürger I. Lumped model for a quasi-continuously operating open metal hydride heat pump system. *Appl Therm Eng.* 2024;241:122250. [[CrossRef](#)].
32. Meier K, Kurtz C, Weckerle C, Hubner M, Bürger I. Air-conditioning system for vehicles with on-board hydrogen. *Appl Therm Eng.* 2018;129:1150–9. [[CrossRef](#)].
33. Satheesh A, Muthukumar P. Performance investigations of a single-stage metal hydride heat pump. *Int J Hydrogen Energy.* 2010;35(13):6950–8. [[CrossRef](#)].
34. Gkanas EI, Grant DM, Stuart AD, Eastwick CN, Book D, Nayeibossadri S, et al. Numerical study on a two-stage Metal Hydride Hydrogen Compression system. *J Alloys Compd.* 2015;645:S18–22. [[CrossRef](#)].
35. Sharma VK, Kumar EA. Thermodynamic analysis of novel multi stage multi effect metal hydride based thermodynamic system for simultaneous cooling, heat pumping and heat transformation. *Int J Hydrogen Energy.* 2017;42(1):437–47. [[CrossRef](#)].
36. Chen C, Cai G, Chen Y, An Y, Xu G, Wang Q. Hydrogen absorption properties of the slurry system composed of liquid C_6H_6 and F-treated Mg_2Ni . *J Alloys Compd.* 2003;350(1–2):275–9. [[CrossRef](#)].
37. Chen C, Cai G, Chen L, An Y, Xu G, Wang Q. Hydrogen absorption properties of a slurry system composed of a magnesium alloy powder and C_6H_6 . *J Alloys Compd.* 2003;356:409–12. [[CrossRef](#)].
38. Muthukumar P, Groll M. Metal hydride based heating and cooling systems: A review. *Int J Hydrogen Energy.* 2010;35(8):3817–31. [[CrossRef](#)].
39. Satheesh A, Muthukumar P. Performance investigation of double-stage metal hydride based heat pump. *Appl Therm Eng.* 2010;30(17–18):2698–707. [[CrossRef](#)].
40. Park J-G, Han S-C, Jang H-Y, Lee S-M, Lee P-S, Lee J-Y. The development of compressor-driven metal hydride heat pump (CDMHHP) system as an air conditioner. *Int J Hydrogen Energy.* 2002;27(9):941–4. [[CrossRef](#)].

41. Mazzucco A, Voskuilen TG, Waters EL, Pourpoint TL, Rokni M. Heat exchanger selection and design analyses for metal hydride heat pump systems. *Int J Hydrogen Energy*. 2016;41(7):4198–213. [[CrossRef](#)].
42. Peng Z, Li Q, Ouyang L, Jiang W, Chen K, Wang H, et al. Overview of hydrogen compression materials based on a three-stage metal hydride hydrogen compressor. *J Alloys Compd*. 2022;895:162465. [[CrossRef](#)].
43. Klopčič N, Grimmer I, Winkler F, Sartory M, Trattner A. A review on metal hydride materials for hydrogen storage. *J Energy Storage*. 2023;72:108456. [[CrossRef](#)].
44. Lototsky MV, Yartys VA, Tarasov BP, Davids MW, Denys RV, Tai S. Modelling of metal hydride hydrogen compressors from thermodynamics of hydrogen–Metal interactions viewpoint: Part I. Assessment of the performance of metal hydride materials. *Int J Hydrogen Energy*. 2021;46(2):2330–8. [[CrossRef](#)].
45. Corgnale C, Hatrick-Simpers J, Sulic M, Weidner J, Lopata J. Experimental assessment of thin film high pressure metal hydride material properties. *Int J Hydrogen Energy*. 2018;43(39):18363–71. [[CrossRef](#)].
46. Yartys VA, Akiba E, Bowman RC, Buckley CE, Graetz J, Hirscher M, et al. Metal hydrides: A historical perspective. *J Alloys Compd*. 2026;1050:185734. [[CrossRef](#)].
47. Afzal M, Gupta N, Mallik A, Vishnula KS, Sharma P. Experimental analysis of a metal hydride hydrogen storage system with hexagonal honeycomb-based heat transfer enhancements-part B. *Int J Hydrogen Energy*. 2021;46(24):13131–41. [[CrossRef](#)].
48. Afzal M, Mane R, Sharma P. Heat transfer techniques in metal hydride hydrogen storage: A review. *Int J Hydrogen Energy*. 2017;42(52):30661–82. [[CrossRef](#)].
49. Madaria Y, Anil Kumar E. Effect of heat transfer enhancement on the performance of metal hydride based hydrogen compressor. *Int J Hydrogen Energy*. 2016;41(6):3961–73. [[CrossRef](#)].
50. Chung C-A, Yang S-W, Yang C-Y, Hsu C-W, Chiu P-Y. Experimental study on the hydrogen charge and discharge rates of metal hydride tanks using heat pipes to enhance heat transfer. *Appl Energy*. 2013;103:581–7. [[CrossRef](#)].
51. Sun D, Deng S. Theoretical study on the heat transfer process in metal hydride beds. *J Chem Eng Chin Univ*. 1989;3(2):64–70. (In Chinese).
52. Hu S, Yang X, Zhang S, Wang J, Chen S, Zhang X, et al. Experimental study on thermal management system based on heat pump with heat storage used in hydrogen storage. *Energy*. 2026;350:139670. [[CrossRef](#)].
53. Hasnain M, Sezer H, Mason JH. Mathematical modeling of heat and mass transfer in metal hydride hydrogen storage systems: A comprehensive review. *Renew Sustain Energy Rev*. 2026;226:116294. [[CrossRef](#)].
54. Su J-W, Tang X-Y, Bai X-S, Yang W-W, Zhang J-F, Qu Z-G. Review on thermal design and thermal management for metal hydride reactors: Current status and future development. *Int J Hydrogen Energy*. 2025;114:295–311. [[CrossRef](#)].
55. Ye J, Li Z, Zhang L, Wang S, Jiang L. Measurement and the improvement of effective thermal conductivity for a metal hydride bed—A review. *RSC Adv*. 2022;12(39):25722–43. [[CrossRef](#)].
56. Malleswararao K, Aswin N, Srinivasa Murthy S, Dutta P. Performance prediction of a coupled metal hydride based thermal energy storage system. *Int J Hydrogen Energy*. 2020;45(32):16239–53. [[CrossRef](#)].
57. Aswathi KB, Krishna PN, Nair HS, Jayakumar OD. LaNi₅ based AB₅ intermetallic hydrides: A structure–composition–performance paradigm for hydrogen storage. *J Alloys Compd*. 2026;1080:190313. [[CrossRef](#)].
58. Schlapbach L, Züttel A. Hydrogen-storage materials for mobile applications. *Nature*. 2001;414(6861):353–8. [[CrossRef](#)].
59. Sun Y, Shen C, Lai Q, Liu W, Wang D-W, Aguey-Zinsou K-F. Tailoring magnesium based materials for hydrogen storage through synthesis: Current state of the art. *Energy Storage Mater*. 2018;10:168–98. [[CrossRef](#)].
60. Sun C, Wang C, Ha T, Lee J, Shim J, Kim Y. A brief review of characterization techniques with different length scales for hydrogen storage materials. *Nano Energy*. 2023;113:108554. [[CrossRef](#)].
61. Shang Y, Pistidda C, Gizer G, Klassen T, Dornheim M. Mg-based materials for hydrogen storage. *J Magnes Alloys*. 2021;9(6):1837–60. [[CrossRef](#)].
62. Nizam A, Chaurasiya PK, Sharma VK, Pai RK. A review on magnesium based metal hydrides for thermal energy storage systems. *Asia-Pac J Chem Eng*. 2026;21(2):e70161. [[CrossRef](#)].
63. Luo S, Park CN, Flanagan TB. Analysis of sloping plateaux in alloys and intermetallic hydrides II. Real systems. *J Alloys Compd*. 2004;384(1–2):208–16. [[CrossRef](#)].

64. Alekseeva S, Fanta ABDS, Iandolo B, Antosiewicz TJ, Nugroho FAA, Wagner JB, et al. Grain boundary mediated hydriding phase transformations in individual polycrystalline metal nanoparticles. *Nat Commun.* 2017;8(1):1084. [[CrossRef](#)].
65. Briki C, de Rango P, Belkhiria S, Dhaou MH, Jemni A. Measurements of expansion of LaNi_5 compacted powder during hydrogen absorption/desorption cycles and their influences on the reactor wall. *Int J Hydrogen Energy.* 2019;44(26):13647–54. [[CrossRef](#)].
66. Nyallang Nyamsi S, Bellosta von Colbe J, Puszkiel JA, Klassen T, Jepsen J. Performance simulation of a metal hydride hydrogen compressor in H_2 refueling stations: The effects of inclined plateau pressure on the H_2 compressor productivity. *Int J Hydrogen Energy.* 2026;237:155239. [[CrossRef](#)].
67. Zohra FT, Webb CJ, Lamb KE, Gray EM. Degradation of metal hydrides in hydrogen-based thermodynamic machines: A review. *Int J Hydrogen Energy.* 2024;64:417–38. [[CrossRef](#)].
68. Hagström MT, Klyamkin SN, Lund PD. Effect of substitution on hysteresis in some high-pressure AB_2 and AB_5 metal hydrides. *J Alloys Compd.* 1999;293:67–73. [[CrossRef](#)].
69. Park J-G, Jang H-Y, Han S-C, Lee P-S, Lee J-Y. Hydrogen storage properties of TiMn_2 -based alloys for metal hydride heat pump. *Mater Sci Eng A.* 2002;329:351–5. [[CrossRef](#)].
70. Hagström MT, Klyamkin SN, Mescheryakova EV, Lund PD. High-pressure AB_2 metal hydrides with low hysteresis. *J Mater Sci.* 2000;35(1):127–31. [[CrossRef](#)].
71. Wang Z, Tian Z, Yao P, Zhao H, Xia C, Yang T. Improved hydrogen storage kinetic properties of magnesium-based materials by adding Ni_2P . *Renew Energy.* 2022;189:559–69. [[CrossRef](#)].
72. Qi Y, Sheng P, Li J, Zhang X, Zhang W, Guo S, et al. Improved hydrogen storage thermodynamics and kinetics of La-Ce-Mg-Ni alloy by ball milling. *J Phys Chem Solids.* 2023;179:111417. [[CrossRef](#)].
73. Kitagawa Y, Tanabe K. Development of a kinetic model of hydrogen absorption and desorption in magnesium and analysis of the rate-determining step. *Chem Phys Lett.* 2018;699:132–8. [[CrossRef](#)].
74. Chen C-Y, Chen H-L, Ma Y-Q, Liu J. Hydrogen desorption kinetics mechanism of Mg-Ni hydride under isothermal and non-isothermal conditions. *Trans Nonferrous Met Soc China.* 2016;26(1):160–6. [[CrossRef](#)].
75. Pan Y-B, Wu Y-F, Li Q. Modeling and analyzing the hydriding kinetics of Mg-LaNi_5 composites by Chou model. *Int J Hydrogen Energy.* 2011;36(20):12892–901. [[CrossRef](#)].
76. Wang H, Lin HJ, Cai WT, Ouyang LZ, Zhu M. Tuning kinetics and thermodynamics of hydrogen storage in light metal element based systems—A review of recent progress. *J Alloys Compd.* 2016;658:280–300. [[CrossRef](#)].
77. Pang Y, Li Q. A review on kinetic models and corresponding analysis methods for hydrogen storage materials. *Int J Hydrogen Energy.* 2016;41(40):18072–87. [[CrossRef](#)].
78. Bösenberg U, Kim JW, Gossler D, Eigen N, Jensen TR, von Colbe JMB, et al. Role of additives in $\text{LiBH}_4\text{-MgH}_2$ reactive hydride composites for sorption kinetics. *Acta Mater.* 2010;58(9):3381–9. [[CrossRef](#)].
79. Chaudhary A-L, Sheppard DA, Paskevicius M, Pistidda C, Dornheim M, Buckley CE. Reaction kinetic behaviour with relation to crystallite/grain size dependency in the Mg-Si-H system. *Acta Mater.* 2015;95:244–53. [[CrossRef](#)].
80. Jander W. Reaktionen im festen Zustande Bei höheren Temperaturen. Reaktionsgeschwindigkeiten endotherm verlaufender Umsetzungen. *Z Anorg Allg Chem.* 1927;163(1):1–30. [[CrossRef](#)].
81. Shao H, Xin G, Zheng J, Li X, Akiba E. Nanotechnology in Mg -based materials for hydrogen storage. *Nano Energy.* 2012;1(4):590–601. [[CrossRef](#)].
82. Huang PG, Lu CH, Sheu TW. Numerical simulation of diffusion-controlled solid-state reactions in spherical particles. *Mater Sci Eng B.* 2004;107(1):39–45. [[CrossRef](#)].
83. Carter RE. Kinetic model for solid-state reactions. *J Chem Phys.* 1961;34(6):2010–5. [[CrossRef](#)].
84. Shimada E, Yamashita H, Matsumoto S, Ikuma Y, Ichimura H. The oxidation kinetics of spherically shaped palladium powder. *J Mater Sci.* 1999;34(16):4011–5. [[CrossRef](#)].
85. Chou KC, Xu K. A new model for hydriding and dehydriding reactions in intermetallics. *Intermetallics.* 2007;15(5–6):767–77. [[CrossRef](#)].
86. Chou KC, Luo Q, Li Q, Zhang JY. Influence of the density of oxide on oxidation kinetics. *Intermetallics.* 2014;47:17–22. [[CrossRef](#)].
87. Kircher O, Fichtner M. Hydrogen exchange kinetics in NaAlH_4 catalyzed in different decomposition states. *J Appl Phys.* 2004;95(12):7748–53. [[CrossRef](#)].

88. Kempen ATW, Sommer F, Mittemeijer EJ. Determination and interpretation of isothermal and non-isothermal transformation kinetics; the effective activation energies in terms of nucleation and growth. *J Mater Sci.* 2002;37(7):1321–32. [[CrossRef](#)].
89. Liu F, Sommer F, Bos C, Mittemeijer EJ. Analysis of solid state phase transformation kinetics: Models and recipes. *Int Mater Rev.* 2007;52(4):193–212. [[CrossRef](#)].
90. Pang Y, Sun D, Gu Q, Chou KC, Wang X, Li Q. Comprehensive determination of kinetic parameters in solid-state phase transitions: An extended jomhson–mehl–avrami–kolomogorov model with analytical solutions. *Cryst Growth Des.* 2016;16(4):2404–15. [[CrossRef](#)].
91. Barkhordarian G, Klassen T, Bormann R. Effect of Nb₂O₅ content on hydrogen reaction kinetics of Mg. *J Alloys Compd.* 2004;364(1–2):242–6. [[CrossRef](#)].
92. Barkhordarian G, Klassen T, Bormann R. Kinetic investigation of the effect of milling time on the hydrogen sorption reaction of magnesium catalyzed with different Nb₂O₅ contents. *J Alloys Compd.* 2006;407(1–2):249–55. [[CrossRef](#)].
93. Khawam A, Flanagan DR. Solid-state kinetic models: basics and mathematical fundamentals. *J Phys Chem B.* 2006;110(35):17315–28. [[CrossRef](#)].
94. Li J, Fan P, Fang ZZ, Zhou C. Kinetics of isothermal hydrogenation of magnesium with TiH₂ additive. *Int J Hydrogen Energy.* 2014;39(14):7373–81. [[CrossRef](#)].
95. Bennett C, Eastwick C, Walker G. Effect of a varying effective thermal conductivity term on heat conduction through a physical model of a hydride bed. *Int J Hydrogen Energy.* 2013;38(3):1692–701. [[CrossRef](#)].
96. Fleming L, Passing M, Puszkiel J, Klassen T, Jepsen J. A metal hydride compressor concept using hydrogen as a heat transfer fluid. *Commun Eng.* 2026;5:49. [[CrossRef](#)].
97. Xu H, Shi T, Xu H, Yu G. Regulation and optimization of solid-state hydrogen storage process in thermochemical reactors with metal hydride by using gradient metal foams. *Appl Therm Eng.* 2025;264:125464. [[CrossRef](#)].
98. Hasnain M, Sezer H, Mason JH. Modeling heat and mass transfer in metal hydride hydrogen storage systems: Impact of operating parameters and reactor geometry. *Int J Hydrogen Energy.* 2024;71:1045–55. [[CrossRef](#)].
99. Bhaskar A, Muduli RC, Kale P. Prediction of hydrogen storage in metal hydrides and complex hydrides: A supervised machine learning approach. *Int J Hydrogen Energy.* 2025;98:1212–25. [[CrossRef](#)].
100. Xiao J. Characteristic coefficients and paired working fluids of hydrogen storage material heat pumps. *Energy Conserv.* 1994;8:5–10. (In Chinese).
101. Alves ES, Costamagna M, von Colbe JB, Barale J, Dematteis EM, Stühff H, et al. Life cycle assessment for the determination of the environmental impacts of an advanced large-scale hydrogen storage system from HyCARE EU project. *J Clean Prod.* 2025;515:145836. [[CrossRef](#)].
102. Puszkiel JA, Neves AM, Warfsmann J, Krause PS, Kaufmann TFJ, Hoberg AR, et al. On the hydrogen storage properties and life cycle evaluation of a room temperature hydride for scale-up applications: The case of an AB₂-alloy. *Int J Hydrogen Energy.* 2025;118:482–99. [[CrossRef](#)].
103. Yashima M. Explosion and fire characteristics of magnesium hydride powder. *J Jpn Soc Saf Eng.* 2022;61(2):102–12. [[CrossRef](#)].
104. Wu XL, Xu S, Pang AM, Cao WG, Liu DB, Zhu XY, et al. Hazard evaluation of ignition sensitivity and explosion severity for three typical MH₂ (M = Mg, Ti, Zr) of energetic materials. *Def Technol.* 2021;17(4):1262–8. [[CrossRef](#)].
105. Yu L, Qu R, Jiang S, Hu C, Wang Y, Xu L, et al. Advancements in the modification of TiFe alloys for enhanced hydrogen Storage: Strategies and future Directions. *Renew Sustain Energy Rev.* 2026;225:116151. [[CrossRef](#)].
106. Liu H, Zhang J, Sun P, Zhou C, Liu Y, Fang ZZ. An overview of TiFe alloys for hydrogen storage: Structure, processes, properties, and applications. *J Energy Storage.* 2023;68:107772. [[CrossRef](#)].
107. Khan HB, Zhang T. Metal hydride hydrogen storage risk assessment: A review. *J Energy Storage.* 2025;129:117273. [[CrossRef](#)].
108. Wu Z, Guo T, Li X, Liu H, Wang B, Yao J, et al. An overview of swelling stress formation and control of metal hydride for high-safety and high-density hydrogen storage applications. *Appl Energy.* 2025;402:126909. [[CrossRef](#)].
109. Lin HC, Lin KM, Wu KC, Hsiung HH, Tsai HK. Cyclic hydrogen absorption–desorption characteristics of TiCrV and Ti_{0.8}Cr_{1.2}V alloys. *Int J Hydrogen Energy.* 2007;32(18):4966–72. [[CrossRef](#)].

110. Yasuda N, Tsuchiya T, Okinaka N, Akiyama T. Thermal conductivity and cycle characteristic of metal hydride sheet formed using aramid pulp and carbon fiber. *Int J Hydrogen Energy*. 2013;38(3):1657–61. [[CrossRef](#)].
111. Gillia O. Hydride breathing and its consequence on stresses applied to containers: A review. *Int J Hydrogen Energy*. 2021;46(72):35594–640. [[CrossRef](#)].
112. Li R, Yu R, Liu X, Wan J, Wang F. Study on the phase structures and electrochemical performances of $\text{La}_{0.6}\text{Gd}_{0.2}\text{Mg}_{0.2}\text{Ni}_{3.15-x}\text{Co}_{0.25}\text{Al}_{0.1}\text{Mn}_x$ ($x = 0-0.3$) alloys as negative electrode material for nickel/metal hydride batteries. *Electrochim Acta*. 2015;158:89–95. [[CrossRef](#)].
113. Li R, Xu P, Zhao Y, Wan J, Liu X, Yu R. The microstructures and electrochemical performances of $\text{La}_{0.6}\text{Gd}_{0.2}\text{Mg}_{0.2}\text{Ni}_{3.0}\text{Co}_{0.5-x}\text{Al}_x$ ($x = 0-0.5$) hydrogen storage alloys as negative electrodes for nickel/metal hydride secondary batteries. *J Power Sources*. 2014;270:21–7. [[CrossRef](#)].
114. Dubey SK, Kumar KR, Tiwari V, Srivastva U. Impacts, barriers, and future prospective of metal hydride-based thermochemical energy storage system for high-temperature applications: A comprehensive review. *Energy Technol*. 2024;12(4):2300768. [[CrossRef](#)].
115. Hang Z, Hu Z, Xiao X, Jiang R, Zhang M. Enhancing hydrogen storage kinetics and cycling properties of NaMgH_3 by 2D transition metal carbide MXene Ti_3C_2 . *Processes*. 2021;9(10):1690. [[CrossRef](#)].
116. Pottmaier D, Pinatel ER, Vitillo JG, Garroni S, Orlova M, Baró MD, et al. Structure and thermodynamic properties of the NaMgH_3 perovskite: A comprehensive study. *Chem Mater*. 2011;23(9):2317–26. [[CrossRef](#)].
117. Corgnale C, Hardy B, Motyka T, Zidan R, Teprovich J, Peters B. Screening analysis of metal hydride based thermal energy storage systems for concentrating solar power plants. *Renew Sustain Energy Rev*. 2014;38:821–33. [[CrossRef](#)].
118. Scarpati G, Di Ilio G, Jannelli E. Design and analysis of an energy-efficient, large scale metal hydride hydrogen storage system using an extended multi-physics numerical model. *Appl Energy*. 2026;409:127452. [[CrossRef](#)].
119. Morgenstern L, Knop L, Turkowski F, Kerscher F, Spliethoff H. Continuous near-equilibrium operation and model validation of a pilot-scale thermochemical energy storage reactor using $\text{CaO}/\text{Ca}(\text{OH})_2$. *Appl Therm Eng*. 2025;258:124528. [[CrossRef](#)].
120. Panwar K, Srivastava S. Theoretical model on the electronic properties of multi-element AB5-type metal hydride. *Int J Hydrogen Energy*. 2021;46(18):10819–29. [[CrossRef](#)].
121. Hariyadi A, Suwarno S, Denys RV, von Colbe JB, Sætre TO, Yartys V. Modeling of the hydrogen sorption kinetics in an AB2 laves type metal hydride alloy. *J Alloys Compd*. 2022;893:162135. [[CrossRef](#)].
122. Matheus FH, Zepon G, Oliveira VB, Leiva DR. Highly reactive hydrogen storage Mg_2Ni alloy prepared by mechanochemistry and H-cycling. *Int J Hydrogen Energy*. 2024;51:320–8. [[CrossRef](#)].
123. Sato T, Saitoh H, Utsumi R, Ito J, Nakahira Y, Obana K, et al. Hydrogen absorption reactions of hydrogen storage alloy LaNi_5 under high pressure. *Molecules*. 2023;28(3):1256. [[CrossRef](#)].
124. Roy N, MacIntosh K, Eid M, Canning G, Rioux RM. Structural chemistry of intermetallic compounds for active site design in heterogeneous catalysis. *Chem Sci*. 2025;16(20):8611–36. [[CrossRef](#)].
125. Lee SY, Ha T, Suh JY, Kim DI, Lee YS, Shim JH. Orientation relationship between TiFeH and TiFe phases in AB-type Ti–Fe–V–Ce hydrogen storage alloy. *J Alloys Compd*. 2024;983:173943. [[CrossRef](#)].
126. Liu Y, Li J, Wang D, Zhao C. Metal hydride hydrogen storage and thermal management at room temperatures. *Renew Sustain Energy Rev*. 2026;242:117350. [[CrossRef](#)].
127. Yoon MS, Hur J, Park SH, Lee UJ, Xu G, Park HK, et al. Role of solute elements in $\text{Mg}-\text{Mg}_2\text{Ni}$ hydrogen storage alloys: A first-principles calculation study. *J Magnes Alloys*. 2024;12(11):4574–93. [[CrossRef](#)].
128. Lys A, Fadonougbo JO, Faisal M, Suh JY, Lee YS, Shim JH, et al. Enhancing the hydrogen storage properties of AxBy intermetallic compounds by partial substitution: A short review. *Hydrogen*. 2020;1(1):38–63. [[CrossRef](#)].
129. Chandra D, Reilly JJ, Chellappa R. Metal hydrides for vehicular applications: The state of the art. *JOM*. 2006;58(2):26–32. [[CrossRef](#)].
130. Révész Á. Improved hydrogen storage performance of novel metal hydrides and their composites. *Energies*. 2023;16(8):3594. [[CrossRef](#)].
131. Ångqvist M, Erhart P. Understanding chemical ordering in intermetallic clathrates from atomic scale simulations. *Chem Mater*. 2017;29(17):7554–62. [[CrossRef](#)].
132. Seo CY, Choi SJ, Choi J, Park CN, Lee PS, Lee JY. The influence of titanium on the electrochemical properties of the AB5-type metal hydrides. *J Alloys Compd*. 2003;350(1–2):324–31. [[CrossRef](#)].

133. Cao Y, Wei Z, Al Maksoud W, Rai R, Kobayashi Y, Kageyama H. Zr-based Laves phases with nitride/hydride ions for ammonia synthesis. *Solid State Sci.* 2023;145:107331. [[CrossRef](#)].
134. Seo CY, Choi SJ, Choi J, Park CN, Lee PS, Lee JY. Effect of Ti and Zr additions on the characteristics of AB₅-type hydride electrode for Ni–MH secondary battery. *Int J Hydrogen Energy.* 2003;28(3):317–27. [[CrossRef](#)].
135. Young K, Chao B, Huang B, Nei J. Studies on the hydrogen storage characteristic of La_{1-x}Ce_x (NiCoMnAlCuSiZr)_{5.7} with a B2 secondary phase. *J Alloys Compd.* 2014;585:760–70. [[CrossRef](#)].
136. Feng L. Research progress of charging and discharging cycle stability of AB₅ type rare-earth hydrogen storage alloys. *Met World.* 2020;1:28–31. (In Chinese). [[CrossRef](#)].
137. Xu J, Chen X, Zhu W, Zhang W, Cui H, Zhu S, et al. Enhanced cycling stability and reduced hysteresis of AB₅-type hydrogen storage alloys by partial substitution of Sn for Ni. *Int J Hydrogen Energy.* 2022;47(53):22495–509. [[CrossRef](#)].
138. Zhang X, Li J, Zhao Y, Zhang G, He X, Bai J, et al. Cycling decay mechanism of AB₅-type hydrogen storage alloy for metal hydride hydrogen compressor. *J Rare Earths.* 2026;44(5):1562–70. [[CrossRef](#)].
139. Wang CS, Wang XH, Lei YQ, Chen CP, Wang QD. The hydriding kinetics of MlNi₅–I. Development of the model. *Int J Hydrogen Energy.* 1996;21(6):471–8. [[CrossRef](#)].
140. Valøen LO, Zaluska A, Zaluski L, Tanaka H, Kuriyama N, Ström-Olsen JO, et al. Structure and related properties of (La, Ce, Nd, Pr)Ni₅ alloys. *J Alloys Compd.* 2000;306(1–2):235–44. [[CrossRef](#)].
141. Zheng Y, Yu Z, Peng Y, Zheng X, Chen X. Advances in research and development of hydrogen storage alloys. *Henan Sci.* 1998;16(4):422–8. (In Chinese). [[CrossRef](#)].
142. Filipek SM, Paul-Boncour V, Liu RS. ZrNi₅-based hydrogenated phases formed under high hydrogen pressure conditions. *Appl Surf Sci.* 2011;257(19):8237–40. [[CrossRef](#)].
143. Weaver JH, Franciosi A, Peterman DJ, Takeshita T, Gschneidner KA Jr. Electronic structure and surface oxidation of the haucke compounds CaNi₅, YNi₅, LaNi₅ and ThNi₅. *J Less Common Met.* 1982;86:195–202. [[CrossRef](#)].
144. Wang X, Chen C, Pan H, Wang Q. Research and development on metal hydride heat pump. *Mater Rep.* 1994;5:16–9. (In Chinese).
145. Sarath Babu K, Anil Kumar E. Thermodynamic analysis of thermochemical energy storage system based on AB₅ type hydride pairs. *Mater Today Proc.* 2022;49:2042–7. [[CrossRef](#)].
146. Joubert JM, Paul-Boncour V, Cuevas F, Zhang J, Latroche M. LaNi₅ related AB₅ compounds: Structure, properties and applications. *J Alloys Compd.* 2021;862:158163. [[CrossRef](#)].
147. Song XY, Chen Y, Zhang Z, Lei YQ, Zhang XB, Wang QD. Microstructure and electrochemical properties of Ti-containing AB₂ type hydrogen storage electrode alloy. *Int J Hydrogen Energy.* 2000;25(7):649–56. [[CrossRef](#)].
148. Humana RM, Ruiz FC, Thomas JE, Peretti HA, Castro EB, Visintin A. Properties of composites of metal hydride alloys synthesized by mechanical milling. *J Solid State Electrochem.* 2017;21(1):153–60. [[CrossRef](#)].
149. Kim DM, Jang KJ, Lee JY. A review on the development of AB₂-type Zr-based Laves phase hydrogen storage alloys for Ni–MH rechargeable batteries in the Korea Advanced Institute of Science and Technology. *J Alloys Compd.* 1999;293:583–92. [[CrossRef](#)].
150. Ivey DG, Northwood DO. Storing hydrogen in AB₂ laves-type compounds. *Z Für Phys Chem.* 1986;147(1–2):191–209. [[CrossRef](#)].
151. Shen H, Zhang J, Paul-Boncour V, Li P, Li Z, Wu Y, et al. AB₂-type rare earth-based compounds with C-15 structure: Looking for reversible hydrogen storage materials. *J Rare Earths.* 2024;42(5):803–16. [[CrossRef](#)].
152. Li M, Han SM, Li Y, Guan W, Mao LR, Hu L. Study on the phase structure and electrochemical properties of RE_{0.93}Mg_{0.07}Ni_{2.96}Co_{0.60}Mn_{0.37}Al_{0.17} hydrogen storage alloy. *Electrochim Acta.* 2006;51(26):5926–31. [[CrossRef](#)].
153. Zhang YH, Zhang W, Song XP, Zhang PL, Zhu YG, Qi Y. Effects of spinning rate on structures and electrochemical hydrogen storage performances of RE–Mg–Ni–Mn-based AB₂-type alloys. *Trans Nonferrous Met Soc China.* 2016;26(12):3219–31. [[CrossRef](#)].
154. Reilly JJ, Wiswall RH. Formation and properties of iron titanium hydride. *Inorg Chem.* 1974;13(1):218–22. [[CrossRef](#)].
155. Niu Y, Li T, Yuan Z, Han Q, Han Z, Liu C, et al. An overview of TiFe-based alloys for hydrogen storage: Structure, element substitution and preparation. *Int J Hydrogen Energy.* 2025;175:151503. [[CrossRef](#)].

156. Park KB, Fadonougbo JO, Park CS, Lee JH, Na TW, Kang HS, et al. Effect of Fe substitution on first hydrogenation kinetics of TiFe-based hydrogen storage alloys after air exposure. *Int J Hydrogen Energy*. 2021;46(60):30780–9. [[CrossRef](#)].
157. Guéguen A, Latroche M. Influence of the addition of vanadium on the hydrogenation properties of the compounds $\text{TiFe}_{0.9}\text{V}_x$ and $\text{TiFe}_{0.8}\text{Mn}_{0.1}\text{V}_x$ ($x = 0, 0.05$ and 0.1). *J Alloys Compd*. 2011;509(18):5562–6. [[CrossRef](#)].
158. Shang H, Li Y, Zhang Y, Qi Y, Guo S, Zhao D. Structure and hydrogenation performances of as-cast $\text{Ti}_{1.1}\text{-RE Fe}_{0.8}\text{Mn}_{0.2}$ (RE = Pr, Sm and Nd; $x = 0, 0.01$) alloys. *Int J Hydrogen Energy*. 2018;43(41):19091–101. [[CrossRef](#)].
159. Shang H, Li Y, Zhang Y, Zhao D, Qi Y, Xu X. Investigations on hydrogen storage performances and mechanisms of as-cast $\text{TiFe}_{0.8}\text{Ni}_{0.2}\text{Co}$ ($m = 0, 0.03, 0.05$ and 0.1) alloys. *Int J Hydrogen Energy*. 2021;46(34):17840–52. [[CrossRef](#)].
160. Mu Y, Zhou Y, Yang G, Xu L, Xu H, Zhu L, et al. Hydrogen storage performance of $\text{Ti}_{0.75}\text{Zr}_{0.25}\text{Mn}_{0.9}\text{CrFe}_{0.1}$ alloy with different preparation methods. *RSC Adv*. 2026;16(10):8623–32. [[CrossRef](#)].
161. Shang H, Zhang Y, Li Y, Gao J, Zhang W, Wei X, et al. Effect of Pr content on activation capability and hydrogen storage performances of TiFe alloy. *J Alloys Compd*. 2022;890:161785. [[CrossRef](#)].
162. Zhai T, Wei Z, Yuan Z, Han Z, Feng D, Wang H, et al. Influences of La addition on the hydrogen storage performances of TiFe-base alloy. *J Phys Chem Solids*. 2021;157:110176. [[CrossRef](#)].
163. Zhang YH, Li C, Yuan ZM, Qi Y, Guo SH, Zhao DL. Research progress of TiFe-based hydrogen storage alloys. *J Iron Steel Res Int*. 2022;29(4):537–51. [[CrossRef](#)].
164. Muthukumar P, Maiya MP, Srinivasa Murthy S, Vijay R, Sundaresan R. Tests on mechanically alloyed Mg_2Ni for hydrogen storage. *J Alloys Compd*. 2008;452(2):456–61. [[CrossRef](#)].
165. Xu Y, Deng Y, Liu W, Zhao X, Xu J, Yuan Z. Research progress of hydrogen energy and metal hydrogen storage materials. *Sustain Energy Technol Assess*. 2023;55:102974. [[CrossRef](#)].
166. Ding X, Cao W, Chen R, Zhang J, Shen H, Guo J. Effects of Cu on the microstructure and hydrogen storage properties of Mg-20Ni alloy. *MATEC Web Conf*. 2024;401:03012. [[CrossRef](#)].
167. Zlatanova Z, Spassov T, Eggeler G, Spassova M. Synthesis and hydriding/dehydriding properties of $\text{Mg}_2\text{Ni-AB}$ (AB = TiNi or TiFe) nanocomposites. *Int J Hydrogen Energy*. 2011;36(13):7559–66. [[CrossRef](#)].
168. Zhong HC, Xu JB, Jiang CH, Lu XJ. Microstructure and remarkably improved hydrogen storage properties of Mg_2Ni alloys doped with metal elements of Al, Mn and Ti. *Trans Nonferrous Met Soc China*. 2018;28(12):2470–7. [[CrossRef](#)].
169. Liang G, Boily S, Huot J, Van Neste A, Schulz R. Hydrogen absorption properties of a mechanically milled Mg–50 wt.% LaNi_5 composite. *J Alloys Compd*. 1998;268(1–2):302–7. [[CrossRef](#)].
170. Liang G, Huot J, Boily S, Van Neste A, Schulz R. Hydrogen storage in mechanically milled Mg– LaNi_5 and $\text{MgH}_2\text{-LaNi}_5$ composites. *J Alloys Compd*. 2000;297(1–2):261–5. [[CrossRef](#)].
171. Tran NE, Ashraf Imam M, Feng CR. Evaluation of hydrogen storage characteristics of magnesium–misch metal alloys. *J Alloys Compd*. 2003;359(1–2):225–9. [[CrossRef](#)].
172. Liu D, Liu X, Zhu Y, Li L. Hydriding combustion synthesis of Mg– CaNi_5 composites. *J Alloys Compd*. 2008;458(1–2):394–7. [[CrossRef](#)].
173. Song M, Kwon S, Mumm DR, Hong SH. Enhancement of hydriding and dehydriding kinetics of Mg by the addition of Ni and nano-structured Fe_2O_3 . *Curr Appl Phys*. 2009;9(1):S118–20. [[CrossRef](#)].
174. Yong H, Guo S, Yuan Z, Qi Y, Zhao D, Zhang Y. Improved hydrogen storage kinetics and thermodynamics of RE-Mg-based alloy by co-doping Ce–Y. *Int J Hydrogen Energy*. 2019;44(31):16765–76. [[CrossRef](#)].
175. Yan H, Xiong W, Wang L, Li B, Li J, Zhao X. Investigations on AB3-, A2B7- and A5B19-type LaYNi system hydrogen storage alloys. *Int J Hydrogen Energy*. 2017;42(4):2257–64. [[CrossRef](#)].
176. Liu J, Han S, Li Y, Yang S, Zhang L, Zhao Y. Effect of Al incorporation on the degradation in discharge capacity and electrochemical kinetics of La–Mg–Ni-based alloys with A2B7-type super-stacking structure. *J Alloys Compd*. 2015;619:778–87. [[CrossRef](#)].
177. Young K, Ouchi T, Shen H, Bendersky LA. Hydrogen induced amorphization of LaMgNi_4 phase in metal hydride alloys. *Int J Hydrogen Energy*. 2015;40(29):8941–7. [[CrossRef](#)].
178. Zhai TT, Yang T, Yuan ZM, Zhang YH. An investigation on electrochemical and gaseous hydrogen storage performances of as-cast $\text{La}_{1-x}\text{Pr}_x \text{MgNi}_{3.6}\text{Co}_{0.4}$ ($x = 0\text{--}0.4$) alloys. *Int J Hydrogen Energy*. 2014;39(26):14282–7. [[CrossRef](#)].

179. Wang W, Qin R, Wu R, Tao X, Zhang H, Ding Z, et al. A promising anode candidate for rechargeable nickel metal hydride power battery: An A5B19-type La–Sm–Nd–Mg–Ni–Al-based hydrogen storage alloy. *J Power Sources*. 2020;465:228236. [[CrossRef](#)].
180. Fan Y, Zhang L, Xue C, Fan G, Liu J, Liu B, et al. Superior electrochemical performances of LaMgNi alloys with A2B7/A5B19 double phase. *Int J Hydrogen Energy*. 2019;44(14):7402–13. [[CrossRef](#)].
181. Zhang J, Villeroy B, Knosp B, Bernard P, Latroche M. Structural and chemical analyses of the new ternary La₅MgNi₂₄ phase synthesized by Spark Plasma Sintering and used as negative electrode material for Ni–MH batteries. *Int J Hydrogen Energy*. 2012;37(6):5225–33. [[CrossRef](#)].
182. Zhao Y, Zhang L, Ding Y, Cao J, Jia Z, Ma C, et al. Comparative study on the capacity degradation behavior of Pr₅Co19-type single-phase Pr₄MgNi₁₉ and La₄MgNi₁₉ alloys. *J Alloys Compd*. 2017;694:1089–97. [[CrossRef](#)].
183. Liu J, Han S, Li Y, Zhao X, Yang S, Zhao Y. Cooperative effects of Sm and Mg on electrochemical performance of La–Mg–Ni-based alloys with A2B7- and A5B19-type super-stacking structure. *Int J Hydrogen Energy*. 2015;40(2):1116–27. [[CrossRef](#)].
184. Liu J, Han S, Han D, Li Y, Yang S, Zhang L, et al. Enhanced cycling stability and high rate dischargeability of (La, Mg)₂Ni7-type hydrogen storage alloys with (La, Mg)₅Ni19 minor phase. *J Power Sources*. 2015;287:237–46. [[CrossRef](#)].
185. Liu J, Han S, Li Y, Yang S, Chen X, Wu C, et al. Effect of Pr on phase structure and cycling stability of La–Mg–Ni-based alloys with A2B7- and A5B19-type superlattice structures. *Electrochim Acta*. 2015;184:257–63. [[CrossRef](#)].
186. Wu F, Zhang MY, Mu DB. Effect of B and Fe substitution on structure of AB3-type co-free hydrogen storage alloy. *Trans Nonferrous Met Soc China*. 2010;20(10):1885–91. [[CrossRef](#)].
187. Yuan Z, Li X, Li T, Zhai T, Lin Y, Feng D, et al. Improved hydrogen storage performances of nanocrystalline RE5Mg41-type alloy synthesized by ball milling. *J Energy Storage*. 2022;46:103702. [[CrossRef](#)].
188. Tian X, Yun G, Wang H, Shang T, Yao Z, Wei W, et al. Preparation and electrochemical properties of La–Mg–Ni-based La_{0.75}Mg_{0.25}Ni_{3.3}Co_{0.5} multiphase hydrogen storage alloy as negative material of Ni/MH battery. *Int J Hydrogen Energy*. 2014;39(16):8474–81. [[CrossRef](#)].
189. Li J, He X, Xiong W, Wang L, Li B, Li J, et al. Phase forming law and electrochemical properties of A2B7-type La–Y–Ni-based hydrogen storage alloys with different La/Y ratios. *J Rare Earths*. 2023;41(2):268–76. [[CrossRef](#)].
190. Wang L, Zhang X, Zhou S, Xu J, Yan H, Luo Q, et al. Effect of Al content on the structural and electrochemical properties of A2B7 type La–Y–Ni based hydrogen storage alloy. *Int J Hydrogen Energy*. 2020;45(33):16677–89. [[CrossRef](#)].
191. Liu Y, Yuan H, Guo M, Jiang L. Effect of Y element on cyclic stability of A2B7-type La–Y–Ni-based hydrogen storage alloy. *Int J Hydrogen Energy*. 2019;44(39):22064–73. [[CrossRef](#)].
192. Xiong W, Yan H, Wang L, Verbetsky V, Zhao X, Mitrokhin S, et al. Characteristics of A2B7-type LaYNi-based hydrogen storage alloys modified by partially substituting Ni with Mn. *Int J Hydrogen Energy*. 2017;42(15):10131–41. [[CrossRef](#)].
193. Friedlmeier G, Wierse M, Groll M. Titanium hydride for high-temperature thermal energy storage in solar-thermal power stations. *Z Für Phys Chem*. 1994;183(1–2):175–83. [[CrossRef](#)].
194. Wu Z, Yang F, Zhu L, Feng P, Zhang Z, Wang Y. Improvement in hydrogen desorption performances of magnesium based metal hydride reactor by incorporating helical coil heat exchanger. *Int J Hydrogen Energy*. 2016;41(36):16108–21. [[CrossRef](#)].
195. Zhou C, Liu H, Liu Y, Shi Q. Metal hydride thermal energy storage and its research progress. *Mater Sci Eng Powder Metall*. 2019;24(5):391–9. (In Chinese).
196. Li C, Zhan W, Liang H, Chen R, Yuan C, Li Y, et al. Role of Nb on initial absorption and effective capacity of Ti–Fe–La-based AB type hydrogen storage alloy. *Chem Eng J*. 2025;523:168384. [[CrossRef](#)].
197. Liu B, Sun H, Guo S, Hou Z, Mu X, Xu L, et al. Structure and hydrogen storage properties of AB2-type (a = Ti, Zr; B = Cr, Mn, Fe, Co, Ni) C14 Laves phase high-entropy alloys. *Intermetallics*. 2026;188:109089. [[CrossRef](#)].
198. Kalita G, Otsuka R, Endo T, Furukawa S. Recent advances in substitutional doping of AB5 and AB2 type hydrogen storage metal alloys for Ni–MH battery applications. *J Alloys Compd*. 2025;1020:179352. [[CrossRef](#)].

199. Ma X, Ding X, Hu S, Zhao Y, Wang Q, Zhang Y, et al. Fast reaction behaviors of AB-type Ti-Fe-Mn hydrogen storage alloys from lattice modification and *in-situ* formed yttrium hydride. *Chem Eng J.* 2025;507:160801. [[CrossRef](#)].
200. Huang Z, Han Z, Zhai T, Gao P, Sun H, Li J, et al. Research progress on theoretical calculation and modification strategy of TiFe-based hydrogen storage materials. *J Alloys Compd.* 2025;1028:180669. [[CrossRef](#)].
201. Paul AR, Mehla S, Bhargava S. Intermetallic compounds for hydrogen storage: Current status and future perspectives. *Small.* 2025;21(14):2408889. [[CrossRef](#)].
202. Van Lai D, Nguyen SH, Nguyen AH, Van Nguyen T, Dinh LC, Doan PD, et al. Tailoring hydrogen storage performance of Mg-Mg₂ Ni alloys: Synergistic effects of composition and phase formation with first-principles insights. *RSC Adv.* 2025;15(38):31240–54. [[CrossRef](#)].
203. Verna D, Berezovets V, Denys R, Deledda S, Pasquini L, Yartys V. Structure and hydrogen sorption properties of multicomponent AB₂ Laves type compounds derived from ZrVNb. *J Alloys Compd.* 2026;1051:185785. [[CrossRef](#)].
204. Bu W, Wang R, Liu Z, Wang X, Hao J, Yong H, et al. Thermodynamic performance of vanadium-modified Mg₂Ni alloy for hydrogen storage. *Adv Compos Hybrid Mater.* 2025;8(5):390. [[CrossRef](#)].
205. Liu Y, Chen Q, Yuan H, Jiang L, Mi J, Hao L. Effect of Mn and Al on the superlattice La-Y-Ni-based hydrogen storage alloys in the long-period electrochemical cycling process. *Int J Hydrogen Energy.* 2025;109:264–74. [[CrossRef](#)].
206. Teng Y, Wang R, Sun X, Liu B, Liu B, Hu B, et al. Composition screening and cycling degradation mechanisms of long-cycle-life superlattice hydrogen storage alloys. *J Alloys Compd.* 2025;1025:180349. [[CrossRef](#)].
207. Sun DW, Deng SJ. Theoretical descriptions and experimental measurements on the effective thermal conductivity in metal hydride powder beds. *J Less Common Met.* 1990;160(2):387–95. [[CrossRef](#)].
208. Hahne E, Kallweit J. Thermal conductivity of metal hydride materials for storage of hydrogen: Experimental investigation. *Int J Hydrogen Energy.* 1998;23(2):107–14. [[CrossRef](#)].
209. Madaria Y, Anil Kumar E, Srinivasa Murthy S. Effective thermal conductivity of reactive packed beds of hydriding materials. *Appl Therm Eng.* 2016;98:976–90. [[CrossRef](#)].
210. Kim KJ, Montoya B, Razani A, Lee KH. Metal hydride compacts of improved thermal conductivity. *Int J Hydrogen Energy.* 2001;26(6):609–13. [[CrossRef](#)].
211. Rodríguez Sánchez A, Klein HP, Groll M. Expanded graphite as heat transfer matrix in metal hydride beds. *Int J Hydrogen Energy.* 2003;28(5):515–27. [[CrossRef](#)].
212. Bennett CMJ, Patman AJ, Milanese C, Eastwick CN, Walker GS. Effect of powder characteristics for a magnesium based metal hydride store. *Int J Hydrogen Energy.* 2014;39(34):19646–55. [[CrossRef](#)].
213. Chibani A, Bougriou C, Merouani S. Simulation of hydrogen absorption/desorption on metal hydride LaNi₅-H₂: Mass and heat transfer. *Appl Therm Eng.* 2018;142:110–7. [[CrossRef](#)].
214. Mazzucco A, Dornheim M, Sloth M, Jensen TR, Jensen JO, Rokni M. Bed geometries, fueling strategies and optimization of heat exchanger designs in metal hydride storage systems for automotive applications: A review. *Int J Hydrogen Energy.* 2014;39(30):17054–74. [[CrossRef](#)].
215. Gkanas EI, Khzouz M. Study on the hydrogenation of an Mm-based AB₅-intermetallic for sustainable building applications. *Int J Energy Res.* 2019;er.4794. [[CrossRef](#)].
216. Gkanas EI, Khzouz M, Panagakos G, Statheros T, Mihalakakou G, Siasos GI, et al. Hydrogenation behavior in rectangular metal hydride tanks under effective heat management processes for green building applications. *Energy.* 2018;142:518–30. [[CrossRef](#)].
217. Raju NN, Kumar A, Malleswararao K, Muthukumar P. Parametric studies on LaNi_{4.7}Al_{0.3} based hydrogen storage reactor with embedded cooling tubes. *Energy Procedia.* 2019;158:2384–90. [[CrossRef](#)].
218. Ghafir MFA, Batcha MFM, Raghavan VR. Prediction of the thermal conductivity of metal hydrides–The inverse problem. *Int J Hydrogen Energy.* 2009;34(16):7125–30. [[CrossRef](#)].
219. Wang H, Prasad AK, Advani SG. Hydrogen storage systems based on hydride materials with enhanced thermal conductivity. *Int J Hydrogen Energy.* 2012;37(1):290–8. [[CrossRef](#)].
220. Popilevsky L, Skripnyuk VM, Amouyal Y, Rabkin E. Tuning the thermal conductivity of hydrogenated porous magnesium hydride composites with the aid of carbonaceous additives. *Int J Hydrogen Energy.* 2017;42(35):22395–405. [[CrossRef](#)].

221. Zheng H, Wang C, Liu Q, Tian Z, Fan X. Thermal performance of copper foam/paraffin composite phase change material. *Energy Convers Manag.* 2018;157:372–81. [[CrossRef](#)].
222. Kapischke J, Hapke J. Measurement of the effective thermal conductivity of a metal hydride bed with chemical reaction. *Exp Therm Fluid Sci.* 1994;9(3):337–44. [[CrossRef](#)].
223. Lloyd G, Kim KJ, Razani A, Feldman KT Jr. Thermal conductivity measurements of metal hydride compacts developed for high-power reactors. *J Thermophys Heat Transf.* 1998;12(2):132–7. [[CrossRef](#)].
224. Ron M, Bershadsky E, Joseph Y. The thermal conductivity of porous metal matrix hydride compacts. *J Less Common Met.* 1991;172:1138–46. [[CrossRef](#)].
225. Suda S, Komazaki Y. The effective thermal conductivity of a metalhydride bed packed in a multiple-waved sheet metal structure. *J Less Common Met.* 1991;172:1130–7. [[CrossRef](#)].
226. Atalmis G, Toros S, Timurkutluk B, Kaplan Y. Effect of expanded natural graphite addition and copper coating on reaction kinetics and hydrogen storage characteristics of metal hydride reactors. *Int J Hydrogen Energy.* 2024;53:647–56. [[CrossRef](#)].
227. Dieterich M, Pohlmann C, Bürger I, Linder M, Röntzsch L. Long-term cycle stability of metal hydride-graphite composites. *Int J Hydrogen Energy.* 2015;40(46):16375–82. [[CrossRef](#)].
228. Madaria Y, Anil Kumar E. Measurement and augmentation of effective thermal conductivity of $\text{La}_{0.8}\text{Ce}_{0.2}\text{Ni}_5$ hydride bed. *J Alloys Compd.* 2017;691:442–51. [[CrossRef](#)].
229. Chaise A, de Rango P, Marty P, Fruchart D, Miraglia S, Olivès R, et al. Enhancement of hydrogen sorption in magnesium hydride using expanded natural graphite. *Int J Hydrogen Energy.* 2009;34(20):8589–96. [[CrossRef](#)].
230. Raju M, Kumar S. System simulation modeling and heat transfer in sodium alanate based hydrogen storage systems. *Int J Hydrogen Energy.* 2011;36(2):1578–91. [[CrossRef](#)].
231. Freni A, Cipiti F, Cacciola G. Finite element-based simulation of a metal hydride-based hydrogen storage tank. *Int J Hydrogen Energy.* 2009;34(20):8574–82. [[CrossRef](#)].
232. Kim KJ, Lloyd GM, Feldman KT, Razani A. Thermal analysis of the $\text{Ca}_{0.4}\text{Mm}_{0.6}\text{Ni}_5$ metal–hydride reactor. *Appl Therm Eng.* 1998;18(12):1325–36. [[CrossRef](#)].
233. Bai XS, Yang WW, Zhang WY, Yang FS, Tang XY. Hydrogen absorption performance of a novel cylindrical MH reactor with combined loop-type finned tube and cooling jacket heat exchanger. *Int J Hydrogen Energy.* 2020;45(52):28100–15. [[CrossRef](#)].
234. Shafiee S, McCay MH. Different reactor and heat exchanger configurations for metal hydride hydrogen storage systems—A review. *Int J Hydrogen Energy.* 2016;41(22):9462–70. [[CrossRef](#)].
235. Wang D, Wang Y, Huang Z, Yang F, Wu Z, Zheng L, et al. Design optimization and sensitivity analysis of the radiation mini-channel metal hydride reactor. *Energy.* 2019;173:443–56. [[CrossRef](#)].
236. Sreeraj R, Aadithiyen AK, Anbarasu S. Integration of thermal augmentation methods in hydride beds for metal hydride based hydrogen storage systems: Review and recommendation. *J Energy Storage.* 2022;52:105039. [[CrossRef](#)].
237. Bai XS, Yang WW, Tang XY, Yang FS, Jiao YH, Yang Y. Optimization of tree-shaped fin structures towards enhanced absorption performance of metal hydride hydrogen storage device: A numerical study. *Energy.* 2021;220:119738. [[CrossRef](#)].
238. Keshari V, Maiya MP. Design and investigation of hydriding alloy based hydrogen storage reactor integrated with a pin fin tube heat exchanger. *Int J Hydrogen Energy.* 2018;43(14):7081–95. [[CrossRef](#)].
239. Wang H, Yi G, Ye J, Feng X, Li Z, Wang S, et al. Intensification of hydrogen absorption process in metal hydride devices with novel corrugated fins: A validated numerical study. *J Alloys Compd.* 2022;926:166759. [[CrossRef](#)].
240. Liu Y, Wang H, Ayub I, Yang F, Wu Z, Zhang Z. A variable cross-section annular fins type metal hydride reactor for improving the phenomenon of inhomogeneous reaction in the thermal energy storage processes. *Appl Energy.* 2021;295:117073. [[CrossRef](#)].
241. Chang H, Tao YB, Wang WY. Numerical study on storage performance of metal hydride reactors with multiple spiral fins. *Int J Hydrogen Energy.* 2023;48(90):35170–84. [[CrossRef](#)].
242. Li H, Wang Y, He C, Chen X, Zhang Q, Zheng L, et al. Design and performance simulation of the spiral mini-channel reactor during H_2 absorption. *Int J Hydrogen Energy.* 2015;40(39):13490–505. [[CrossRef](#)].

243. Bai XS, Yang WW, Tang XY, Dai ZQ, Yang FS. Parametric optimization of coupled fin-metal foam metal hydride bed towards enhanced hydrogen absorption performance of metal hydride hydrogen storage device. *Energy*. 2022;243:123044. [[CrossRef](#)].
244. Tiwari S, Sharma P. Integration of metal hydride reactor with thermocline based heat storage system. *J Energy Storage*. 2023;59:106506. [[CrossRef](#)].
245. Lewis SD, Chippar P. Analysis of heat and mass transfer during charging and discharging in a metal hydride—Phase change material reactor. *J Energy Storage*. 2021;33:102108. [[CrossRef](#)].
246. Wan J, Li R, Wang F, Ding C, Yu R, Wu Y. Effect of Ni substitution on hydrogen storage properties of $Zr_{0.8}Ti_{0.2}Co_{1-x}Ni_x$ ($x = 0, 0.1, 0.2, 0.3$) alloys. *Int J Hydrogen Energy*. 2016;41(18):7408–18. [[CrossRef](#)].
247. He X, Zhang X, Li B, Zhou S, Zhao Y, Wang L, et al. Capacity degradation mechanism of ternary La–Y–Ni-based hydrogen storage alloys. *Chem Eng J*. 2023;465:142840. [[CrossRef](#)].
248. Li Q, Tang G, Cai B, Wu K, Qin L, Chen D, et al. Effect of silicone oil additive on swelling stress alleviation in the metal hydride reactor. *Int J Hydrogen Energy*. 2022;47(18):10308–14. [[CrossRef](#)].
249. Kim KJ, Lloyd G, Razani A, Feldman KT. Development of $LaNi_5/Cu/Sn$ metal hydride powder composites. *Powder Technol*. 1998;99(1):40–5. [[CrossRef](#)].
250. Liu F, Suda S. Hydriding properties of the ternary Mm-based AB₅ alloys modified by surface treatment. *J Alloys Compd*. 1996;232(1–2):204–11. [[CrossRef](#)].
251. Desai FJ, Uddin MN, Rahman MM, Asmatulu R. A critical review on improving hydrogen storage properties of metal hydride *via* nanostructuring and integrating carbonaceous materials. *Int J Hydrogen Energy*. 2023;48(75):29256–94. [[CrossRef](#)].
252. Pohlmann C, Kieback B, Röntzsch L. Composite materials of melt-spun $Mg_{90}Ni_{10}$ and graphite: Microstructural changes during cyclic hydrogenation and the impact on gas and heat transport characteristics. *Int J Hydrogen Energy*. 2014;39(16):8331–9. [[CrossRef](#)].
253. Le-Quoc H, Coste M, Lacoste A, Laversenne L. Magnesium hydride films deposited on flexible substrates: Structure, morphology and hydrogen sorption properties. *J Alloys Compd*. 2023;955:170272. [[CrossRef](#)].
254. Jangid MK, Sharma SS, Ray J, Yadav DK, Lal C. Structural, optical and electrical characterizations of Mg/Ti/Ni multilayer thin films deposited by DC magnetron sputtering for hydrogen storage. *Int J Hydrogen Energy*. 2023;48(96):37921–9. [[CrossRef](#)].
255. Souqui L, Caroff CM, Lastowski RJ, Shrivastav S, Girolami GS, Krogstad JA, et al. MgH_2 thin films and nanowires deposited by CVD from a magnesium diamidodiborane precursor. *Mater Today Commun*. 2026;50:114615. [[CrossRef](#)].
256. Wu Y, Yu H, Guo Y, Zhang Y, Jiang X, Sun B, et al. Promoting hydrogen absorption of liquid organic hydrogen carriers by solid metal hydrides. *J Mater Chem A*. 2019;7(28):16677–84. [[CrossRef](#)].
257. Lamb KE, Webb CJ. A quantitative review of slurries for hydrogen storage—Slush hydrogen, and metal and chemical hydrides in carrier liquids. *J Alloys Compd*. 2022;906:164235. [[CrossRef](#)].
258. Chen CP, Wang XH, Cai GM, Chen LX, Wang QD. Surface structure of F-treated $La_{1.8}Ca_{0.2}Mg_{14}Ni_3$ alloy and hydrogenation properties of solid–liquid system composed of the alloy and benzene. *Int J Hydrogen Energy*. 2006;31(10):1261–5. [[CrossRef](#)].
259. Wu Y, Scarponi J, Powell A, Jayachandran J. Magnesium hydride slurry: A potential net-zero carbon dioxide emitting aviation fuel. *Fuel*. 2023;333:126232. [[CrossRef](#)].
260. Huang LJ, Lin HJ, Wang H, Ouyang LZ, Zhu M. Amorphous alloys for hydrogen storage. *J Alloys Compd*. 2023;941:168945. [[CrossRef](#)].
261. Han L, Huang H, Zhang P, Ma C, Wang X, Sang G, et al. Hydrogen storage properties of Zr_2Co crystalline and amorphous alloys. *Int J Hydrogen Energy*. 2021;46(2):2312–21. [[CrossRef](#)].
262. Han B, Yu S, Wang H, Lu Y, Lin HJ. Nanosize effect on the hydrogen storage properties of Mg-based amorphous alloy. *Scr Mater*. 2022;216:114736. [[CrossRef](#)].
263. Zhou H, Ding Z, Chen YA, Lan ZQ, Guo SF, Spieckermann F, et al. Enhancement of hydrogen storage properties from amorphous $Mg_{85}Ni_5Y_{10}$ alloy. *J Non Cryst Solids*. 2023;605:122167. [[CrossRef](#)].
264. Chibani A, Merouani S, Bougriou C. The performance of hydrogen desorption from a metal hydride with heat supply by a phase change material incorporated in porous media (metal foam): Heat and mass transfer assessment. *J Energy Storage*. 2022;51:104449. [[CrossRef](#)].

265. Baldi A, Dam B. Thin film metal hydrides for hydrogen storage applications. *J Mater Chem*. 2011;21(12):4021–6. [[CrossRef](#)].
266. Wang QD, Wu J, Chen CP, Li ZP. An investigation of the mechanical behaviour of hydrogen storage metal beds on hydriding and dehydriding and several methods of preventing the damage of hydride containers caused by the expansion of hydrogen storage metals. *J Less Common Met*. 1987;131(1–2):399–407. [[CrossRef](#)].
267. Ron M, Bershadsky E, Josephy Y. Thermal conductivity of PMH compacts, measurements and evaluation. *Int J Hydrogen Energy*. 1992;17(8):623–30. [[CrossRef](#)].
268. Klein HP, Groll M. Heat transfer characteristics of expanded graphite matrices in metal hydride beds. *Int J Hydrogen Energy*. 2004;29(14):1503–11. [[CrossRef](#)].
269. Zheng X, Kong H, Chu D, Hu F, Wang Y, Yan Y, et al. Stress reduction of a V-based BCC metal hydride bed using silicone oil as a glidant. *Inorganics*. 2022;10(10):167. [[CrossRef](#)].
270. Nnabuife SG, Hamzat AK, Darko CK, Udemu C, Quainoo KA, Yang J, et al. Low-carbon energy storage *via* liquid organic hydrogen carriers: From new developments to global initiatives. *Next Energy*. 2026;11:100533. [[CrossRef](#)].
271. Henseler J, Geißelbrecht M, Tippkötter N, Wasserscheid P. Storage stability in the liquid organic hydrogen carrier system benzyltoluene/perhydro benzyltoluene. *Int J Hydrogen Energy*. 2026;226:154460. [[CrossRef](#)].
272. Geißelbrecht M, Mandon H, Wasserscheid P, Lauterbach L. Bio inspired design principles for next generation liquid organic hydrogen carriers: Bridging molecular biocatalysis and chemical hydrogen storage. *Renew Sustain Energy Rev*. 2026;241:117216. [[CrossRef](#)].
273. Reilly JJ, Johnson JR. The kinetics of the absorption of hydrogen by LaNi_5H_x -*n*-undecane suspensions. *J Less Common Met*. 1984;104(1):175–90. [[CrossRef](#)].
274. Reilly JJ, Johnson JR, Gamo T. The effect of methane on the rate of hydrogen absorption by LaNi_5H_x in liquid suspension. *J Less Common Met*. 1987;131(1–2):41–9. [[CrossRef](#)].
275. Gamo T, Johnson JR, Reilly JJ. The kinetics of the absorption of hydrogen by LaNi_5H_x suspended in aqueous solutions. *J Less Common Met*. 1987;131(1–2):81–8. [[CrossRef](#)].
276. An Y, Chen CP, Xu GH, Cai GM, Wang QD. Study on kinetics of hydrogen absorption by metal hydride slurries I. Absorption of hydrogen by hydrogen storage alloy MmNi_5 suspended in benzene. *J Rare Earths*. 2002;20:113–5. [[CrossRef](#)].
277. Cai GM, Chen CP, An Y, Xu GH, Chen L, Wang QD. Hydrogen absorption thermodynamic properties of rare earth based hydrogen storage alloy in benzene. *J Rare Earths*. 2002;20:28–35. [[CrossRef](#)].
278. Ulmer U, Cholewa M, Diemant T, Bonatto Minella C, Dittmeyer R, Behm RJ, et al. Thermochemical energy storage through de/hydrogenation of organic liquids: Reactions of organic liquids on metal hydrides. *ACS Appl Mater Interfaces*. 2016;8(22):13993–4003. [[CrossRef](#)].
279. Guettel R, Turek T. Comparison of different reactor types for low temperature Fischer–Tropsch synthesis: A simulation study. *Chem Eng Sci*. 2009;64(5):955–64. [[CrossRef](#)].
280. Platzer-Björkman C, Mongstad T, Mæhlen JP, Baldi A, Karazhanov S, Holt A. Deposition of magnesium hydride thin films using radio frequency reactive sputtering. *Thin Solid Films*. 2011;519(18):5949–54. [[CrossRef](#)].
281. Adachi G, Niki K, Nagai H, Shiokawa J. The effect of hydrogen absorption on the electrical resistivities of LaNi_5 and $\text{MmNi}_{4.5}\text{Mn}_{0.5}$ films (Mm = misch metal). *J Less Common Met*. 1982;88(1):213–6. [[CrossRef](#)].
282. Singh SK, Singh AK, Ramakrishna K, Srivastava ON. Investigations on the structural and hydrogenation characteristics of LaNi_5 , HoNi_5 , GdNi_5 , SmNi_5 , MmNi_5 , and $\text{CFMmNi}_{4.5}\text{Al}_{0.5}$ thin films. *Int J Hydrogen Energy*. 1985;10(7–8):523–9. [[CrossRef](#)].
283. Matsuda J, Uchiyama N, Kanai T, Harada K, Akiba E. Effect of Mg/Ni ratio on microstructure of Mg–Ni films deposited by magnetron sputtering. *J Alloys Compd*. 2014;617:47–51. [[CrossRef](#)].
284. Le-Quoc H, Lacoste A, Miraglia S, Béchu S, Bès A, Laversenne L. MgH_2 thin films deposited by one-step reactive plasma sputtering. *Int J Hydrogen Energy*. 2014;39(31):17718–25. [[CrossRef](#)].
285. Ivanov AG, Karpov DA, Chebukov ES, Yurchenkov MI. Investigation of multilayer Ni–Mg–Ni–Mg film structures and development of a prototype of film metal-hydride hydrogen accumulator. *Clean Energy Sci Technol*. 2025;3(3):374. [[CrossRef](#)].

286. Shchelkanov IA, Schmid M, Paul R, Papa F, Stubbers RA, Jurczyk BE. IMPULSE® +Positive Kick™ scalable in-line bipolar HiPIMS for resilient Cr/SiC coatings on accident tolerant nuclear fuels claddings. *Surf Coat Technol.* 2026;519:132971. [CrossRef].
287. Kumar A. Metal Hydride Heat Pumps for Thermal Management of Devices. In: Chemical and materials engineering. Reno, NV, USA: University of Nevada; 2013.
288. Abere MJ, Gallegos RJ, Moorman MW, Rodriguez MA, Kotula PG, Kellogg RA, et al. Normally closed thermally activated irreversible solid state erbium hydrides switches. *Micro Nano Eng.* 2024;23:100243. [CrossRef].
289. Zhang QA, Zhang LX, Wang QQ. Crystallization behavior and hydrogen storage kinetics of amorphous $\text{Mg}_{11}\text{Y}_2\text{Ni}_2$ alloy. *J Alloys Compd.* 2013;551:376–81. [CrossRef].
290. Bu W, Zhang W, Gao J, Qi Y, Zhao D, Zhang Y. Hydrogen storage properties of amorphous and nanocrystalline $(\text{Mg}_{24}\text{Ni}_{10}\text{Cu}_2)_{100-\text{Nd}}$ ($x = 0-20$) alloys. *Int J Hydrogen Energy.* 2019;44(11):5365–73. [CrossRef].
291. Żywczak A, Rusinek D, Czub J, Sikora M, Stępień J, Gondek Ł, et al. Amorphous hydrides of the $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17-x}\text{Co}_x$ nano-powders. *Int J Hydrogen Energy.* 2015;40(45):15534–9. [CrossRef].
292. Li C, Liu J, Li C, Fu X, Li X, Kou S. Research progress on the effect of hydrogen on structure and properties of amorphous alloys. *Rare Met Mater Eng.* 2025;54(10):2660–70. (In Chinese). [CrossRef].
293. Chang Z, Bi W, Ge Y, Xu H, Song Y. The micro-zones characteristics and mechanical properties of Nb-reinforced Zr-based bulk metallic glass composites prepared by selective laser melting. *J Alloys Compd.* 2025;1033:181336. [CrossRef].
294. Pan L, Li Y, Cheng M, Ma S, Duan X, Wada T, et al. Unraveling influence of entropy on thermal stability and glass-forming ability of (Fe, Co)–(Ta)–B amorphous alloys: Insights from local atomic structure simulated by *ab initio* molecular dynamics. *Intermetallics.* 2024;166:108179. [CrossRef].
295. Goo NH, Lee KS. The electrochemical hydriding properties of Mg–Ni–Zr amorphous alloy. *Int J Hydrogen Energy.* 2002;27(4):433–8. [CrossRef].
296. Spassov T, Solsona P, Suriñach S, Baró MD. Nanocrystallization in $\text{Mg}_{83}\text{Ni}_{17-x}\text{Y}_x$ ($x = 0, 7.5$) amorphous alloys. *J Alloys Compd.* 2002;345(1–2):123–9. [CrossRef].
297. QYResearch. Global solid-state hydrogen storage alloy materials sales market report, competitive analysis and regional opportunities 2026–2032. 2026 [cited 2026 Sep 15]. p. 120. Available from: <https://www.qyresearch.com/reports/6123195/solid-state-hydrogen-storage-alloy-materials>.
298. IndexBox. Asia hydrogen storage materials-market analysis, forecast, size, trends and insights. 2026 [cited 2026 Sep 15]. Available from: <https://www.indexbox.io/store/asia-hydrogen-storage-materials-market-analysis-forecast-size-trends-and-insights/>.
299. QYResearch. Metal hydride alloys—Global market share and ranking, overall sales and demand forecast 2025–2031. 2025 [cited 2026 Sep 15]. p. 124. Available from: <https://www.qyresearch.com/reports/4941132/metal-hydride-alloys>.
300. Wang X, Peng P, Witman MD, Stavila V, Allendorf MD, Breunig HM. Technoeconomic insights into metal hydrides for stationary hydrogen storage. *Adv Sci.* 2025;12(21):2415736. [CrossRef].
301. Li M, Liu B. A comprehensive review of China's hydrogen energy industry chain: Technologies, economics, and policy implications. *J Pipeline Sci Eng.* 2026;100431. [CrossRef].
302. Bürger I, Linder MP. H2HP-efficient hydrogen based heat pumps for sector coupling. In: 4TunaTES meets its sisters and brothers—Creating synergies between EU-projects. Messina, Italy: Electronic Library—Blättern nach Dokumentenart; 2025.
303. Muñoz C, Reininghaus N, Puszkil J, Pistor A, Kroener M, Dyck A, et al. Economic dispatch optimization of a metal hydride storage system for supplying heat and electricity in a residential application. *Energy Convers Manag X.* 2026;30:101579. [CrossRef].
304. Krane P, Ziviani D, Braun JE, Jain N, Marconnet A. Techno-economic analysis of metal-hydride energy storage to enable year-round load-shifting for residential heat pumps. *Energy Build.* 2022;256:111700. [CrossRef].
305. QYResearch. Hydrogen storage alloy—Global market share and ranking, overall sales and demand forecast 2026–2032. 2026 [cited 2026 Sep 15]. p. 158. Available from: <https://www.qyresearch.com/reports/5496443/hydrogen-storage-alloy>.
306. Beyazit Nİ. Comparative study of hydrogen storage and metal hydride systems: Future energy storage solutions. *Processes.* 2025;13(5):1506. [CrossRef].

307. Zohra FT, Webb CJ, Gray EM. Degradation of intermetallic hydrogen storage alloys under isochoric thermal cycling: Compressor-like conditions. *J Alloys Compd.* 2026;1059:187087. [[CrossRef](#)].
308. Sheft I, Gruen DM, Lamich G, Mendelsohn MH, Charlson LW, Knox AE, et al. HYCSOS: A chemical heat pump and energy conversion system based on metal hydrides. Argonne, IL, USA: Argonne National Laboratory; 1979. p. 16334.
309. Sheft I, Gruen DM, Lamich GJ, Carlson LW, Knox AE, Nixon JM, et al. Performance characteristics of the hycsos chemical heat pump system based on rare earth transition metal AB5 hydrides. In: *The rare earths in modern science and technology*. Boston, MA, USA: Springer; 1978. p. 17–24. [[CrossRef](#)].
310. Kim KJ, Feldman TK Jr, Lloyd GM, Razani A. Compressor-driven heat pump development employing porous metal hydride compacts. In: *Proceedings of the 1998 ASHRAE Winter Meeting*; 1998 Jan 18–21; San Francisco, CA, USA.
311. Weckerle C, Dörr M, Linder M, Bürger I. A compact thermally driven cooling system based on metal hydrides. *Energies.* 2020;13(10):2482. [[CrossRef](#)].