Niche applications of metal hydrides and related thermal management issues

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Article info
Article history:
Available online 30 January 2015

Keywords:
Metal hydrides
Hydrogen storage
Hydrogen compression
Heat management
Thermal management issues

Abstract
This short review highlights and discusses the recent developments and thermal management issues related to metal hydride (MH) systems for hydrogen storage, hydrogen compression and heat management (refrigeration, pump and upgrade, etc.). Special attention is paid to aligning the system features with the requirements of the specific application. The considered system features include the MH material, the MH bed on the basis of its corresponding MH container, as well as the layout of the integrated system.

1. Introduction

Metal hydride (MH) materials are able to reversibly absorb and desorb large amounts of hydrogen in a wide range of temperatures and pressures. They are characterised by some unique properties, including extremely high volume density of H atoms incorporated in the metal matrix [1–5], wide “tuneability” of thermodynamic performances [3–7] and fast kinetics of hydrogenation/dehydrogenation [3–9]. MH technologies utilising such features are typical application-driven niche areas able to provide very efficient solutions for hydrogen handling, particularly for end-use applications, by the tuning of component and phase composition of the parent MH material, system layout and operation parameters. MHS offer several advantages over traditional hydrogen storage (e.g. compressed hydrogen, liquefied hydrogen, etc.) and processing systems, such as compactness, safety (due to low pressures <10 bar), possibilities of hydrogen supply at pre-defined pressures, absence of moving parts, long operation lifetime, efficient and technologically flexible energy conversion between low-grade heat and the energy of pressurised H2 [7,10]. These systems have found a number of promising gas phase applications including hydrogen storage and supply, hydrogen compression, heat management (refrigeration, pump, and upgrade), etc. [1–10].

The present work herein briefly highlights features of the most important gas-phase niche applications of MH. Methods for improving heat transfer performances of the corresponding MH reactors are also described and discussed.

2. Thermodynamic properties of MH and main applications

The chemical bonding of gaseous hydrogen in MH can be written as:

\[ \text{M(s)} + \frac{x}{2}\text{H}_2(g) \rightarrow \text{MH}_x(s) + Q; \]  

(1)

where M is the metal, alloy or intermetallic compound forming hydride, MHx, (s) and (g) denote solid and gas phase, respectively.

The direct process of reaction (1), hydride formation/hydrogen absorption is an exothermic reaction, and the generated heat, Q, is approximately equal to the absolute value of the enthalpy of reaction (1). The heat has to be effectively removed in order to achieve the desired H2 charge rate. Accordingly, the endothermic hydride decomposition/H2 desorption (reverse process of reaction (1)) needs efficient supply of the approximately same amount of the heat to provide the necessary rates of H2 discharge.

It has to be noted that the driving force of both direct and reverse processes of reaction (1) strongly depends upon the deviation of the actual hydrogen pressure, P, from the value, \( P_{eq} \), of equilibrium dissociation pressure of the MH which is an important property of hydride forming materials. Temperature dependence of \( P_{eq} \) in the plateau region of a Pressure–Composition Isotherm (PCI) is expressed by the van’t Hoff equation:
45 J mol$^{-1}$H$_2$ for the reaction (1), of $\Delta S_1$ [mol H$_2$ K$^{-1}$] and $\Delta H_1$ [kJ mol$^{-1}$ H$_2$] represent the associated changes in enthalpy and entropy, and $P_0$ is the reference pressure (1 atm)$^{-1}$.

Fig. 1 shows $\Delta S$ and $\Delta H$ values for 278 metal hydride materials [7,10]. For the most of the MH materials, $\Delta S$ does not vary significantly around $-111$ J mol$^{-1}$ K$^{-1}$ which is close to the change of entropy of gaseous H$_2$ for the reaction (1), of $-130$ J mol$^{-1}$ H$_2$ K$^{-1}$. The plateau pressure, $P_{eq}$, is mainly determined by the reaction enthalpy, $\Delta H_1$, which varies from $-166$ to $-6.6$ kJ mol$^{-1}$ H$_2$ for ZrH$_2$ [11,12] and AlH$_3$ [13], respectively. At the same time, in some MH materials the contribution of the entropy of the solid into the total entropy change for reaction (1) can be significant thus resulting in significant deviations of $\Delta S$ from the average value specified above. Binary metal hydrides and solid solution alloys exhibit lower $\Delta S$, down to $-150$ J mol$^{-1}$ H$_2$ K$^{-1}$, while multicomponent A$\beta$$_{2x}$ metal hydrides can have hydrogenation entropy as high as $-45$ J mol$^{-1}$ H$_2$ K$^{-1}$.

Fig. 1 can guide in selecting metal hydrides for different gas phase applications including:

A – Heat pumps: for efficient operation, the MH material should have high heat effects (|$\Delta H_1$| > 30 kJ mol$^{-1}$ H$_2$) while providing moderate H$_2$ pressures during the operation. The absolute value of the reaction entropy should be as low as possible (|$\Delta S_1$| < 110 J mol$^{-1}$ H$_2$ K$^{-1}$).

B – Heat storage: similarly, the MH material has to have high heat effects (|$\Delta H_1$| > 30 kJ mol$^{-1}$ H$_2$), but highly exothermic MH should have not too low H$_2$ pressures at operating temperatures (|$\Delta S_1$| > 110 J mol$^{-1}$ H$_2$ K$^{-1}$).

C – H$_2$ storage: for this type of application, low energy consumption for hydrogen release is important (|$\Delta H_1$| < 30 kJ mol$^{-1}$ H$_2$), and highly exothermic MH should have not too high H$_2$ pressures at operating temperatures (|$\Delta S_1$| > 110 J mol$^{-1}$ H$_2$ K$^{-1}$).

D – H$_2$ compression: this application requires compromise between energy consumption for hydrogen desorption and high compression ratio; accordingly the MH materials should have medium heat effects (|$\Delta H_1$| = 20–30 kJ mol$^{-1}$ H$_2$) and high absolute values of the hydrogenation entropy (|$\Delta S_1$| > 100 J mol$^{-1}$ H$_2$ K$^{-1}$).

3. Thermal management issues

3.1. General features

When the rates of heat dissipation (exothermic H$_2$ absorption) or heat supply (endothermic H$_2$ desorption) from/to the MH material are lower than the rates of its heating/cooling due to heat effect, $\Delta H_1$ of reaction (1), the material reaches an equilibrium temperature, $T_{eq}$ when $P = P_{eq}$ and no further absorption or desorption occurs. The value of $T_{eq}$ can be estimated by a solution of Eq. (2) with respect to the temperature for each actual pressure (“dynamic van’t Hoff equation”) as it was suggested by Goodell [14]. Thus, further rates of hydrogen absorption/desorption in any part of the MH material in a reactor will be limited by the rate of heat exchange between the material (elementary volume in MH bed) at $T = T_{eq}$ and the cooling/heating means at $T = T_0$. Accordingly, the integral H$_2$ absorption/desorption rates in a MH reactor can be determined only in the course of the solving of, in 3D statement, the Fourier heat equation with a source term [3]:

$$\frac{\partial T}{\partial t} = \nabla \cdot \left( \frac{k}{\rho c_p} \nabla T \right) \pm \frac{\Delta H}{\rho c_p},$$

where $T$ [K] is the MH temperature, $t$ [s] is time, $k$ [W m$^{-1}$ K$^{-1}$] is the effective thermal conductivity, $\rho$ [kg m$^{-3}$] is the apparent specific weight and $c_p$ [J kg$^{-1}$ K$^{-1}$] is the specific heat capacity of the packed material, “+” and “−” correspond to H$_2$ desorption and absorption, respectively.

This approach has been taken in numerous investigations for the modelling of heat-and-mass transfer in MH beds [15–17]. At the same time, the details of the task statement strongly depend upon a number of factors, first of all, effective heat conductivity of the MH bed, its geometry, ways of heat supply and its removal. These parameters related to heat management issues may significantly differ in numerous applications. However, the common strategy in the improvement of heat transfer performances of MH beds should include the “maximizing” of the term $\frac{\partial T}{\partial t}$, first of all, by increasing the effective thermal conductivity, $k$. The shortening of the characteristic heat transfer distance is also very important.

3.2. Augmentation of hydride bed heat transfer

Enhancing the effective thermal conductivity forms the central objective of all techniques applied to porous MH beds. Impregnations of heat conduction matrices have been found to be very useful. The approach includes 2D and 3D structures made of heat conductive metals, e.g., copper or aluminium. Common impedi-ments to the above solution include the parasitic weight of the heat conductive material, disintegration and deterioration upon cycling, and high cost. Representative values of effective thermal conductivity and void fraction achieved by different augmentation techniques are listed in Table 1.

Suda et al. [24] carried out experimental investigations aimed at improving the effective thermal conductivity of activated MH. A 3D structure of porous aluminium foam increases $k_0$ in 9–10 times (4 W m$^{-1}$ K$^{-1}$ at 0.5 MPa H$_2$) as compared to the unmodified hydride bed. Laurencelle and Gayot [19] numerically studied the impact of aluminium foam to enhance hydrogenation reactions. The effective thermal conductivity of the hydride bed was improved to 10 W m$^{-1}$ K$^{-1}$. The reaction rate in the reactor with foam depends upon the resistance inside the foam cells, and also along the path to the reactor wall. With foam, the MH bed thickness could be increased without hampering the charging time. The foams with pore density less than 20 PPI (Pores Per Inch) were not recommended due to poor heat transfer. Fleming et al. [25] showed that
adding metallic foam significantly improved the rate of metal-hydrate based hydrogen separation process.

Expanded Natural Graphite (ENG)–MH compacts provide a cost effective solution to the problem [22,23]. Recompressed ENG offers (i) high plasticity under compression loads, (ii) high thermal conductivity and (iii) gas permeability in the direction perpendicular to the direction of the compacting. Hydrogen absorption rates were found to decrease slightly compared to that of the MH powder–Al foam reaction bed. Further improvement of heat transfer in MH/ENG compacts was suggested by De Rango et al. [26], as an alternative arrangement with heat conductive fins within an MH hydrogen storage tank. This layout was successfully applied for large-scale H storage tanks comprising stable MH (MgH₂) taken for the compacting with ENG in the hydrogenated state [27]. For the MH materials which form hydrides with dissociation pressure higher than 1 bar at the room temperature, some variations of the compacting technology have been recently suggested by the South African co-authors of this review (ML, BGP, VL) [28].

Implementation examples of the heat transfer augmentation techniques are presented in Fig. 2.

In addition to the internal heat transfer, the solutions intensifying heat exchange between the MH bed and the heating–cooling fluid can be very efficient as well, especially, when they are combined with the shortening of the characteristic heat transfer distance. The best achievement for this approach was realised by Ergenics Inc. [32,33] whereby MH materials were loaded into a tubular containment of a small outer diameter, down to 1/16 in. (1.588 mm). The intensification of heat exchange between the outer surface of the hydride tube and heating/cooling fluid was achieved by fins formed by steel wire wound and soldered onto the hydride tube. The hydride beds in such hydride “ring manifolds” (the images can be found in [7,30,32,33]) enable very short reaction kinetics of about 95 s for desorption and 80 s for absorption and the reported specific cooling power was 850 W kg⁻¹ for 95 s cooling time (in other words 425 W kg⁻¹ for the complete cycle). Recently, Anbarasu et al. [36] studied the effect of different arrangements of cooling tubes embedded in the hydride bed on the hydriding and dehydriding characteristics. Using 2.75 kg of LmNi₄ₓSn₀.₁, the absorption time was significantly reduced to 5 min when the number embedded cooling tubes was increased from 36 to 60.

3.3. Specific niche applications

3.3.1. Hydrogen storage

The use of MH materials for hydrogen storage is characterised by high compactness, safety and ease of operation and consumption of low “quality” energy (waste heat) for H₂ desorption. Even taking into account low hydrogen storage weight capacity for “low-temperature” MH materials, they can be successfully used for a number of wide-scale stationary and special mobile applications when the system weight is not a major and critical issue [37]. However, the main issue related to the thermal management is in poor H₂ charge/discharge dynamics due to heat transfer limitations. This effect is especially pronounced for the larger-scale hydrogen storage systems and can be mitigated by the improvement of heat transfer inside MH bed (see Section 3.2).

3.3.2. Heat pumps. Heat transformers. Heat storage

The use of Chloro-Fluro-Carbon refrigerants (CFCs) is well-known to be significant source of pollution to the global environment and great effort has been undertaken to tackle and minimize this problem through the promotion of the alternative refrigeration and air-conditioning systems. One of the most promising alternatives is the use of hydrogen as refrigerant in the metal hydride based heat pumps (MHHP) [30,38]. MHHPs are characterised by safe and easy operation (no moving parts), and enable to use the waste heat (T ~ 150 °C). The main problem to be solved in the development of all heat management applications of MH, including MHHP, is in the careful selection of materials with thermodynamic properties for the high- and low-temperature system sides need to be aligned. The selection must take into account the required operation temperatures: low (T₁), medium (T₉) and high (T₉); hydrogen pressures; as well as reversible hydrogen storage capacities of the materials at the operation conditions. Thus for example, the combination Z₉₋₀.₅₉₋₀.₉MnFe/LaN₅ allows operations at T₁ = 25.7 °C, T₉ = 50 °C, T₉ = 145.2 °C and P(H₂) = 1.77–5.5 atm. This example was taken from the publication by Dantzer and Orgaz [39] where detailed guidance for the selection of the MH materials for heat management applications was presented.

Another problem is in the low efficiency of MHHPs as the Coefficients of Performance (COP) of single-stage MHHPs are typically below 0.5. The efficiency can be increased by minimizing the contribution of containment and auxiliary elements (heat exchangers) into the total system weight, without compromising on fast dynamics of H₂ exchange between MH beds and high heat exchange rates between the MH beds and the heat transfer fluid. The use of CTRBs allowed the system to achieve fast reaction kinetics [35].
increase of COP and specific cooling power per MH unit mass can be achieved using a Compressor-Driven (CD) MH systems for cooling and heating applications. Magnetto et al. [32] described the development of a CD-MHHP for automotive applications (with COPs in the range of 2.57–2.76) which was superior to conventional R-134a refrigerant system.

Apart from the increase in the effective thermal conductivity of the MH bed, special attention in the course of the development of high-efficiency MHHP has to be paid to the balance between the rate of hydrogen transfer and the capacity rate of heat transfer fluids. A lumped parameter model suggested by Bjurström and Suda in 1989 [40] can be useful for such analysis.

MHHP can be used in various energy saving technologies, including Combined Heat and Power (CHP), utilisation of low-potential industrial heat, residential energy systems, etc.

Metal hydride based heat transformer (MHHT) is a type of MHHP which can upgrade the temperature of low grade heat such as industrial waste heat, solar energy, and geothermal energy up to the temperature in the range of 150–220 °C. It also provides higher heat storage capacity and offers wider range of working temperatures as compared to other conventional heat pumps/heat transformers. MHHTs use hydrogen as a working fluid which is environment friendly, noise free and vibration free. The performance of MHHT can be improved by (i) sensible heat recovery, (ii) employing compact reactors with embedded heat transfer fluid tubes and (iii) optimizing heat transfer enhancement and thermal capacity of the reactor [41,42].

Heat storage is another important heat management application of MH. Unlike the latent and the sensible heat storages utilising phase change materials, in chemical energy storage systems on the basis of MH, heat can be stored for a longer period without any thermal insulation [43]. MH based energy storage systems are high energy dense, deliver heat at near constant temperature, and offer wide range of operating temperatures. They can provide energy densities as high as 2814 kJ kg\(^{-1}\) of hydride [44]. The system performance depends upon careful selection of hydride forming alloy within its operating range. Hydrides with high heat of formation, flat plateau, low hysteresis, fast kinetics, easy activation, and high melting point are desirable. The other desirable properties of metal hydride alloys are: high hydrogen storage capacity, flat plateau, low hysteresis, fast kinetics, easy activation, and high melting point. Hydrides on the basis of Mg alloys (hydrogen storage capacity of MgH\(_2\) is 7.6 wt.% H; \(\Delta H = -74\) kJ mol\(^{-1}\) H\(_2\); \(P_{eq} = 1\) bar at \(T \approx 300\) °C) are suitable for energy storage applications.

An interesting and promising approach in the development of the hydride-based heat management systems is in the combination of MH (“low-temperature” side) and catalysed organic hydrides (“high-temperature” side) characterised by wide range...
of the operation temperatures (≥100–500 °C) and high hydrogenation-heat effects (about 70 kJ mol⁻¹ H₂ that is close to the heat of formation of MgH₂). This solution [45] could potentially extend the operating temperature range of the MHHP and increase the efficiency, providing that the problem with slow H transfer kinetics in organic hydride systems is solved.

3.3.3. MH hydrogen compressors
Thermally-driven MH sorption compression is an efficient and reliable method allowing conversion of energy from heat into a compressed hydrogen gas. This technology offers a good alternative to both conventional (mechanical) and newly developed (electrochemical, ionic liquid pistons, etc.) methods of hydrogen compression. MH hydrogen compression is characterised by safe and easy operation (no moving parts); practically unlimited, up to kilobar-range, discharge pressures; good scalability, from few litres to several m³ H₂ (at STP) per hour; modular design; easy replenishment/maintenance; possibility to utilise waste heat instead of electricity. A comprehensive review on MH hydrogen compression technology was recently published by Lototskyy et al. [7]. Similarly to the MH heat management systems, the main disadvantages of MH compressors are associated to low efficiency and low productivity originated from slow dynamics of hydrogen uptake and release in MH reactors (compression elements). Similarly to MHHPs, the efficiency can be increased by the minimization of thermal masses of MH containers and their auxiliary elements (heat exchangers, filters, etc.); the use of heat recovery solutions is promising as well. The productivity can be increased by the improvement of heat transfer performances of the MH reactors, as described above.

Promising niche applications of the MH compressors cover very wide areas, including laboratory facilities, cryogenics, space, H₂ filling stations, utilisation of waste heat, temperature sensors & actuators, as well as a number of special H₂-consuming technological processes (e.g., powder metallurgy).

4. Concluding remarks
This paper briefly describes thermal management issues in various niche applications of MH including (i) H₂ charge/discharge dynamic performance and (ii) energy efficiency.

The main factors influencing the H₂ charge/discharge dynamics are as follows:

- MH material characteristics (H storage capacity, thermodynamic and thermal properties).
- Pressure/temperature operating conditions.
- Reactor configuration and geometric parameters.
- Thermal design of the overall MH reactor.

The optimisation mainly relates to the improvement of heat transfer performances, by the introduction of a heat transfer matrix in the MH bed, including wire meshes (copper or aluminium), metal foams, expanded graphite. An alternative approach can be in the development of MH containers with short characteristic heat transfer distance in the MH bed and improved heat transfer coefficient between the container wall and heating–cooling fluid.

Note that for portable and mobile hydrogen storage applications, heat transfer intensification may be counterproductive due to the added weight of the thermally conductive materials which do not participate in H₂ sorption. This problem can be mitigated by: (i) the use of ENG, and/or (ii) the development of “hybrid” systems using unstable MH in combination with gaseous H₂ at moderately high pressures [46].

The following main factors affect the efficiency of MH systems:

- Thermal masses of MH container and auxiliary elements (heat exchangers, filters, etc.).
- Heat recovery.
- Heat transfer.

Heat transfer is the major factor directly controlling H₂ sorption/desorption rates in MH beds and affecting the efficiency of energy conversion. The improvement of the heat transfer characteristics is crucial.

Special attention and care in the optimisation of MH reactors related to the heat management issues has to be paid to aligning system features (MH material, MH bed on its basis in MH container, as well as layout of the integrated system) with the requirements of the specific application.

For hydrogen storage, as well as for the increase of energy efficiency in other applications, the mass of the MH container and auxiliary elements (heat exchangers, filters, etc.) should be decreased.

Acknowledgements
The contribution of South African co-authors into this work was supported by the Department of Science and Technology (DST) within the HySA Programme (project KP3-S02 – On-Board Use of Metal Hydrides for Utility Vehicles), Eskom Holdings Limited, and Impala Platinum Limited; South Africa. Investments from the industrial funders have been leveraged through the Technology and Human Resources for Industry Programme (THRIP), jointly managed by the South African National Research Foundation (NRF) and the Department of Trade and Industry (DTI); projects TP1207254249, TP2010071200039, and TP2011070800020. ML also acknowledges NRF support via incentive funding grant 76735.

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