Performance analysis of cylindrical metal hydride beds with various heat exchange options

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Abstract
A 3D numerical heat-and-mass transfer model was used for the comparison of H$_2$ uptake performances of powdered cylindrical MH beds comprising MmNi$_4$Al$_{0.4}$ hydrogen storage material. The considered options of heat exchange between the MH and a heat transfer fluid included internal cooling using straight (I) or helically coiled (II) tubing, as well as external cooling of the MH bed without (III) and with (IV) transversal fins. The dynamic performances of these layouts were compared based on the numerical simulation. The effect of heat transfer coefficient was also analysed.

1. Introduction

Metal hydrides (MH) have the ability to reversibly absorb and desorb relatively large amounts of hydrogen in wide ranges of temperatures and pressures. They have many potential applications including hydrogen storage, hydrogen compression and related thermal management systems (heat storage, pumping and upgrade) [1–5].

Hydrogen absorption in MH is an exothermic reaction when the generated heat has to be effectively removed to achieve the desired H$_2$ charge rate. Similarly, the endothermic H$_2$ desorption needs supply of the heat to MH. Thus, the performance of any MH based thermal device is essentially determined by heat transfer processes, and the thermal management of a hydrogen storage container (MH tank) is very important.

In recent years, many researchers have made numerous attempts to improve the heat transfer in the MH reactors, by enhancing the effective thermal conductivity of the reaction beds [6–9] and incorporating heat exchangers [10,11]. Kim et al. [6] presented the experimental results for the coupled metal-hydrider reactors comprising Ca$_{0.8}$Mm$_{0.2}$Ni$_2$ (Mm = Mischmetal) with hydrogen pumped by the compressor. In order to augment heat transfer in the reactor, the MH powder particles were copper-coated and compressed into porous MH compacts. Botzung et al. [8] presented a hydrogen storage tank using MH for a combined heat and power system. During H$_2$ absorption/desorption, the heat was dissipated/supplied by fluid circulation. An integrated plate-fin type heat exchanger was designed to obtain good capacity and to reach high absorption/desorption rates.

In effect, incorporating heat exchangers into MH reactors has been proven to be an effective way to enhance the heat and mass transfer, thus improving hydrogen storage performance. Recently, employing 4 kg of Ti$_{1.1}$CrMn, Visaria et al. [12,13] studied the hydriding performance of MH reactor with coiled tube heat exchanger and modular tube – fin heat exchangers but they tested the MH reactor at higher pressures, from 70 to 330 bar. The aforementioned research was mainly focused on the MH reactors equipped with a straight pipe heat exchanger. In order to further enhance the heat transfer and improve the hydrogen storage process in MH reactors, more attention has been paid to the reactors incorporating helical coil heat exchanger, which has the superior effect on the enhancement of heat and mass transfer due to its secondary circulation [14].

Minko et al. [15] studied heat-and-mass transfer in an MH bed of cylindrical geometry for thermal-sorption hydrogen compression. The numerical model was verified on LaNi$_5$ at the operating conditions from 4 atm/20°C (H$_2$ absorption) to 40 atm/150°C (H$_2$ desorption). There was also analysed the effect of introduction of aluminium framework in the MH powder on the H$_2$ absorption/desorption dynamic performance. It was shown that the aluminium framework allowed to increase the thickness of the MH bed in three times without compromising H$_2$ charge/discharge dynamics.

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A key issue in the development of any gas phase MH application is the selection of optimal layout of the MH tank which, from the one hand, should fit in space and weight constraints of the end-user, and, from the other, has to provide fast H₂ charge/discharge dynamics at the required hydrogen storage capacity and minimal costs. The acceleration of the H₂ charge/discharge, first of all, depends on the intensity of the heat exchange between a heat transfer fluid (HTF) and the MH [5]. Apart from the methods of augmentation of the bed heat transfer overlooked above, a general system layout at similar bed sizes and geometries is very important for the optimisation. As a first optimisation step, a proper comparative modelling of various heat exchange layouts has to be carried out at the similar conditions. Despite of numerous modelling activities [8,10,12–19, etc.], there is a lack of such a comparison in the literature.

In the present study, a 3D numerical model of heat-and-mass transfer in MH beds has been developed using typical simulation approaches [16,17]. The model has been further applied for the comparison of hydrogen uptake performance for cylindrical MH beds with four MH cooling layouts: straight pipe (I) and helically coiled (II) internal heat exchangers, and external cooling of the MH powder without (III) and with (IV) transversal fins. The selected layouts are simple for manufacturing and MH powder loading. All reactors contained the same AB₅ type hydrogen storage material. The selected external dimensions of the modelled MH beds were close to typical size of MH containers for on-board hydrogen storage and supply system for hydrogen-fuelled utility vehicle (forklift).

2. Summary of modelling details

Fig. 1 shows the model of four MH beds discussed in this paper. The considered options of heat exchange between the MH powder and the HTF included (I, II) internal cooling using straight (I) and helically coiled (II) tube, as well as (III, IV) external cooling of the MH without (III) and with (IV) transversal fins (copper, 0.5 mm thick, 5 mm pitch).

The main characteristics of the MH beds considered in the present work are presented in Table 1. For the correct comparison, the MH bed was assumed to have the same dimensions (60 mm in diameter and 500 mm in length) in all four cases, and the MH loading density¹ (4031 kg/m³, or about 48% of the alloy density, see Table 2) was also assumed to be the same. As it can be seen from Table 1, the main difference between the internal (I, II) and the external (III, IV) cooling is the area of the heat exchange between the MH and the HTF (I < II < III = IV). The smaller differences are in the MH material volumes resulting in the decrease of hydrogen storage capacity from ~8% (I and IV) to ~24% (II) as compared to case III where whole volume of the MH bed is occupied by MH powder.

The simulations were performed using COMSOL Multiphysics, versions 4.2 and 4.4.

The exact mathematical formulation of heat and mass transfer mechanism within the MH bed is difficult due to the influence of numerous factors most of which are related to the properties of the used MH material. The assumptions made for the simplified treatment of the problem are listed below.

1. Hydrogen is treated as an ideal gas as the pressure within the bed is moderate.
2. The solid and the gas are at the same temperature (local thermal equilibrium).
3. Effect of radiative heat transfer is negligible. This assumption is valid for all hydride forming alloys whose operation temperatures are well below 100 ºC.

¹ We assumed the MH loading density to be equal to 60% of the density of the material in the hydrogenated state that is the maximum safe limit of filling the MH containers [5]. The value of 4031 kg/m³ is close to the effective MH density (~4200 kg/m³) assumed in [16].
4. The thermal conductivity and specific heat of the hydride bed are assumed to be constant. This assumption underestimates the bed performance slightly, because in the actual case the effective thermal conductivity varies with hydrogen pressure and concentration.

5. Other thermo-chemical properties, such as enthalpy of formation, entropy of formation and activation energy of the metal hydride, are independent on temperature and pressure.

6. Only heat exchange between MH and HTF is taken into account (no loss/gain of heat to/from the environment).

7. The heat exchange between MH and HTF is accounted by the value of the overall heat transfer coefficient, \( U \), without consideration of the wall thermal resistance. As it was shown in [18], this assumption is valid even for stainless steel \((k = 17 \text{ W m}^{-1} \text{ K}^{-1})\) as a wall material.

The following equations were included in COMSOL while simulating the metal-hydrogen reaction process:

1. **Equilibrium pressure**, \( P_{eq} \), was modelled using the modified van't Hoff equation:

   \[
   P_{eq} = \exp\left(\frac{\Delta H}{RT} + \frac{\Delta S}{R} + (\varphi - \varphi_0) \tan \left(\pi \frac{X}{X_f} - \frac{1}{2}\right)\right),
   \]
   
   where \( \Delta H \) and \( \Delta S \) are reaction enthalpy and entropy, respectively; \( \varphi \) and \( \varphi_0 \) are the slope factors; \( \beta \) is the hysteresis factor; \( X \) and \( X_f \) denote the actual and final hydrogen concentrations, respectively. Eq. (1) first suggested by Nishizaki et al. [19] was used in a number of works on modelling of heat and mass transfer in MH (see e.g., [16,17,19]). It describes well the PCT features of metal-hydrogen systems in not too wide temperature ranges when the changes of hydrogen concentrations corresponding to the transitions from (to) \( \alpha \) - (\( \beta \)) - to (form) (\( \alpha + \beta \))-regions of the pressure-composition isotherm can be neglected.

2. **Mass flow equation** determining the rate of mass of hydrogen absorbed by the metal hydride, \( m \), per unit time and per unit volume was represented as a kinetic equation with Arrhenius-like, \( \exp \left( -\frac{E_a}{k_B T}\right) \), and pressure-dependent, \( \ln \left( \frac{P}{P_{eq}}\right) \), factors [17], where \( E_a \) is activation energy, \( k_B \) is the universal gas constant, \( T \) is temperature, \( P \) and \( P_{eq} \) are the actual and equilibrium H2 pressures, respectively.

3. **Energy equation**. It was noted that even if to account the heat exchange between solid and gas phase in MH systems, the temperatures of the phases during H2 absorption/desorption will be practically equal [15]. Assumimg thermal equilibrium between the hydride bed and hydrogen, a combined energy equation with a source term was introduced instead of separate equations for both solid and gas phases. The equation was supplemented by the expressions for the calculation of the source term, equivalent heat capacity and effective thermal conductivity.

4. **Hydrogen mass balance equation**. The hydrogen mass balance is expressed using the continuity equation where the velocity of hydrogen inside the hydride bed is calculated using Darcy’s law. The gas density is determined by the equation of ideal gas.

5. **Initial and boundary conditions**. The fraction, \( X_1 \), of the reacted MH is assumed to be uniform and equal to 0.1. Also, the temperature in the reactor is assumed to be uniform.

   **Initial conditions:**
   \[
   P_g = P_i; \quad T_m = T_{ini}; \quad T_f = T_{ini}; \quad X = X_{ini} = 0.1X_f;
   \]
   
   where \( P \) is H2 pressure, \( T \) is temperature, \( X \) is hydrogen concentration in the solid; indexes \( g \), \( s \), \( m \) and \( f \) relate to gas, supply, metal, initial and final states, respectively.

   **Boundary conditions:**
   The outer boundary of the MH tank (cases I and II) is assumed to be adiabatic:
   \[
   \frac{\partial T}{\partial r} = 0.
   \]
   
   The heat transfer fluid flows through the heat exchanger inside/outside the reactor bed and convective boundary condition is given by:
   \[
   -k_c \frac{\partial T}{\partial r} = U(T - T_0),
   \]
   
   where \( U \) is the overall heat transfer coefficient, \( T \) and \( T_0 \) are the temperature of the MH and the average temperature of HTF, respectively.
The thermo-physical properties of MnNi₄.₆Al₀.₄ and hydrogen used to compute the present simulation were taken from [16,17] and are listed in Table 2. More details related to the calculation procedure and validation of the model are presented in the Supplementary information.

3. Results and discussion

Fig. 2 displays distributions of hydrogen concentration and temperature for four layouts of the MH bed – straight pipe (I), helical coil (II) and external cooling/no fins, and IV – external cooling/transversal fins.
the MH powder without (III) and with (IV) transversal fins. The calculations have been done for H₂ uptake (absorption process) at $t = 300$ s, $P_g = 3$ MPa and $T_0 = 303$ K. The temperature distributions were found to be quite similar to the concentration ones, when the “hot” regions of the MH bed corresponded to the regions with the lower H concentrations. Since the hydrogenation process is mainly driven by the pressure difference between the actual and equilibrium H₂ pressures, the hydrogenation ceases in the “hot” regions far away from the heat exchange surface. Further cooling of the MH bed, by the heat removal through the HTF, results in the decrease of the H₂ equilibrium pressure, and the H absorption resumes.

It is clearly seen from Fig. 2 that in average the hydrogen concentrations in the beds II and IV are higher than those in the beds I and III. It is associated with the longer pathway, in the latter case, of the heat transfer through the MH powder characterised by a poor effective thermal conductivity. In turn, due to the higher heat exchange area (Table 1), the external cooling (III) is more effective than the internal one (I) resulting in more complete H absorption in the former case at the same moment. Further introduction of copper fins (case IV) results in practically uniform temperature distributions along the fins (see Supplementary information, Fig. S2), and the heat transfer in the MH powder in between the adjacent fins limits the H absorption rate. The shorter characteristic heat transfer distance results in the significant improvement of hydrogen sorption performance.

Fig. 3 shows a comparison of time dependencies of average hydrogen concentrations presented as a ratio of the actual and final/maximum values, $X/X_f$, and temperatures (B) in the MH beds of the studied layouts. The improvement of the H₂ absorption dynamic performances in the order: inner straight tube < external cooling/no fins < inner helical HE ≈ external cooling/transversal fins can be clearly observed.

The effect of the overall heat transfer coefficient, $U$, between HTF and the MH bed on H₂ charge performance of the reactor incorporating the helical coil tubing (case II) is illustrated by Fig. 4. The modelling was carried out at the initial H₂ pressure of 3 MPa and the average HTF temperature of 303 K.

It can be seen that for the considered case the intensity of the heat transfer is important at $U \leq 600$ W m⁻² K⁻¹, and its further increase does not significantly accelerate H₂ absorption. Thus, the optimisation of MH storage tanks should not only be focused on the intensification of the heat exchange between HTF and MH but, rather on the selection of the design characterised by a suitable $U$ value, taking into account required H₂ absorption time, supply pressure, storage capacity and costs. The observed tendency is typical for all heat exchange layouts considered in this work. As it can be seen from Fig. 5, the shortening of time necessary for 56% (A) and 72% (B) saturation of the MH with hydrogen with the increase of the overall heat transfer coefficient is more pronounced at $U < 500$ W m⁻² K⁻¹, and at $U > 800$ W m⁻² K⁻¹ the improvements of hydrogen absorption dynamics become negligible. At $U = 1000$ W m⁻² K⁻¹ the reaction for the helical coil HE (case II)
and external cooling/transversal fins (case IV) approaches equilibrium in ~650 s, while for the case III it takes nearly 900 s, and for the case I more than 2500 s.

Summarizing the simulation results we can conclude that for the cylindrical MH beds of sizes close to the ones considered in the present work, external cooling is more efficient than the internal one in the improvement of dynamic performances of hydrogen uptake due to the higher heat exchange area between HTF and MH in the former case. In addition, the making of MH containers realising this option is less labour-consuming and thus less expensive because of the absence of additional leak-proof penetrations for the installation of the internal heat exchanger. The introducing of heat-conductive fins in the externally cooled/heated MH beds results in further improvement of the dynamic performances, similar to the ones for helically cooled internal heat exchangers, without noticeable reduction of hydrogen storage capacity at the same external dimensions.

4. Conclusions

A 3D numerical model has been developed for the comparison of hydrogen uptake and release performances of cylindrical reactors filled with powdered MH material. A comparison of hydrogen uptake performances for different layouts of the MH bed of the same dimensions has been carried out. The considered options included straight tube (I) and helical (II) inner heat exchangers (HE), as well as the external cooling of the MH without (III) and with (IV) transversal heat distribution fins in the MH bed.

For the considered layouts, the dynamics of hydrogen absorption are improved in the series: inner straight tube HE < external cooling/no fins < inner helical HE < external cooling/transversal fins.

The external cooling was shown to be more efficient than the internal one in the improvement of dynamic performances of hydrogen uptake due to the higher heat exchange area between HTF and MH in the former case. Additional motivation for the selection of the external cooling/heating option includes (i) simplicity and lower costs and (ii) less pronounced reduction of the hydrogen storage capacity at the same dimensions of the MH bed.

The increase of the overall heat transfer coefficient between the heat transfer fluid and the MH bed above 800 W m⁻² K⁻¹ does not improve significantly the dynamic performances of hydrogen absorption in the MH reactors of the studied geometry and size.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jallcom.2014.12.272.

References


