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ARISTON PUBLICATIONS
EEA Energy & Environment Advances
ISSN: 3066-5728 https://aristonpubs.com/energy-environment-advances https://doi.org/10.69626/eea.2024.0162

REVIEW ARTICLE

Advancement in Magnesium Based Alloys for Hydrogen Storage: A Review

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ABSTRACT: The growing global demand for clean and sustainable energy solutions, driven by the expanding population and developing economies, has highlighted the need to address the environmental impact of fossil fuels. Hydrogen-based fuels have emerged as a promising alternative, offering a pathway to achieving energy sustainability. However, the efficient storage of hydrogen remains a significant challenge in the development of hydrogen-based energy systems. Magnesium alloys have garnered attention as a potential solution due to their high volumetric hydrogen storage capacity, making them particularly suitable for onboard hydrogen storage in applications such as transportation. This review provides an in-depth analysis of magnesium-based hydrogen storage materials, focusing on their fundamental properties, hydrogenation and dehydrogenation mechanisms, and the latest advancements in the field. Magnesium hydride (MgH_2) is highlighted as a key material, known for its high hydrogen content and excellent energy density, although it faces challenges such as slow hydrogenation rates and high temperature and pressure requirements for effective hydrogen absorption. To address these issues, innovative approaches such as Severe Plastic Deformation (SPD) are explored. SPD techniques, which refine the grain structure of magnesium alloys to the nanoscale, have demonstrated the ability to accelerate hydrogenation and dehydrogenation kinetics, improving the overall efficiency of magnesium-based hydrogen storage systems. This review examines the potential of magnesium hydrides in overcoming current limitations and discusses strategies for enhancing their performance. By focusing on material development, surface modification, and new processing techniques, the review underscores the importance of magnesium alloys in advancing hydrogen storage technologies.

Keywords: Hydrogen Storage; Magnesium Alloys; Severe Plastic Deformation.

Received: 08 May 2024; Revised: 21 June 2024; Accepted: 16 July 2024; Published Online: 11 August 2024

1. INTRODUCTION

The exponential growth in energy consumption is propelled by the burgeoning worldwide population, industrialization, and urbanization [1]. Currently, coal, natural gas, and oil make up over 85% of global energy consumption, exacerbating existing political, economic, and environmental challenges like global warming [2]. These fossil fuels are limited in supply, and as they become scarcer, their costs increase. Overcoming the depletion of finite fossil resources is crucial for achieving sustainable energy in the future.

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Renewable energy is becoming more important globally due to its sustainability advantages [2, 3]. The global community is now undergoing a transformative energy transition motivated by the imperative to identify an inexhaustible, sustainable energy source for future energy provision while simultaneously addressing the impacts of climate change. Recent research has explored various renewable energy sources, including nuclear, solar, and wind, to address these challenges [1]. However, wind, solar, and nuclear power face limitations due to weather and geographical factors, preventing them from fully supporting a global green economy. The exceptional environmental advantages and energy efficiency of hydrogen have positioned it as the fuel of the future [3]. Hydrogen, the most plentiful element in the cosmos, can chemically store and generate electrical energy rather than relying on combustion. Its versatility is demonstrated by its usage in many applications, including vehicle propulsion and residential

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heating while producing just heat and water as byproducts [4]. Figure 1 illustrates that hydrogen has a greater energy density per unit mass (120 MJ/kg) compared to gasoline [5].

However, for hydrogen to be practical, it must first be produced economically and then transported and stored in a usable form. Hydrogen does not naturally exist as a free gas and requires an energy source for its production, which can be either renewable or non-renewable, such as fossil fuels, solar, wind, and biomass energy. Anticipated to emerge as a key energy source in the next years, the production of hydrogen from renewable energy sources will be crucial in attaining the 2050 goal of net-zero emissions [5]. The progress of hydrogen applications in industries is greatly dependent on efficient hydrogen storage. Thus, the establishment of a clean hydrogen economy would necessitate the implementation of storage technologies that are both highly efficient and reliable. The storage of hydrogen presents difficulties because of its great flammability and its exceptionally low density (0.082 kg/m³ at STP) [5]. Compressed hydrogen storage carries risks of leakage and explosion. Hydrogen storage systems may be broadly classified into two primary categories: material-based and physical-based. Within the physical-based classification, hydrogen is held in the form of a liquid, cold/cryo-compressed, or compressed gas. Material-based storage can be categorized into two main subgroups: physical sorption (physisorption) and chemical sorption (chemisorption) [6].

The keyword “Magnesium based materials for Hydrogen Storage” was searched in the SCOPUS database under ‘topic’, ‘abstract’, and ‘keywords’ for articles published within a time 10-year time span from 2015 and 2024. The initial search yielded 220 articles. Further the results were refined via "search within results" by applying the keywords “Magnesium Alloys”, and “Severe Plastic Deformation” which resulted in 100 articles respectively. All 100 papers were reviewed to determine their suitability for the scope of the present work. Irrelevant articles were omitted. During this process, it was found that 30 papers had the subject as a major sub-theme. Consequently, 70 papers were removed, resulting in a final sample of 30 items for detailed consideration. Moreover, the network map of co-occurring keywords is displayed in Figure 2 providing an intuitive visualization of the relationships between keywords related to “Magnesium-Based Alloys for Hydrogen Storage”. The size of each node represents the frequency of keyword occurrences, with larger nodes indicating higher occurrence frequency.

Hydrogen is the predominant chemical element found in abundance in the natural world. The International Energy Agency (IEA) has estimated that the worldwide demand for hydrogen as a fuel has significantly grown fourfold since 1975, reaching an annual volume of 70 million tonnes by 2018. In contrast to fossil fuels like coal and oil, green hydrogen is an environmentally friendly energy source that just emits water vapor and does not produce any detrimental by-products in the atmosphere. Since the early 1800s, hydrogen has played a crucial role in modern industry by providing power to automobiles, airships, and spaceships. Given the ongoing global economic shift towards decarbonization, which is an inevitable trend, the significance of hydrogen will persistently increase.

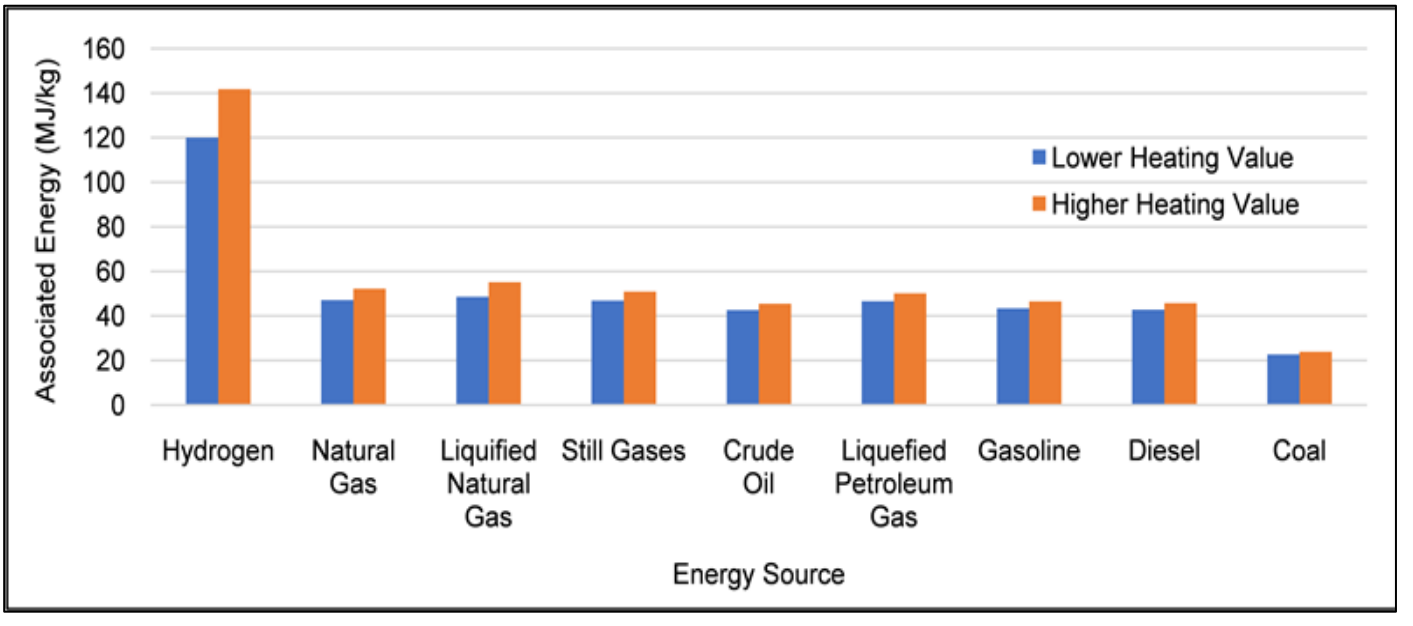

Fig. 1. Comparison of energy associated with different sources. Reprinted with permission from ref. [5], Wei, T.Y., Lim, K.L., Tseng, Y.S. and Chan, S.L.I., 2017. A review on the characterization of hydrogen in hydrogen storage materials. *Renewable and Sustainable Energy Reviews*, *79*, pp.1122-1133. Copyright © Elsevier.

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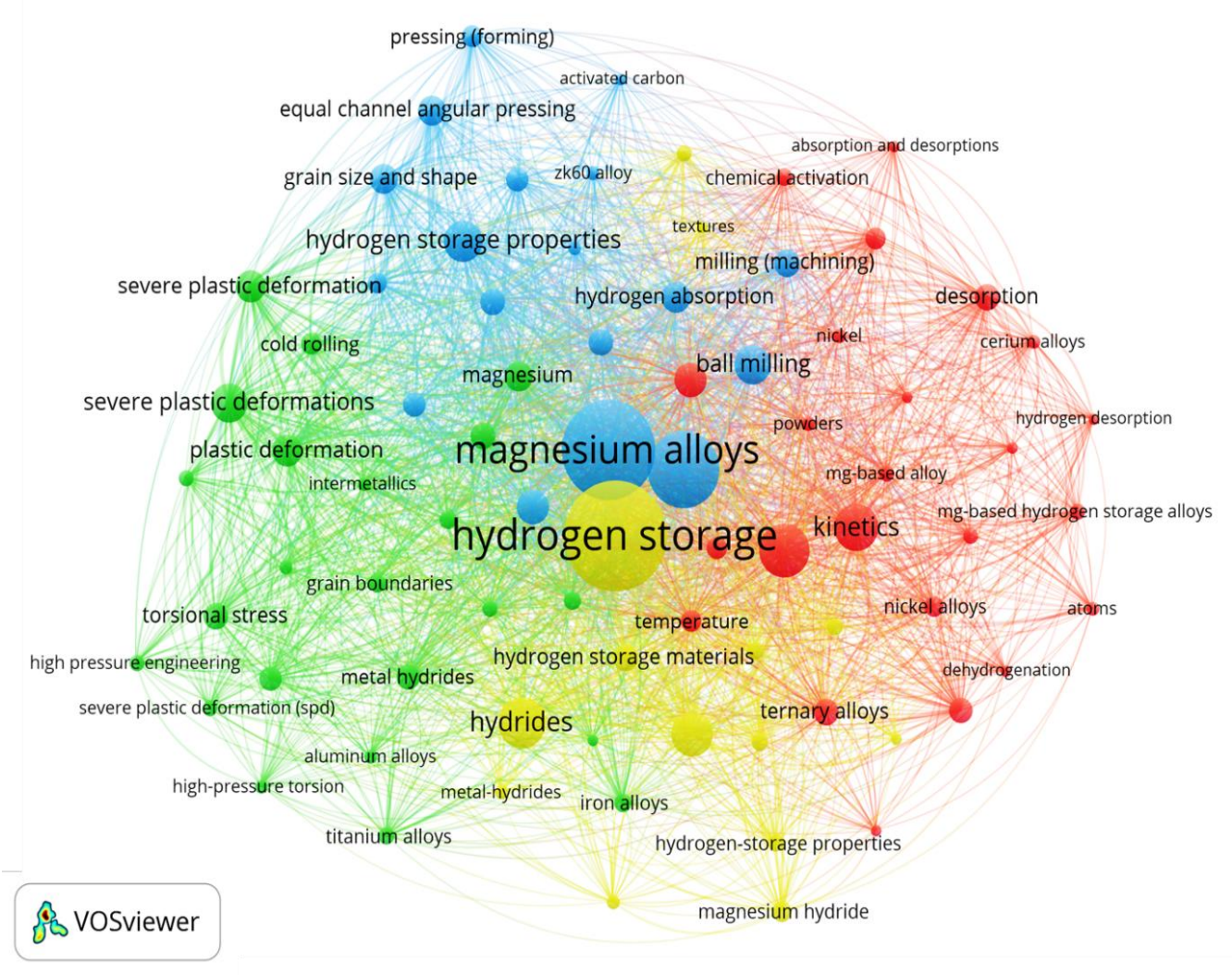

Fig. 2. VOS viewer showing the network of co-occurring keywords.

Furthermore, if the production prices of hydrogen fall by 50% by 2030, as forecasted by the World Hydrogen Council, hydrogen will unquestionably emerge as one of the future fuels. Some of the most notable advantages of hydrogen include:

Completely sustainable: Green hydrogen does not release any harmful gases during its production or combustion.

Easily storable: Hydrogen can be stored effectively, allowing for use beyond the time of synthesis and across various future applications.

Versatile: Green hydrogen can be converted into synthetic gas or electricity, making it suitable for transportation, commercial, and industrial uses.

Hydrogen has many benefits, but challenges related to its production, use, and storage still need to be addressed. The primary method of producing hydrogen is gas reforming, which generates a substantial amount of CO_2. Despite the inadequate efficiency of photocatalysis at present, substantial endeavors are being undertaken to generate hydrogen via the process of water splitting, utilizing renewable energy through electrolysis and photocatalysis. Fuel cells are highly efficient at utilizing hydrogen, but widespread adoption faces several major hurdles, including reducing operating temperatures, developing effective catalysts, and lowering costs. Additionally, there are limitations on how hydrogen can be stored, whether as a solid, liquid, or high-pressure gas.

Due to safety concerns, high-pressure hydrogen storage necessitates specialized tanks that occupy significant space. Although the process of liquefying hydrogen necessitates energy and liquid hydrogen has the tendency to evaporate over time, it offers a convenient, compact means of storage. The optimal and reliable method for storing hydrogen is by using solid-state techniques, namely with metal and complex hydrides. Nevertheless, some hydrides face obstacles such as sluggish kinetics, challenging activation, extensive thermodynamic stability (necessitating elevated working

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temperatures), or limited gravimetric storage capacity. The ideal hydrogen storage system should include the following characteristics [7]: high density of hydrogen by volume and weight, complete reversibility, sufficient safety measures, and feasibility for operation under normal environmental conditions.

At present, hydrogen is stored in three primary forms: compressed gas [8], liquid [9], and solid-state storage using hydrides like metal and complex metal hydrides [10]. Compressed hydrogen is most commonly used [11], but it presents several challenges. First, manufacturing lightweight carbon-fiber tanks is both difficult and costly. Second, the volumetric energy density of compressed hydrogen is significantly lower than that of gasoline. For example, at a pressure of 700 bar, hydrogen has an energy density of only 5.6 MJ/L, whereas gasoline has an energy density of 32.0 MJ/L, which is about 6 times higher[12]. Additionally, compressing hydrogen to 700 bar requires substantial energy, consuming 13 to 18% of the Lower Heating Value (LHV) of hydrogen [12]. The storage of hydrogen in liquid form necessitates a significantly low temperature of -253°C, which is energetically unfavorable. According to theoretical calculations, the energy required for liquefaction is around 10% of the overall energy content. Nevertheless, in typical application, this percentage might increase to 20-30% [13]. Furthermore, the problem of boil-off results in a daily hydrogen loss ranging from 1% to 2%, which needs to be taken into account [14].

By comparison, solid-state storage provides a high attainable volumetric hydrogen density and improved safety, therefore presenting itself as a highly attractive option. The concept of metal-based systems for hydrogen storage dates back to 1866, when Graham first observed the high affinity of hydrogen for Palladium (Pd). Nevertheless, the exploration of metal hydrides for hydrogen storage started in the 1960s. In the realm of hydride systems, magnesium hydride has garnered significant attention owing to its notable volumetric density of 110 kg H/m³ and gravimetric density of 7.6 wt% of hydrogen. The density values of these substances much exceed those of compressed hydrogen, which are calculated to be around 23 kg H/m³ at 350 pressure and 38 kg H/m³ at 700 bar, as well as liquid hydrogen at 71 kg H/m³ [15, 16].

2. PROPERTIES OF MAGNESIUM FOR HYDROGEN STORAGE

Magnesium (Mg) stands out as a promising material for hydrogen storage due to its high hydrogen concentration, remarkable energy density, and unique structural properties. Magnesium can store up to 7.6 wt% hydrogen, which is nearly double the volumetric density of liquid hydrogen [17]. This high storage capacity makes it particularly suitable for applications requiring compact and efficient energy storage, such as onboard hydrogen storage in vehicles. Moreover, the abundance and cost-effectiveness of magnesium enhance its appeal as a sustainable and economical hydrogen storage solution [18]. Magnesium-based hydrides, particularly magnesium hydride (MgH_2), exhibit several functional advantages, including recyclability, reversibility, vibration absorption, and excellent heat resistance. These attributes make MgH_2 a viable candidate for practical hydrogen storage systems. Within the group of reversible hydrides, MgH_2 boasts the highest energy density, measured at 9 MJ/kg, surpassing many other metal hydrides [19]. This makes it an attractive choice for applications that require high energy output and reliability.

The chemical and structural properties of MgH_2 further enhance its suitability for hydrogen storage. The Mg–H bonds in MgH_2 closely resemble ionic hydrides typically found in alkali and alkaline earth metals, giving it a stoichiometric ratio of approximately 0.99 ± 0.01 for H/Mg [20]. Under standard conditions, MgH_2 exists in the α-MgH_2 phase with a tetragonal rutile crystal structure. This phase, while stable, can transition into two other polymorphs under high-pressure conditions: γ-MgH_2, which adopts an orthorhombic structure, and β-MgH_2, which has a hexagonal structure [21]. These polymorphic transformations provide MgH_2 with versatility in various operating conditions and environments.

Despite its numerous advantages, MgH_2 faces certain challenges in practical applications. The slow hydrogenation and dehydrogenation reaction rates, coupled with the high temperatures (350–400°C) and pressures (over 3 MPa) required for effective hydrogen absorption, present significant barriers [22]. Surface oxidation of magnesium (forming MgO) when exposed to air further hinders its ability to absorb hydrogen efficiently. Addressing these challenges requires advanced activation procedures to remove the oxide layer and enhance the hydrogenation process. Iterative cycling of heating and cooling in a hydrogen atmosphere or vacuum is often employed to activate magnesium and improve hydrogen absorption.

The potential of MgH_2 in hydrogen storage extends beyond its basic properties. Magnesium-based materials have demonstrated unique capabilities in structural and functional integration, making them ideal for next-generation hydrogen storage technologies. For instance, the MgH_2 phase's formation and stability are influenced by factors such as hydrogen pressure and thermodynamic stimuli, which can be optimized for specific applications. Additionally, the development of novel fabrication techniques, such as Severe Plastic Deformation (SPD), can refine magnesium's grain structure to nanoscale dimensions. This refinement accelerates hydrogenation and dehydrogenation kinetics, significantly improving the overall performance of magnesium-based hydrogen storage systems.

The unique properties of magnesium and magnesium hydride, combined with ongoing advancements in material processing and activation methods, position Mg as a key material in the development of efficient, sustainable, and cost-effective hydrogen storage technologies. With continued research and innovation, MgH_2 has the potential to play a central role in the transition to hydrogen-based energy

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systems.

3. PREPARATION OF Mg HYDRIDE

The preparation of magnesium hydride (MgH_2) has undergone significant evolution since its first reported synthesis, reflecting the progression of experimental techniques and material understanding. Researchers documented the earliest synthesis of MgH_2 through the pyrolysis of ethyl magnesium iodide under vacuum conditions at 448 K. While this method was groundbreaking for its time, it lacked scalability and practicality. The direct production of MgH_2 from its elemental components was not achieved until 1951 when Wiberg et al. [24] accomplished this feat under highly controlled conditions, achieving a modest yield of only 68%. These stringent conditions highlighted the complexity of magnesium hydride synthesis, especially when aiming for higher yields and purity.

Subsequent progress was made by Dymova and colleagues [25], who succeeded in producing MgH_2 with an impressive purity of 97–98%. This represented a considerable improvement in synthesis efficiency and laid the groundwork for further innovations. In 1984, Bogdanovic [26] introduced an alternative method based on homogeneous catalysis. This two-step process involved dissolving metallic magnesium into a soluble state, followed by its reaction with gaseous hydrogen in the presence of catalysts such as $CrCl_3$ or $TiCl_4$. While this approach was effective in producing MgH_2, it also generated soluble contaminants, which posed challenges for the purity and practical application of the product. The breakthrough in achieving pure MgH_2 came with the adoption of mechano-chemical activation techniques. This approach involves milling magnesium under a controlled atmosphere, thereby inducing solid-phase processes that enhance hydrogen absorption and reaction kinetics. The mechanical milling process significantly increases the surface area of the material, introduces lattice defects, and creates micro-stresses within the crystal structure, all of which contribute to improved hydrogenation properties [27, 28]. Unlike earlier methods, mechano-chemical activation enables the hydrogenation of magnesium at ambient temperatures without the need for additional heat, making it more energy-efficient and practical.

One of the critical advantages of this method is its ability to form novel nucleation sites, which facilitate the initiation of the hydrogenation process. These sites enable a more uniform and efficient distribution of hydrogen within the magnesium matrix. Additionally, mechanical milling promotes enhanced diffusion of hydrogen atoms across the material's layers, ensuring a more complete conversion to MgH_2 [29]. This technique has also been instrumental in overcoming one of the significant challenges in MgH_2 preparation: the sluggish hydrogenation kinetics and high activation energy required for hydrogen dissociation on the magnesium surface.

The development of mechano-chemical activation has not only improved the quality and yield of MgH_2 but has also made it possible to tailor the material's properties for specific applications. By controlling the milling parameters, such as time, pressure, and atmosphere, researchers can optimize the material's microstructure and hydrogen storage capacity. Furthermore, the incorporation of catalytic additives during the milling process has been shown to enhance the hydrogenation and dehydrogenation rates, making MgH_2 a more viable candidate for practical hydrogen storage systems. The preparation of MgH_2 has advanced from early, rudimentary methods to highly refined techniques like mechano-chemical activation. These advancements have significantly improved the material's purity, yield, and hydrogen storage performance, addressing many of the challenges that hindered its early development. The ongoing refinement of these methods continues to hold promise for the widespread adoption of MgH_2 in hydrogen storage applications, particularly in sectors requiring lightweight, high-capacity storage solutions such as transportation and renewable energy systems.

4. CONSTRAINTS OF MgH_2 FOR PRACTICAL APPLICATION

The use of magnesium hydride (MgH_2) for hydrogen storage presents notable challenges that hinder its practicality in many applications. Although MgH_2 exhibits promising hydrogen storage properties, such as a high hydrogen concentration and reversibility, its real-world application is constrained by significant drawbacks. These limitations are primarily related to its slow hydrogenation and dehydrogenation reaction rates and the elevated temperatures and pressures required for these processes to occur efficiently. Specifically, MgH_2 only functions effectively at temperatures between 350 and 400°C and hydrogen pressures exceeding 3 MPa, which are impractical for many onboard and commercial storage systems.

One of the primary obstacles to the efficient hydrogenation of magnesium is the formation of a surface oxide layer (MgO) when magnesium is exposed to air. This oxide layer acts as a barrier, preventing hydrogen molecules from interacting with the magnesium surface and initiating the hydrogenation process. To overcome this issue, an activation procedure is required to remove or disrupt the MgO layer. Common activation techniques involve repeated cycles of heating and cooling under a hydrogen atmosphere or vacuum. However, these processes are energy-intensive and time-consuming. Even after extensive activation, magnesium still requires temperatures around 400°C and prolonged reaction times to achieve complete hydride formation. This reliance on high-temperature conditions presents a significant drawback for practical hydrogen storage applications, especially those requiring rapid and efficient cycling.

Another critical factor that slows the hydrogenation process is the sluggish dissociation rate of hydrogen

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molecules on the surface of magnesium. For hydrogen molecules to be absorbed, they must first dissociate into atomic hydrogen—a process that demands considerable energy. Even after dissociation, the hydrogen atoms face additional challenges in penetrating the magnesium matrix. The interaction between hydrogen atoms and magnesium involves a high activation energy barrier, which further delays the formation of MgH_2. Consequently, the overall hydrogen absorption rate remains low, limiting the efficiency of the storage system.

The hydrogen pressure also plays a pivotal role in the kinetics of MgH_2 formation. Higher hydrogen pressures provide greater thermodynamic driving forces for the reaction, but even under these conditions, the process is not without complications. During the initial stages of hydrogenation, a surface layer of MgH_2 forms rapidly. This layer, while indicative of progress, acts as a diffusion barrier for subsequent hydrogen absorption. The dense MgH_2 surface layer inhibits hydrogen molecules from migrating deeper into the magnesium core, effectively stalling further hydride formation. This phenomenon necessitates hydrogen diffusion at the interface between magnesium and the newly formed MgH_2, a process that is inherently slow. As a result, the advancement of the MgH_2 phase becomes progressively sluggish, posing a significant bottleneck in the hydrogenation process. Additionally, the dehydrogenation of MgH_2 is equally challenging. Releasing hydrogen from the hydride requires reversing the reaction under similarly high temperatures and pressures. The slow kinetics of hydrogen desorption further complicate the cycling process, making MgH_2 unsuitable for applications demanding rapid hydrogen release, such as fuel cells or onboard vehicle storage systems.

Researchers have identified several approaches to mitigate these constraints, but each solution introduces its own set of challenges. For instance, the use of catalysts, such as transition metals, can enhance the dissociation rate of hydrogen molecules and reduce the activation energy required for hydrogen absorption and desorption. However, the inclusion of catalysts increases material costs and may introduce additional complexities in material preparation and long-term stability. Alloying magnesium with other elements, such as nickel or aluminum, has also been explored to improve hydrogenation kinetics and lower operational temperatures. While these strategies show promise, they often result in reduced hydrogen storage capacity, which diminishes one of the key advantages of MgH_2. Another potential solution is the application of nanostructuring techniques, such as severe plastic deformation or ball milling, to produce magnesium powders with nanoscale grains. These methods increase the surface area and introduce defects into the crystal lattice, providing more nucleation sites for hydrogen absorption. Nanostructuring also improves hydrogen diffusion within the material, addressing the issue of surface layer impedance. Despite these benefits, nanostructured magnesium hydrides are challenging to produce at scale, and their stability over multiple hydrogenation-dehydrogenation cycles remains a concern. While magnesium hydride exhibits exceptional potential as a hydrogen storage material, its practical application is constrained by slow reaction kinetics, high operational temperatures and pressures, and diffusion limitations caused by surface oxidation and MgH_2 layer formation. Although various strategies, such as catalysis, alloying, and nanostructuring, offer potential pathways to address these issues, further research and development are required to overcome the inherent challenges. Achieving a balance between improving performance, maintaining storage capacity, and ensuring scalability will be critical for realizing the widespread adoption of MgH_2 in hydrogen storage technologies.

5. THERMODYNAMIC AND KINETIC PROPERTIES

Magnesium, with lattice parameters "a = b = 0.32094 nm and c = 0.52112 nm", belongs to a hexagonal system (P63/mmc) and can combine with H_2 to form MgH_2. Magnesium hydride is an ionic compound existing in three structural types: "α-MgH_2", "β-MgH_2", and "γ-MgH_2", with hydrogen present as H^- ions. In the hexagonal close-packed (hcp) α phase, magnesium first undergoes hydrogen absorption to generate an interstitial solid solution. The tetragonal β-MgH2 phase is formed upon further hydrogenation, which can then convert into a metastable orthorhombic γ phase when subjected to substantial compressive stress. A combination of β and γ phases can be obtained by processing at 293 K and 8 GPa for one hour, with the γ phase reverting to the β phase upon heating to 623 K. Both phases share the same packing type and coordination number, though the β phase has a straight hydrogen chain, whereas the γ phase forms a zigzag octahedral chain around a magnesium atom. The most common phase upon hydrogenation of magnesium is β-MgH_2, a tetragonal system "(P42/mmc, a = b = 0.45170 nm, c = 0.30205 nm)".

Pressure-concentration-temperature (PCT) plots show the thermodynamics of hydride formation in Figure 3. At the thermodynamic level, the Mg/MgH_2 system exhibits reversibility in both hydrogenation and dehydrogenation processes. The kinetic process of the Mg/MgH_2 system can be categorized into four primary stages: Adsorption and dissociation of H_2 molecules on the magnesium surface; diffusion of H atoms into the solid-state interface; formation of a Mg-H solid solution (α phase); and conversion of this solid solution into MgH_2 (β phase) as H concentration reaches saturation.

The process of hydrogen sorption has a modest energy demand, usually ranging from 1 to 10 kJ mol^{-1}. Nevertheless, the energy threshold for dissociation is considerably greater, reaching a maximum of 432 kJ mol^{-1}. The high dissociation energy arises from the incapacity of magnesium to offer d-orbitals for the interaction with the antibonding H molecular orbital, therefore inhibiting the dissociation of H_2 on the magnesium surface. Furthermore, the surface of magnesium readily undergoes oxidation, which impedes the dissociation

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and diffusion of H_2. One further constraint is the minimal rate at which hydrogen atoms dissociate in magnesium and magnesium hydroxide (4.5×10^{-13} and 1.5×10^{-16} m^2 s^{-1}, respectively).

6. HYDROGENATION AND DEHYDROGENATION MECHANISMS

A crucial factor to take into account when choosing a hydrogen storage system is the kinetic characteristics of the material. Obtaining rapid rates of hydrogenation and dehydrogenation is essential for many hydrogen storage materials, such as MgH_2. In their study, Pedersen et al. [30] found that magnesium has the ability to absorb 6.4 wt.% hydrogen at 363°C when subjected to a pressure of 22.7 bar of H_2 for 1500 seconds. They also discovered that magnesium can release around 6.0 wt.% hydrogen at 390°C when subjected to a pressure of 1.5 bar of H_2 for 500 seconds. The reversible hydrogen storage capacity of MgH_2 is influenced by several parameters, such as material fabrication techniques, operational parameters, and the incorporation of additives [31]. During hydrogenation at 375°C at 40 bar H_3 pressure and dehydrogenation at 350°C under vacuum circumstances, about 75% of the theoretical capacity of pure magnesium is attained. However, after 70 cycles, the hydrogen storage capacity diminishes to 70% of the maximum value predicted by theory [30]. The activation energy and rate-limiting stages play a crucial role in the hydrogenation and dehydrogenation processes of Mg/MgH_2.

An energy input, referred to as activation energy (Ea), is required to commence these processes. Two commonly utilized approaches for estimating the activation energy (Ea) are often employed to evaluate this process:

Kissinger Method [32]:

This approach employs calorimetric measurements for calculating activation energy (Ea). The equation employed is:

$$\ln \frac{\beta}{T_{max}^{\ 2}} = \frac{E_a}{RT_{max}} + \ln \frac{AR}{E_a} \quad (1)$$

Where, β is the heating rate, Tmax is the peak temperature in the calorimetric curve, A is the pre-exponential factor, and R is the gas constant.

Arrhenius Equation [33]:

This method determines the rate constant (k):

$$k = A.\mathrm{e}^{\left(\frac{-E_a}{RT}\right)}.\ln\left(\frac{p}{p_{eq}}\right) \quad (2)$$

Where, A is the pre-exponential factor, p is the pressure, $_{eq}$ is the equilibrium pressure, T is the temperature.

Experimental studies have demonstrated a broad spectrum of activation energy values for MgH_2/Mg, ranging from 90 to 130 kJ/mol for absorption and from 120 to 195.3 kJ/mol for desorption [34-36]. Fernandez et al. [34] documented an electrochemical activation energy (Ea) of 160 ± 10 kJ/mol for desorption and 90 ± 10 kJ/mol for absorption.

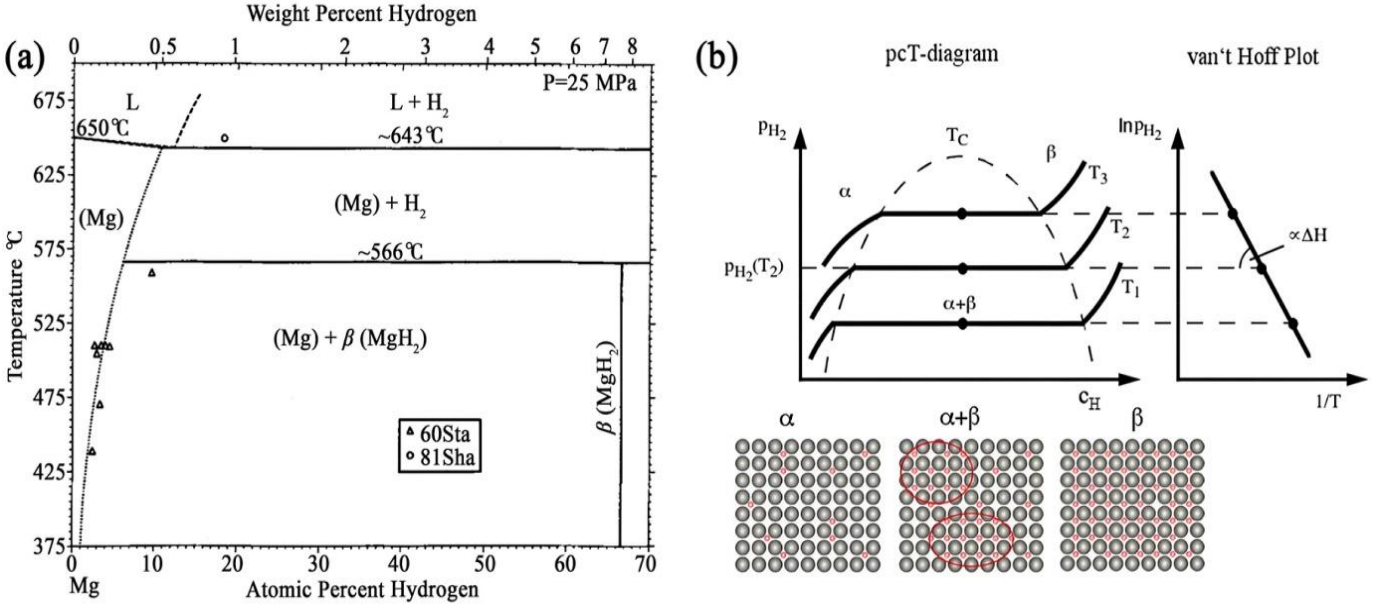

Fig. 3. Schematic PCT diagram and corresponding Van't Hoff plot. Reprinted with permission from ref. [56], Dornheim, M. **2011**. Thermodynamics of Metal Hydrides: Tailoring Reaction Enthalpies of Hydrogen Storage Materials', in *Thermodynamics - Interaction Studies - Solids, Liquids and Gases* (Ed. Juan Carlos Moreno-Pirajan), IntechOpen. Copyright © IntechOpen.

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The activation energies (E_a) of MgH_2 are also affected by the particle size, in which smaller particles exhibit lower values. This benefit, however, decreases over time as a result of particle coarsening. The processes of hydrogenation and dehydrogenation include several stages, including surface reactions, diffusion, and phase formation. The total reaction kinetics are determined by the slowest step, which, in the case of hydrogen absorption in Mg, is the diffusion process through the surface layer of $MgO/Mg(OH)_2$ and then through the second layer of MgH_2. An oxide layer serves as a barrier, impeding hydrogenation, however, this may be reduced by altering microstructures or including additives. The formation of MgH_2 exacerbates the obstruction of hydrogen transport by virtue of its inferior diffusion coefficient in comparison to Mg.

7. ENHANCEMENTS IN MAGNESIUM-BASED HYDROGEN STORAGE BY SEVERE PLASTIC DEFORMATION

Diverse approaches have been investigated to surmount the thermodynamic and kinetic obstacles in magnesium-based hydrogen storage materials. These methods encompass the alloying of magnesium, the development of composites, the integration of catalysts, and the modification of the microstructure. Within the last twenty years, processing methods like severe plastic deformation (SPD), initially proposed by Skripnyuk et al. [37], have demonstrated their efficacy in enhancing the kinetics and thermodynamics of hydrogen storage in magnesium-based compositions. Severe Plastic deformation (SPD) causes substantial distortion in materials, resulting in the creation of bulk products with very small or nanograins and a high concentration of crystal lattice defects. Equal-channel angular pressing (ECAP) [38], high-pressure torsion (HPT) [39], and friction stir processing (FSP) [40, 41] are the most often utilized SPD procedures. Additionally, there is increasing interest in using conventional methods like shot peening, fast forging, and intensive rolling to apply severe strain to hydrogen storage materials. The formation of a compact arrangement of grain boundaries and crystal lattice defects by SPD leads to an improvement in hydrogen transport, thereby enhancing the kinetics of hydrogenation. In contrast to ball milling, which generates hydrogen storage materials in powder form with extensive surface areas, SPD techniques yield bulk materials with reduced surface areas, resulting in enhanced activation and heightened resistance to oxidation. Moreover, ultra-SPD methods, which generate very high shear stresses, have the capability to produce a variety of magnesium-based hydrogen storage materials.

HPT is a well-regarded deformation method that is particularly successful in producing significant and uninterrupted stresses at high pressure. This makes it very efficient in the process of refining microstructures and introducing flaws in magnesium-based materials. By contrast, techniques such as ECAP and intense rolling, which include repeated cycles and intermittent straining, yield less substantial microstructure refinement and strain in comparison to HPT. Nevertheless, these methods are more appropriate for the production of longer fragments of hydrogen storage materials, therefore conferring them with advantages for commercial applications. Although fast forging may generate significant strain in a single cycle, it typically produces a lower degree of strain and grain refinement compared to HPT.

7.1. Equal-channel angular pressing (ECAP)

ECAP is a key method among SPD procedures for improving the hydrogen storage characteristics of magnesium alloys. ECAP is a highly utilized approach for SPD and was the first to be acknowledged for its efficacy in enhancing the hydrogenation kinetics of magnesium alloys [42]. This procedure involves subjecting a rod or bar-shaped billet to iterative compression via a channel at a bending angle, resulting in the introduction of simple shear strain. The ECAP process is renowned for its ability to achieve significant grain refinement, frequently reaching the submicron scale, in magnesium and related alloys.

The initial success of ECAP in enhancing hydrogen absorption and desorption was demonstrated with the magnesium-based ZK60 alloy "Mg-4.95Zn-0.71Zr", a widely used material for structural purposes [37]. Additional improvements in dehydrogenation kinetics were reported for the ZK60 alloy processed with different ECAP setups. ECAP significantly reduces particle size, bringing it down to submicron levels during hydrogenation and dehydrogenation. While some studies combined ECAP with methods like cold rolling or accumulative roll bonding (ARB), these combinations were less effective compared to using ECAP alone.

Experimental studies have demonstrated that ECAP is as effective as or even more effective than traditional ball milling in enhancing hydrogenation kinetics. Ball-milled ZK60 exhibited a hydrogenation curve that was comparable to, but somewhat lower than, that of the ECAP-processed alloy. An important benefit of ECAP is its capacity to manufacture large quantities of hydrogen storage materials, therefore circumventing the hazards traditionally connected with the manipulation of ball-milled powders. A multitude of investigations have employed ECAP and other SPD methods to treat different magnesium-based alloys, such as the eutectic $Mg_{89}Ni_{11}$ alloy with a refined lamellar structure [43], showcasing its capacity to enhance the kinetics of hydrogenation and dehydrogenation. An effective strategy for further improving this kinetics is to develop composites that include metal hydrides or carbon-based particles. Research conducted on a magnesium-based composite including 2 wt% multiwall carbon nanotubes, which was treated by ECAP, shown that the inclusion of nanotubes greatly enhances the rate of hydrogen desorption [44]. Furthermore, this approach eradicates pressure hysteresis. ECAP, being one of the first technologies employed to

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improve hydrogenation kinetics in Mg-based alloys, continues to be a feasible choice for the development of large-scale hydrogen storage systems. Figure 4 depicts the impact of ECAP on the kinetics of dehydrogenation.

7.2. High Pressure Torsion

HPT is a very efficient approach among bulk SPD techniques for producing various hydrogen storage materials. This is because HPT can apply very high shear strain to bulk samples [39]. In HPT, a disc-shaped sample is placed between two anvils and exposed to intense uniaxial pressure, frequently exceeding several GPa's, as well as torsional strain caused by repeated rotations. This approach has been extensively employed on materials based on magnesium.

When MgH_2 powders are processed using HPT, they undergo substantial grain refinement, develop a pronounced (002) texture, and form a metastable γ-MgH_2 phase, all of which enhance overall hydrogen storage performance [45, 46]. Both particle and grain size are critical factors in hydrogen absorption kinetics, and HPT has been demonstrated to improve hydrogenation kinetics by creating a bimodal microstructure that includes both nanocrystals and larger recrystallized grains.

In commercially processed magnesium via HPT, the dislocation density reaches a high level of 10^{15} m^{-2}, providing effective sites for hydrogen transport [47]. For ZK60 Mg-based alloys processed with HPT, the hydrogen storage capacity remains stable for up to 100 hydrogenation cycles [48]. Additionally, ball-milled Mg-Ni nanopowders show a 50% increase in maximum hydrogen capacity after HPT processing, reaching theoretical limits as a result of the creation of additional hydrogen transport sites in close proximity to dislocations [49]. Stacking faults and other lattice defects significantly improve the hydrogenation kinetics in Mg_2Ni when subjected to HPT processing. Fractures in ultrafine Mg+ 2 Wt% nickel powder provide routes for hydrogen to pass through the surface of discs produced using HPT. This method can stimulate the absorption of hydrogen in the $MgNi_2$ phase, which previously exhibited negligible hydrogen absorption. Furthermore, HPT is advantageous in the development of novel magnesium-based composites or alloys for hydrogen storage. A powder combination consisting of Mg + 5 wt% Ni + 2 wt% Nb2O5 has a satisfactory hydrogenation capability when subjected to high-pressure thermal treatment at a temperature of 423 K [50], as shown in Figure 5.

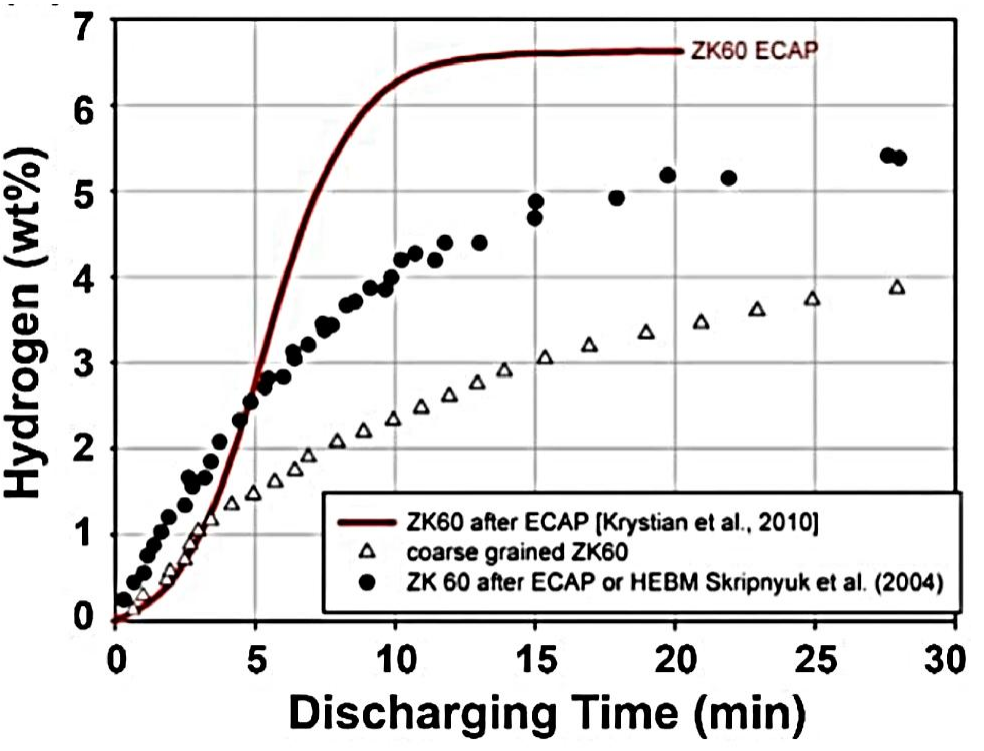

Fig. 4. Dehydrogenation kinetics of the ZK60 alloy processed through various methods: ECAP (shown by triangles) [37], ECAP combined with high-energy ball milling (shown by filled circles) [57], and ECAP using a different route (shown by red curve) [37]. Reprinted with permission from ref. [37], Skripnyuk, V.M., Rabkin, E., Estrin, Y. and Lapovok, R., 2004. The effect of ball milling and equal channel angular pressing on the hydrogen absorption/desorption properties of Mg–4.95 wt% Zn–0.71 wt% Zr (ZK60) alloy. *Acta Materialia*, *52*(2), pp.405-414. Copyright © Elsevier, and Ref. [57], Krystian, M., Zehetbauer, M.J., Kropik, H. et al. (2011) 'Hydrogen storage properties of bulk nanostructured ZK60 Mg alloy processed by Equal Channel Angular Pressing', *Journal of Alloys and Compounds*, 509, S449–S455. Copyright © Elsevier.

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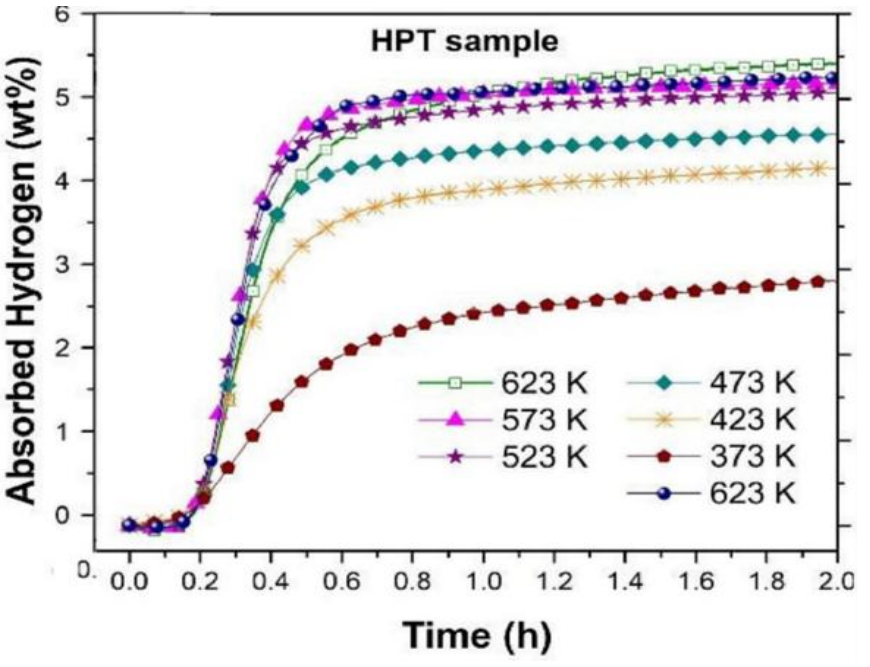

Fig. 5. Hydrogenation curves at different temperatures for Mg + 5 wt% Ni + 2 wt.% Nb_2O_5 powder composite processed by HPT. Reprinted with permission from ref. [50], Osorio-García, M., Suárez-Alcántara, K., Todaka, Y., Tejeda-Ochoa, A., Herrera-Ramírez, M., Hernández-Silva, O., Cruz-Gandarilla, F. and Cabañas-Moreno, J.G., 2021. Low-temperature hydrogenation of Mg-Ni-Nb_2O_5 alloy processed by high-pressure torsion. *Journal of Alloys and Compounds*, *878*, p.160309. Copyright © Elsevier.

The integration of ball milling with high-pressure machining (HPT) enhances the rate at which nanocrystalline magnesium is produced, facilitated by Nb2O5 and/or carbon nanotubes. These nanotubes stay undamaged during both plastic deformation and hydrogen transport cycles [51]. The catalytic properties of metal-oxide particles and carbon nanotubes can be augmented by utilizing metal-oxide nanotubes in isolation. Although HPT has potential for a wide variety of materials, its present constraint is the limited sample sizes it generates, which presents difficulties for expanding to commercial applications.

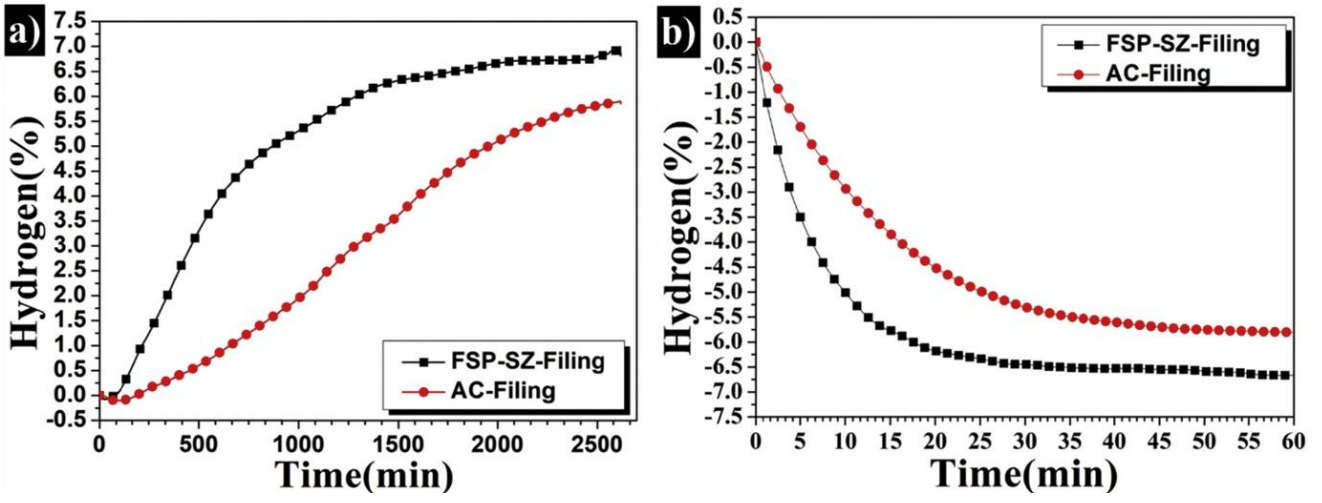

Fig. 6. Kinetic curves for the filings from the AC and SZ samples include: (a) activation, (b) initial desorption. Reprinted with permission from ref. [55], Silva, E.P.D., Leiva, D.R., Pinto, H.C., Floriano, R., Neves, A.M. and Botta, W.J., 2018. Effects of friction stir processing on hydrogen storage of ZK60 alloy. *International Journal of Hydrogen Energy*, *43*(24), pp.11085-11091. Copyright © Elsevier.

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7.3. Friction Stir Processing

FSP is an SPD method that efficiently generates precisely refined and homogenous microstructures, alters alloys, and develops nanocomposites [52]. The process does this by subjecting the material to high temperatures, and significant strain. During FSP, a rotating tool with proper geometry is employed to incise material and move it in the intended direction [53], which leads to grain refinement in the stirred zone (SZ) due to SPD. The base metal (BM) zone, meanwhile, remains essentially unaltered. The enhanced microstructure across the SZ region enhances the mechanical characteristics of materials being processed. [54].

Silva et al. [55], reported that FSP of the ZK60 alloy causes significant grain refinement and full recrystallization, resulting in a nanostructure that is randomly oriented. The grain size has decreased from more than 150 µm to around 1-2 µm, including the fragmentation of intermetallic phases. The reinforcement filings from the FSP-SZ area exhibit significantly enhanced hydrogenation kinetics. Specifically, during the activation phase, they assimilate approximately 6.3 wt% hydrogen during a 24-hour period, whereas filings from the as-cast alloy absorb 3.5 wt%. FSP further improves the rate at which hydrogen is absorbed in the first and second cycles, achieving a 5.0 wt% absorption in precisely 10 minutes. Furthermore, the rate of desorption is doubled in SZ files as compared to as-cast filings. Figure 6 illustrates the kinetic characteristics of hydrogen absorption and desorption for filings derived from both as-cast (AC) and SZ samples. Panels (a) and (b) display the kinetics curves for activation (initial absorption) and desorption, respectively. FSP technique is an economical approach for treating magnesium alloys, resulting in a refined microstructure characterized by evenly distributed intermetallic phases and the absence of oxides and inclusions. Furthermore, the incorporation of reinforcement particles results in further improvements in hydrogen storage characteristics, mostly attributed to the fragmentation of intermetallics and the enlarged surface area.

8. CONCLUSION

Magnesium-based alloys are promising candidates for hydrogen storage, owing to their high volumetric capacity and eco-friendliness. However, practical challenges such as slow hydrogenation-dehydrogenation rates, high operating temperatures, and susceptibility to surface oxidation limit their broader application. Research has shown that severe plastic deformation (SPD) techniques, including Equal Channel Angular Pressing (ECAP), High-Pressure Torsion (HPT), and Friction Stir Processing (FSP), significantly enhance the performance of magnesium hydrides. These techniques produce ultrafine grain structures and induce crystal lattice defects, leading to faster hydrogen absorption/desorption rates, improved activation, and better cyclic stability. Furthermore, advancements in preparation techniques, such as mechano-chemical activation, have enabled hydrogenation at ambient temperatures by enhancing surface properties and promoting diffusion. Despite these advancements, achieving practical applicability requires overcoming thermodynamic and kinetic barriers. For instance, reducing the temperature and pressure requirements for hydrogenation while maintaining material stability remains a priority. Surface oxidation, a persistent issue, demands effective protective strategies to maintain magnesium's reactivity over extended use. Additionally, scalable and cost-effective fabrication techniques are essential for transitioning magnesium-based hydrogen storage systems from research to commercial applications. By addressing these challenges, magnesium-based materials could play a transformative role in advancing hydrogen storage technologies, supporting the global shift toward clean and sustainable energy systems.

9. Future Directions

The future of magnesium-based hydrogen storage systems hinges on overcoming current limitations related to material stability, kinetics, and scalability. Research efforts should focus on several key areas to make these materials more practical and efficient for large-scale applications.

Material Stabilization and Surface Modifications: One of the critical challenges for magnesium-based hydrogen storage is the tendency of magnesium to oxidize, which significantly reduces its reactivity and hydrogen absorption efficiency. Future research should focus on developing advanced coating technologies or surface treatments that protect magnesium from oxidation while enhancing its hydrogen absorption capacity. Protective coatings, such as carbon-based layers or metal oxide films, could prevent the formation of the magnesium oxide layer, thus facilitating more efficient hydrogenation. Additionally, introducing alloying elements like rare earth metals, which improve the oxidation resistance and thermal stability of magnesium, may provide a viable solution.

Enhancing Hydrogenation Kinetics: Magnesium hydrides typically exhibit slow hydrogenation and dehydrogenation rates, especially at lower temperatures and pressures. To address this, research could focus on optimizing the grain size and crystal structures of magnesium-based alloys. The application of Severe Plastic Deformation (SPD) techniques such as Equal Channel Angular Pressing (ECAP) and High-Pressure Torsion (HPT) has already shown promise in refining the microstructure of magnesium hydride, improving hydrogenation kinetics. However, further exploration into hybrid methods combining SPD with other mechanical or chemical activation techniques could further enhance these properties. For example, using catalysts in conjunction with SPD processes might promote faster dissociation of hydrogen molecules at the magnesium surface, improving the overall hydrogenation and dehydrogenation rates.

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Alloying and Composite Materials: Developing new magnesium alloys or composite materials is another promising direction. Magnesium hydride can benefit from alloying with metals such as aluminum, zinc, or calcium, which could modify the thermodynamic properties of magnesium, lowering the temperature and pressure requirements for hydrogen absorption. Composite materials that combine magnesium with other hydride-forming elements, such as lithium or sodium, could also be explored to create more efficient and stable hydrogen storage systems. Additionally, integrating magnesium hydrides with carbon nanotubes, graphene, or other advanced nanomaterials could enhance the overall hydrogen storage capacity and improve the mechanical properties of the material.

Optimizing the Hydrogen Storage Cycle: Improving the cycle life of magnesium-based hydrogen storage systems is essential for their commercial viability. Research should focus on enhancing the long-term stability of magnesium hydrides under repeated hydrogenation and dehydrogenation cycles. Investigating the effects of repeated cycling on the material's microstructure, hydrogen absorption kinetics, and overall performance could provide insights into minimizing degradation. Furthermore, developing efficient methods for reactivating or regenerating spent magnesium hydride could extend its lifetime and reduce operational costs.

Lowering Operating Temperatures and Pressures: To make magnesium-based hydrogen storage more practical, reducing the high temperatures and pressures required for hydrogenation is crucial. Future research could explore methods to lower the activation energy for hydrogen absorption, possibly by using catalytic materials, modifying the alloy composition, or introducing novel chemical processes. Reducing the operating conditions of magnesium hydride systems could lead to more energy-efficient and cost-effective storage solutions, making them suitable for applications such as automotive or portable energy storage systems.

Scalable Fabrication Techniques and Cost-Effectiveness: As magnesium-based hydrogen storage technologies advance, scaling up the production of magnesium hydride materials will be essential for commercial application. Developing cost-effective manufacturing techniques, such as large-scale SPD or roll-to-roll processing, will be crucial for meeting market demands. Additionally, integrating cost analysis and lifecycle assessments into the development process will ensure that these materials are economically competitive with other energy storage systems. Reducing the cost of raw materials, energy consumption during processing, and material waste will be key to improving the overall feasibility of magnesium-based hydrogen storage technologies.

Environmental Impact and Sustainability: Alongside performance improvements, the environmental impact of magnesium-based hydrogen storage systems should be considered. Future research should include comprehensive lifecycle assessments to evaluate the environmental footprint of these materials, including the mining, production, and disposal stages. The goal will be to ensure that magnesium-based hydrogen storage technologies are not only efficient but also sustainable, minimizing their ecological impact throughout their lifecycle. Additionally, recycling strategies for magnesium hydride materials should be developed to ensure that used materials can be reused or repurposed, reducing the overall demand for raw magnesium.

Integration with Renewable Energy Systems: The ultimate goal of hydrogen storage technologies is to integrate them with renewable energy sources, such as solar or wind, to create a sustainable energy ecosystem. Magnesium-based hydrogen storage could play a pivotal role in storing excess energy generated from renewable sources during periods of high production and releasing it when demand is high or when renewable energy generation is low. Research should focus on developing systems that can efficiently store and release hydrogen in a controlled manner, ensuring reliable integration with renewable energy grids. This could lead to the development of hybrid storage systems that combine magnesium-based hydrogen storage with other energy storage solutions, such as batteries, to enhance grid stability and energy security.

By addressing these challenges and advancing the performance and scalability of magnesium-based hydrogen storage systems, these materials can become a cornerstone of the hydrogen economy, helping to support the transition toward clean, sustainable, and efficient energy solutions.

DECLARATIONS

Ethical Approval

We affirm that this manuscript is an original work, has not been previously published, and is not currently under consideration for publication in any other journal or conference proceedings. All authors have reviewed and approved the manuscript, and the order of authorship has been mutually agreed upon.

Funding

Not applicable

Availability of data and material

All of the data obtained or analyzed during this study is included in the report that was submitted.

Conflicts of Interest

The authors declare that they have no financial or personal

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interests that could have influenced the research and findings presented in this paper. The authors alone are responsible for the content and writing of this article.

Authors' contributions

All authors contributed equally in the preparation of this manuscript.

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