Gas-phase applications of metal hydrides

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ARTICLE INFO

Keywords:
- Metal hydrides
- Hydrogen storage and compression
- Hydrogen separation and purification
- Thermal energy storage and heat conversion
- Vacuum-plasma technologies

ABSTRACT

Applications of metal hydrides (MHs) utilise a reversible interaction of hydride-forming metals, alloys and intermetallic compounds with hydrogen. The reversible process of the formation-decomposition of the MH when interacting with hydrogen allows to utilise several unique features of the hydrogenation-dehydrogenation process. These features enable efficient storage of hydrogen gas resulting in a high volumetric efficiency of hydrogen storage while also storing thermal energy and converting it to the energy of compressed hydrogen gas or utilising the hydrides for the electrochemical energy conversion and storage. Thus, MH applications are very important as the components of the hydrogen energy systems integrating hydrogen supply from the metal hydride store and PEM fuel cells. Compact and safe hydrogen storage together with utilisation of the waste heat opens up for the commercial market of the hydrogen energy systems of green energy storage and supply.

1. Introduction: historical outlook

The revolutionary discovery in 1866 by Thomas Graham of the ability of palladium metal to reversibly absorb significant amounts of hydrogen [1,2] resulted in several practical applications of this phenomenon. Later a similar behaviour was observed for several other metals [3], and unique properties of the “metal – hydrogen” systems became a subject of numerous detailed studies. As mentioned by Sandrock in his published 30 years ago review [4], during the early period of the studies of metal hydrides, already in 1866–1946, there were published around 1500 works on the topic “Hydrogen in Metals”. Later, the intensity of research in this field steadily increased until discovery of the hydrides of intermetallic compounds (ZrNiH2, Libowitz et al., 1958 [5]; LaNi5H6, Philips Research Laboratories, 1970s [6]) which initiated a dramatic growth of the R&D activities in the field. The well-known IEA/DOE/SNL hydride database [7,8] includes 2706 records on (pseudo)binary, intermetallic and complex hydrides published in 1616 references, while 373 records are related to the hydride applications, even though systematic introduction of new entries was discontinued in the first decade of 2000s. Thus, the authors who compiled this database [7] were well aware that the collected information is incomplete. The volume and variety of the metal hydride-related activities evaluated when using Scopus database (Fig. 1) are very significant. Since 1918 until January 2023, 11,591 relevant publications have been published of which >20% (2465 entries for 1924–2023) are based on the applications of these materials. Since 1950s, the metal hydride publication activities exhibit exponential growth. Similar growth of the applications of the metal hydrides is now taking place, even though being less intense while starting after a gap of two decades.

The first comprehensive monograph [3] describing the applications of the metal hydrides was published in 1968 and focused on binary hydrides for nuclear technologies. Besides, the monograph also considered various applied aspects including use of metal hydrides as laboratory sources of pure hydrogen, preparation of the fine metal powders and metal foams, deposition of coatings, creating ceramic – metal junctions, as well as considering hydrogen embrittlement issues.

An important milestone in the development of the metal hydride applications was achieved in 1970s. As already mentioned, that time was characterised by a rapid growth of the research of newly discovered intermetallic hydrides characterised by reversible and very fast formation/decomposition at near-ambient conditions. Apart from the fundamental studies, this resulted in the development of prototypes of hydrogen storage and compression systems on the basis of intermetallic hydrides [9]. During the same time, a new concept of hydrogen energy systems suggesting transition of energy supply, industry and transport to use of hydrogen as an energy carrier appeared being catalysed by the...
global oil supply crisis. Metal hydride technologies related to the development of compact and safe hydrogen storage systems were one of the key focus areas in this concept [10]. The time interval 1975–1990 was characterised by in-depth fundamental research, and a large number of the works on the topic were published worldwide. These studies were reviewed by Buschow, Bouten and Miedema [11], Lynch and Snape [12], Reilly and Wiswall [13, 14], Buchner [15], Podgorny [16, 17], and many others. The applications covered hydrogen storage, purification and extraction of hydrogen from the gas mixtures, thermosorption compression of hydrogen together with its supply at controlled pressures. Some works (e.g., [17]) demonstrated an advantage of combining several working functions in a unified multipurpose metal hydride apparatus that allows to benefit from the advantages of the metal hydride technologies against the alternative available technology solutions. Various potential consumers spanned among power engineering, metallurgy, chemical industry, petrol refineries and other industries.

In the second half of 1980s, the changes in the world market of energy supply resulted in a decline of the growth rates in the R&D related to hydrogen energy technologies, first of all of the topic related to the broad use of metal hydrides. This was caused by economic factors related to a high market price of hydrogen as compared to the conventional energy carriers. This motivated the work towards improvements of techno-economic parameters of hydrogen production and increase of the efficiency of the processes of its utilisation. The issues of hydrogen storage were not prioritised, when compared to the focus area of joint hydrogen production and utilisation at a particular chemical plant/enterprise [18].

After the environment impact started to be seriously accounted and later prioritised from the societal considerations, the environment friendly nature of hydrogen utilisation improved profitability of the industrial processes [19]. At the same time, a broader implementation of the concept of hydrogen energy faces challenges in realising its efficient storage and transportation. Thus, various related applications of the metal hydrides including hydrogen storage, hydrogen separation and purification, and thermally driven compression of hydrogen gas attracted a significant interest of the international community of academia and industry [20–23].

Beginning of 1990s was marked by an explosive development of the metal hydrides batteries using MH as anode electrodes. Based on in-depth international fundamental and applied research, commercial production of nickel – metal hydride (NiMH) batteries started in Japan [24]. Presently, NiMH batteries represent the most important global application of the metal hydrides. Furthermore, other applications of metal hydride technologies demonstrate a transition from the prototypes to the commercialisation. Though the speed of this process is slower than expected, the worldwide continuous growth remains stable.

In 1980s – early 2000s, there were published numerous reviews which presented R&D results on the fundamentals and applications of the metal hydrides (MH). The most significant contributions to the topic were made by Sandrock [9, 25–28], Dantzer [29, 30], Suda [25, 31], Züttel [32–34], Bowman, Jr. [27, 28, 35], Latroche [36, 37] and the authors of the present review [38–41]. Reviews and book chapters published during 2007–2017 covered various aspects of MH applications including: application-related properties of hydrogen storage materials [42–48], hydrogen storage using metal hydrides [49–53] and other gas-phase applications including hydrogen compression [54–57], heat management [56, 58–60], hydrogen separation and purification [54, 61, 62], as well as electrochemical applications of MH [43, 46–48, 52, 60] in the NiMH batteries.

Recently, several comprehensive reviews on fundamentals and applications of metal hydrides have been delivered by the International Energy Agency (IEA) expert groups (Tasks 32 “Hydrogen Based Energy Storage” and 40 “Energy Storage and Conversion based on Hydrogen”) [63–66]. Various applications of metal hydrides have been also reviewed by other research teams [67–73].

MH applications are very important for hydrogen-based energy storage and conversion technologies including hydrogen driven PEM fuel cells. They allow to combine the processes of compact and safe hydrogen storage and supply, along with the utilisation of the waste heat released during operation of other system components [52].

This article aims at overview of the gas-phase applications of the metal hydrides that utilise several unique features of the hydrogenation/dehydrogenation reaction and focuses on the following topics:

- Safe, compact and technologically flexible hydrogen storage.
- Thermally driven hydrogen compression.
- Efficient heat management (refrigeration, heat storage, heat upgrade and conversion) with a focus on the utilisation of the low-potential heat (T < 160 °C).
- Hydrogen separation and purification at near ambient conditions.
- Hydrogen getters and sources of low-pressure hydrogen and its heavy isotopes.

2. Fundamentals of the hydrogen – metal interaction

2.1. General considerations

The process of formation/decomposition of the MH involves two mechanisms. The first one (Eq. (1)) is the interaction of the parent metal/intermetallic compound with hydrogen gas while the second (Eq. (2)) is electrochemical hydrogenation of the metal (or hydride decomposition) in an electrolyte, e.g., aqueous alkaline solution:

\[ \text{M} (s) + x/2 \text{H}_2 (g) \rightleftharpoons \text{MH}_x (s) + Q; \quad (1) \]

\[ \text{M} (s) + x/2 \text{H}_2 \text{O} (l) + e^- \rightleftharpoons \text{MH}_x (s) + \text{OH}^- (l); \quad (2) \]

where M is hydride-forming metal (intermetallic); Q is heat released during hydride formation or absorbed during its decomposition; the indexes x, g and l correspond to solid, gas and liquid phases, respectively. Both reactions are reversible, so it is possible to change their direction by small changes of the external conditions (temperature and hydrogen pressure for Eq. (1); electrode potential and temperature for Eq. (2)).

The principal difference between the mechanisms (1) and (2) is in the source of atomic hydrogen which is required in both Eqs. (1) and (2) and in a way this atomic hydrogen is generated either by splitting
molecular H₂ (process 1) or from water molecules (process 2).

Accordingly, the applications of MHs can be generally classified as the gas-phase (Eq. (1)) and electrochemical (Eq. (2)) ones. The latter include NiMH batteries; air – MH batteries and fuel cells and are a subject of a separate consideration [46,67,69].

The hydride formation processes taking place during the hydrogenation are schematically shown in Fig. 2. Hydrogen penetration into hydride forming metal is preceded by dissociative chemisorption of H₂ molecules on its surface followed by further diffusion of H atoms into the bulk through the interstitials in the metal matrix. It results in the formation of interstitial solid solution (α-phase) of hydrogen in the host metal. As the concentration of hydrogen in the α-solid solution increases, a phase transition is taking place in the M-H system causing the formation of hydride (β-phase) characterised by a high H/M ratio (from ~1 for M = Pd [74] to 3.75 for M = Th [75]) and partially (intermetallic hydrides) or completely (binary hydrides) ordered hydrogen sublattice.¹ Metal sublattice expands when accommodating H atoms, most frequently without changes in its original symmetry (see example in the mid-bottom inset).

The H – M interactions can be described by the following features:

• Fast and reversible hydrogen uptake and release take place.
• Host metal/alloy matrix accommodates H atoms in the interstitial sites forming MH.
• Volume density of the accommodated H atoms by 1.5–2.0 times exceeds the value for the liquid H₂.
• The MH can be formed and decomposed within very broad ranges of the operating temperatures (from <0 to >300 °C) and hydrogen pressures (from <1 mbar to >1 kbar), as defined by the alloy’s composition and structure type.
• Significant heat effects, Q, accompany the exothermic hydrogenation and endothermic decomposition of the hydride. They vary between <25 and >70 kJ/mol H₂. The Q’s depend on the alloy’s composition.
• Significant volume change of the host metal occurs upon the hydrogenation/dehydrogenation (dilatation effects).
• The effects associated with non-equilibrium state of the gas phase when hydrogenation/dehydrogenation reaction takes place, including high catalytic activity of the MH in the hydrogen transfer reactions [76].
• 100 % selectivity of hydrogen absorption from the H₂-rich gas mixtures.

2.2. Thermodynamic features and application requirements

Operating temperatures and hydrogen pressures are the most important parameters of the gas-phase applications of the metal hydrides defined by their thermodynamic properties.

Thermodynamics of Reaction (1) follows the relationship between the hydrogen equilibrium pressure (P_{eq}), hydrogen concentration in the solid (C=H/M) and temperature (T) described by a PCT diagram built as a family of pressure – composition isotherms. An example of such a family is presented in Fig. 3(a) and describes an equilibrium condition during hydrogen desorption in the H₂–LaNi₄₅Sn₀₂ system [78]. At moderate temperatures each isotherm has three segments two of which show a pronounced increase of Peq with the increase of H/M and correspond to the formation of solid solution of hydrogen in the host metal (α) and in the hydride (β). The third segment is characterised by a constant equilibrium pressure (P_{eq} = P_6; plateau) and shows the area where the saturated α-solution and β-hydride coexist, that resembles a transformation of gas (α) into a liquid (β phase). The temperature increase causes the “shrinking” of the miscibility gap (α + β region) as shown by the dashed line in Fig. 3(a), and degeneration of the plateau into the sloppy dependence with an inflection point at a critical temperature (T_C).

The temperature dependence of plateau pressure, P₀(T), exhibits linearity in coordinates 1/T – ln(P₀). Here the intercept of the straight line with the Y-axis and its slope are proportional to the negated standard entropy and the standard enthalpy of the α–β transition, respectively. The linear dependence between 1/T and ln(P₀) (van’t Hoff plot; see Fig. 3(b)) is described by a well-known equation:

\[
\ln(P₀) = -\frac{\Delta S^0}{R} + \frac{\Delta H^0}{RT},
\]

where P₀ [atm] is the plateau pressure, T [K] is temperature, ΔS^0 [J/(mol H₂ K)] and ΔH^0 [J/mol H₂] are standard enthalpy and entropy of the α–β transition, respectively, and R = 8.314 J/(mol K) is the universal gas constant.

Additional features of the real hydrogen – metal systems include hysteresis of the plateau pressures for H₂ absorption and desorption, sloping plateaux, as well as frequent appearance of the multiplateau segments. For further details please consult [79] and references therein.

The gas phase applications of metal hydrides include:

- Hydrogen stores. These provide benefits of compact hydrogen storage and supply systems operating at ambient pressure-temperature conditions.
- Metal hydride compressors. These compressors convert thermal energy into the energy of compressed H₂ gas. Hydrogen can be compressed from 1 bar to 800 bar by performing a multistage compression and by using appropriate composition of the MH alloys.
- Heat storage and conversion.
- Hydrogen getters and vacuum-plasma technologies.

The corresponding ranges for some of them are shown as rectangular regions in Fig. 4. As it can be seen, for every application a suitable MH material for which equilibrium conditions of Reaction (1) match well into the corresponding range can be found.

Table 1 presents main types of MH materials used in gas-phase applications. Suitability of a particular material for a particular target application mostly depends on the matching between the range of operating temperatures/hydrogen pressures determined by the thermodynamics of H–M interaction (Fig. 4) and the pressure/temperature operation conditions for the specific application. Obviously, a number of the additional application-related properties of the MHs should be taken into account to achieve the required efficiency and reliability of the end-user system.

The interrelation between the properties of hydrogen – metal systems and their performances in specific applications have been considered in detail in numerous reviews [25–30,42,55,65,67].

2.3. Application-related properties of metal hydrides

The most comprehensive consideration of application-related properties of MHs has been given by Dantzer [29]. According to the proposed classification, these include:

- Thermochemical reactivity, viz:
- Thermodynamics of H–M interaction.
- Surface effects affecting hydrogen sorption performance by impurities present in H₂ gas.
- Cycling stability.
- Transport properties – hydrogenation/dehydorgenation kinetics.
- Thermal properties – heat transfer efficiency.
- Dynamics of heat-and-mass exchange between the MH bed and its surrounding.

¹ The values of H/M for the α-solid solution (<0.1) and β-hydride (>1) presented in Fig. 2 show their typical values exhibiting a significant difference between the H concentrations in these phases at temperatures well below the critical temperature of α–β transition (see Fig. 3(a)).
Of the listed groups of properties, the thermochemical reactivity (a) and hydrogen absorption/desorption kinetics (b) are related to the properties of the hydride-forming material while the other ones (c, d) – to the design and operational performance of the MH reactors whose hydrogen charge/discharge dynamics is mainly limited by macro-kinetics determined by heat transfer performance of the MH beds.

Furthermore, the material-related features include the preparation routes of the alloys and hydrides [77, 83, 84], activation of the metal-hydrogen interaction [9, 61, 85–89], as well as the dilatation effects related to the expansion of the unit cells upon the hydrogenation [90–99]. The latter feature was recently reviewed by Gillia [99] and is very important for achieving the safe operation of the MH containers since the dilatation effects may cause unacceptably high stresses of their walls if the filling density of the MH material is too high. At the same time, increasing the filling density results in the improvement of hydrogen sorption capacity and dynamic performance of H2 charge and discharge [55]. To achieve a compromise between the successful performances and safety, a careful design of the MH container including specification of the acceptable MH filling density and some technological procedures providing a uniform distribution of the material in the container should be drawn. The most reliable starting data for this stage of development include the quantitative information about the structure of the parent and hydrogenated material and lattice periods of the constituent phases to allow the calculations of the ideal (crystallographic) density of the material in the non-hydrogenated and hydrogenated states.

Another material-related feature important for the gas phase applications of MHs is the stability of their hydrogen sorption properties during the cyclic hydrogenation-dehydrogenation. Most of hydride-forming metals and alloys exhibit degradation of their reversible hydrogen sorption capacities, gradual transformation of their pressure–composition isotherms and deterioration of hydrogen absorption/desorption kinetics during the repeated cycling in H2. The cycle stability issues may be related to the influence of several factors including surface poisoning by the impurities present in H2 (will be considered in Section 3.4) and sintering of the solid particles at high temperatures which results in the elongation of H diffusion pathways (typical for the MgH2-based materials [100]). However, the most frequently observed degradation phenomenon is related to the disproportionation of the multicomponent intermetallic hydrides during performing multiple H
absorption/desorption cycles that negatively impacts hydrogen compression (Section 3.2) and heat management (Section 3.3) applications.

The disproportionation of the intermetallic $AB_n$ alloy in hydrogen results in the formation of a stable binary hydride of the A-component along with a release of the component B in elemental or B-enriched alloy forms; the latter two do not form hydrides at the applied experimental conditions. This process is thermodynamically favourable (see Fig. 5) but it requires a diffusion of the metallic atoms enabling phase separation. As the diffusion is slow or hindered at low temperatures, then the formation of the insertion type homogeneous intermetallic hydride $AB_nH_Y$ prevails. However, the disproportionation quickly accelerates when the temperature increases, and even a minor extent of the disproportionation process when accumulated from cycle to cycle becomes very pronounced after a completion of several thousand hydrogenation/dehydrogenation cycles or when the intermetallic alloy is subjected to high temperatures and high hydrogen pressures.

The disproportionation process of the hydride-forming intermetallics was intensively studied since the 1970s, see Refs. [101–105] (1970s–1980s), [106–110] (1990s), and [111–115] (2000 and later) representing the studies that made a noticeable contribution to the subject.

As it can be seen from the Fig. 5, the disproportionation is favoured by the increased values of the heat (negated enthalpy) of formation of the binary hydride, $AH_Y$, and the decreased values of heat of formation of $AB_n$ intermetallic. Thus, the disproportionation is more pronounced for the A-components which form stable hydrides (REH$_n$) where RE is a

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**Table 1**

Types of MH materials for the gas-phase applications [9,29,52,56,61,63,67,71,77,80–82].

<table>
<thead>
<tr>
<th>Type</th>
<th>Operating temperatures [°C]</th>
<th>Operating H$_2$ pressures [bar]</th>
<th>H storage capacity [wt %]</th>
<th>Hydrogenation heat effect (Q in Eq. (1)) [kJ/mol H$_2$]</th>
<th>Suitable for applications</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binary (e.g., MgH$_2$) and complex (e.g., NaAlH$_4$, Mg$_2$FeH$_6$) hydrides</td>
<td>150…500</td>
<td>&lt;1…200</td>
<td>4…7.6</td>
<td>45…80</td>
<td>High-temperature (T &gt; 200 °C) heat management</td>
<td>Nanostructuring and/or use of catalysts is required to provide reversibility and improve H absorption/desorption kinetics</td>
</tr>
<tr>
<td>$AB_n$ (A = RE; B=Ni,Al, Sn,Mn, ...)</td>
<td>0…200</td>
<td>&lt;1…200</td>
<td>1.2…1.5</td>
<td>25…40</td>
<td>Operating pressures can be tuned by variation of alloy composition</td>
<td></td>
</tr>
<tr>
<td>$AB_n$ (A = Zr; B=V, V + Fe)</td>
<td>20…300</td>
<td>$10^{-7}$…$10^{-3}$</td>
<td>1.9…2.2</td>
<td>−80</td>
<td>Hydrogen getters and sources of H isotopes</td>
<td></td>
</tr>
<tr>
<td>$AB_n$ (A = Ti,Zr; B=Mn, Cr,Fe,V, ...)</td>
<td>−50…150</td>
<td>1…1000</td>
<td>1.5…1.9</td>
<td>15…30</td>
<td>Operating pressures can be tuned in very broad ranges by varying the alloy’s composition</td>
<td></td>
</tr>
<tr>
<td>$AB_n$ (A = Zr; B=Ni,Co)</td>
<td>20…250</td>
<td>$10^{-6}$…$10^{-3}$</td>
<td>0.7…1.9</td>
<td>45…75</td>
<td>Hydrogen getters and sources of H isotopes</td>
<td>Performance is very sensitive to impurities in both H$_2$ gas and host alloy</td>
</tr>
<tr>
<td>$AB_n$ (A = Ti; B=Fe,Mn, V)</td>
<td>0…150</td>
<td>1…100</td>
<td>1.7…2.0</td>
<td>28…32</td>
<td>Efficient H storage at ambient conditions</td>
<td></td>
</tr>
<tr>
<td>RCC solid solution alloys on the basis of V and Ti-Cr</td>
<td>0…100</td>
<td>&lt;1…300</td>
<td>2.5…3.0</td>
<td>30…40</td>
<td>Difficulties in the preparation and further processing</td>
<td></td>
</tr>
</tbody>
</table>

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Fig. 4. Van’t Hoff plots for several pseudo-binary, complex and intermetallic hydrides and the related gas-phase applications: VPT – vacuum-plasma technologies (getters and low-pressure sources of H isotopes), MHHS – MH hydrogen storage systems MHHP – MH heat management systems (heat storage, conversion & upgrade), MHHC – thermally driven MH H$_2$ compressors. (Adopted from [77].)

Fig. 5. Schematic energy (enthalpy) diagram illustrating thermodynamic favourability of the disproportionation reaction. (Adopted from refs. [101, 102].)
rare-earth element or CaH$_2$ ($\Delta H = -(180 \text{–} 200)$ kJ/mol H$_2$ [3]), and for the relatively less stable intermetallics (e.g., LaNi$_5$, $\Delta H = -90$ kJ/mol [116] against LaNi$_5$, $\Delta H = -159$ kJ/mol [117]). Thus, the possibilities to suppress the disproportionation process include increase of the stability of the parent intermetallic alloy (e.g., by a substitution of La by Ce [112], or Ni with Sn [108,118], Co [113] or Al [119,120] in LaNi$_5$) and/or decrease of the stability of the binary hydrides formed by A-components of the intermetallic (e.g., by substituting a rare-earth element with Mg in RENi$_3$ [121]).

We note that the stability of AB$_5$ intermetallic compounds and, accordingly, the resistance against the disproportionation increases with an increase of the B/A ratio, i.e., the value of n in AB$_n$. [11] The disproportionation may include several intermediate processes comprising of lattice disordering/appearance of defects, amorphization, and formation of intermetallics enriched with B-component [118,122,125].

AB$_5$ [124-126] and, particularly, AB$_2$-type [109,110] intermetallics where A = Ti and/or Zr were shown to be less prone to the disproportionation as compared to the intermetallic compounds of the rare-earth elements and calcium. The origin of this difference is in a lower stability of TiH$_2$ and ZrH$_2$ ($\Delta H = -131$ and $-160$ kJ/mol H$_2$, respectively [3]) as compared to the RE and calcium dihydrides (see above). However, taking into account the lower stability of the Ti- and/or Zr-based AB$_5$ and AB$_2$-type intermetallics as compared to the RE-based AB$_2$-type ones [11], the thermodynamic considerations alone are insufficient. As an example, the Gibbs free energy of hydrogen-induced disproportionation of TiFe calculated at $T = 300 \, ^\circ\text{C}$ ($-83.7$ kJ/mol H$_2$ assuming formation of TiH$_2$ and TiFe$_2$) was found to be not much less negative than that for LaNi$_5$ ($-96.2$ kJ/mol H$_2$ assuming formation of LaH$_3$ and Ni) while for TiFe the disproportionation at $T = 300 \, ^\circ\text{C}$ and 40 bar H$_2$ was not observed, in contrast to LaNi$_5$ which exhibits a noticeable disproportionation at the same conditions [124]. Studies clarifying the effect of additional factors (e.g., diffusivity of the metal atoms) which contribute to the disproportionation mechanism of AB- and AB$_2$-type alloys where A = Ti and/or Zr are, therefore, required to further enlighten the controlling features of the interaction process.

The degradation effects upon cycling also occur for the individual hydride-forming BCC metal vanadium and solid solution type BCC alloys. As it was noted in the review paper describing fundamental and applied features of the use of the metal hydrides in the MH compressors published by the authors of this article (ML, VY) [55], the origin of the degradation is in the structural-morphological changes of the metallic matrix resulting in the reduction of H sorption capacity, particularly at low-temperature hydrogen saturation of the alloys inhibits the degradation effect.

Hydrogen sorption properties of the AB$_5$-type intermetallics can be recovered by several hours-long heating in vacuum or under near-atmospheric H$_2$ pressure [104,110,118]. This is caused by the recombination reaction when the stable binary hydride decomposes and the initial intermetallic alloy forms upon a completion of the hydrogen desorption process. However, upon further cycling, the recovered alloys frequently degrade faster than the “fresh” ones [104].

Advanced in situ diffraction studies contribute as a highly valuable tool to probe the structure and reacting mechanisms of hydrogen and energy storage materials including hydrogenation-disproportionation-desorption-recombination (HDDR) [128]. A completeness of the HDDR process when using in situ studies has been demonstrated for a broad range of chemical compositions of hydrogen storage alloys. These include Zr-rich Zr$_2$Fe, Zr$_2$Fe and Zr$_2$FeO$_{1-x}$ [129], Mg-rich LaMg$_{12}$ [130,131], and MgCo$_{3}$ [132]. Furthermore, hydrogen desorption properties of a series of binary hydrides of the rare earth metals have been characterised [133,134] and related to the HDDR behaviours in the rare-earth rich Nd$_3$Fe$_2$B$_6$ [135] and Nd$_3$Fe$_2$Co$_6$ [136]. All these studies showed that because of the nanostructured morphologies of the hydrogenated materials typical for the alloys subjected to the HDDR process and increased diffusion mobility of the metal atoms caused by hydrogen dissolved in the metal lattice, the recombination process in the multi-component disproportionated mixtures often proceeds at much lower temperatures as compared to the binary hydrides. One example is Mg-assisted low temperature hydrogen desorption from the disproportionated in hydrogen LaMg$_{12}$ when initial intermetallic LaMg$_{12}$ recombines already below 450 °C which is 400 °C lower as compared to the binary hydride LaH$_2$ releasing hydrogen at 850 °C only [131].

The material-related information about thermodynamics of H-M interaction including reaction heat effect, equilibrium pressure-temperature-concentration—temperature (PCT) relationships, as well as kinetics of hydrogen uptake and release is a starting point in the design optimisation of the MH reactors where these parameters along with other properties of the hydride-forming material (particle size distribution, density, heat capacity, etc.) are used during optimisation of the MH reactors via modelling of heat-and-mass transfer (refs [137–150] represent typical articles from several dozen of the works published since 2015).

2.4. From material to system

We can conclude that MH material properties are the key factors defining the development of any gas-phase application of metal hydrides, and the general strategy of the system development should realise the down-top approach “From material to system” (see Fig. 6) when the first stage includes a comprehensive studies of various properties of the selected MH materials followed by the development of the MH reactors and their integration in the end-use hydrogen energy systems. At the same time, selection criteria of the MH materials should account conditions of their use in the specific applications (dashed arrow in Fig. 6) including ranges of operating temperatures and hydrogen pressures, system size and weight, presence of impurities gas species in the hydrogen feed, required cycle and calendar lifetime. These requirements are application-specific and will be considered later in this review.

3. Main applications of MHs using hydrogen gas

3.1. Hydrogen storage

Hydrogen produced by water electrolysis with the use of green energy is a clean and zero-emission fuel. As is well recognised, one main challenge limiting the widespread use of hydrogen fuel cell technology in various applications is in the development of efficient hydrogen storage and supply systems [150–156]. The main problem is in finding an efficient way to deliver hydrogen to the consumer as at normal conditions H$_2$ is a low-density gas (0.09 kg/m$^3$), thus requiring a densification by using physical (compression or liquefaction) or chemical methods. Even at high pressures, the density of compressed H$_2$ remains too low, about 20 kg/m$^3$ at $P = 350$ bar and $T = 25$ °C. Accordingly, the size of the high-pressure cylinders for the storage of necessary amount of hydrogen becomes too large that prevents their use.
in the applications which experience strict space constrains. Storage of hydrogen as a cryogenic liquid (density 70 kg/m$^3$; $T = -253$ °C) is associated with high energy consumption, up to 30 % of hydrogen higher heating value (HHV) for the liquefaction of H$\textsubscript{2}$ gas. Similar energy consumption (up to 25 % HHV) is characteristic of the chemical hydrogen storage methods, e.g., Liquid Organic Hydrogen Carriers (LOHC).

Metal hydrides (hydrogen storage density up to 150 kg/m$^3$) present a promising alternative to the above-mentioned H$\textsubscript{2}$ storage technologies, with a possibility to select materials compositions as required by the specification requirements from the end-use applications. Advantages of MHs as a hydrogen storage medium include simplicity, high safety, and flexibility of hydrogen storage systems on their basis (based on a proper selection of the H storage materials) which provides a high hydrogen storage density per unit volume and high purity of the supplied H$\textsubscript{2}$. Improvement of the operational safety is achieved due to the lower pressure of the stored hydrogen and the limited rate of hydrogen release in case of accidental leaks or even rupture of the hydrogen storage tank. Decomposition of “low-temperature” metal hydrides with release of H$\textsubscript{2}$ consumes 20–30 kJ/mol H$\textsubscript{2}$ [157] that is about two times lower than the energy necessary for the H$\textsubscript{2}$ release from LOHC (55–70 kJ/mol H$\textsubscript{2}$ [156]). Finally, thermal integration of the “low temperature” MHs based on AB$\textsubscript{m}$- and AB$\textsubscript{m}$-type intermetallics allows utilisation of heat produced during operation of the electrolyser and a fuel cell stack, thus improving the overall system efficiency [52,67,81,155,158]. Other advantages of MH-based hydrogen storage technologies include their flexibility and ability to be well-aligned with certain niche applications including combination of several functions in a unified MH system, in addition to hydrogen storage [17,35,52,67,73,155,158]. Competitive advantages of metal hydride hydrogen storage technologies over the alternative ones also include simpler and less expensive H$\textsubscript{2}$ refuelling infrastructure due to a low standby H$\textsubscript{2}$ pressure (1–50 bar at the ambient temperature). According to the estimations presented in ref. [159], the replacement of compressed gas H$\textsubscript{2}$ storage tank ($P = 700$ bar) with the MH one on-board of a fuel cell vehicle allows to achieve 36–39 % reduction of the refuelling costs due to significant reduction of the costs for H$\textsubscript{2}$ compression.

The low weight capacity of the “low-temperature” (inter)metallic hydrides usually considered as the major disadvantage to their use in passenger vehicles [157], is not critical for the stationary applications and becomes an advantage for hydrogen storage on-board heavy duty utility vehicles, in maritime, railroad and other applications which require use of the ballast lowering centre of gravity of the donor vehicle [63].

The main problems hindering a broader commercialisation of the MH H$\textsubscript{2}$ storage systems include [63,157,160–162]:

(i) Excessive costs of the MH materials and MH reactors/containers.
(ii) Necessity to shorten initially long charge/discharge time of the MH tanks.
(iii) Insufficiently fast kinetics, particularly for H$\textsubscript{2}$ absorption.
(iv) Difficulties in aligning the compositions of the MH materials with thermodynamic properties of their interaction with H$\textsubscript{2}$ gas, to provide matching with the pressure – temperature conditions required for the application, lowering hydrogenation enthalpy, and increasing the volumetric hydrogen storage density.

Due to the vast amount of the available experimental data on hydrogen sorption performance of various metallic hydride forming materials accumulated since the beginning of 1970s, empirical statistical analysis of the regularities in interrelations between the alloy’s composition and its hydrogenation/dehydrogenation properties can become a powerful tool for optimising compositions of hydrogen storage alloys in the specific hydrogen storage applications (iv). Such analyses including the use of machine-learning approach were carried out for a number of hydrogen storage alloys including AB$\textsubscript{m}$ [77,161,163–165] and AB$\textsubscript{m}$-type [166] intermetallics, “high-entropy” BCC solid solution alloys [167], as well as some “high-temperature” hydrides including Mg-based and complex compositions [168–170]. Furthermore, modelling attempts were undertaken to describe the performance of the hydrogen storage and compression MH materials belonging to the different types [157,171,172]. Successful correlations identified by the analysis of several hundred entries were obtained for the multi-component AB$\textsubscript{m}$-type alloys, well describing the relationships between their composition and the Gibbs energy of hydride formation, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = RT\ln P^\circ$, or characteristic temperature which corresponds to the atmospheric plateau pressure, $T_s < \frac{\Delta G^\circ}{R}$ [77].

Resolving kinetic issues (iii) is another important problem in the development of the MH hydrogen storage materials and systems. Studies of hydrogenation – dehydrogenation kinetics are in a focus of the metal hydrides research; a brief review of the application-related kinetic studies can be found in ref. [173]. Mostly, kinetics improvements are required for the “high-temperature” Mg-based and complex hydrides as they are generally characterised by the slow H absorption – desorption rates. The improvements are caused by adding of catalysts, nano-structuring or combination of these methods [64,65,174–184]. A very promising approach is in the preparation of hydrogen storage composites which include nanoscale carbon (e.g, graphene-like materials) with catalytic metal nanoparticles deposited onto it [185,186]. In addition to the accelerating hydrogenation/dehydrogenation kinetics due to the
facilitation of dissociative H\textsubscript{2} chemisorption/H recombination on the catalytic nanoparticles and shortening the H diffusion pathways in the nanosstructured material, such composites are characterised by improved effective thermal conductivity of the MH beds on their basis and high stability of their hydrogen sorption performance during the cycling at high temperatures.

Hydrogenation/dehydrogenation kinetics and mechanisms are strongly dependent on the pressure acting as a driving force of the process [187]. This factor is particularly critical for the applications which require low-pressure H\textsubscript{2} absorption, for example, when storing H\textsubscript{2} supplied from a solid oxide electrolyser or another source of low
temperature. The decrease of pressure driving force also happens during the operation of the MH containers for hydrogen storage and other gas-phase applications (e.g., H\textsubscript{2} compression) due to the heating (exothermic H absorption) or cooling (endothermic H desorption) of the MH bed usually characterised by a low (<1 W/(m K)) effective thermal conductivity. As a result, the pressure/temperature conditions approach the equilibrium ones [188], and H absorption/desorption rates slow down, so the process becomes rate-limited by the heat transfer issues (issue ii). Detailed analysis of this effect requires numerical modelling of heat-and-mass transfer in the MH beds where PCT (iv) [79, 189, 190] and kinetic (iii) [191–193] relationships/models are included in the model as the governing equations [140–142, 150, 194–196].

Most of the methods for the acceleration of H\textsubscript{2} charge/discharge of metal hydride reactors are aimed at the increase of the effective thermal conductivity of the MH bed, by placing MH powder in a heat-conductive matrix (metal foam, internal finning or their combination [148, 197–199]), compacting MH powder with a heat-conductive binder (metal, expanded natural graphite, carbon nanomaterials [200–205]), as well as introducing internal heat exchangers of various layouts [206–210], heat pipes [211–213], phase change materials [213–216]. These methods and corresponding designs of metal hydride hydrogen storage reactors have been recently reviewed in refs [217–219].

We note that the methods of heat transfer augmentation specified above are applicable to the most of the gas-phase applications of MH (hydrogen compression, heating/cooling, conversion systems), in addition to hydrogen storage.

Apart from the improvement of the charge/discharge dynamic performances by intensifying heat exchange between the MH bed and its heating/cooling means, special attention in the development of the MH containers for hydrogen storage and compression must be paid to avoid or mitigate the stresses which appear on the containment wall due to the dilatation of the MH material when it is hydrogenated. The main technological approach is in the keeping safe density of filling the MH material into container which roughly should not exceed 50 % of the crystallographic density of the material in the hydrogenated state [90]. Some increase of the safe filling density can be achieved by mixing the MH powder with a plastic additive like Expanded Natural Graphite (ENG). The mixture can be either left in the powdered form or further compacted [205, 220–222]. Alternatively, the stress alleviation can be achieved by introducing minor additives which provide lubricating effect – a recent study [223] showed that addition of 3 wt% of silicone oil to AB\textsubscript{9}-type MH powder almost eliminates stresses in the reactor at the filling density increased to 60 %.

Compact, safe, and flexible hydrogen storage remains the main gas-phase application of the metal hydrides. One example of a commercial product for one of the applications is the integrated hybrid hydrogen battery recently developed by the company Lavo (Australia; [https://lavo.com.au]). The LAVO\textsuperscript{TM} Energy Storage System intended for the use in residential applications consumes renewable energy from the PV panels and a tap water which is further purified inside the system. Hydrogen generated by an electrolyser is stored in four metal hydride containers at a pressure about 30 bar and further supplied to a PEM fuel cell stack which, together with Li-ion battery, provides on-demand supply of up to 5 kW power of electricity. The system can store 40 kWh of electricity. The details about the system performance and cost can be found in [224, 225].

In summary, the use of metal hydrides allows to build various hydrogen energy systems. The companies involved in the manufacturing and sales of the metal hydride hydrogen storage systems for the laboratory and stationary applications include GRZ Technologies/ Switzerland (http://grz-technologies.com/), GKN Hydrogen/Germany (https://www.gknhydrogen.com/), Pragma Industries/ France (http://wwwPragma-industries.com/hydrogen-storage/), HBank/Taiwan (http://www.hbank.com.tw), Whole Bin (Beijing)/China (http://www.bjhaoyun.com/indexen.php).

Metal hydrides allow to create compact, safe and technologically flexible hydrogen storage systems for portable, stationary and mobile applications ranged in the amount of the stored H\textsubscript{2} from several grams to several dozens of kilograms. Some examples representing developments at HySA Systems Centre of Competence in South Africa [222, 226, 227] are described below.

Fig. 7 shows a cartridge-type MH tank for hydrogen storage on-board of a light fuel cell vehicle (scooter) [226]. The tank has hydrogen storage capacity of up to 1 Nm\textsuperscript{3} (90 g) H\textsubscript{2} and comprises of two MH containers made of aluminium, filled with AB\textsubscript{9}-type hydrogen storage alloy powder and equipped with internal copper and external aluminium heat-conductive fins which provide the rated performance of the H\textsubscript{2} charge (~1 h time at supply pressure up to 40 bar) and discharge (2 tanks connected in parallel provide stable operation of 1.1 kW fuel cell stack) when cooled and heated with ambient air at T = 15–25 °C. H\textsubscript{2} input/output pipeline of the tank is equipped with quick connector which allows for a quick replacement of the used tank with the one refuelled off-board.

The MH tank for the storage of up to 1.8 kg (20 Nm\textsuperscript{3}) H\textsubscript{2} on-board of a 3-t fuel cell forklift (see Fig. 8) is made as an assembly of eight metal hydride cassettes each comprising of 5 tubular (Ø48x800 mm) MH containers filled with the AB\textsubscript{9}-type hydrogen storage alloy powder and equipped with internal heat conductive copper fins. To provide a safe operation of the forklift when lifting the maximum load, each liquid heated/cooled cassette is encased in a lead thus combining the functions of hydrogen storage unit and vehicle ballast. The tank is characterised by a reasonable refuelling time (up to 20 min at the refuelling pressure up to 150 bar and ambient temperature) and provides stable operation of 11 kW fuel cell stack at the maximum load [227].

Recently HySA Systems has developed a prototype hydrogen storage tank for the stationary fuel cell applications (Fig. 9). The liquid heated/cooled tank filled with AB\textsubscript{9}-type hydrogen storage alloy stores up to 4 kg (45 Nm\textsuperscript{3}) H\textsubscript{2} and is made of a stainless-steel pipe (Ø219x2500 mm) with flanged ends. One of the flanges is intended for H\textsubscript{2} input/output while the other carries an internal heat exchanger. For the temperature measurements in different points of the MH bed, the tank is equipped with several thermocouple probes installed at the ports of the cylindrical containment.

Fig. 10(a–c) presents the estimated breakdowns of the costs incurred by HySA Systems for the making the MH tanks described above.

As it can be seen, a frequently expressed opinion that the cost of the metal hydride hydrogen storage systems is mainly determined by the cost of MH material is valid only for the large MH tanks made as individual containers (Fig. 10(c)). For the tanks made as assemblies of several small-size MH containers in order to improve the H\textsubscript{2} charge/discharge dynamic performance (Fig. 10(a, b)), quite labour-intensive MH containers, due to their individual manufacturing in a larger number by a custom order, become the main cost component. Taking into account that high costs for the MH containers are mainly related to not yet well-established market associated with absence of the mass production, it is expected that when mass produced, the cost of the containers will become lower than the one for the MH material. The latter might be further reduced due to the increase of its market demand associated with the increase of the production volume, and/or by the use of cheaper MH materials, e.g., based on TiFe which can potentially be
3-5 times cheaper (per unit weight of the stored H\textsubscript{2}) than the AB\textsubscript{5}- and AB\textsubscript{2}-type hydrogen storage alloys conventionally used for hydrogen storage applications due to their favourable hydrogen sorption performances [9]. However, inexpensive methods of the improvement of the activation performance, hydrogenation/dehydrogenation kinetics and poisoning tolerance of TiFe \cite{9,85,87-89,228} are necessary to be developed first.
3.2. Thermally driven hydrogen compression

Almost any application of hydrogen gas requires its compression. The major problems in hydrogen compression technologies are in achieving high safety, reliability, and energy efficiency of the compressor systems [229]. The use of conventional mechanical hydrogen compressors is associated with unacceptably high capital and operational costs and frequent safety-related incidents. For hydrogen refuelling stations with dispensing pressures 350 to 700 bar, hydrogen compressors take from 48 to 58% of the capital costs, up to 65% of the operational costs (including service and maintenance which take about 1/4 of the total maintenance hours) and cause 18% of the incidents [160, 188, 230].

Thermally driven hydrogen compression utilising metal hydrides has several advantages over conventional methods, including simple compressor design, the absence of moving parts, high purity of the delivered hydrogen, the possibility of utilisation of low-potential heat, reliability and safety in operation [55, 57, 63, 66, 160, 188, 231]. The main disadvantages of the MH hydrogen compressors include low efficiency limited by Carnot efficiency in the operating temperature range [232], as well as limited cycle and calendar life of the MH materials for hydrogen compression [112, 233].

Metal hydride technology of hydrogen compression is in demand for several applications including:

- H₂ filling stations.
- Space exploration.
- Utilisation of low-potential heat.
- Powder metallurgy and other special H₂-consuming technological processes.
- Laboratory supply of compressed H₂.
- Temperature sensors & actuators.

Despite a possibility to generate very high, up to 7.5 kbar, H₂ discharge pressures utilising vanadium hydride as a hydrogen compression material [234], the hydrogen compression productivity acceptable for medium-to-large scale applications (e.g., hydrogen refuelling stations) is presently limited by the pressures 200–250 bar H₂ [160, 188, 230]. On-going R&D activities are aimed at further increase of the discharge pressure while reaching the productivity suitable for the refuelling of fuel cell buses and utility vehicles (>350 bar) and passenger vehicles (>700 bar) [63, 160, 161, 188]. The relevant recent publications are mainly focused on the development of MH materials suitable for high-pressure hydrogen compression mostly based on C14-AB₂-type intermetallics where A = Ti or Ti + Zr [235–245]; in some works [246, 247] the application of V–Ti—Cr BCC alloys for hydrogen compression has also been studied.

Fig. 11(a) presents the isotherms of hydrogen absorption at T = 20 °C and hydrogen desorption at T = 150 °C for C14-AB₂-type intermetallic (A = Ti + Zr, B = Cr + Fe + Mn + Ni) recently developed by HySA Systems in South Africa. The isotherms were calculated on the basis of fitting the experimental PCT data for this alloy taken in the range T = 20… + 20 °C, P = 0.1…200 bar, using the model of phase equilibria in hydrogen–metal systems which allows for the realistic extrapolation of the results outside pressure– temperature ranges where the experimental data were collected [79]. As it can be seen, this alloy allows for hydrogen compression from P_L = 100 bar (T_L = 20 °C) to P_H = 500 bar (T_H = 150 °C) with cycle productivity ΔC = 115 NL/kg.

Fig. 11(b) illustrates hydrogen discharge performance (backpressure regulator setpoint of 500 bar) of a prototype composite metal hydride container for high-pressure hydrogen compression developed by HySA.

Fig. 10. Breakdown of the costs incurred by HySA Systems for the manufacturing of the MH hydrogen storage tanks: a – 90 g H₂ MH tank for scooter (Fig. 7), b – 1.8 kg H₂ MH tank for forklift (Fig. 8), c – stationary 4 kg H₂ MH tank (Fig. 9).
The principle of operation described above is used for the thermal energy storage (TES) [64,65,70,150,208], as well as heat conversion comprising of cooling, heat transforming and heat upgrade [56,58,70,158]. These applications use the concept of metal hydride heat pump (MHHP) which is a heat engine similar to a metal hydride hydrogen compressor, however, operating in the reverse mode. Then, depending on the hydrogen pressure applied to MH bed, Reaction (1) proceeds either directly (heat release) or in reverse direction (heat absorption). Thermodynamics of MHHPs was analysed by Dantzer and Orgaz [258,259]; more recent works include refs [58, 70, 260].

The cyclic operation of a metal hydride bed in MHHP is illustrated by Fig. 12 and includes two stages: H₂ absorption at a higher pressure, P₂, accompanied by the release of heat, Q₁, at a higher temperature, T₁ (a), followed by H₂ desorption at a lower pressure, P₁, accompanied by absorption of heat, Q₂, at a lower temperature, T₂ (b). An idealized (not accounting H₂ absorption/desorption hysteresis) van’t Hoff plot for the used MH material is presented in Fig. 12(c).

The principle of operation described above is used for the thermal energy storage (TES) [T₁ ≈ T₀] and heat conversion [T₁ < T₀].

The MH-based TES is a highly competitive solution as compared to the systems utilising molten salts. The use of “high-temperature” binary and complex hydrides allows to store medium-to-high grade heat including the one supplied by concentrated solar energy plants at $T = 300\ldots> 1000$ °C with energy storage densities per unit volume and weight close to and even exceeding the values for the alternative thermochemical heat storage materials ([261–264]; see Fig. 13). Storage and conversion of heat at lower temperatures is also possible using “low-temperature” intermetallic hydrides [263].

The use of heat pumps on the basis of “low temperature” MH allows to utilise low-grade heat with temperature potential below 100 °C. This is a promising energy saving technology for industrial and domestic applications, particularly in the case of combined cooling, heating and power (CCHP) systems.

Most frequently used configurations of MHHPs include one-bed compressor-driven and multi-bed thermally driven systems which use two or more MH materials differing by their thermal stabilities [58,70,260].

The one-bed MHHPs (Fig. 12) are mainly used for the cooling purposes (refrigeration and air conditioning) [265–268]. The technical solution is simple in the implementation and has the highest efficiency (above 80 %) and coefficient of performance (3.85) among alternative configurations of the MHHPs [260]. At the same time, it seems to be quite challenging to use this configuration in large-scale applications due to consumption of expensive electricity to drive hydrogen compressor, as well as other problems associated with its operation (see Section 3.2).
In the multi-bed configuration, hydrogen compression from $P_L$ to $P_H$ (see Fig. 12 (a, b)) is provided by another MH bed which uses low-grade heat to compress $H_2$. The simplest case is a two-bed configuration (Figs. 14, 15) which includes the less stable (LT-MH) and more stable (HT-MH) hydride beds forming the “cold” and “hot” sides of the MHHP, respectively. The gas spaces above the beds are connected allowing the hydrogen gas to flow between them, and the operation is driven by the heating and/or cooling the MH beds maintaining them at three temperature levels: high ($T_H$), medium ($T_M$) and low ($T_L$); $T_L < T_M < T_H$. As it can be seen from the bottom parts of Figs. 14 and 15, the operation follows the cycle ABCD coupling van’t Hoff plots (simplified similar to the Fig. 12) for HT-MH between $T_M$ and $T_H$ and LT-MH between $T_L$ and $T_M$. Generally, the mode of operation of the two-bed MHHP depends on the values of $T_L$, $T_M$ and $T_H$, and thermodynamic properties of LT-MH and HT-MH. These parameters determine the differences between hydrogen equilibrium pressures in points A (LT-MH at $T_L$) and B (HT-MH at $T_M$), and in points C (HT-MH at $T_H$) and D (LT-MH at $T_M$). Consequently, the pressure differences determine direction of $H_2$ flow between the two beds. When $P_A > P_B$ and $P_C > P_D$, the hydrogen flow follows the paths A → B and C → D as shown in Fig. 14, and the cyclic process ABCD provides cooling of the “cold” side to the lower temperature $T_L$ driven by the heating of the “hot” side to the higher temperature $T_H$ while a periodic cooling of the “cold” and “hot” sides set the equilibrium at the medium temperature $T_M$. Accordingly, the MHHP provides cooling of the LT-MH to $T_L$ driven by the heating of HT-MH to $T_H$ and the cooling of both beds to $T_M$. Alternatively, this mode can provide heat upgrade at $T_M$ by the heat transfer from both “hot” ($T_H$) and “cold” ($T_L$) sides.
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When $P_A < P_B$ and $P_C < P_D$ (Fig. 15), the cycle ABCD changes its direction. Indeed, hydrogen transfer between HT-MH at $T_M$ and LT-MH at $T_L$ follows the path B → A thus absorbing heat at $T_A$ and releasing heat at $T_L$. The reverse $H_2$ transfer from LT-MH to HT-MH follows the path D → C accompanied by heat absorption in LT-MH at $T_M$ and heat release from HT-MH at $T_H$. In doing so, the heat transforming mode is realised: the release of heat from HT-MH at $T_H$ is driven by its heating to $T_M$ and cooling of LT-MH to $T_L$ followed by its heating to $T_M$.

The first and the main task in the development of the multi-bed MHHP is a proper selection of the pairs of MH materials for the connected LT-MH and HT-MH beds. The thermodynamic performances of the materials in the pair should be carefully aligned towards achievement of maximum efficiency and coefficient of performance (COP) for the selected mode of operation at the specified operating temperatures ($T_L$, $T_M$ and $T_T$). They should also provide maximum absolute values of pressure driving forces ($P_A$–$P_B$) and ($P_C$–$P_D$) and, in turn, to improve dynamics of hydrogen transfer. Additionally, the operating pressures should not be too high to minimise the material consumption of the MH containment thus reducing losses for its alternating heating and cooling.

The approach for the selection of hydride pairs for MHHPs [259] was significantly extended by accounting the vast growth of the amount of the available data on the properties of the MH materials and development of the advanced data processing algorithms. The work [269] reported screening of the suitable pairs based on the analysis of 336 (pseudo)binary, complex and intermetallic hydrides for the heat management applications. The study also included dynamic simulations allowing to select around 1900 (from >10,000 available) hydride pairs characterised by the dynamic COP above 1 and specific heating power between 25 and 60 W/kg in the temperature range 25 to 140 °C.

Industrial-scale implementation of the metal hydride heat pumps started in the first decade of 2000s in Japan. One example is a freezer/refrigerator system developed by the Japan Steel Works, Ltd. and comprising of two rooms, 67 m³ each, cooled to −30 and 0–5 °C, respectively. The system uses four MH beds, two (120 kg each) for the “cold” and two (137 kg each) for the “hot” side, based on AB$_2$-type materials. The system is driven by industrial heat at $T_H = 160$ °C and intermediate cooling to $T_M = 10–17$ °C using ground water [270].

The reference data describing the recent developments in the application of metal hydrides for heat storage and conversion can be found in the Refs [70,73,271–275].

3.4. Hydrogen separation and purification

Selectivity of the reversible interaction of gaseous hydrogen with hydride forming metals and intermetallics (Reaction (1)) when subjecting the metals to the mixtures of hydrogen-containing gases allows for the development of simple and low energy-consuming absorption/desorption systems for hydrogen separation and purification based on pressure – temperature swing [25,27,29,54,61,62,276–281].

The main problem of the application of metal hydrides for hydrogen separation and purification is in a high sensitivity of the MH materials towards poisoning by the selected gas impurities of active gases including carbon dioxide and, particularly, carbon monoxide which may be present as an admixture in hydrogen synthesized from hydrocarbons [61,62,73,282–286]. The Ti-based hydride forming alloys (TiFe and AB$_2$-type) are also sensitive to oxygen and water vapour/moisture which may be present in $H_2$ produced by electrolysis [9,287–290].

The origin of “poisoning” of hydride materials with gas impurities is in the passivation of active centres responsible for the dissociative $H_2$ chemisorption on the material surface (see Fig. 2) by forming strong bonds with active gases thus making these centres inaccessible for the splitting of hydrogen molecules. Accordingly, the poisoning tolerance of the MH substrate can be improved by either preventing the migration of the impurities to its surface, or by a creation of the additional catalytically active centres thereon. These approaches are schematically illustrated by Fig. 16. The first approach (1) is in covering the particles of the MH substrate with a very fine polycrystalline fluoride layer which is permeable for hydrogen but not for the species of the active gases, O$_2$, H$_2$O, CO, CO$_2$, which may cause the degradation of the hydrogen sorption performance. The protective layer is formed during the treatment of the substrate powder with an aqueous solution of a soluble fluoride in presence of HF. The best results have been obtained for the rare-earth containing AB$_2$- and A$_2$B$_7$-type substrate materials and for hydrogen storage alloys (e.g., AB$_2$-type intermetallics) doped by rare-earth elements [291–294].

The second approach (2) is in the surface deposition of the metals capable to catalyse a dissociative chemisorption of $H_2$. Efficient catalysts include Platinum Group Metals (PGM), with Pd being most abundantly utilised [295–301]. The most frequently applied technique is electroless plating which results in a discontinuous coating of the substrate by the PGM particles with the size of x10 nm [302]. Improvement of the PGM deposition process allowed increasing of the PGM loading and the
coating density (and, in turn, poisoning tolerance of the surface-modified MH), even at a low concentration of the PGM plating solution, can be achieved by functionalisation of the oxidised substrate surface by aqueous solutions of aminosilanes [299,303].

A combination of the approaches described above (1 + 2 in Fig. 16) provides a very pronounced synergetic effect [61,302]. Of the possible options of realisation of this approach (a–c), the deposition of PGM onto fluoride layer (b) seems to be the most promising. It was shown [302] that electroless deposition of Pd onto fluorinated AB2-type material results in plugging the micro-cavities of the fluoride layer by Pd nanoparticles to form advanced composite material characterised by exceptionally good hydrogenation performance. These materials even after long (several months) exposure of the AB2 powder to air actively form the hydrides without a need for the preliminary activation.

Table 2 presents the data allowing to compare hydrogen absorption characteristics of the same AB2-type alloy surface modified by different methods. It can be seen that the hydrogenation performance is improved following the series “unmodified < Pd coating without aminosilane functionalisation ≈ fluorination < Pd coating with aminosilane functionalisation < fluorination followed by aminosilane functionalisation and Pd coating”.

Surface modification by fluorination and deposition of metallic catalysts significantly improves both gas-phase and electrochemical hydrogenation properties of MH materials including easy activation and suppression of the degradation rate during the cycling [293,304,305].

A prototype hydrogen separation unit based on the AB2-type material surface-modified using “fluorination – aminosilane functionalisation – Pd coating” route showed a stable hydrogen separation and purification performances over ~200 cycles when exposed to the feedstocks containing CO2 and CO at the concentrations of up to 30 % and 100 ppm, respectively [62,282].

The recent studies (2020–2023) on hydrogen separation and purification utilising MH materials were mainly focused on the experimental investigations of the influence of gas admixtures (up to 50 % of CH4 or CO2) on hydrogen sorption properties of the AB2-type alloys [286,306–308]. Interesting data concerning the influence of the temperature on the poisoning tolerance of AB2-type alloys when exposed to H2 + CO mixtures were reported in ref. [285]. It was shown that the increase of the operating temperatures improved poisoning tolerance towards CO. Similar results were reported in ref. [309]. The work [310] which studied the poisoning resistance of fluorinated Mg/MgH2 during the hydrogenation using the mixture H2 + CO2 (up to 50 %) + CO (up to 100 ppm) at T = 300 °C is also of interest.

Many recent works reported modelling approaches describing MH hydrogen separation and purification systems [309,311–314]. The problems related to the selection of the suitable MH materials and design of hydrogen purification reactors were considered in the Ref. [315].

3.5. MH getters and low-pressure sources of hydrogen isotopes used in vacuum-plasma technologies

One of the promising gas-phase applications of the metal hydrides is their use in the supply systems of vacuum-plasma facilities, which include ion sources for the accelerators, injectors for the fusion installations, and other components which use hydrogen isotopes as a working fluid. These materials can provide compact storage of a moderate amount (around x100 normal litres) of hydrogen (deuterium, tritium), evacuation of the excessive gas from an ion source to the vacuum systems to \( P = 10^{-7} \cdot 10^{-3} \) Pa, involving its purification and further supply to the ion source at \( P = 0.1–100 \) Pa. Additionally, the use of the MH in the vacuum-plasma technologies allows to significantly increase the efficiency and operation stability of the corresponding components of vacuum-plasma installations [316].

Reversibility of the Reaction (1) even for the very stable hydrides, e. g., formed by the multi-phase alloys \( \alpha - \text{Zr} + \text{C14-Zr(V,Fe)} + \eta - \text{Zr}_4 \text{V}_2 \) (B, O)\(_5\) (317) or \( \alpha - \text{Zr} + \text{C15-ZrV}_2 + \eta - \text{Zr}_4 \text{V}_2 \)O\(_5\) (318), builds up of the very efficient sources of both positive (\( H^+ \), \( H_2 \), \( H_3 \)) and negative (\( H^- \)) hydrogen ions comprising electrodes made of the hydrogenated getter type alloy. Schematic representation of a prototype ion source utilising such material as a part of anode of the gas discharge chamber is shown in Fig. 17. Introducing MH into the anode results in the significant improvements of the H ions generation including easier ignition (lower value of the discharge voltage, \( U_0 \)), and higher stability of the discharge burning, as well as significant increase of the yield of hydrogen ions (by 30–50 % for \( H_2 \) and by 15 % for \( H_3 \)) [316,319]. The later feature was associated with the effect of hydrogen “activation” during the \( H_2 \) desorption from a MH [76], via vibrational excitation of the \( H_2 \) molecules formed by recombination of H atoms on the MH surface [320,321].

Introducing reversible MH getters into cathode of the gas discharge chamber is particularly efficient. The bombardment of the MH cathode by positive ions of the discharge plasma results in hydrogen desorption, and the desorption rate increases with the increase of intensity of the ion bombardment. As a result, the processes in hydrogen plasma contacting with the MH cathode acquire internal dynamic feedback between the discharge current and hydrogen pressure established in a closed gas discharge chamber. The so-called “pressure auto-stabilisation” effect [322] is promising in the development of very efficient applications of MH (reversible hydrogen getters) in vacuum-plasma technologies by the creation of compact, autonomous, and simple in operation facilities characterised by a high gas efficiency [323–326].

![Fig. 16. Approaches to increase the tolerance of the MH substrate towards “poisoning” with gas species by blocking the \( H_2 \) chemisorption active centres. 1 – covering with the protective fluoride layer not permeable to the species of active gases but permeable to \( H_2 \) molecules. 2 – deposition of the catalytically active metals. 1 + 2 – combination of the above techniques.](image-url)
Feasibility of a thin film source of H₂ ions formed due to electron stimulated hydrogen desorption from TH₂ thin films followed by H₂ ionisation has been demonstrated in ref. [327].

Applications of MH hydrogen getters in vacuum-plasma technologies also include targets for the laser sources of protons (MgH₂, ZrH₂) [328] and neutron generators (titanium tritide); the latter application also uses deuterium-saturated getter alloy for the supply of low-pressure deuterium gas [329].

Recently published review [330] considers Zr and V-based intermetallics and multiphase alloys as promising non-evaporable hydrogen getters. Other recent publications on the topic can be found in the references of the corresponding section of review [77], as well as in the refs [331–336].

4. Discussion

Use of metal hydrides because of versatility of their thermodynamic properties thus covering an extremely broad range of hydrogen pressures spanning 10 orders of magnitude (see Fig. 4), allows to efficiently utilise them for hydrogen storage, hydrogen compression, heat storage and conversion, and in vacuum-plasma technologies.

The rich chemistry of metal hydrides extends this application landscape to the processes of hydrogen generation by the hydrolysis of the MH [337–340], catalysis of the chemical reactions involving transfer of hydrogen [73,341–343], powder metallurgy processing of the metals including HDDR route [132,136,344,345]. Each of these mentioned applications owns a vast amount of individual specific features and deserves to be considered in separate reviews.

Use of the approach “From material to system” (Fig. 6), allows to properly select relevant for the specific application MH and to optimise their properties making them suitable to fulfill the requirements of the targeted engineering solutions. When developing various gas-phase applications of metal hydrides, a joint use of the metal hydride technologies together with other suitable hydrogen energy technologies appears to be particularly fruitful because of their synergy thus bringing benefits by mitigating the effect of disadvantageous features while amplifying the advantages of the combined methods. One example is the development of hybrid hydrogen compression technology by integrating electrochemical hydrogen supply system providing hydrogen gas with an output pressure of 10–200 bar and metal hydride hydrogen compression technology boosting this pressure to 200–875 bar. Such integrated system offers a higher reliability and energy efficiency as compared to 10–875 bar electrochemical and metal hydride hydrogen compressors when operating separately [346]. Another example is the application of AB₅-type hydride-forming material surface-modified by Pd acting as a very efficient catalyst in the hydrogenation/dehydrogenation of liquid organic hydrogen carriers [347].

We believe that further R&D in the development of gas phase applications of metal hydrides will be focused on addressing system integration issues by introducing multi-functional MH units into balance of plant (BoP) of small-to-medium (up to 100–200 kW) hydrogen-based renewable energy systems [348]. Along with compact hydrogen storage, such units can provide utilisation of heat losses from the system components (e.g., electrolyser and fuel cell), heat storage and conversion, hydrogen compression for dispensing to the fuel cell vehicles, together with other useful features which will eventually result in the extension of system functionality and increase of the round-trip efficiency.

Successful implementation of this approach requires in-depth application-targeted studies of MH materials including:

- Selection of the compositions of multi-component hydride-forming alloys and catalysed hydride composites whose hydrogen sorption properties will be well aligned with the requirements of end-use applications as concerns of operating temperatures and hydrogen pressures. The search could be done using computer modelling (including machine learning tools) followed by the experimental validation of the PCT behaviours of the selected materials.
- In-depth experimental studies of hydrogen absorption – desorption kinetics for the promising MH materials including the influence of impurities in H₂ gas and H₂ absorption/desorption cycling on the kinetic parameters.
- Studies of the upscaling on the preparation of the MH materials as related to their phase-structural characteristics, morphology, and hydrogen sorption properties.

Along with the material studies, in-depth investigations of the engineering aspects of the use of MH materials will be continued. The focus will be on the augmentation of heat-and-mass transfer in the MH reactors, by the optimisation based on their simulation results together with the experimental validation. Special attention in these works should be paid to simplified modelling approaches which would allow to adequately predict H₂ charge/dischage dynamic performances of the MH reactors without excessive workload to assess the data concerning, e.g., spatial temperature distributions requiring use of significant computation resources and not always helpful in optimising the reactors design. This approach should provide a set of criterial equations where dimensionless criteria would describe the principal reactor parameters responsible for the charge/discharge dynamics. Examples of use of such approach can be found in refs [196, 349].

An extra component contributing to the improvement of H₂ charge/discharge dynamics via acceleration of reaction kinetics and optimisation of the heat transfer is in the development of advanced MH-based composites with additives which combine functions of hydrogenation/dehydrogenation catalyst and increase of the effective thermal conductivity of the MH bed. One good example is in use of graphene-like materials doped by nanoparticles of catalytically active metals [186].

Development of the MH reactors should also focus on addressing the safety concerns associated with the dilatation effects in MH materials, and, at the same time, maximising the MH loading density. Furthermore, elaboration of efficient and labour-saving procedures of the MH loading into the reactors is in a great demand.

For the high-pressure hydrogen compression applications, development of the MH containers for hydrogen compression combining sufficient strength with minimal material consumption (to reduce energy losses during the thermal cycling) is required.

Finally, future breakthroughs in the gas-phase metal hydride technologies can be achieved by proposing new solutions of their combination with the alternative technologies as has been already mentioned in this section.
5. Conclusions

The unique features of the reversible processes of formation/decomposition of metal hydrides make possible to efficiently use these materials for various applications. The applications based on heat-driven reversible interaction of hydride-forming materials with hydrogen gas are the most versatile. The MH systems for the gas-phase applications allow to tailor operating H₂ pressures in extremely broad range, while being compact, safe in operation, offering excellent absorption/desorption kinetics, and being easy to scale up based on the concept of modular design. Further to hydrogen storage, several other important technologies, including hydrogen compression, heat management, H₂ separation and purification, should be in focus in the development of the MH technologies. A success in realising this approach will be in a fine tuning of the properties of the MH materials, and in the optimisation of the system design addressing consumer’s specification. MH applications are very important for energy storage and conversion technologies including hydrogen and fuel cell-based hydrogen energy systems. They allow to combine the processes of compact and safe hydrogen storage and its supply, along with the utilisation of waste heat released during operation of other system components.

Future progress in the gas-phase applications of metal hydrides will include in-depth application-targeted studies of metal hydride materials and development of advanced engineering solutions of the efficient metal hydride reactors aimed at integration of multi-functional metal hydride units into balance of plant of hydrogen-based renewable energy systems.

Acknowledgements

ML and BPT acknowledge support from the Ministry of Science and Higher Education of the Russian Federation, mega grant, agreement no. 075-15-2022-1126.

ML acknowledges support from the Department of Science and Innovation (DSI) of South Africa, Hydrogen South Africa/HySA RDI Strategy, Key Programme KP6 “Metal hydride materials and technologies”; and South African National Research Foundation (NRF), grant number 132454.

VY and ML acknowledge support from EU Horizon 2020 programme in the frame of the H2020-MSCA RISE-2017 action, HYDRIDE4MOBILITY project, with grant agreement 778307.

VY thanks IFE for the support.

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