Review

Enhancing the Hydrogen Storage Properties of A_xB_y Intermetallic Compounds by Partial Substitution: A Short Review

Andrii Lys ^{1,2}, Julien O. Fadonougbo ^{1,*}, Mohammad Faisal ¹, Jin-Yoo Suh ^{1,2} , Young-Su Lee ¹ , Jae-Hyeok Shim ¹, Jihye Park ³ and Young Whan Cho ¹

¹ Center for Energy Materials Research, Korea Institute of Science and Technology, Seoul 02792, Korea; 519006@kist.re.kr (A.L.); faisal@kist.re.kr (M.F.); jinyoo@kist.re.kr (J.-Y.S.); lee0su@kist.re.kr (Y.-S.L.); jhshim@kist.re.kr (J.-H.S.); oze@kist.re.kr (Y.W.C.)

² Division of Nano & Information Technology, University of Science and Technology KIST School, Seoul 02792, Korea

³ Strategy & Technology Division, Hyundai Motor Company, Uiwang 16082, Korea; jihyepark@hyundai.com

* Correspondence: julien.fadonougbo@kist.re.kr; Tel.: +82-2-958-6807

Received: 6 October 2020; Accepted: 9 December 2020; Published: 15 December 2020

Abstract: Solid-state hydrogen storage covers a broad range of materials praised for their gravimetric, volumetric and kinetic properties, as well as for the safety they confer compared to gaseous or liquid hydrogen storage methods. Among them, A_xB_y intermetallics show outstanding performances, notably for stationary storage applications. Elemental substitution, whether on the A or B site of these alloys, allows the effective tailoring of key properties such as gravimetric density, equilibrium pressure, hysteresis and cyclic stability for instance. In this review, we present a brief overview of partial substitution in several A_xB_y alloys, from the long-established AB_5 and AB_2 -types, to the recently attractive and extensively studied AB and AB_3 alloys, including the largely documented solid-solution alloy systems. We not only present classical and pioneering investigations, but also report recent developments for each A_xB_y category. Special care is brought to the influence of composition engineering on desorption equilibrium pressure and hydrogen storage capacity. A simple overview of the A_xB_y operating conditions is provided, hence giving a sense of the range of possible applications, whether for low- or high-pressure systems.

Keywords: metal hydrides; A_xB_y intermetallics; elemental substitution; low/high pressure applications

1. Introduction

Humankind is on the verge of facing a worldwide energy crisis considering the soon-to-come fossil fuels shortage. The transition to environmentally friendly energy sources is a challenge that many countries are already tackling by reformatting their economy to implement alternative and sustainable solutions. As such, the hydrogen-based economy became one of the main candidates for the transition towards cleaner energy source, in the light of hydrogen's positive impact on the environment and its intrinsic great potential as an abundant energy carrier: (i) high gravimetric energy density of 142 MJ kg^{-1} (against only 47 MJ kg^{-1} for petroleum) and (ii) high energy efficiency (fuel cells electrochemical processes show ~50–60% efficiency whereas that of combustion engines is as low as 25% for hydrogen-air mixtures, but still slightly higher than petrol-air) [1].

In the most general context, there are three different hydrogen storage methods: (i) compressed gas, (ii) liquid (cryogenic liquid H_2 or liquid organic hydrogen carriers) or (iii) solid state storage as metal hydrides (see the flow chart in Figure 1, which elaborates the different techniques for hydrogen storage).

To this day, gaseous storage of hydrogen is the most utilized method due to its relative simplicity. However, the low volumetric energy density of hydrogen at ambient temperature and atmospheric pressure (1 kg H₂ occupies 11 m³) remains a major technical limitation to the widespread use of gaseous hydrogen [2,3]. Indeed, a high level of pressurizing is needed to meet the volume efficiency requirement of industrial-scale energy storage systems, causing additional energy consumption and costs. Liquid-state hydrogen storage greatly improves volumetric characteristics (from lower than 40 kg H₂ m⁻³ of compressed hydrogen gas to 70.8 kg H₂ m⁻³), but requires either cryogenic conditions (~21.2 K at ambient pressure) to avoid boil-off (hydrogen critical temperature is 33 K), or up to 10⁴ atm of pressure for room temperature closed storage systems [2]. Either way, liquid-state hydrogen storage has to overcome technical and economic barriers for actual applications [4], since hydrogen liquefaction process (compressing and cooling) consumes about 30% of the energy stored [5], and 10⁴ atm is challenging on an engineering point of view.

Hydrogen storage in solids has the advantage of bypassing the aforementioned limitations of gaseous and liquid-state storage, and provides safe and efficient storage conditions [6,7]. Solid-state hydrogen storage in metal hydrides appears to be the safest way of storing hydrogen since metal hydrides can be operated at relatively moderate temperatures and pressures compared to other storage states. Besides, some metal hydrides can be regarded as heat-storage systems, since hydrogen absorption/desorption is an exothermic/endothermic process [8], respectively, that can easily be triggered by operating at conditions different from the equilibrium (above or below the equilibrium pressure for a fixed temperature) [9]. Up to this date, various metal hydrides have been investigated due to their high hydrogen volumetric and gravimetric density. As such, complex hydrides like MBH₄ (M = Li, Mg and Na, displaying 18.5 wt% H₂ for LiBH₄, 14.8 wt% H₂ for Mg(BH₄)₂, and 10.6 wt% H₂ for NaBH₄) [10–14], and AlH₃ (10.1 wt% H₂) [15] were studied. Additionally, the properties of MgH₂ (7.6 wt% H₂) [16] enhanced with various catalysts (metal oxides, carbides, nitrides or metalloids like Si) [17–21], or even with transition metals to form ternary hydrides (Ni, Co and Fe respectively forming Mg₂NiH₄ (3.6 wt% H₂), Mg₂CoH₅ (4.4 wt% H₂), and Mg₂FeH₆ (5.5 wt% H₂)) [22–35] were also explored. Although attractive, these high capacity hydrides all suffer major limitations absolutely preventing mass production and their use at ambient conditions; namely a high thermal stability (MBH₄ and Mg-based ternary hydrides), a low reversibility (MBH₄), and the need of extreme conditions for mechanochemical synthesis (AlH₃) [10,15,26].

For this reason, room temperature hydrides such as intermetallics have drawn significant attention. Not only their thermodynamics is suitable for large-scale applications, but also they display high reversibility and a decent energy density per unit volume superior to those of gaseous and liquid phase (see Table 1) [36].

Table 1. Storage properties of intermetallic hydrides compared to gas and liquid hydrogen [36].

Material	H Density		Energy Density	
	wt%	kg m ⁻³	MJ kg ⁻¹	MJ dm ⁻³
Gas H ₂ , 700 bar	100	42	120.0	5
Liquid H ₂ (20 K)	100	71	120.0	8.5
LaNi ₅ H ₆	1.4	90	1.7	10.8
TiFeH ₂	1.9	105	2.3	12.6
MgH ₂	7.6	110	9.2	13.3

In the simplest case, intermetallic hydrides are A_xB_yH_z ternary compounds, because variations in elemental nature and their amount allow tailoring the sorption and storage properties of these hydrides. Element A is usually rare earth or transition metal and tends to form a stable hydride. Element B, on the other hand, is often a transition metal and does not form stable hydrides. It has been found that B:A ratios of 0.5, 1, 2, 5 form hydrides with a hydrogen-to-metal ratio of up to two [2]. The main hydride families are summarized in Table 2.

Table 2. Some of the most important families of hydride-forming intermetallic compounds, with the corresponding reference alloys and structures [2,37].

Intermetallic Compound	Reference Alloy	Structure
AB ₅	LaNi ₅	Haucke phase, hexagonal
AB ₂	TiMn ₂	Laves phase, hexagonal or cubic
AB	TiFe	Cubic, CsCl-type or orthorhombic, CrB-type
AB ₃	CeNi ₃	Hexagonal, NbBe ₃ -type
Solid solutions	V, Ti–V	Body centered cubic

The main requirements for a large scale application of metal hydrides for on-board applications are (i) low hydrogen release temperature in the typical working conditions of a PEM fuel cell, (ii) high hydrogen absorption and desorption rates, (iii) acceptable costs and most importantly (iv) high storage capacity of 8 wt% according to the recent European VII FP call [38], which sets the bar even higher than the 6 wt% targeted by the American Department of Energy (DOE) [39]. It is difficult to achieve the gravimetric capacity target, especially for intermetallic hydrides. Hence, the main application for the intermetallic hydrides would be stationary applications, which are essential parts of renewable energy systems.

Many research groups have been trying to improve the characteristics of existing alloys in order to meet the EU's and DOE's requirements. Past, present and future developments in the field of hydrogen-based energy storage have been extensively documented recently (since 2016) in several exhaustive review articles, from general energy storage methods and delivery systems [40–42], to more specific storage technologies such as metal hydrides [8,43,44], including for instance Mg-based materials for energy storage [45–47]. However, to our knowledge, there are only very little recent reviews focusing on room temperature A_xB_y hydrides, aside from the comprehensive and comparative overview of AB₃ alloys for stationary fuel-cell applications by Liu et al. [48], and that of vanadium-based hydrides for hydrogen storage by Kumar et al. [49]. Therefore, in this review article, we provide a brief overview of partial substitution in A_xB_y intermetallics and solid solutions for room temperature applications. We compare some of the most promising achievements and findings for each A_xB_y alloy category to identify and suggest the most promising representatives for further development. Material capabilities and performance are compared and discussed for both classical and recent works on the topic, notably in terms of desorption pressure-composition-isotherm, hysteresis, cycling performance and storage capacity.

Figure 1. Flow chart representation of hydrogen storage methods (adapted from Hydrogen Storage Technology Materials and Applications, Page 67 [50]).

2. AB₅-Type Alloys

The AB₅-type hydrides have been intensively studied during the last decades for their high potential for practical applications [51]. They have reversible and fast hydrogen absorption/desorption kinetics at near-ambient temperatures, simple activation process, and moderate pressure-temperature conditions of hydrogenation/dehydrogenation, which can easily be controlled. However, the maximum discharge capacity is limited to only around 1.5 wt% for the single CaCu₅-type hexagonal structure [8,52,53].

In this section, LaNi₅ is taken as the reference material of the AB₅ family, in the light of its remarkable properties and features in comparison with other AB₅ compounds that were recently studied. Indeed, LaNi₅-based hydrides show good hydrogen absorption/desorption characteristics under near-atmospheric conditions and excellent kinetics [54,55]. The amount of hydrogen desorbed from a typical LaNi₅-type metal-hydride system ranges from much less than 1 wt% up to 1.2 wt% H₂ between room temperature and 373 K, with a theoretical maximum reversible storage capacity of 1.5 wt% H₂ (still below the DOE's target) [39,56]. Despite attractive properties, LaNi₅-based compounds have a high cost in comparison with other alloys and show a significant capacity loss (higher than 30% after 800 cycles under impure hydrogen gas containing 100 ppm of O₂ [57]), therefore urging to develop other materials with higher discharge capacity, better cyclic stability and lower cost [58].

The costly lanthanum in LaNi₅ can thus be replaced by cheaper rare earth elements such as Ce [59], or by a cheaper rare earth mixture called mischmetal (Mm) consisting of La, Ce, Pr and Nd [60], which was investigated in many studies. MmNi₅ possesses a hexagonal crystal structure similar to that of LaNi₅ and tends to form stable hydrides. However, it shows a very high activation pressure (120 atm at 298 K), a high hydride formation pressure (30–60 atm at 298 K), large hysteresis between the absorption and desorption pressures and a maximum storage capacity of about 20% lower than that of LaNi₅ [61,62]. Many groups have attempted to reduce the high hydride formation pressure in MmNi₅ by partially substituting A and B components with various elements [61,63–65].

To enhance the hydrogen storage capacity, Ca may partially replace Mm in MmNi₅ because of its lightweight (at. wt. 40) in comparison to Mm (at. wt. 140, corresponding to the following composition: La 22%, Ce 52%, Nd 15% and Pr 11%). Hence, for H/M = 1.0 the storage capacity of MmNi₅H₆ is 1.38 wt%, while that of Mm_{0.66}Ca_{0.34}Ni₅H₆ corresponds to 1.5 wt% [66,67]. The studies on Mm_{1-x}Ca_xNi₅ were first reported by Sandrock [68] and Shinar et al. [69]. Sandrock's results show that the hydride dissociation pressure decreased with increasing Ca content, while Shinar's results indicate that the substitution of Ca for Mm or La caused an increase in hydride dissociation pressure. Such contradictory behaviour results from the variation in Ca content, as elucidated by Wang et al. [70]. Indeed, they reported that the dissociation pressure of the hydrides (at 298 K) increased when $x < 0.3$ but decreased when $0.3 < x < 0.9$, which was attributed to the effect of geometrical and electronic factors. In addition, the first hydrogenation incubation time shortened and its absorption rate increased along with increasing x in Mm_{1-x}Ca_xNi₅, and the hysteresis reduced.

Different from Mm and Ca (A substitutes), substitutions for B element were reported to be effective in tailoring the plateau pressure. Among them, Al was used for reducing the plateau pressure, for instance from 50 atm for MmNi₅ down to 0.5 atm for MmNi_{4.2}Al_{0.8}. However, the maximum storage capacity decreased from 1.44 to 1.3 wt% and the plateau slope increased [71]. Meanwhile, Fe is known to increase hydrogen storage capacity (1.5 wt% for MmNi_{4.6}Fe_{0.4}), and reduce sloping and hysteresis [72,73].

Srivastava et al. [66,67] reported the effects of simultaneously substituting Ca, Al and Fe by preparing a series of Mm_{1-x}Ca_xNi_{5-y-z}Al_yFe_z alloys. This composition turned out to compensate some drawbacks of previously described alloys, and result in a larger storage capacity. Mm_{0.9}Ca_{0.1}Ni_{4.7}Fe_{0.2}Al_{0.1} is thus showing a maximum storage capacity of 2.2 wt%, however Mm_{0.9}Ca_{0.1}Ni_{4.8}Fe_{0.1}Al_{0.1} (smaller Fe content) desorbed 1.9 wt% (see desorption PCIs plotted in Figure 2). The desorption behaviour of Mm_{1-x}Ca_xNi_{5-y-z}Al_yFe_z alloys is plotted in Figure 2, together with those of the reference alloys (LaNi₅ and MmNi₅). Additional information on the alloys is available

in Table 3, which summarizes key properties and main remarks for each alloy shown in the figure. From all the above alloy modifications, we can note the overall increase of desorption plateau pressures, and of the reversible storage capacity from 1 and 1.25 wt% (MmNi₅ and LaNi₅, respectively) to 1.65 wt% in Mm_{0.9}Ca_{0.1}Ni_{4.6}Fe_{0.3}Al_{0.1} at ambient temperature and pressure up to 60 atm.

Figure 2. Desorption pressure-composition isotherms (PCI) of Mm_{0.9}Ca_{0.1}Ni_{5-x}Al_{0.1}Fe_x at 300 K [67] with desorption PCI of reference LaNi₅ at 303 K [74] and MmNi₅ at 273 K [75].

Table 3. Summary of the main properties of AB₅ alloys presented in this section and plotted in Figure 2.

Alloy	Temperature (K)	Structure Type	Lattice Parameters (nm)	Maximum/Reversible Capacity (wt%)	P _a /P _d (atm)	Remarks on the Effects of Partial Substitution
LaNi ₅ [74]	303	CaCu ₅	a = 0.5020 c = 0.3980	1.56/1.25	2.90/2.50	-
MmNi ₅ [75]	273	CaCu ₅	a = 0.4934 c = 0.3998	1.29/1.00	~5.20	Easy activation process, increased hysteresis and maximum storage capacity ~20% lower than that of LaNi ₅ .
Mm _{0.9} Ca _{0.1} Ni _{4.8} Fe _{0.1} Al _{0.1} [67]	300	CaCu ₅	a = 0.4949 c = 0.4013	1.90/1.25	~24.00/18.00	Ca enhances the hydrogen storage capacity, reduces the incubation time of the first hydrogenation, increases the absorption rate (with increasing Ca concentration), and reduces the hysteresis. Al reduces the plateau pressure, but also the maximum hydrogen storage capacity. Fe increases the storage capacity and reduces sloping and hysteresis.
Mm _{0.9} Ca _{0.1} Ni _{4.7} Fe _{0.2} Al _{0.1} [67]	300	CaCu ₅	a = 0.4952 c = 0.4019	2.20/1.50	~16.00/13.00	
Mm _{0.9} Ca _{0.1} Ni _{4.6} Fe _{0.3} Al _{0.1} [67]	300	CaCu ₅	a = 0.4962 c = 0.4018	1.96/1.65	~10.00/5.00	

Other than Al and Fe, various elements have also been used for B site substitutions. For instance, in 2000, Rożdżyńska-Kiełbik et al. [76] prepared a series of pseudo binary LaNi₅ alloys by substituting 0, 5, 10, 15 and 20 at% of Zn for Ni. For an increasing Zn content, the produced LaNi_{5-x}Zn_x alloys showed a linear increase of the unit cell volume, accompanied with a decrease of the absorption plateau pressures (in the range of 293 to 353 K) as well as a slight decrease in the hydrogen storage capacity as compared to the parent LaNi₅ compound.

A lowered absorption plateau pressure and decreased hydrogen content is similarly observed when substituting by metalloids like Si (forming La_{28.9}Ni_{67.55}Si_{3.55} which yields a H/M ratio of 1.0 at

1.04 atm against 1.2 for LaNi_5 at 1.3 atm) [77], while Sn mostly yields a better degradation resistance to thermal cycling [78].

Recently, more complex composition manipulations have been attempted by alloying Co, Al and Mn. The experimental study conducted by Briki et al. [79] reports that the synthesized $\text{LaNi}_{3.6}\text{Mn}_{0.3}\text{Al}_{0.4}\text{Co}_{0.7}$ (hexagonal CaCu_5 -type structure) reversibly absorbs/desorbs hydrogen in normal operating conditions (293 K and 6 bar), exhibits a significant reduction of hysteresis between hydriding and dehydriding, and a larger size of interstitial voids leading to a higher number of hydrogen atoms in the cell. Similar improvements without storage capacity decrease were also achieved thanks to Al in multicomponent alloys such as melt-spun $\text{LaNi}_{4.7-x}\text{Al}_{0.3}\text{Bi}_x$ ($x = 0.0, 0.1, 0.2, 0.3$), whereas Bi substitution increased the absorption/desorption plateau pressure and reduced the hydrogen capacity [80]. In this investigation, Yilmaz et al. also evidenced the formation of BiLa and AlNi_3 intermetallic phases at the grain boundaries, which results in an increased pulverization resistance of the alloy.

3. AB_2 -Type Alloys

AB_2 Laves phase is another type of alloy with high potential for hydrogen storage. Usually, these alloys exist in three different crystal structures: cubic C15 (for instance MgCu_2 , ZrV_2), hexagonal C14 (MgZn_2 , ZrMn_2) and double hexagonal C36 (MgNi_2). Laves phases with $A = \text{Zr}$ show relatively high capacities ($\text{ZrV}_2\text{H}_{5.3}$, $\text{ZrMn}_2\text{H}_{3.6}$, $\text{ZrCr}_2\text{H}_{3.4}$), faster kinetics, longer lifetime and a relatively low cost in comparison to the LaNi_5 -based alloys. However, their hydrides are too stable at room temperature and more sensitive to contaminants [38,81]. This high stability of Zr-containing alloys is also seen in various type of materials, notably in amorphous structures in which hydrogen is irreversibly immobilized either in trapping sites [82–84], or by forming stable ZrH_2 phase [85,86].

In this section, we take Ti–Mn Laves phase alloys as the reference material of the AB_2 family, because of their easy activation, good hydriding-dehydriding kinetics, high hydrogen storage capacity and relatively low cost. Besides, they display high plateau pressure at room temperature (over 20 atm) and a sloping plateau often accompanied with a large hysteresis that requires major improvements [87,88].

In 2005, Toyota's group demonstrated the use of $\text{Ti}_{1.1}\text{MnCr}$ alloys in a high-pressure metal hydride (MH) tank. This alloy has a maximum storage capacity of 1.9 wt%, but it has been reached only for a hydrogen pressure of around 350 atm at room temperature [89]. Kandavel et al. [90] substituted Zr in $\text{Ti}_{1.1}\text{CrMn}$ to provide favorable hydrogen sorption conditions and maximize the storage capacity. The increase in Zr content leads to a decrease in the equilibrium plateau pressure and faster absorption kinetics, together with an increase in the hydrogen storage capacity from 1.9 to 2.2 wt% for $\text{Ti}_{1.1}\text{CrMn}$ and $(\text{Ti}_{0.9}\text{Zr}_{0.1})_{1.1}\text{CrMn}$, respectively. Besides, Park et al. [87] conducted studies on Ti–Zr–Mn–Cr based metal hydrides and concluded that when Zr/Ti ratio increases, the lattice strain increases. This is partially responsible for a drastic increase of sloping, while the use of Cu was found very effective to mitigate the sloping.

In 1995, Morii et al. [91] prepared and investigated $(\text{Ti}, \text{Zr})(\text{Ni}, \text{Mn}, \text{X})_2$ alloys, where X is V or/and Fe. The results showed that V lowers both hysteresis and plateau pressure. On the other hand, Ni raises the plateau pressure and reduces the width of the plateau region, while Fe flattens and lengthens it.

Improvements of the hydrogen storage properties of Laves phase AB_2 -type alloys at 303–308 K and 1–15 atm have been achieved by introducing non-stoichiometry at the A site of $(\text{Ti}_{0.65}\text{Zr}_{0.35})_{1+x}\text{MnCr}_{0.8}\text{Fe}_{0.2}$ alloys. From pressure-composition-temperature (PCT) measurements, the maximum hydrogen storage capacity was found to be around 2.2 wt% at 35 atm and 305 K for $(\text{Ti}_{0.65}\text{Zr}_{0.35})_{1.1}\text{MnCr}_{0.8}\text{Fe}_{0.2}$, which is approximately 16% higher than that of the commercially available “Hydralloy C5” ($\text{Ti}_{0.955}\text{Zr}_{0.045}\text{Mn}_{1.52}\text{V}_{0.43}\text{Fe}_{0.12}\text{Al}_{0.03}$). These alloys show remarkable hydrogenation kinetics: the full capacity is reached within 10 min without any need for activation [92].

Alloys without zirconium (such as $\text{Ti}_{1.02}\text{Cr}_{1.0}\text{Fe}_{0.75}\text{Mn}_{0.25}$) display 1.55 wt% of reversible hydrogen storage capacity when the temperature is as low as 233 K. However, without zirconium the effective

hydrogen capacity is optimal only when the pressure is higher than 70 atm [93], proving the effectiveness of Zr in Laves phase alloys. Figure 3 shows the desorption behavior of some noteworthy AB₂ alloys.

Figure 3. Desorption pressure-composition isotherms of TiMn_{1.5} [94], (Ti_{1-x}Zr_x)_{1+y}Mn_{0.8}Cr_{1.2} [87], Ti_{0.8}Zr_{0.1}Mn_{1.2}Cr_{0.2}V_{0.1}Fe_{0.1} [94], (Ti_{0.9}Zr_{0.1})_{1.1}Cr_{1.5}Fe_{0.2}Mn_{0.3} [95], Ti_{0.2}Zr_{0.8}Ni_{1.3}Mn_{0.7} and Ti_{0.4}Zr_{0.6}Ni_{1.1}Mn_{0.6}V_{0.1}Fe_{0.2} at 303 K [91]. (Ti_{0.65}Zr_{0.35})_{1.05}MnCr_{0.8}Fe_{0.2} on the other hand was measured at 305 K [92].

Recent developments (<5 years) on AB₂-type materials have highlighted their significant potential for high-pressure compressors, notably (Ti,Zr)(Mn,Cr)-based alloys. Indeed, Corgnale et al. [96] proposed a techno-economic analysis of metal hydride systems for efficient and novel high-pressure compressors. Among various materials, TiCr_{1.9}, Ti_{1.1}CrMn, TiCrMn_{0.4}Fe_{0.4}V_{0.2}, and (Ti_{0.97}Zr_{0.03})_{1.1}Cr_{1.6}Mn_{0.4}, they suggested the last one as the best candidate for their novel two-stage hybrid electrochemical and metal hydride compression system, since pressures about 863 atm can be reached with a thermal power provided at approximately 423 K.

Pickering et al. [97] further demonstrated the high capability of (Ti,Zr)(Mn,Cr)-based alloys for both hydrogen storage and high-pressure compression by producing industrial volumes (~10 kg) of tailored AB₂ intermetallics (A = Ti + Zr, B = Cr + Mn + Ni+Fe + V) by means of vacuum induction melting process. They successfully tuned the hydrogenation properties of the alloy, showing that at a fixed quite low Zr/(Ti + Zr) ratio the PCT properties of the materials can be adjusted in a wide range by the variation of V content which, in addition, results in the increase of the hydrogen storage capacity. Cheaper alternatives to pristine Ti and V nevertheless exist, notably by replacing those high purity raw materials by their low-cost and low-purity counterparts, namely Ti sponge and ferrovanadium (FeV), respectively. Such substitution in (Ti,Zr)(V,Fe,Cr,Mn) reduces the raw material cost by 83%, without altering the dissociation pressure (15 atm), nor the reversibility (1.4 and 1.5 wt% H₂ after 1000 cycles, against an initial capacity of 2 and 1.7 wt% H₂ for pristine and modified alloys, respectively) [98].

The development of hybrid hydrogen storage system is equally appealing to the scientific community. For instance, rare earth elements (RE) such as La, Ce or Ho in Ti_{1.02}Cr_{1.1}Mn_{0.3}Fe_{0.6}RE_{0.03} have been shown in 2018 to yield better activation behaviour, larger storage capacity but lower desorption plateau pressure [99]. This study suggests Ti_{1.02}Cr_{1.1}Mn_{0.3}Fe_{0.6}La_{0.03} alloy as the best overall candidate since it can be fully activated at room temperature, and has a hydrogen storage capacity as high as ~1.7 wt%. Another example of hybrid system is reported by Puszkiel et al. [100], who demonstrated that mixing expanded natural graphite (ENS) into (Ti_{0.9}Zr_{0.1})_{1.25}Cr_{0.85}Mn_{1.1}Mo_{0.05} alloy not only improves the heat transfer properties, but also yields a reversible capacity of about 1.5 wt%, together with decent cycling stability and rapid reaction kinetics (25 to 70 s).

Although all the above-mentioned (Ti,Zr)(Mn,Cr)-based Laves phase alloys are widely investigated in the light of their superior potential for high-pressure compressors (and hybrid hydrogen storage), Zr-based AB₂ materials are nevertheless not to be discarded although they display significantly lower desorption plateau pressures. Wu et al. [101] thus elucidated the role of Ni addition on the hydrogen storage characteristics of Zr(V_{1-x}Ni_x)₂ ($x = 0.02, 0.05, 0.1, 0.15, 0.25$) intermetallic compounds. The hydrogen absorption capacity turns out to decrease, and the equilibrium pressure increases with increasing Ni content. The alloys exhibit fast absorption kinetics at room temperature and a remarkable cyclic stability even after 100 hydrogen absorption/desorption cycles.

Owing to fast kinetics, high equilibrium pressure and impressive volumetric hydrogen storage density at ambient temperature, ZrFe₂ based alloys are similarly good candidates for high pressure compressed hydrogen tanks. To bypass its rather large hysteresis, Mn, Ti, V and Cr addition [102,103] has been considered. On one hand, V addition is suggested to improve the hysteresis, while Ti helps to lower plateau sloping as well as to increase the plateau pressure. Zr_{1.05}Fe_{1.6}Mn_{0.4} shows a relatively high dehydriding pressure of 20.6 atm at 298 K, while (Zr_{0.5}Ti_{0.5})_{1.05}Fe_{0.95}MnV_{0.05} delivers a maximum capacity of 1.64 wt% H₂ and shows a dehydriding pressure of 6.8 atm at 298 K (calculated from Van't Hoff plots) [102]. Additionally, the simultaneous Cr/V substitution for Fe decreases the equilibrium pressure (due to the enlarged unit cell), and Zr_{1.05}Fe_{1.85}Cr_{0.075}V_{0.075} seems to exhibit decent overall hydrogen storage properties (1.54 wt%, and a desorption equilibrium pressure of 9.7 atm at 243 K) [103].

Figure 4 summarizes desorption PCT curves of some representative materials for high pressure compressor described above. Unlike Figure 3, most of alloys shown here display significantly higher desorption plateau pressures that seem to be achieved at the expense of the storage capacity. It is interesting to note the excellent capacity of AB₂ alloys to cover this broad range of properties with relatively simple manipulations of the composition. Indeed, essential properties such as absorption/desorption plateau pressures, maximum/reversible storage capacity, activation and cyclic performance (among others) can be tuned to adapt the alloy to the requirements of the target applications. This outstanding ability is even more obvious when carefully comparing the effect of substitutional modifications on each alloy presented in Figures 3 and 4, as shown in the comparative Table 4.

Figure 4. Recently reported desorption pressure-composition isotherms of Ti_{0.98}Zr_{0.02}V_{0.43}Fe_{0.09}Cr_{0.05}Mn_{1.5} and its FeV and Ti sponge counterpart acquired at 298 K [98], Ti_{1.02}Cr_{1.1}Mn_{0.3}Fe_{0.6} and Ti_{1.02}Cr_{1.1}Mn_{0.3}Fe_{0.6}La_{0.03} measured at 263 K [99], (Ti_{0.9}Zr_{0.1})_{1.25}Cr_{0.85}Mn_{1.1}Mo_{0.05} at 296 K [100], Zr_{1.05}Fe_{1.6}Mn_{0.4} and (Zr_{0.5}Ti_{0.5})_{1.05}Fe_{0.95}MnV_{0.05} at 288 K [102], and finally Zr_{1.05}Fe_{1.85}Cr_{0.075}V_{0.075} at 288 K [103].

Table 4. Summary of the main properties of AB₂ alloys presented in this section and plotted in Figures 3 and 4.

Alloy	Temperature (K)	Structure Type	Lattice Parameters (nm)	Maximum/Reversible Capacity (wt%)	P _a /P _d (atm)	Remarks on the Effects of Partial Substitution
TiMn _{1.5} [94]	303	MgZn ₂	a = 0.4878 c = 0.7976	1.42/0.75	-/5.45	-
(Ti _{0.8} Zr _{0.2}) _{1.00} Mn _{0.8} Cr _{1.2} [87]	303	MgZn ₂	a = 0.4902 c = 0.8044	1.79/1.35	12.00/10.52	Increasing Zr content decreases the equilibrium plateau pressure, accelerates absorption kinetics, and increases the storage capacity. Cr increases hydrogen storage capacity and reduces equilibrium pressure. Lattice strain increases along with Zr/Ti ratio and partially results in important sloping
(Ti _{0.8} Zr _{0.2}) _{1.05} Mn _{0.8} Cr _{1.2} [87]	303	MgZn ₂	-	1.90/1.55	8.40/7.54	
(Ti _{0.75} Zr _{0.25}) _{1.00} Mn _{0.8} Cr _{1.2} [87]	303	MgZn ₂	a = 0.4912 c = 0.8064	1.86/1.50	8.72/6.99	
(Ti _{0.75} Zr _{0.25}) _{1.05} Mn _{0.8} Cr _{1.2} [87]	303	MgZn ₂	-	1.91/1.60	5.23/4.47	
(Ti _{0.9} Zr _{0.1}) _{1.1} Cr _{1.5} Fe _{0.2} Mn _{0.3} [95]	303	MgZn ₂	a = 0.4897 c = 0.8026	1.84/1.30	2.54/2.17	Partial substitution of Mn by Fe shrinks the cell volume and increases the plateau pressure, but the hydrogen capacity does not change noticeably.
Ti _{0.2} Zr _{0.8} Ni _{1.3} Mn _{0.7} [91]	303	MgCu ₂	-	1.65/1.35	1.40/0.38	V lowers both hysteresis and plateau pressure. Ni raises the plateau pressure and reduces the plateau width, while Fe flattens and lengthens it.
Ti _{0.4} Zr _{0.6} Ni _{1.1} Mn _{0.6} V _{0.1} Fe _{0.2} [91]	303	MgCu ₂	-	1.64/1.25	1.22/0.75	
(Ti _{0.65} Zr _{0.35}) _{1.05} MnCr _{0.8} Fe _{0.2} [92]	305	MgZn ₂	-	2.2/1.75	5.30/2.80	Unit cell volume and storage capacity increase, charge time reduces along with non-stoichiometry on the A site.
Ti _{0.8} Zr _{0.1} Mn _{1.2} Cr _{0.2} V _{0.1} Fe _{0.1} [94]	303	MgZn ₂	-	2.03/1.60	18.06/9.02	-
Ti _{0.98} Zr _{0.02} V _{0.43} Fe _{0.09} Cr _{0.05} Mn _{1.5} [98]	298	MgZn ₂	a = 0.4875 c = 0.7994	1.89/1.36	23.3/12.1	Replacing Ti by Ti sponge does not change the initial storage capacity, whereas it is reduced after substitution of V by FeV. Substitutions do not affect microstructural properties.
Ti _{sp0.98} Zr _{0.02} (FeV) _{0.43} Fe _{0.09} Cr _{0.05} Mn _{1.5} [98]	298	MgZn ₂	a = 0.4872 c = 0.7989	1.62/1.12	23.4/13.8	
Ti _{1.02} Cr _{1.1} Mn _{0.3} Fe _{0.6} [99]	263	MgZn ₂	a = 0.4854 c = 0.7968	1.38/1.05	208/143	RE improves the activation behaviour, the sorption properties and storage capacity (saturation reached at RT), but decreases the hydrogen desorption plateau pressure.
Ti _{1.02} Cr _{1.1} Mn _{0.3} Fe _{0.6} La _{0.03} [99]	263	MgZn ₂	a = 0.4862 c = 0.7975	1.7/1.2	218/137	
(Ti _{0.9} Zr _{0.1}) _{1.25} Cr _{0.85} Mn _{1.1} Mo _{0.05} [100]	296	MgZn ₂	a = 0.4884 c = 0.801	1.45/1.25	54/34	The equilibrium pressure increases with Mo amount, mostly due to the larger bulk modulus of Mo (compared to Cr) rather than the increase in cell volume. For Mo higher than x = 0.05, the hydrogen capacity greatly drops.
Zr _{1.05} Fe _{1.6} Mn _{0.4} [102]	288	MgCu ₂	a = 0.7086	1.32/1.12	60/24	V addition improves the hysteresis, while an adequate Ti amount helps to achieve low slope and high plateau pressure.
(Zr _{0.5} Ti _{0.5}) _{1.05} Fe _{0.95} MnV _{0.05} [102]	288	MgZn ₂	a = 0.4935 c = 0.8079	1.64/1.32	23/6.7	
Zr _{1.05} Fe _{1.85} Cr _{0.075} V _{0.075} [103]	288	MgCu ₂	a = 0.7086	1.54/1.08	61/44	Cr and V substitutions effectively decrease the equilibrium pressure due to the enlarged unit cell, while the V substitution improves the hysteresis. Too high Cr addition induces a transition from MgCu ₂ to MgZn ₂ structure type.

4. AB-Type Alloys

AB-type alloys are attractive materials for hydrogen storage because of their light molar mass and high weight capacities. TiFe alloys with cubic CsCl-type structures are the most known alloys of this class and stand among the best hydrogen storage materials up to this date [8,104].

TiFe intermetallic compound is one of the most promising hydrogen storage alloys, due to its relatively high theoretical hydrogen storage capacity (1.9 wt%) at near-ambient conditions compared to other A_xB_y families. Besides, its economical merit based on the abundance and low cost of the constituting elements encourages extensive investigations on the TiFe system.

The hydrogen sorption and desorption in TiFe was first described by Reilly and Wiswall in the year 1974 [105]. They reported two stable intermetallics of TiFe system (TiFe and $TiFe_2$) and a third, Ti_2Fe that forms only above 1273 K (dissociates to TiFe and Ti below that temperature). Only TiFe is known to make two ternary hydrides, $TiFeH$ and $TiFeH_2$.

The hydrogen absorption in TiFe alloy depends on two factors: (i) the Fe/Ti ratio and (ii) the oxygen amount in the alloy. TiFe intermetallic exists over a narrow composition range of ~2.5 at% (from 49.5 to 52 at% Ti). Slightly less than 49.5 at% Ti results in a two-phase mixture of $TiFe_2$ and TiFe, the first being of no use since it is a non-hydride former. If Ti content is higher than 52 at%, the alloy consists of TiFe and (α or β) Ti solid solution [105]. Although Ti itself readily forms hydrides, they are highly stable and are non-reversible at the temperatures of interest (ambient).

The lower plateau level and general shape of the curve is not significantly affected but the maximum hydrogen storage capacity substantially reduces with the increase in oxygen content (Figure 5) [106]. Additionally, TiFe usually requires heating over 573 K for activation, which again suggests the low poisoning tolerance resulting in significant deterioration of hydrogen sorption even for trace amounts of gas species (oxygen and water vapor for instance) [105,107,108]. Most importantly, surface oxidation issues induce significant difficulties notably in the first hydrogenation. The problem with first activation can be resolved by partial replacement of the base element [109–114], mechanical alloying [115,116], surface modifications [108], groove rolling and high-pressure torsion [107,117]. Most of these studies did not lead to an improvement in hydrogen storage properties, and the result was usually a decreased maximum hydrogen absorption capacity and increased desorption temperature of the intermetallic hydrides.

Figure 5. The effect of oxygen content (in the inlet gas) on the hydrogen desorption isotherm of the reference un-modified TiFe alloy at 313 K [106]. Oxygen content ranges from 0.010 to 0.87 wt%.

There is 10% volume increase when initial hydrogenation occurs. This exerts stresses on unhydrided core, thus results in cracks. The presence of second phase particles (TiFe_2 , $\text{Ti}_{10}\text{Fe}_7\text{O}_3$, Ti) promotes activation: (i) lowers fracture toughness of TiFe and (ii) provides interface for preferential hydride nucleation and penetration [106].

The intimacy of the alloy to a minor level of oxygen creates another feature to be noted; TiFe microstructure with minor oxygen contamination exhibits at least two phases (TiFe and an oxygen stabilized $\text{Ti}_{10}\text{Fe}_7\text{O}_3$ as fine eutectic distribution). For this oxygen stabilized phase, each oxygen binds with 5.7 metal atoms, so even 1 wt% O-contamination results in 19 wt% $\text{Ti}_{10}\text{Fe}_7\text{O}_3$ phase, which does not form any hydride [106].

The level of plateau pressure determines the stability of the hydride. Partial substitution of Fe by 3d-transition metals can disrupt and thus modify the stability of the resulting hydride ($\text{TiFe}_{1-x}\text{M}_x$). This allows the alloy to be tailor-made with appropriate properties for particular application. Mn can be used in that purpose, for instance by providing a heat-treatment free novel activation route [118]. Shang et al. [119] synthesized $\text{Ti}_{1.1}\text{Fe}_{0.8}\text{Mn}_{0.2}$ (Figure 6), and demonstrated that partial replacement of Fe with Mn as well as excess Ti helped to reduce the activation process temperature from 573 K to 423 K and to increase the amount of stored hydrogen from 1.35 to 1.5 wt% (mostly due to Mn) under ambient temperature and a pressure of 30 atm (first plateau).

Comparable improvements of the activation procedure are also reported for off-stoichiometric $\text{TiFe}_{0.9}$ alloys, for which Mn substitution for Fe is additionally shown to reduce the equilibrium pressure at room temperature [113]. Plateau pressures can also be tuned by Cu substitution for which the cell parameter linearly increases with Cu content [120]. Hence, the combination of Cu, Mn and off-stoichiometry is of great interest for tailoring the properties of TiFe-based alloys, as recently demonstrated by Dematteis et al. [121]. They investigated the effect of Mn and Cu substitution for Fe in $\text{TiFe}_{0.9}$ system, and the thorough structural and thermodynamic study shows that all synthesized alloys display fast kinetics and high storage capacity. The report suggests that (i) both Mn and Cu substitutions increase the cell parameter of TiFe (decreased first plateau pressure), whereas (ii) Cu substitution increases the second plateau pressure, and (iii) the hydride stability is not solely driven by cell volume, but may also strongly depend on the electronic properties of the substituting elements.

Jang et al. in 1986 [111] studied Zr substituting Ti, rather than Fe, in TiFe alloy for improved activation properties. Particularly, $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Fe}$ activated at room temperature and required no heat treatment. There was a visible enhancement in the β phase hydride (TiFeH) formation and suppression of γ phase (TiFeH_2). Nagai et al. [122] in the year 1988 further studied the result of Zr addition in TiFe. Partial substitution of Zr (~1–15 at%) results in TiFe and two other phases ($(\text{Ti}_{1-y}\text{Zr}_y)_2\text{Fe}$, a hydride former, and $\text{Ti}(\text{Fe}_{1-x}\text{Zr}_x)_2$, a non-hydride former). They reported activation of the alloy at ambient temperatures with reduced incubation time for hydrogenation kinetics, without any loss in hydrogen storage capacity.

Lee and Perng in 1999 [123] studied partial substitution of Co, Ni and Al in TiFe. They observed that Co and Ni (similar size with Fe) addition led to the formation of a small fraction of α phase (solid solution) with hydriding characteristics similar to that of pure TiFe, but the addition of Al (large atomic size as compared to Fe) resulted in a much larger α phase fraction (see Figure 6). All three alloys did not require any activation treatment.

Kuziora et al. [124] very recently explored the effect of refractory metals (Ta and Mo) on the hydrogen storage properties of TiFe alloys prepared via suspended droplet alloying (SDA). The resultant alloys, $\text{Ti}_{0.5}\text{Fe}_{0.45}\text{Ta}_{0.05}$ and $\text{Ti}_{0.5}\text{Fe}_{0.4}\text{Mo}_{0.1}$, absorbed ~1 and 1.4 wt% H_2 , respectively. The alloys displayed sloping plateau, and despite the encouraging results, the correlation between alloy composition and absorption plateau pressure could not be established.

Figure 6. Desorption pressure-composition isotherms of TiFe and $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Fe}$ at 303 K [111], and $\text{Ti}_{1.1}\text{Fe}_{0.8}\text{Mn}_{0.2}$ at 313 K [119]. The graph also plots the PCI of alloys with varying Fe/Ti ratios at 313 K: (a) 60.5 wt% Fe and 39.5 wt% Ti, (b) 50.5 wt% Fe and 49.2 wt% Ti, (c) 36.7 wt% Fe and 63.2 wt% Ti [105] and of TiFe alloy with 4 wt% Zr [125]. Finally, $\text{TiFe}_{0.9}\text{Ni}_{0.1}$, $\text{TiFe}_{0.9}\text{Co}_{0.1}$ and $\text{TiFe}_{0.9}\text{Al}_{0.1}$ at 323 K [123].

Different from refractory metals, recent research is focused on the use of Zr and other alloying elements for possible room temperature activation. Jain et al., in 2015, presented a comparative study on the effect of Zr, Ni and $\text{Zr}_7\text{Ni}_{10}$ alloy on the TiFe hydrogenation properties [125]. They concluded that Zr addition annihilates the initial activation requirements and reduces the incubation time without affecting the reversible storage capacity.

Very recently, in the year 2020, Yang et al. [126], documented the effect of Cr, Mn and Y substitution for Fe on the hydrogen storage properties. They concluded that Cr substituted alloys ($\text{TiFe}_{0.9}\text{Cr}_{0.1}$, $\text{TiFe}_{0.9}\text{Cr}_{0.1}\text{Y}_{0.05}$) have lower equilibrium pressure and sloped plateaus, thus providing better hydrogenation kinetics as compared to Mn substituted alloys ($\text{TiFe}_{0.9}\text{Mn}_{0.1}$, $\text{TiFe}_{0.9}\text{Mn}_{0.1}\text{Y}_{0.05}$), which have higher equilibrium pressure but flat plateaus and thus better dehydrogenation kinetics. Y substitution in Ti–Fe–Mn and Ti–Fe–Cr based alloys resulted in αY phase, which transforms to YH_3 during hydrogenation.

Ha et al. [127] investigated the contrast in the microstructure of as cast and heat treated TiFe-6 wt% ZrCr_2 alloys. They reported that the as cast alloy has 65 wt% TiFe and 35 wt% TiFe_2 (C14 Laves phase) while the heat-treated alloy has a portion of TiFe_2 transformed to TiFe phase (84 wt%). The activation profile reveals that both the alloys can be activated at room temperature under 30.6 atm H_2 but the as cast alloy displays enhanced absorption kinetics (activation starts without any delay while its heat-treated counterpart requires 40 h of incubation time). Both specimens show approximately equal maximum hydrogen storage capacity of 1.7 wt%. The first plateau for the annealed alloy is flatter in shape and the desorption isotherm shows less retained hydrogen as compared to the as cast alloy. In parallel, Jung et al. [128] conducted a study on tailoring the equilibrium plateau pressure of TiFe monohydride and dihydride via V substitution for both Ti and Fe, in order to achieve maximum reversible capacity under a narrow pressure range. When V substitutes for Ti, the monohydride plateau pressure rises whereas a pronounced opposite trend is seen if V substitutes for Fe. Interestingly, the plateau pressure for dihydride is lowered in both the cases.

To summarize all the above, similarly to AB_2 alloys, there exists an appreciable opportunity to fabricate TiFe based AB alloys with ternary element substitution resulting in tailored hydrogen storage and hydrogenation kinetics properties as per the application requirement, as summarized in Table 5.

Table 5. Summary of the main properties of AB alloys presented in this section and plotted in Figure 6.

Alloy	Temperature (K)	Structure Type	Lattice Parameters (nm)	Maximum/Reversible Capacity (wt%)	P _a /P _d (atm)	Remarks on the Effects of Partial Substitution
TiFe [111]	303	CsCl	-	~1.73/~1.60	-/6	Enthalpy of β hydride (TiFeH) formation is $-5.68 \text{ kcal (mol H}_2\text{)}^{-1}$ and the enthalpy for hydrogen desorption is $6.31 \text{ kcal (mol H}_2\text{)}^{-1}$.
Ti _{1.1} Fe _{0.8} Mn _{0.2} [119]	313	CsCl	a = 0.2990	~1.75/~1.65	-/~1.0 (mid-point)-	Dehydrogenation enthalpy is $5.65 \text{ kcal (mol H}_2\text{)}^{-1}$. The addition of over-stoichiometric Ti leads to reduction in hydrogen storage capacity and substitution of Mn for Fe results in more stable hydride and improved hydrogen storage capacity with easy activation.
Ti ₃₆ Fe ₆₄ (60.5 wt% Fe and 39.5 wt% Ti) [105]	313	CsCl	-	~0.80/~0.71	-/7.0	Second plateau is sloping.
Ti _{45.5} Fe _{54.5} (50.5 wt% Fe and 49.2 wt% Ti) [105]	313	CsCl	-	~1.98/~1.74	-/~4 (mid-point)	Sloping plateau.
Ti _{59.6} Fe _{40.4} (36.7 wt% Fe and 63.2 wt% Ti) [105]	313	CsCl	-	~2.1/~0.90	-/~1.5	Second plateau is sloping. The desorption is not complete due to the presence of excess Ti, which forms very stable hydride.
Ti _{0.9} Zr _{0.1} Fe [111]	303	CsCl	-	~1.1/~0.99	-/3	Enthalpy of β hydride formation is $-6.25 \text{ kcal (mol H}_2\text{)}^{-1}$ and the enthalpy for hydrogen desorption is $6.91 \text{ kcal (mol H}_2\text{)}^{-1}$. Zr substitution increases the hydride stability and reduces the storage capacity.
TiFe _{0.9} Ni _{0.1} [123]	323	CsCl	-	~1.4/~1.27	-/~1.0	Enthalpy for hydrogen desorption is $8.51 \text{ kcal (mol H}_2\text{)}^{-1}$. Partial substitution greatly influences the stability of the monohydride, as reflected in the broad enthalpy range reported in this table. Easy activation at RT.
TiFe _{0.9} Co _{0.1} [123]	323	CsCl	-	~1.46/~1.29	-/~5.0	Enthalpy for hydrogen desorption is $7.32 \text{ kcal (mol H}_2\text{)}^{-1}$. Easy activation at RT.
TiFe _{0.9} Al _{0.1} [123]	323	CsCl	a = 0.2997	~1.27/~1.15	-(sloping plateau)	Sloping plateau. Easy activation at RT.
TiFe + 4 wt% Zr [125]	313	CsCl	a = 0.2983	~1.2/~0.83	-(sloping plateau)	Addition of Zr results in multiphase alloy (formation of a Zr-rich inter-granular phase), RT activation but incomplete desorption at RT.

5. AB₃-Type Alloys

Research on AB₃ alloys, whose structure consist of combined AB₂ and AB₅ (see equation below), was initially motivated by their strong potential for Ni-MH batteries [48,129]. Indeed, negative electrode materials based on AB₃ can offer a higher hydrogen storage capacity than AB₅-types alloys (already commercialized), but unfortunately suffer a severe degradation of their cyclic properties due to pulverization and oxidation/corrosion [130,131].

Most frequently based on La₂MgNi₉, AB₃ alloys however turn out to be promising for stationary hydrogen storage applications as well, considering their good activation and hydrogenation/dehydrogenation kinetics on one hand, and their relatively high storage capacity

and low cost on the other (thus combining the best features of AB_5 and AB_2 respectively) [48]. Additionally, the phase composition of AB_3 alloys (hence their properties) can be tuned by means of element substitution, heat treatment and different material processing methods, similarly to AB_2 alloys [48].

Pioneering work in the seventies [132,133] first reported hydrogen solubility and hydride forming ability of AB_3 alloys based on rare earth elements (A side) and transition metals (B side). Later on, Kadir et al. further investigated such alloys, by providing exhaustive reports on the effect of rare earth elements on the hydrogenation properties of AB_3 alloys (La, Ce, Pr, Nd, Sm, Gd) [134], as well as on the effect of La and Mg partial replacement by Ca and/or Y in La-Mg-Ni based alloys [135,136].

The hydriding characteristics of $LaNi_3/CaNi_3$ and RT_3 phases ($R = Dy, Ho, Er, Tb, Gd$; $T = Fe$ or Co) showed that the hydrogen storage capacity of the AB_3 phases exceeds that of the well-known hydrogen absorber $LaNi_5$ [137]. Due to the special crystal structure of AB_3 compounds, it is possible to combine Mg, Ca, and rare earth elements in the A side. Kadir et al. [136] synthesized $(La_{0.65}Ca_{0.35})(Mg_{1.32}Ca_{0.68})Ni_9$ which absorbs ~ 1.87 wt% H_2 at ~ 33 atm H_2 and 283 K. Under identical pressure condition, Chen et al. [137] reached up to 1.8 wt% H_2 at 293 K for $LaCaMgNi_9$.

In order to improve the performance of La-Mg-Ca-Ni AB_3 -type alloy, Lim et al. investigated the effects of partial substitution with Ce and Al on the hydrogenation properties of $La_{0.65-x}Ce_xCa_{1.03}Mg_{1.32}Ni_{9-y}Al_y$ alloys [138]. Their results indicated that the hydrogen storage capacity significantly decreased after Ce and Al substitution. Xin et al. [139] investigated the effects of Y partial substitution on overall hydrogen storage properties of $(La_{0.65}Ca_{0.35})(Mg_{1.32}Ca_{0.68})Ni_9$. At 1 atm H_2 , the hydrogen desorption capacity of $La_{0.60}Y_{0.05}Mg_{1.32}Ca_{1.03}Ni_9$ was approximately 1.624, 1.616, and 1.610 wt% at 298, 313, and 333 K, respectively. In addition, the equilibrium pressure could be tailored by altering the Y amount to range 1–10 atm.

The effect of half replacement of Ca by R ($R = Nd, Gd$ and Er) on the phase structure and hydrogen storage property of Ca_2MgNi_9 compound was investigated in 2019 by Zang et al. [140]. Results showed that alloys with Gd, Er or Nd instead of La have lower maximum storage capacity (1.4, 1.2, and 1.5 wt% H_2 , respectively, against 1.87 wt% H_2 for La). Desorption behaviours of some remarkable AB_3 alloys (plotted in Figure 7) show flatter plateau pressures than some AB_2 and AB alloys (Figures 3, 4 and 6) while displaying comparable storage capacity (see detailed summary in Table 6).

Figure 7. Desorption pressure-composition isotherms of $LaCaMgNi_9$ at 293 K [137], $(La_{0.65}Ca_{0.35})(Mg_{1.32}Ca_{0.68})Ni_9$ at 283 K [136] and $La_{(0.65-x)}Y_xMg_{1.32}Ca_{1.03}Ni_9$ at 298 K [139].

Table 6. Summary of the main properties of AB₃ alloys presented in this section and plotted in Figure 7.

Alloy	Temperature (K)	Structure Type	Lattice Parameters (nm)	Maximum/Reversible Capacity (wt%)	P _a /P _d (atm)	Remarks on the Effects of Partial Substitution
LaCaMgNi ₉ [137]	293	NbBe ₃	a = 0.4924 c = 2.3875	1.8/1.25	3.20/2.64	AB ₃ alloys can be tuned by different material processing methods similarly to AB ₂ and AB ₅ alloys.
(La _{0.65} Ca _{0.35})(Mg _{1.32} Ca _{0.68})Ni ₉ [136]	283	NbBe ₃	a = 0.4952 c = 2.3907	1.87/1.35	2.21/1.65	
La _{0.65} Mg _{1.32} Ca _{1.03} Ni ₉ [139]	298	NbBe ₃	a = 0.4961 c = 2.3926	1.83/1.3	2.28/1.61	AB ₅ phase fraction increases with Y substitution, and becomes the dominant phase inducing a reduction of the maximum capacity. Y substitution significantly increases both the hydrogen absorption/desorption plateau pressures due to the lattice contraction.
La _{0.60} Y _{0.05} Mg _{1.32} Ca _{1.03} Ni ₉ [139]	298	NbBe ₃	a = 0.4955 c = 2.3935	1.79/1.4	5.31/3.11	
La _{0.45} Y _{0.20} Mg _{1.32} Ca _{1.03} Ni ₉ [139]	298	NbBe ₃	a = 0.4948 c = 2.3942	1.75/1.5	13.32/8.37	

To summarize, partial substitution in the B site of Ni for elements with larger atomic radius increases the unit cell volume and results in a decrease of the absorption and desorption plateau pressures. As such, increasing Co concentration (in La_{0.7}Mg_{0.3}Ni_{3.4-x}Mn_{0.1}Co_x [141] or in La₂Mg(Ni_{1-x}Co_x)₉ (x = 0.1–0.5) [142]), or Al and Mo (in La_{0.7}Mg_{0.3}Ni_{3.5-x}(Al_{0.5}Mo_{0.5})_x with x = 0–0.8 [143]) decreased the desorption equilibrium pressure.

“Pseudo AB₃” alloys like A₂B₇ (Ce₂Ni₇-type structure) or even A₅B₁₉ (Ce₅Co₁₉) with stacked super structures were also considered both for battery and hydrogen storage applications. As such, in the aim of developing a new type of Mg-free AB₃-type alloy system, Yan et al. [144] investigated the effect of La and Mg replacement by Y on one side, and that of Ni by Mn and Al on the other. Similar to La-Mg-Ni based system, the studied LaY₂Ni_{8.2}Mn_{0.5}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) alloys are multiphase structures, with hydrogen storage capacities at 313 K of 0.85, 1.48 and 1.45 wt% for AB₃, A₂B₇ and A₅B₁₉-type alloys, respectively (A₂B₇ and A₅B₁₉ being larger than that of the AB₅-type alloy they used for comparison purpose: 1.38 wt%). However, such alloy system still needs major improvement, since the decomposition pressure is very low, ranging from about 10⁻² to 0.4 atm, which is still impractical for solid-state hydrogen storage applications.

6. Solid Solutions

Metallurgically speaking, the term “solid solution alloy” designates a primary element (solvent) into which one or more minor elements (solutes) are dissolved. Unlike the intermetallic compound, the solute does not need to be present at an integer or near-integer stoichiometric ratio and is present in a random (disordered) substitutional or interstitial distribution within the basic crystal structure. Several solid solution alloys form reversible hydrides, in particular those based on Pd, Ti, Zr, Nb and V solvents [145].

Despite excellent properties such as fast absorption/desorption kinetics and large hydrogen gravimetric density of maximum 3.8 wt% at moderate temperatures, V-based alloys suffer major drawbacks preventing their rapid and widespread applications. These limitations are (i) the relatively difficult first activation, and (ii) the high thermal stability of its hydride phases yielding poor cyclic performance (reversible capacity down to ~2 wt% H₂ at room temperature) [49,146].

Upon hydrogenation, V forms a solid solution α followed by β phase (V₂H with body-centered tetragonal structure) and then the γ phase (VH₂ with CaF₂ crystal structure), whose respective thermal stability drastically differs. Indeed, the β phase is so stable that its hydrogen desorption reaction never occurs under moderate conditions, its desorption pressure usually ranging 10⁻⁵–0.1 atm. On the other hand, the γ phase is not as stable as its β counterpart and its hydrogen absorption/desorption reaction occurs at moderate temperatures and pressures (over 1 atm at room temperature). Therefore, due to

the stability of the β phase, only about half of the amount of hydrogen absorbed in vanadium metal can be used in the hydrogen absorption and desorption processes under practical conditions [146].

Thermodynamic destabilization of the β phase of pristine V stands out as the main solution to tackle the issues mentioned above. Hence, similarly to any other A_xB_y alloy category, the use of alloying elements of diverse nature and simultaneous addition (binary, ternary and quaternary systems for instance) can destabilize the hydride phases, by altering the ionicity, electronic density of states and lattice parameters [49].

Binary V-based systems cover a broad range of elements, with Ti being the most studied one in the light of its high solubility in V [147], the improved hydrogenation rates and increased terminal solid solubility (TSS) of hydrogen [49]. Although Ti is widely utilized, other elements such as Si, Al and Fe are also considered, but turn out to decrease the hydrogenation rates [148,149], while Mo addition increases hydrogenation-dehydrogenation pressure and decreases the hydrogen storage capacity for instance [150].

To push further the enhancement brought by binary alloys, ternary systems have been developed, notably V–Ti–Cr which remains the most documented ternary alloy due to its excellent improvement of the cyclic stability (as compared to its former binary V–Ti counterpart) while maintaining high effective capacity at room temperature [151–153]. Storage capacity can be controlled and increased by tuning the compositional ratio of those three elements, for instance in a mixture of 60 at% V, 15 at% Ti and 25 at% Cr which reaches as high as 2.62 wt% [154]. V–Ti–Cr alloys however show a steep slope of hydrogen absorption–desorption plateaus, requiring homogenization by heat treatment [155,156] and melt-quenching treatment [157,158]. Besides, the formation of an enriched Ti phase during heat treatment and the oxidation of Ti during melt-quenching both reduce the amount of stored hydrogen and complicate the activation process [159].

In spite of the attractive storage capacity of V–Ti–Cr alloys, they remain expensive since the price of pure V is very high. Fe can thus be used as a replacement of V in ternary systems, and excellent storage capacity of 3.9 wt% with a reversible capacity of 2.4 wt% are reported for $Ti_{43.5}V_{49}Fe_{7.5}$ (at 253 K) [160]. Fe also shows a great potential for tailoring plateau pressures, for instance in $(V_{0.9}Ti_{0.1})_{1-x}Fe$ alloys (with $x = 0-0.075$) [161]. The reduction of costs by Fe addition has also been attempted for quaternary alloys, notably by Luo et al. [162] who synthesized $V_{48}Fe_{12}Ti_{15}Cr_{25}$. The maximum hydrogen storage capacity of this alloy reached 1.98 wt% at 315 K, which is lower than that of other V–Ti–Cr series alloys, due to smaller lattice constant and cell volume.

The lattice constant of the alloys is closely related to the amount of hydrogen absorbed/desorbed [154,163,164]: $V_{48}Fe_{12}Ti_{15}Cr_{25}$ has smaller interstitial sites, which could lead to a lower hydrogen storage capacity, higher plateau pressure, and smaller hysteresis. Similar to Fe addition, the use of Ce is shown by Liu et al. [165] to improve the flatness of plateau of the $Ti_{32}Cr_{46}V_{22}$ BCC alloy, as a result of the microstructural homogenization during heat-treatment (Ce also increases the hydrogen capacity by lowering the oxygen concentration). The heat-treated $Ti_{32}Cr_{46}V_{22}Ce_{0.4}$ alloy can release 2.00 and 2.52 wt% H_2 at 343 and 298 K, respectively, under 1 atm.

In general, quaternary alloys compile the advantages of the already optimized properties of ternary V–Ti–Cr alloys, and display an improved cyclic stability without noticeable change of the storage capacity after the addition of various atoms such as Fe [166], Nb [167] or even C [168]. However, even more complex systems exist, as shown by Yang et al. [169], who conducted partial substitution studies on V–Ti–Cr–Fe alloys using Co and Zr for improving the storage and cyclic properties. They found out that the hydrogen absorption-desorption capacities of the $(VFe)_{60}(TiCrCo)_{40-x}Zr_x$ alloys decrease with increasing Zr content. The maximum desorption capacity reaches 2.10 wt% when $x = 0$, against 1.88 wt% when $x = 2$. This could be ascribed to the decrease of the volume fraction of the BCC phase while the other phases increase with the Zr content. At the same time, the rate of cyclic degradation decreases with higher Zr content, from 10.9% after 10 cycles (for $x = 0$) down to 4.5% (when $x = 2$). Moreover, as the Zr content increases, the hydriding incubation period shortens from 120 s for $x = 0$ down to 4 s for $x = 2$. Additionally, more than 90% of the maximum hydrogen

absorption capacity is achieved in 400 s when $x = 0$, while only about 150 s when $x = 2$. Figure 8 shows the desorption behaviour of some representative solid solution alloys described in this section (see Table 7 for more information on the plotted alloys).

Figure 8. Desorption pressure-composition isotherms of V and V-Fe at 313 K [146], $\text{Ti}_{32}\text{Cr}_{46}\text{V}_{22}\text{Ce}_{0.4}$ at 298 K and 318 K [165], $\text{V}_{48}\text{Fe}_{12}\text{Ti}_{15}\text{Cr}_{25}$ at 295 K [162] and $(\text{VFe})_{60}(\text{TiCrCo})_{39.5}\text{Zr}_{0.5}$ at 298 K [169].

Table 7. Summary of the main properties of Solid Solutions presented in this section and plotted in Figure 8.

Alloy	Temperature (K)	Structure Type	Lattice Parameters (nm)	Maximum/Reversible Capacity (wt%)	P_a/P_d (atm)	Remarks on the Effects of Partial Substitution
V [146]	313	BCC	-	3.63/1.8	-/4.57	-
V-Fe [146]	313	BCC	-	3.50/1.6	-/6.99	Fe (smaller radius) increases the plateau pressure and inhibits the diffusion of hydrogen.
$\text{Ti}_{32}\text{Cr}_{46}\text{V}_{22}\text{Ce}_{0.4}$ [165]	298 318	BCC	-	3.63/2.5 3.44/2.0	-/1.41 -/3.40	Cr and Ti additions improve cyclic stability, reaction rates, and terminal solid solubility. Ce increases the hydrogen capacity by lowering the oxygen concentration.
$\text{V}_{48}\text{Fe}_{12}\text{Ti}_{15}\text{Cr}_{25}$ [162]	295	BCC	$a = 0.2967$	1.98/1.1	1.91/1.01	Commercial ferrovanadium substitution for V lowers the alloy costs, reduces hydrogen storage capacity, hysteresis and cycle stability, and makes higher plateau pressure.
$(\text{VFe})_{60}(\text{TiCrCo})_{39.5}\text{Zr}_{0.5}$ [169]	298	BCC	$a = 0.3081$	3.61/1.6	-/1.89	Co and Zr enhance the storage and cyclic properties, but the hydrogen absorption/desorption capacities decrease with increasing Zr content. The rate of cyclic degradation decreases with higher Zr content and the hydriding incubation period shortens.

In summary, the effect of partial substitution on the microstructure and subsequent hydrogenation properties (plateau pressure, storage capacity, hysteresis and so on) shown in this section are not limited to solid solutions like Ti-V-Cr mentioned earlier. Similar observations can be made on other classes of alloys, as described earlier in this review. In principle, the substitution by a smaller element (smaller radius) leads to a smaller cell volume and induces an increased plateau pressure, for instance in (Ti,Mn)-based AB_2 -type alloys (Fe substitution for Mn [95], or simply by increasing Mn content to contract the lattice [170]), in La-Mg-Ni-based AB_3 alloys (Y substitution for La [139]), or in V solid

solution (Fe substitution for V [146]). On the other hand, the use of larger radius enlarges the cell volume and decreases the plateau pressure, for LaNi₅ (increasing Zn substitution for Ni) [76], for TiFe (Mn substitution for Fe) [119], and also for La–Mg–Ni-based AB₃ alloy (Co, Mo and Al substitution for Ni) [141–143] for example. It is however difficult to generalize the trends from this non-exhaustive list, notably to establish clear effects on the storage capacity. Indeed, since the substitution may lead to the formation of multicomponent systems, the formation of secondary phases may additionally alter the storage properties (see Tables 3–7 for a more detailed case-by-case comparison).

7. Conclusions

Hydrogen is a sustainable energy carrier that can totally redefine and transform the future global energy industry. The actual barrier for implementing hydrogen economy is not only the lack of adequate infrastructures, but also the safe and long-term storage methods. As described in this review, solid-state storage systems based on intermetallic compounds and solid solutions are recognized as one of the most feasible solutions to store hydrogen for hydrogen-powered systems. Overall, the alloys described here cannot store large quantities of hydrogen (most gravimetric densities being around and under 2 wt%). Therefore, developing new kinds of metal hydrides with larger hydrogen storage capacities remains a significant challenge for scientists and engineers. In this review, we evaluated and compared several alloys and presented the most successful and promising modifications aiming to improve their hydrogen sorption properties. In an attempt to overview the most promising representatives of each alloy category, both classical and recent publications have been reviewed. In our opinion, Mm_{0.9}Ca_{0.1}Ni_{4.6}Fe_{0.3}Al_{0.1} (AB₅), (Ti_{0.65}Zr_{0.35})_{1.05}MnCr_{0.8}Fe_{0.2} and Ti_{1.02}Cr_{1.1}Mn_{0.3}Fe_{0.6}La_{0.03} (low/high pressure AB₂), Ti_{1.1}Fe_{0.8}Mn_{0.2} (AB), La_{0.60}V_{0.05}Mg_{1.32}Ca_{1.03}Ni₉ (AB₃), and Ti₃₂Cr₄₆Y₂₂Ce_{0.4} (solid solutions) all gather some of the best properties among other compounds presented here (see Table 8). The enhancement of room temperature properties they show deserves additional investigations to open the route to further developments.

Partial substitution, even as trivial as a few weight percent of one element for another, can induce drastic changes in all hydrogen-related properties of A_xB_y alloys. This unique potential for tuning the properties by manipulating the composition enables the development of tailor-made alloys as per specific application targets. Whether for storage or high-pressure compression of hydrogen, AB₅ and AB₂ alloys illustrate particularly well this fact, which explains the extensive research they have undergone. Hence, tremendous progress has been made especially in the past two decades, leading to actual commercialization. Those are few among many examples, which encourage application-driven research, stimulating the hope to see one day A_xB_y alloys move from laboratory to industrial-scale in a society based on hydrogen economy.

Table 8. Summary of the main properties of most promising alloys presented in each section.

Alloy	Temperature (K)	Structure Type	Lattice Parameters (nm)	Maximum/Reversible Storage Capacity (wt%)	P _a /P _d (atm)
Mm _{0.9} Ca _{0.1} Ni _{4.6} Fe _{0.3} Al _{0.1} [67]	300	CaCu ₅	a = 0.4962 c = 0.4018	1.96/1.65	10.00/5.00
(Ti _{0.65} Zr _{0.35}) _{1.05} MnCr _{0.8} Fe _{0.2} [92]	305	MgZn ₂	-	2.2/1.75	5.30/2.80
Ti _{1.02} Cr _{1.1} Mn _{0.3} Fe _{0.6} La _{0.03} [99]	263	MgZn ₂	a = 0.4862 c = 0.7975	1.7/1.2	218/137
Ti _{1.1} Fe _{0.8} Mn _{0.2} [119]	313	CsCl	a = 0.2990	~1.75/~1.65	~1.0 (mid-point)
La _{0.60} Y _{0.05} Mg _{1.32} Ca _{1.03} Ni ₉ [139]	298	NbBe ₃	a = 0.4955 c = 2.3935	1.79/1.4	5.31/3.11
Ti ₃₂ Cr ₄₆ V ₂₂ Ce _{0.4} [165]	298 318	BCC	-	3.63/2.5 3.44/2.0	-1.41 -3.40

Author Contributions: Conceptualization, A.L., J.O.F., J.P. and J.-Y.S.; Writing—Original Draft Preparation, A.L., J.O.F. and M.F.; Writing—Review and Editing, J.O.F., J.-Y.S., Y.-S.L., J.-H.S., J.P. and Y.W.C.; Visualization, A.L., J.O.F. and M.F.; Supervision, J.O.F. and J.-Y.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the “Technology Development Program to Solve Climate Changes” of the National Research Foundation (NRF) funded by the Ministry of Science, ICT & Future Planning (Grant number: 2015M1A2A2074688) and the APC was funded by Korea Institute of Science and Technology (2E30201).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Schlapbach, L.; Züttel, A. Hydrogen-Storage Materials for Mobile Applications. In *Materials for Sustainable Energy: A Collection of Peer-Reviewed Research and Review Articles from Nature Publishing Group*; World Scientific: Singapore, 2011; pp. 265–270.
2. Orimo, S.; Matsushima, T.; Fujii, H.; Fukunaga, T.; Majer, G.; Züttel, A.; Schlapbach, L. Nanostructured graphite-hydrogen systems prepared by mechanical milling method. *Mol. Cryst. Liq. Cryst.* **2002**, *386*, 173–178. [[CrossRef](#)]
3. Von Colbe, J.B.; Ares, J.-R.; Barale, J.; Baricco, M.; Buckley, C.; Capurso, G.; Gallandat, N.; Grant, D.M.; Guzik, M.N.; Jacob, I.; et al. Application of hydrides in hydrogen storage and compression: Achievements, outlook and perspectives. *Int. J. Hydrog. Energy* **2019**, *44*, 7780–7808. [[CrossRef](#)]
4. Liu, T.; Wang, C.; Wu, Y. Mg-based nanocomposites with improved hydrogen storage performances. *Int. J. Hydrog. Energy* **2014**, *39*, 14262–14274. [[CrossRef](#)]
5. Trudeau, M.L. Advanced Materials for Energy Storage. *MRS Bull.* **1999**, *24*, 23–26. [[CrossRef](#)]
6. Wang, P.; Kang, X.-D. ChemInform Abstract: Hydrogen-Rich Boron-Containing Materials for Hydrogen Storage. *ChemInform* **2009**, *40*, 5400–5413. [[CrossRef](#)]
7. Hong, S.-H.; Song, M.Y. Hydrogen desorption and absorption properties of Pd and MgO or nano-sized Ni-added MgH₂ + LiBH₄ composites. *Mater. Res. Bull.* **2013**, *48*, 3453–3458. [[CrossRef](#)]
8. Rusman, N.; Dahari, M. A review on the current progress of metal hydrides material for solid-state hydrogen storage applications. *Int. J. Hydrog. Energy* **2016**, *41*, 12108–12126. [[CrossRef](#)]
9. Jain, I.; Lal, C.; Jain, A. Hydrogen storage in Mg: A most promising material. *Int. J. Hydrog. Energy* **2010**, *35*, 5133–5144. [[CrossRef](#)]
10. Dolotko, O.; Gupta, S.; Kobayashi, T.; McDonald, E.; Hlova, I.; Majzoub, E.; Balema, V.P.; Pruski, M.; Pecharsky, V.K. Mechanochemical reactions and hydrogen storage capacities in MBH₄–SiS₂ systems (MLi or Na). *Int. J. Hydrog. Energy* **2019**, *44*, 7381–7391. [[CrossRef](#)]
11. Jiang, Z.; Yuan, J.; Han, H.; Wu, Y. Effect of carbon nanotubes on the microstructural evolution and hydrogen storage properties of Mg(BH₄). *J. Alloy. Compd.* **2018**, *743*, 11–16. [[CrossRef](#)]
12. Afonso, G.; Bonakdarpour, A.; Wilkinson, D.P. Hydrogen Storage Properties of the Destabilized 4NaBH₄/5Mg₂NiH₄ Composite System. *J. Phys. Chem. C* **2013**, *117*, 21105–21111. [[CrossRef](#)]
13. Javadian, P.; Zlotea, C.; Ghimbeu, C.M.; Latroche, M.; Jensen, T.R. Hydrogen Storage Properties of Nanoconfined LiBH₄–Mg₂NiH₄ Reactive Hydride Composites. *J. Phys. Chem. C* **2015**, *119*, 5819–5826. [[CrossRef](#)]
14. Severa, G.; Ronnebro, E.; Jensen, C.M. Direct hydrogenation of magnesium boride to magnesium borohydride: Demonstration of >11 weight percent reversible hydrogen storage. *Chem. Commun.* **2010**, *46*, 421–423. [[CrossRef](#)] [[PubMed](#)]
15. Duan, C.; Cao, Y.; Hu, L.; Fu, D.; Ma, J.; Youngblood, J. An efficient mechanochemical synthesis of alpha-aluminum hydride: Synergistic effect of TiF₃ on the crystallization rate and selective formation of alpha-aluminum hydride polymorph. *J. Hazard. Mater.* **2019**, *373*, 141–151. [[CrossRef](#)] [[PubMed](#)]
16. Bogdanović, B.; Hartwig, T.; Spliethoff, B. The development, testing and optimization of energy storage materials based on the MgH₂ Mg system. *Int. J. Hydrog. Energy* **1993**, *18*, 575–589. [[CrossRef](#)]
17. 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. Alloy. Compd.* **2006**, *407*, 249–255. [[CrossRef](#)]
18. Barkhordarian, G.; Klassen, T.; Bormann, R. Fast hydrogen sorption kinetics of nanocrystalline Mg using Nb₂O₅ as catalyst. *Scr. Mater.* **2003**, *49*, 213–217. [[CrossRef](#)]

19. Oelerich, W.; Klassen, T.; Bormann, R. Comparison of the catalytic effects of V, V_2O_5 , VN, and VC on the hydrogen sorption of nanocrystalline Mg. *J. Alloy. Compd.* **2001**, *322*, L5–L9. [[CrossRef](#)]
20. Sargent, A.-L.; Sheppard, D.A.; Paskevicius, M.; Pistidda, C.; Dornheim, M.; Buckley, C.E. Reaction kinetic behaviour with relation to crystallite/grain size dependency in the Mg–Si–H system. *Acta Mater.* **2015**, *95*, 244–253. [[CrossRef](#)]
21. Vajo, J.J.; Mertens, F.; Ahn, C.C.; Bowman, J.R.C.; Fultz, B. Altering Hydrogen Storage Properties by Hydride Destabilization through Alloy Formation: LiH and MgH_2 Destabilized with Si. *J. Phys. Chem. B* **2004**, *108*, 13977–13983. [[CrossRef](#)]
22. Su, W.; Zhu, Y.; Zhang, J.; Liu, Y.; Yang, Y.; Mao, Q.; Li, L. Effect of multi-wall carbon nanotubes supported nano-nickel and TiF_3 addition on hydrogen storage properties of magnesium hydride. *J. Alloy. Compd.* **2016**, *669*, 8–18. [[CrossRef](#)]
23. Asselli, A.A.C.; Botta, W.J.; Huot, J. Formation reaction of Mg_2FeH_6 : Effect of hydrogen absorption/desorption kinetics. *Mater. Res.* **2013**, *16*, 1373–1378. [[CrossRef](#)]
24. Huot, J.; Hayakawa, H.; Akiba, E. Preparation of the hydrides Mg_2FeH_6 and Mg_2CoH_5 by mechanical alloying followed by sintering. *J. Alloy. Compd.* **1997**, *248*, 164–167. [[CrossRef](#)]
25. Bogdanovic, B.; Hofmann, H.; Neuy, A.; Reiser, A.; Schlichte, K.; Spliethoff, B.; Wessel, S. Ni-doped versus undoped Mg– MgH_2 materials for high temperature heat or hydrogen storage. *J. Alloy. Compd.* **1999**, *292*, 57–71. [[CrossRef](#)]
26. Felderhoff, M.; Bogdanović, B. High Temperature Metal Hydrides as Heat Storage Materials for Solar and Related Applications. *Int. J. Mol. Sci.* **2009**, *10*, 325–344. [[CrossRef](#)] [[PubMed](#)]
27. Puzskiel, J.; Riglos, M.V.C.; Ramallo-López, J.M.; Mizrahi, M.; Gemming, T.; Pistidda, C.; Larochette, P.A.; Von Colbe, J.B.; Klassen, T.; Dornheim, M.; et al. New Insight on the Hydrogen Absorption Evolution of the Mg–Fe–H System under Equilibrium Conditions. *Metals* **2018**, *8*, 967. [[CrossRef](#)]
28. Witek, K.; Karczewski, K.; Karpowicz, M.; Polański, M. Mg_2FeH_6 Synthesis Efficiency Map. *Crystals* **2018**, *8*, 94. [[CrossRef](#)]
29. Polański, M.; Nawra, D.; Zasada, D. Mg_2FeH_6 synthesized from plain steel and magnesium hydride. *J. Alloy. Compd.* **2019**, *776*, 1029–1040. [[CrossRef](#)]
30. Fadonougbo, J.O.; Jung, J.-Y.; Suh, J.-Y.; Lee, Y.-S.; Shim, J.-H.; Cho, Y.W. Low temperature formation of Mg_2FeH_6 by hydrogenation of ball-milled nano-crystalline powder mixture of Mg and Fe. *Mater. Des.* **2017**, *135*, 239–245. [[CrossRef](#)]
31. Jung, J.Y.; Fadonougbo, J.O.; Suh, J.-Y.; Lee, Y.-S.; Huh, J.-Y.; Cho, Y.W. Synthesis of Mg_2FeH_6 by hydrogenation of Mg/Fe powder mixture prepared by cold roll milling in air: Effects of microstructure and oxygen distribution. *Int. J. Hydrog. Energy* **2018**, *43*, 16758–16765. [[CrossRef](#)]
32. Fadonougbo, J.O.; Jung, J.-Y.; Suh, J.-Y.; Lee, Y.-S.; Shim, J.-H.; Fleury, E.; Cho, Y.W. The role of Fe particle size and oxide distribution on the hydrogenation properties of ball-milled nano-crystalline powder mixtures of Fe and Mg. *J. Alloy. Compd.* **2019**, *806*, 1039–1046. [[CrossRef](#)]
33. Bobet, J. Study of Mg–M (M = Co, Ni and Fe) mixture elaborated by reactive mechanical alloying: Hydrogen sorption properties. *Int. J. Hydrog. Energy* **2001**, *26*, 493–501. [[CrossRef](#)]
34. Rzeszotarska, M.; Czujko, T.; Polański, M. $Mg_2(Fe, Cr, Ni)Hx$ complex hydride synthesis from austenitic stainless steel and magnesium hydride. *Int. J. Hydrog. Energy* **2020**, *45*, 19440–19454. [[CrossRef](#)]
35. Fadonougbo, J.O.; Kim, H.-J.; Suh, B.-C.; Suh, J.-Y.; Lee, Y.-S.; Shim, J.-H.; Yim, C.D.; Cho, Y.W. Kinetics and thermodynamics of near eutectic Mg– Mg_2Ni composites produced by casting process. *Int. J. Hydrog. Energy* **2020**, *45*, 29009–29022. [[CrossRef](#)]
36. Shao, H.; He, L.; Lin, H.; Li, H.-W. Progress and Trends in Magnesium-Based Materials for Energy-Storage Research: A Review. *Energy Technol.* **2018**, *6*, 445–458. [[CrossRef](#)]
37. Iba, H.; Akiba, E. Hydrogen absorption and modulated structure in Ti–V–Mn alloys. *J. Alloy. Compd.* **1997**, *253*, 21–24. [[CrossRef](#)]
38. Principi, G.; Agresti, F.; Maddalena, A.; Russo, S.L. The problem of solid state hydrogen storage. *Energy* **2009**, *34*, 2087–2091. [[CrossRef](#)]
39. US Department of Energy. *DOE Technical Targets for Onboard Hydrogen Storage for Light-Duty Vehicles*; Office of Energy Efficiency and Renewable Energy: Washington, DC, USA, 2017.

40. Hirscher, M.; Yartys, V.; Baricco, M.; Von Colbe, J.B.; Blanchard, D.; Bowman, R.C.; Broom, D.P.; Buckley, C.E.; Chang, F.; Chen, P.; et al. Materials for hydrogen-based energy storage—past, recent progress and future outlook. *J. Alloy. Compd.* **2020**, *827*, 153548. [[CrossRef](#)]
41. Moradi, R.; Groth, K.M. Hydrogen storage and delivery: Review of the state of the art technologies and risk and reliability analysis. *Int. J. Hydrog. Energy* **2019**, *44*, 12254–12269. [[CrossRef](#)]
42. Ren, J.; Musyoka, N.M.; Langmi, H.W.; Mathe, M.; Liao, S. Current research trends and perspectives on materials-based hydrogen storage solutions: A critical review. *Int. J. Hydrog. Energy* **2017**, *42*, 289–311. [[CrossRef](#)]
43. Abe, J.; Popoola, A.; Ajenifuja, E.; Popoola, O. Hydrogen energy, economy and storage: Review and recommendation. *Int. J. Hydrog. Energy* **2019**, *44*, 15072–15086. [[CrossRef](#)]
44. Bannenberg, L.; Heere, M.; Benzidi, H.; Montero, J.; Dematteis, E.; Suwarno, S.; Jaroń, T.; Winny, M.; Orłowski, P.; Wegner, W. Metal (boro-) hydrides for high energy density storage and relevant emerging technologies. *Int. J. Hydrog. Energy* **2020**, *45*, 33687–33730. [[CrossRef](#)]
45. Yartys, V.; Lototsky, M.; Akiba, E.; Albert, R.; Antonov, V.; Ares, J.; Baricco, M.; Bourgeois, N.; Buckley, C.; Von Colbe, J.B.; et al. Magnesium based materials for hydrogen based energy storage: Past, present and future. *Int. J. Hydrog. Energy* **2019**, *44*, 7809–7859. [[CrossRef](#)]
46. Crivello, J.-C.; Denys, R.V.; Dornheim, M.; Felderhoff, M.; Grant, D.M.; Huot, J.; Jensen, T.R.; De Jongh, P.E.; Latroche, M.; Walker, G.; et al. Mg-based compounds for hydrogen and energy storage. *Appl. Phys. A* **2016**, *122*, 1–17. [[CrossRef](#)]
47. Baran, A.; Polański, M. Magnesium-Based Materials for Hydrogen Storage—A Scope Review. *Materials* **2020**, *13*, 3993. [[CrossRef](#)]
48. Liu, W.; Webb, C.; Gray, E. Review of hydrogen storage in AB₃ alloys targeting stationary fuel cell applications. *Int. J. Hydrog. Energy* **2016**, *41*, 3485–3507. [[CrossRef](#)]
49. Kumar, S.; Jain, A.; Ichikawa, T.; Kojima, Y.; Dey, G. Development of vanadium based hydrogen storage material: A review. *Renew. Sustain. Energy Rev.* **2017**, *72*, 791–800. [[CrossRef](#)]
50. Klebanoff, L. Hydrogen storage technology: Materials and applications. *Choice Rev. Online* **2013**, *50*, 50. [[CrossRef](#)]
51. Borzone, E.; Baruj, A.; Blanco, M.; Meyer, G. Dynamic measurements of hydrogen reaction with LaNi_{5-x}Sn_x alloys. *Int. J. Hydrog. Energy* **2013**, *38*, 7335–7343. [[CrossRef](#)]
52. Modibane, K.; Lototsky, M.V.; Davids, M.; Williams, M.; Hato, M.; Molapo, K. Influence of co-milling with palladium black on hydrogen sorption performance and poisoning tolerance of surface modified AB₅-type hydrogen storage alloy. *J. Alloy. Compd.* **2018**, *750*, 523–529. [[CrossRef](#)]
53. Pan, H.; Liu, Y.; Gao, M.; Zhu, Y.; Lei, Y. The structural and electrochemical properties of La_{0.7}Mg_{0.3}(Ni_{0.85}Co_{0.15})_x (x = 3.0–5.0) hydrogen storage alloys. *Int. J. Hydrog. Energy* **2003**, *28*, 1219–1228. [[CrossRef](#)]
54. Sharma, V.K.; Kumar, E.A. Effect of measurement parameters on thermodynamic properties of La-based metal hydrides. *Int. J. Hydrog. Energy* **2014**, *39*, 5888–5898. [[CrossRef](#)]
55. Prigent, J.; Joubert, J.-M.; Gupta, M. Modification of the hydrogenation properties of LaNi₅ upon Ni substitution by Rh, Ir, Pt or Au. *J. Alloy. Compd.* **2012**, *511*, 95–100. [[CrossRef](#)]
56. Georgiadis, M.C.; Kikkinides, E.; Makridis, S.S.; Kouramas, K.; Pistikopoulos, E.N. Design and optimization of advanced materials and processes for efficient hydrogen storage. *Comput. Chem. Eng.* **2009**, *33*, 1077–1090. [[CrossRef](#)]
57. Liu, J.J.; Li, K.; Cheng, H.H.; Yan, K.; Wang, Y.; Liu, Y.; Jin, H.M.; Zheng, Z. New insights into the hydrogen storage performance degradation and Al functioning mechanism of LaNi_{5-x}Al_x alloys. *Int. J. Hydrog. Energy* **2017**, *42*, 24904–24914. [[CrossRef](#)]
58. Zhu, Y.; Yang, C.; Zhu, J.; Li, L. Structural and electrochemical hydrogen storage properties of Mg₂Ni-based alloys. *J. Alloy. Compd.* **2011**, *509*, 5309–5314. [[CrossRef](#)]
59. Pęska, M.; Dworecka-Wójcik, J.; Płociński, T.; Polański, M. The Influence of Cerium on the Hydrogen Storage Properties of La_{1-x}Ce_xNi₅ Alloys. *Energies* **2020**, *13*, 1437. [[CrossRef](#)]
60. Chen, J.; Dou, S.; Liu, H.K. Effect of partial substitution of La with Ce, Pr and Nd on the properties of LaNi₅-based alloy electrodes. *J. Power Sources* **1996**, *63*, 267–270. [[CrossRef](#)]
61. Balasubramaniam, R.; Mungole, M.; Rai, K. Hydriding properties of MmNi₅ system with aluminium, manganese and tin substitutions. *J. Alloy. Compd.* **1993**, *196*, 63–70. [[CrossRef](#)]

62. Mungole, M. Hysteresis in MmNi_5 systems with aluminium, manganese and tin substitutions. *Int. J. Hydrog. Energy* **1995**, *20*, 151–157. [[CrossRef](#)]
63. Molinas, B.; Pontarollo, A.; Scapin, M.; Peretti, H.; Melnichuk, M.; Corso, H.; Aurora, A.; Gattia, D.M.; Montone, A. The optimization of $\text{MmNi}_{5-x}\text{Al}_x$ hydrogen storage alloy for sea or lagoon navigation and transportation. *Int. J. Hydrog. Energy* **2016**, *41*, 14484–14490. [[CrossRef](#)]
64. Iosub, V.; Latroche, M.; Joubert, J.-M.; Percheron-Guégan, A. Optimisation of $\text{MmNi}_{5-x}\text{Sn}_x$ ($\text{Mm} = \text{La, Ce, Nd}$ and Pr , $0.27 < x < 0.5$) compositions as hydrogen storage materials. *Int. J. Hydrog. Energy* **2006**, *31*, 101–108.
65. Zhou, W.; Tang, Z.; Zhu, D.; Ma, Z.; Wu, C.; Huang, L.; Chen, Y. Low-temperature and instantaneous high-rate output performance of AB_5 -type hydrogen storage alloy with duplex surface hot-alkali treatment. *J. Alloy. Compd.* **2017**, *692*, 364–374. [[CrossRef](#)]
66. Srivastava, S.; Upadhyaya, R. Investigations on synthesis, characterization and hydrogenation behavior of hydrogen storage alloys, $\text{Mm}_{1-x}\text{Ca}_x\text{Ni}_{5-y-z}\text{Al}_y\text{Fe}_z$ ($x = 0, 0.05, 0.1, 0.2, 0.3$; $y = 0, 0.1$; $z = 0, 0.1$) $\text{Mm}_{1-x}\text{Ca}_x\text{Ni}_{5-y-z}\text{Al}_y\text{Fe}_z$ ($x = 0, 0.05, 0.1, 0.2, 0.3$; $y = 0, 0.1$; $z = 0, 0.1$). *Int. J. Hydrog. Energy* **2007**, *32*, 4195–4201. [[CrossRef](#)]
67. Srivastava, S.; Upadhyaya, R. Investigations of AB_5 -type hydrogen storage materials with enhanced hydrogen storage capacity. *Int. J. Hydrog. Energy* **2011**, *36*, 7114–7121. [[CrossRef](#)]
68. Sandrock, G. A New Family of Hydrogen Storage Alloys Based on the System Nickel-Mischmetal-Calcium. In Proceedings of the 12th Intersociety Energy Conversion Engineering Conference, Washington, DC, USA, 28 August–2 September 1977; pp. 951–958.
69. Shinar, J.; Shaltiel, D.; Davidov, D.; Grayevsky, A. Hydrogen sorption properties of the $\text{La}_{1-x}\text{Ca}_x\text{Ni}_5$ and $\text{La}(\text{Ni}_{1-x}\text{Cu}_x)_5$ systems. *J. Less Comm. Metals* **1978**, *60*, 209–219. [[CrossRef](#)]
70. Wang, X.; Chen, C.; Wang, C.; Wang, Q. Hydrogen storage properties of $\text{Ml}_{1-x}\text{Ca}_x\text{Ni}_5$ pseudobinary intermetallic compounds. *J. Alloy. Compd.* **1996**, *232*, 192–196. [[CrossRef](#)]
71. Kumar, E.A.; Sharma, V. Simulation of Pressure Concentration Isotherms of $\text{MmNi}_{5-x}\text{Al}_x$ Hydrides. In Proceedings of the 13th International Conference on Fuel Cell & Hydrogen Technologies, Kuala Lumpur, Malaysia, 22–23 November 2011.
72. Sarma, V. On the mechanically pulverized $\text{MmNi}_{4.6}\text{Fe}_{0.4}$ as a viable hydrogen storage material. *Int. J. Hydrog. Energy* **2001**, *26*, 231–236. [[CrossRef](#)]
73. Apostolov, A.; Stanev, N.; Tcholakov, P. Hydrogen desorption characteristics of $\text{MmNi}_{5-x}\text{Fe}_x$ compounds. *J. Less Common Metals* **1985**, *110*, 127–129. [[CrossRef](#)]
74. An, X.; Gu, Q.; Zhang, J.; Chen, S.; Yu, X.; Li, Q. Experimental investigation and thermodynamic reassessment of La-Ni and $\text{LaNi}_5\text{-H}$ systems. *Calphad* **2013**, *40*, 48–55. [[CrossRef](#)]
75. Verbetsky, V.; Sirotina, R.; Umerenko, E. Absorption of hydrogen by MmNi_5 alloys. *Int. J. Hydrog. Energy* **1996**, *21*, 935–938. [[CrossRef](#)]
76. Rozdzyńska-Kielbik, B.; Iwasieczko, W.; Drulis, H.; Pavlyuk, V.; Bala, H. Hydrogenation equilibria characteristics of $\text{LaNi}_{5-x}\text{Zn}_x$ intermetallics. *J. Alloy. Compd.* **2000**, *298*, 237–243. [[CrossRef](#)]
77. Abu Dakka, M.I.; Jain, I. Comparative study of hydrogen in $\text{La(28.9)Ni(67.55)Si(3.55)}$ and LaNi . *Int. J. Hydrog. Energy* **2000**, *25*, 773–777. [[CrossRef](#)]
78. Bowman, R., Jr.; Luo, C.; Ahn, C.; Witham, C.; Fultz, B. The effect of tin on the degradation of $\text{LaNi}_{5-y}\text{Sn}_y$ metal hydrides during thermal cycling. *J. Alloy. Compd.* **1995**, *217*, 185–192. [[CrossRef](#)]
79. Briki, C.; Belkhiria, S.; Dhaou, M.H.; De Rango, P.; Jemni, A. Experimental study of the influences substitution from Ni by Co, Al and Mn on the hydrogen storage properties of $\text{LaNi}_{3.6}\text{Mn}_{0.3}\text{Al}_{0.4}\text{Co}_{0.7}$ alloy. *Int. J. Hydrog. Energy* **2017**, *42*, 10081–10088. [[CrossRef](#)]
80. Yilmaz, F.; Ergen, S.; Hong, S.-J.; Uzun, O. Effect of Bismuth on hydrogen storage properties of melt-spun $\text{LaNi}_{4.7-x}\text{Al}_{0.3}\text{Bi}_x$ ($x = 0.0, 0.1, 0.2, 0.3$) ribbons. *Int. J. Hydrog. Energy* **2018**, *43*, 20243–20251. [[CrossRef](#)]
81. Bououdina, M.; Grant, D.M.; Walker, G. Review on hydrogen absorbing materials—structure, microstructure, and thermodynamic properties. *Int. J. Hydrog. Energy* **2006**, *31*, 177–182. [[CrossRef](#)]
82. Kim, M.-H.; Debnath, M.R.; Wang, Y.-I.; Suh, J.-Y.; Fleury, E.; Kim, D. Effect of Co on the degradation of the hydrogen permeability of Ni-Nb-Zr amorphous membranes. *Metals Mater. Int.* **2014**, *20*, 215–219. [[CrossRef](#)]
83. Zhao, Y.; Choi, I.-C.; Seok, M.-Y.; Kim, M.-H.; Kim, D.-H.; Ramamurty, U.; Suh, J.-Y.; Jang, J.-I. Effect of hydrogen on the yielding behavior and shear transformation zone volume in metallic glass ribbons. *Acta Mater.* **2014**, *78*, 213–221. [[CrossRef](#)]

84. Zhao, Y.; Choi, I.-C.; Seok, M.-Y.; Ramamurty, U.; Suh, J.-Y.; Jang, J.-I. Hydrogen-induced hardening and softening of Ni–Nb–Zr amorphous alloys: Dependence on the Zr content. *Scr. Mater.* **2014**, *93*, 56–59. [[CrossRef](#)]
85. Fadonougbo, J.O.; Suh, J.-Y.; Han, S.; Shim, C.-H.; Kim, G.-H.; Kim, M.-H.; Fleury, E.; Cho, Y.W. Hydrogen-induced decomposition of Cu–Zr binary amorphous metallic alloys. *J. Alloy. Compd.* **2016**, *660*, 456–460. [[CrossRef](#)]
86. Fadonougbo, J.O.; Suh, J.-Y.; Shim, C.-H.; Kim, G.-H.; Fleury, E.; Cho, Y.W. Nanometer-scale phase separation and formation of delta ZrH₂ in Cu–Zr binary amorphous alloys. *J. Alloy. Compd.* **2017**, *721*, 646–652. [[CrossRef](#)]
87. Park, J.-G.; Jang, H.-Y.; Han, S.-C.; Lee, P.S.; Lee, J.-Y. The thermodynamic properties of Ti–Zr–Cr–Mn laves phase alloys. *J. Alloy. Compd.* **2001**, *325*, 293–298. [[CrossRef](#)]
88. Liu, B.-H.; Kim, N.-M.; Lee, K.-Y.; Lee, J.-Y. Hydrogen storage properties of TiMn₂-based alloys. *J. Alloy. Compd.* **1996**, *240*, 214–218. [[CrossRef](#)]
89. Kojima, Y.; Kawai, Y.; Towata, S.-I.; Matsunaga, T.; Shinozawa, T.; Kimbara, M. Development of metal hydride with high dissociation pressure. *J. Alloy. Compd.* **2006**, *419*, 256–261. [[CrossRef](#)]
90. Kandavel, M.; Bhat, V.; Rougier, A.; Aymard, L.; Nazri, G.-A.; Tarascon, J.-M. Improvement of hydrogen storage properties of the AB₂ Laves phase alloys for automotive application. *Int. J. Hydrog. Energy* **2008**, *33*, 3754–3761. [[CrossRef](#)]
91. Morii, K.; Shimizu, T. Hydriding characteristics in (Ti,Zr)(Ni,Mn,X)₂ alloys. *J. Alloy. Compd.* **1995**, *231*, 524–527. [[CrossRef](#)]
92. Manickam, K.; Grant, D.M.; Sardari, P.T. Optimization of AB₂ type alloy composition with superior hydrogen storage properties for stationary applications. *Int. J. Hydrog. Energy* **2015**, *40*, 16288–16296. [[CrossRef](#)]
93. Li, J.; Jiang, X.; Li, G.; Li, X. Development of Ti_{1.02}Cr_{2-x-y}Fe_xMn_y (0.6 ≤ x ≤ 0.75, y = 0.25, 0.3) alloys for high hydrogen pressure metal hydride system. *Int. J. Hydrog. Energy* **2019**, *44*, 15087–15099. [[CrossRef](#)]
94. Lee, J.-Y.; Lee, K.-Y.; Lee, H.-H.; Kim, D.-M.; Yu, J.-S.; Jung, J.-H.; Lee, S.-G. Hydrogen-Storage Material Employing Ti–Mn Alloy System. U.S. Patent 5,888,317A, 30 March 1999.
95. Li, J.; Xu, L.; Jiang, X.; Li, X. Study on the hydrogen storage property of (TiZr_{0.1})_xCr_{1.7-y}Fe_yMn_{0.3} (1.05 < x < 1.2, 0.2 < y < 0.6) alloys. *Prog. Nat. Sci. Mater. Int.* **2018**, *28*, 470–477.
96. Corgnale, C.; Sulic, M. Techno-Economic Analysis of High-Pressure Metal Hydride Compression Systems. *Metals* **2018**, *8*, 469. [[CrossRef](#)]
97. Pickering, L.; Lototsky, M.V.; Davids, M.W.; Sita, C.; Linkov, V. Induction melted AB₂-type metal hydrides for hydrogen storage and compression applications. *Mater. Today Proc.* **2018**, *5*, 10470–10478. [[CrossRef](#)]
98. Ulmer, U.; Dieterich, M.; Pohl, A.; Dittmeyer, R.; Linder, M.P.; Fichtner, M. Study of the structural, thermodynamic and cyclic effects of vanadium and titanium substitution in laves-phase AB₂ hydrogen storage alloys. *Int. J. Hydrog. Energy* **2017**, *42*, 20103–20110. [[CrossRef](#)]
99. Yao, Z.; Liu, L.; Xiao, X.; Wang, C.; Jiang, L.; Chen, L. Effect of rare earth doping on the hydrogen storage performance of Ti_{1.02}Cr_{1.1}Mn_{0.3}Fe_{0.6} alloy for hybrid hydrogen storage application. *J. Alloy. Compd.* **2018**, *731*, 524–530. [[CrossRef](#)]
100. Puszkiel, J.; Bellosta von Colbe, J.M.; Jepsen, J.; Mitrokhin, S.V.; Movlaev, E.; Verbetsky, V.; Klassen, T. Designing an AB₂-Type Alloy (TiZr–CrMnMo) for the Hybrid Hydrogen Storage Concept. *Energies* **2020**, *13*, 2751. [[CrossRef](#)]
101. Wu, T.; Xue, X.; Zhang, T.; Hu, R.; Kou, H.; Li, J. Role of Ni addition on hydrogen storage characteristics of ZrV₂ Laves phase compounds. *Int. J. Hydrog. Energy* **2016**, *41*, 10391–10404. [[CrossRef](#)]
102. Qin, C.; Zhou, C.; Ouyang, L.; Liu, J.; Zhu, M.; Sun, T.; Wang, H. High-pressure hydrogen storage performances of ZrFe₂ based alloys with Mn, Ti, and V addition. *Int. J. Hydrog. Energy* **2020**, *45*, 9836–9844. [[CrossRef](#)]
103. Zhou, C.; Wang, H.; Ouyang, L.; Liu, J.; Zhu, M. Achieving high equilibrium pressure and low hysteresis of Zr–Fe based hydrogen storage alloy by Cr/V substitution. *J. Alloy. Compd.* **2019**, *806*, 1436–1444. [[CrossRef](#)]
104. Blasius, A.; Gonster, U. Mössbauer surface studies on Tife hydrogen storage material. *Appl. Phys. A* **1980**, *22*, 331–332. [[CrossRef](#)]
105. Reilly, J.J.; Wiswall, R.H. Formation and properties of iron titanium hydride. *Inorg. Chem.* **1974**, *13*, 218–222. [[CrossRef](#)]

106. Sandrock, G.D.; Reilly, J.J.; Johnson, J.R. Metallurgical Considerations in the Production and use of FeTi Alloys for Hydrogen Storage. In Proceedings of the Intersociety Energy Conversion Engineering Conference, State Line, NV, USA, 12 September 1976.
107. Edalati, K.; Matsuda, J.; Iwaoka, H.; Toh, S.; Akiba, E.; Horita, Z. High-pressure torsion of TiFe intermetallics for activation of hydrogen storage at room temperature with heterogeneous nanostructure. *Int. J. Hydrog. Energy* **2013**, *38*, 4622–4627. [[CrossRef](#)]
108. Davids, M.W.; Lototsky, M.V.; Nechaev, A.; Naidoo, Q.; Williams, M.; Klochko, Y. Surface modification of TiFe hydrogen storage alloy by metal-organic chemical vapour deposition of palladium. *Int. J. Hydrog. Energy* **2011**, *36*, 9743–9750. [[CrossRef](#)]
109. Qu, H.; Du, J.; Pu, C.; Niu, Y.; Huang, T.; Li, Z.; Lou, Y.; Wu, Z. Effects of Co introduction on hydrogen storage properties of Ti–Fe–Mn alloys. *Int. J. Hydrog. Energy* **2015**, *40*, 2729–2735. [[CrossRef](#)]
110. Yamashita, I.; Tanaka, H.; Takeshita, H.; Kuriyama, N.; Sakai, T.; Uehara, I. Hydrogenation characteristics of $\text{TiFe}_{1-x}\text{Pd}_x$ ($0.05 \leq x \leq 0.30$) alloys. *J. Alloy. Compd.* **1997**, *253*, 238–240. [[CrossRef](#)]
111. Jang, T.; Han, J.; Jai-Young, L. Effect of substitution of titanium by zirconium in TiFe on hydrogenation properties. *J. Less Common Metals* **1986**, *119*, 237–246. [[CrossRef](#)]
112. Bronca, V.; Bergman, P.; Ghaemmaghami, V.; Khatamian, D.; Manchester, F. Hydrogen absorption characteristics of an FeTi + misch metal alloy. *J. Less Common Metals* **1985**, *108*, 313–325. [[CrossRef](#)]
113. 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. Alloy. Compd.* **2011**, *509*, 5562–5566. [[CrossRef](#)]
114. Lee, S.M.; Perng, T.P. Microstructural Correlations with the Hydrogenation Kinetics of $\text{FeTi}_{1+\epsilon}$ Alloys. *J. Alloy. Compd.* **1991**, *177*, 107–118. [[CrossRef](#)]
115. Emami, H.; Edalati, K.; Matsuda, J.; Akiba, E.; Horita, Z. Hydrogen storage performance of TiFe after processing by ball milling. *Acta Mater.* **2015**, *88*, 190–195. [[CrossRef](#)]
116. Chiang, C.-H.; Chin, Z.-H.; Perng, T.-P. Hydrogenation of TiFe by high-energy ball milling. *J. Alloy. Compd.* **2000**, *307*, 259–265. [[CrossRef](#)]
117. Edalati, K.; Matsuda, J.; Yanagida, A.; Akiba, E.; Horita, Z. Activation of TiFe for hydrogen storage by plastic deformation using groove rolling and high-pressure torsion: Similarities and differences. *Int. J. Hydrog. Energy* **2014**, *39*, 15589–15594. [[CrossRef](#)]
118. Johnson, J.; Reilly, J. The Use of Manganese Substituted Ferrotitanium Alloys for Energy Storage. In Proceedings of the The Use of Manganese Substituted Ferrotitanium Alloys for Energy Storage, Miami Beach, FL, USA, 5–7 December 1977.
119. Shang, H.; Zhang, M.; Li, Y.; Qi, Y.; Guo, S.; Zhao, D. Effects of adding over-stoichiometrical Ti and substituting Fe with Mn partly on structure and hydrogen storage performances of TiFe alloy. *Renew. Energy* **2019**, *135*, 1481–1498. [[CrossRef](#)]
120. Wu, C.Y.; Li, J.C. Phase-Structure of the Ti1cu1-Xfex System. *Metall. Trans. A Phys. Metall. Mater. Sci.* **1989**, *20*, 981–985. [[CrossRef](#)]
121. Dematteis, E.M.; Cuevas, F.; Latroche, M. Hydrogen storage properties of Mn and Cu for Fe substitution in $\text{TiFe}_{0.9}$ intermetallic compound. *J. Alloy. Compd.* **2021**, *851*, 156075. [[CrossRef](#)]
122. Nagai, H.; Kitagaki, K.; Shoji, K.-I. Hydrogen Storage Characteristics of FeTi Containing Zirconium. *Trans. Jpn. Inst. Metals* **1988**, *29*, 494–501. [[CrossRef](#)]
123. Lee, S.-M.; Perng, T.-P. Correlation of substitutional solid solution with hydrogenation properties of $\text{TiFe}_{1-x}\text{M}_x$ ($\text{M} = \text{Ni}, \text{Co}, \text{Al}$) alloys. *J. Alloy. Compd.* **1999**, *291*, 254–261. [[CrossRef](#)]
124. Kuziora, P.; Kuncze, I.; McCain, S.; Adkins, N.J.E.; Polański, M. The influence of refractory metals on the hydrogen storage characteristics of FeTi-based alloys prepared by suspended droplet alloying. *Int. J. Hydrog. Energy* **2020**, *45*, 21635–21645. [[CrossRef](#)]
125. Jain, P.; Gosselin, C.; Huot, J. Effect of Zr, Ni and Zr 7 Ni 10 alloy on hydrogen storage characteristics of TiFe alloy. *Int. J. Hydrog. Energy* **2015**, *40*, 16921–16927. [[CrossRef](#)]
126. Yang, T.; Wang, P.; Xia, C.Q.; Liu, N.; Liang, C.Y.; Yin, F.X.; Li, Q. Effect of chromium, manganese and yttrium on microstructure and hydrogen storage properties of TiFe-based alloy. *Int. J. Hydrog. Energy* **2020**, *45*, 12071–12081. [[CrossRef](#)]

127. Ha, T.; Lee, S.-I.; Hong, J.; Lee, Y.-S.; Kim, D.-I.; Suh, J.-Y.; Cho, Y.W.; Hwang, B.; Lee, J.; Shim, J.-H. Hydrogen storage behavior and microstructural feature of a TiFe–ZrCr₂ alloy. *J. Alloy. Compd.* **2021**, *853*, 157099. [\[CrossRef\]](#)
128. Jung, J.-Y.; Lee, Y.-S.; Suh, J.-Y.; Huh, J.-Y.; Cho, Y.W. Tailoring the equilibrium hydrogen pressure of TiFe via vanadium substitution. *J. Alloy. Compd.* **2021**, *854*, 157263. [\[CrossRef\]](#)
129. Ouyang, L.; Huang, J.; Wang, H.; Liu, J.; Zhu, M. Progress of hydrogen storage alloys for Ni–MH rechargeable power batteries in electric vehicles: A review. *Mater. Chem. Phys.* **2017**, *200*, 164–178. [\[CrossRef\]](#)
130. Liu, Y.; Pan, H.; Yue, Y.; Wu, X.; Chen, N.; Lei, Y. Cycling durability and degradation behavior of La–Mg–Ni–Co-type metal hydride electrodes. *J. Alloy. Compd.* **2005**, *395*, 291–299. [\[CrossRef\]](#)
131. Liao, B.; Lei, Y.; Chen, L.; Lü, G.; Pan, H.; Wang, Q. The effect of Al substitution for Ni on the structure and electrochemical properties of AB₃-type La₂Mg(Ni_{1–x}Al_x)₉ (x = 0–0.05) alloys. *J. Alloy. Compd.* **2005**, *404*, 665–668. [\[CrossRef\]](#)
132. Takeshita, T.; Wallace, W.E.; Craig, R.S. Solubility of hydrogen in rare earth-tricobalt compounds. *Inorg. Chem.* **1974**, *13*, 2283–2284. [\[CrossRef\]](#)
133. Oesterreicher, H.; Clinton, J.; Bittner, H. Hydrides of La–Ni Compounds. *Mater. Res. Bull.* **1976**, *11*, 1241–1247. [\[CrossRef\]](#)
134. Kadir, K.; Sakai, T.; Uehara, I. Synthesis and structure determination of a new series of hydrogen storage alloys; RMg₂Ni₉ (R = La, Ce, Pr, Nd, Sm and Gd) built from MgNi₂ Laves-type layers alternating with AB₅ layers. *J. Alloy. Compd.* **1997**, *257*, 115–121. [\[CrossRef\]](#)
135. Kadir, K.; Sakai, T.; Uehara, I. Structural investigation and hydrogen capacity of YMg₂Ni₉ and (Y_{0.5}Ca_{0.5})(MgCa)Ni₉: New phases in the AB₂C₉ system isostructural with LaMg₂Ni₉. *J. Alloy. Compd.* **1999**, *287*, 264–270. [\[CrossRef\]](#)
136. Kadir, K.; Sakai, T.; Uehara, I. Structural investigation and hydrogen storage capacity of LaMg₂Ni₉ and (La_{0.65}Ca_{0.35})(Mg_{1.32}Ca_{0.68})Ni₉ of the AB₂C₉ type structure. *J. Alloy. Compd.* **2000**, *302*, 112–117. [\[CrossRef\]](#)
137. Chen, J.; Kuriyama, N.; Takeshita, H.; Tanaka, H.; Sakai, T.; Haruta, M. Hydrogen Storage Alloys with PuNi₃-Type Structure as Metal Hydride Electrodes. *Electrochem. Solid State Lett.* **2000**, *3*, 249–252. [\[CrossRef\]](#)
138. Lim, K.L.; Liu, Y.; Zhang, Q.-A.; Chan, S.L.I. Effects of partial substitutions of cerium and aluminum on the hydrogenation properties of La (0.65–x) CexCa_{1.03}Mg_{1.32}Ni (9–y) Alloy. *Int. J. Hydrog. Energy* **2014**, *39*, 10537–10545. [\[CrossRef\]](#)
139. Xin, G.; Wang, S.; Yuan, H.; Yang, K.; Jiang, L.; Liu, X. Promising hydrogen storage properties of cost-competitive La(Y)–Mg–Ca–Ni AB₃-type alloys for stationary applications. *RSC Adv.* **2016**, *6*, 21742–21748. [\[CrossRef\]](#)
140. Zang, J.; Zhang, Q.; Sun, D. Hydrogen storage performances of RCaMgNi₉ (R = Nd, Gd and Er) compounds. *J. Alloy. Compd.* **2019**, *794*, 45–52. [\[CrossRef\]](#)
141. Liu, Y.; Pan, H.; Gao, M.; Li, R.; Lei, Y. Effect of Co content on the structural and electrochemical properties of the La_{0.7}Mg_{0.3}Ni_{3.4–x}Mn_{0.1}Co_x hydride alloys: II. Electrochemical properties. *J. Alloy. Compd.* **2004**, *376*, 304–313. [\[CrossRef\]](#)
142. Liao, B.; Lei, Y.; Chen, L.; Lü, G.; Pan, H.; Wang, Q. Effect of Co substitution for Ni on the structural and electrochemical properties of La₂Mg(Ni_{1–x}Co_x)₉ (x = 0.1–0.5) hydrogen storage electrode alloys. *Electrochim. Acta* **2004**, *50*, 1057–1063. [\[CrossRef\]](#)
143. Zhang, X.; Sun, D.; Yin, W.; Chai, Y.; Zhao, M. Crystallographic and electrochemical characteristics of La_{0.7}Mg_{0.3}Ni_{3.5–x}(Al_{0.5}Mo_{0.5})_x (x = 0–0.8) hydrogen storage alloys. *J. Power Sources* **2006**, *154*, 290–297. [\[CrossRef\]](#)
144. 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. Hydrog. Energy* **2017**, *42*, 2257–2264. [\[CrossRef\]](#)
145. Sandrock, G. A panoramic overview of hydrogen storage alloys from a gas reaction point of view. *J. Alloy. Compd.* **1999**, *293*, 877–888. [\[CrossRef\]](#)
146. Yukawa, H.; Takagi, M.; Teshima, A.; Morinaga, M. Alloying effects on the stability of vanadium hydrides. *J. Alloy. Compd.* **2002**, *330*, 105–109. [\[CrossRef\]](#)
147. Seo, C.-Y.; Kim, J.-H.; Lee, P.S.; Lee, J.-Y. Hydrogen storage properties of vanadium-based b.c.c. solid solution metal hydrides. *J. Alloy. Compd.* **2003**, *348*, 252–257. [\[CrossRef\]](#)
148. Kumar, S.; Taxak, M.; Krishnamurthy, N. Hydrogen absorption kinetics of V–Al alloy. *J. Therm. Anal. Calorim.* **2013**, *112*, 5–10. [\[CrossRef\]](#)

149. Kumar, S.; Taxak, M.; Krishnamurthy, N. Synthesis and hydrogen absorption kinetics of V_4Cr_4Ti alloy. *J. Therm. Anal. Calorim.* **2012**, *112*, 51–57. [\[CrossRef\]](#)
150. Verbetsky, V.N.; Zotov, T.A.; Movlaev, E.A. Absorption of hydrogen by V–Mo and V–Mo–Ti alloys. *Inorg. Mater. Appl. Res.* **2014**, *5*, 70–74. [\[CrossRef\]](#)
151. Tamura, T.; Kazumi, T.; Kamegawa, A.; Takamura, H.; Okada, M. Protium absorption properties and protide formations of Ti–Cr–V alloys. *J. Alloy. Compd.* **2003**, *356*, 505–509. [\[CrossRef\]](#)
152. Okada, M.; Kuriwa, T.; Tamura, T.; Takamura, H.; Kamegawa, A. Ti–V–Cr bcc alloys with high protium content. *J. Alloy. Compd.* **2002**, *330*, 511–516. [\[CrossRef\]](#)
153. Kagawa, A.; Ono, E.; Kusakabe, T.; Sakamoto, Y. Absorption of Hydrogen by Vanadium-Rich V–Ti-Based Alloys. *J. Less Common Metals* **1991**, *172*, 64–70. [\[CrossRef\]](#)
154. Tsukahara, M. Hydrogenation Properties of Vanadium-Based Alloys with Large Hydrogen Storage Capacity. *Mater. Trans.* **2011**, *52*, 68–72. [\[CrossRef\]](#)
155. Tamura, T.; Tominaga, Y.; Matsumoto, K.; Fuda, T.; Kuriwa, T.; Kamegawa, A.; Takamura, H.; Okada, M. Protium absorption properties of Ti–V–Cr–Mn alloys with a bcc structure. *J. Alloy. Compd.* **2002**, *330*, 522–525. [\[CrossRef\]](#)
156. Shudo, Y.; Ebisawa, T.; Itoh, H. Characterization of Ti–Zr–Mn–V-based Laves phase alloys for MH refrigeration system. *J. Alloy. Compd.* **2003**, *356*, 497–500. [\[CrossRef\]](#)
157. Yu, X.; Wu, Z.; Xia, B.; Xu, N. Hydrogen storage performance of quenched Ti–V-based alloy. *J. Alloy. Compd.* **2004**, *373*, 134–136. [\[CrossRef\]](#)
158. Yu, X.; Wu, Z.; Xu, N. Effects of melt-quenching rates on the hydrogen storage properties of Ti-based BCC phase alloy. *Phys. B Condens. Matter* **2004**, *344*, 456–461. [\[CrossRef\]](#)
159. Yu, X.; Wu, Z.; Xia, B.; Xu, N. Improvement of activation performance of the quenched Ti–V-based BCC phase alloys. *J. Alloy. Compd.* **2005**, *386*, 258–260. [\[CrossRef\]](#)
160. Nomura, K.; Akiba, E. H_2 Absorbing-desorbing characterization of the TiVFe alloy system. *J. Alloy. Compd.* **1995**, *231*, 513–517. [\[CrossRef\]](#)
161. Lynch, J.F.; Maeland, A.J.; Libowitz, G.G. Lattice Parameter Variation and Thermodynamics of Dihydride Formation in the Vanadium-Rich V–Ti–Fe/ H_2 System. *Z. Phys. Chem.* **1985**, *145*, 51–59. [\[CrossRef\]](#)
162. Luo, L.; Li, Y.; Zhai, T.; Hu, F.; Zhao, Z.; Bian, X.; Wu, W. Microstructure and hydrogen storage properties of $V_{48}Fe_{12}Ti_{15-x}Cr_{25}Al_x$ ($x = 0, 1$) alloys. *Int. J. Hydrog. Energy* **2019**, *44*, 25188–25198. [\[CrossRef\]](#)
163. Akiba, E.; Iba, H. Hydrogen absorption by Laves phase related BCC solid solution. *Intermetallics* **1998**, *6*, 461–470. [\[CrossRef\]](#)
164. Yan, Y.; Chen, Y.; Liang, H.; Wu, C.; Tao, M.; Mingjing, T. Effect of Al on hydrogen storage properties of $V_{30}Ti_{35}Cr_{25}Fe_{10}$ alloy. *J. Alloy. Compd.* **2006**, *426*, 253–255. [\[CrossRef\]](#)
165. Liu, X.; Jiang, L.; Li, Z.; Huang, Z.; Wang, S. Improve plateau property of $Ti_{32}Cr_{46}V_{22}$ BCC alloy with heat treatment and Ce additive. *J. Alloy. Compd.* **2009**, *471*, L36–L38. [\[CrossRef\]](#)
166. Aoki, M.; Noritake, T.; Ito, A.; Ishikiriya, M.; Towata, S.-I. Improvement of cyclic durability of Ti–Cr–V alloy by Fe substitution. *Int. J. Hydrog. Energy* **2011**, *36*, 12329–12332. [\[CrossRef\]](#)
167. Towata, S.-I.; Noritake, T.; Itoh, A.; Aoki, M.; Miwa, K. Effect of partial niobium and iron substitution on short-term cycle durability of hydrogen storage Ti–Cr–V alloys. *Int. J. Hydrog. Energy* **2013**, *38*, 3024–3029. [\[CrossRef\]](#)
168. Shen, C.-C.; Li, H.-C. Cyclic hydrogenation stability of γ -hydrides for $Ti_{25}V_{35}Cr_{40}$ alloys doped with carbon. *J. Alloy. Compd.* **2015**, *648*, 534–539. [\[CrossRef\]](#)
169. Yang, S.; Yang, F.; Wu, C.; Chen, Y.; Mao, Y.; Luo, L. Hydrogen storage and cyclic properties of $(VFe)_{60}(TiCrCo)_{40-x}Zr_x$ ($0 \leq x \leq 2$) alloys. *J. Alloy. Compd.* **2016**, *663*, 460–465. [\[CrossRef\]](#)
170. Nayeibossadri, S.; Book, D. Development of a high-pressure Ti–Mn based hydrogen storage alloy for hydrogen compression. *Renew. Energy* **2019**, *143*, 1010–1021. [\[CrossRef\]](#)

Publisher’s Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).