Heat and mass transfer of hydrogen storage in metal-hydrogen reactors

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Abstract

Hydrogen energy is the best alternative to fossil fuels due to its high calorific value and being environmentally friendly. Hydrogen also produces more energy per unit weight than any other fuel. However, storage problem of hydrogen prevents its wide usage and commercialization.

Hydrogen absorption in two LaNi5-H2 reactors is experimentally and theoretically investigated. In the experimental program, two tanks are filled with LaNi5 alloy and hydrogen is charged with a constant pressure. The temperature changes in the tanks are measured at several locations and recorded in a computer. Hydriding process is identified from measured temperature histories. An experimental set up is designed to study main characteristics of hydriding process and effect of bed geometry and heat transfer on the hydriding process.

Hydriding process is characterized by exothermic reaction between LaNi5 and H2 and rapid temperature increase due the heat release. Hydriding time mainly depend on the successful heat removal from the bed. A bed geometry which provides more heat transfer area significantly reduces hydriding time.

In the theoretical program, a two dimensional mathematical model, which considers complex heat and mass transfer and fluid flow is developed and numerically solved. The governing equations are numerically solved and calculated results are compared with experimental data. It is found that mathematical model adequately captures the main physics of the hydriding process and can be employed for a better hydride bed design to reduce hydriding time.

A reasonable agreement between the numerical results and experimental data is obtained.

Keywords: Hydrogen storage, Hydriding time, Heat and mass transfer, Mathematical model

1. Introduction

Hydrogen energy is the best alternative to fossil fuels due to its high calorific value and being environmentally friendly. Hydrogen also produces more energy per unit weight than any other fuel. However, storage problem of hydrogen prevents its wide usage and commercialization.

Low density of hydrogen exposes several storage problems such as high pressure and large volume requirements, weight and safety risks. Some intermetallic compounds, have been found to absorb and release relatively large amounts of hydrogen rapidly at a relatively low pressure; therefore they are under consideration as a practical means of storing hydrogen. Thus, the metal hydride reactors lead the scientist to focus on rare metal alloys that have several advantages including reversibility of absorption/desorption, unit volume of metal hydride holds, low pressure equipment, safety implication and little energy requirements.
As far as chemically storage in a metal alloys in the form of metal hydrides is concerned, there has been great interest on many metals such as Mg, Na, La, Li etc [1-5]. The critical issues for storage materials are amount of hydrogen absorbed/desorbed, thermal stability of the hydride, hydrating/dehydrating kinetics, thermodynamic and thermo-physical properties, crystal structures, surface processes like segregation, carbonization. Therefore, efficient conditions to form metal alloys has been the main target for chemists, metallurgist, and engineers.

Developments in metal hydride technology show that metal-hydrides provide opportunity for hydrogen storage to a high standard of safety both for mobile and for stationary applications. There are continuous efforts to enhance properties of hydriding alloys. Addition of other alloying materials significantly changes the working temperature of the La-Ni system. Using La-Ni-Al system as hydrogen absorbing alloy, Asakuma et al. [4] performed experiments from -80 °C to +140 °C and from $10^{-6}$ to 100 bar. Argon, helium and nitrogen gases were used as the filling gases. Thermal conductivity of the metal hydride bed is analyzed by the homogenization method using multi-scale alloy; specifically changing contact area of hydrogen with metal surface, Asakuma et al. [4] also developed a model for prediction of thermal conductivity in such system. However, the value of conductivity calculated with the model over predicts the measured one at high pressure. They indicate that differences between their experimental data and results at high pressure are caused by the assumption that the hydride bed is expressed by the simple cell model, which has the minimum contact points between particles and the minimum surface area between particles and gas.

It is experimentally found that addition of some organic and inorganic materials enhance the hydriding process. Güvendiren and Öztürk [9] analyzed on the effects of additives on mechanical milling and hydrogenation of magnesium. Some substances like graphite and Al$_2$O$_3$ are the most effective additives for the hydrogen absorption for the magnesium powder which accelerate the absorption capacity to the 6.0wt %.

Chi and his co-workers performed mechanical ball milling with benzene [2]. They indicated that the ball milling in a a-polar organic solvent offers a new way for magnesium based hydrogen storage materials, exploiting their higher capacity and higher equilibrium pressure while operating at lower temperature. Results show that there are obvious differences in the surface morphology for different ball milling conditions [2].

Theoretical studies also shed light on hydriding process and much useful information is obtained. Sun et al. [1], Choi and Mills [5], Ben Nasrallah and co workers [6-8], Mat and co-workers [10-13] developed several mathematical models for detailed analysis of metal-hydride bed operations. Jemni and Nasrallah [6] developed two mathematical models, one based on solid and gaseous phase and other consider solid and gaseous phases as a mixture. Based on Jemni and Nasrallah’s continuum mixture model Mat and co-workers [10-13] carried out a detailed analysis and parameters effecting the hydriding process, and extended analysis to three dimensional cases. A prediction of heat and mass transfer in a closed metal hydrogen reactor is based on mathematical and numeric model besides measured evolutions of pressure in the reservoir which reported by Askri at al. [8]. This study contains development a theoretical model that makes it possible to predict the transient heat and mass transfer in a closed cylindrical reactor. They also discuss some governing operating conditions such as gaseous part volume, height to the radius ratio of the reactor and the initial hydrogen to metal atomic ratio, temperature.

Although there are several theoretical and experimental studies in the literature on the various aspects of the hydrogen storage processes. There are very limited studies validating theoretical models and investigating various bed geometries on hydriding process. Therefore, the objective of this study is to study theoretically and experimentally hydrogen absorption in metal-hydride reactors and analyze various bed geometries and configurations in order to reduce the storage time.
2. Mathematical Model

Metal hydride formation is considered in two-dimensional metal hydride reactors shown in Figure 1a and 1b. Two different reactors were designed for experiments. The first reactor is a cylindrical tank with 40 mm radius and 120 mm height (Figure 1a). The second reactor consists of two co-eccentric cylinders and the space between the cylinders is used as a bed (Figure 1b). The inner radius of the bed is 20 mm while outer radius and height were calculated as 40 mm and 160 mm respectively in order to have some volume with the first reactor.

The differential equations governing the hydriding process are mass balance of hydrogen and metal, momentum and energy equations [10].

**Mass Balance for Hydrogen**

\[
\frac{\partial \rho_S}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \rho_S u_r \right) + \frac{\partial}{\partial z} \left( \rho_S u_z \right) = -m
\]  

(1)

**Mass Balance for Metal**

\[
(1 - \varepsilon) \frac{\partial \rho_S}{\partial t} = \dot{m}
\]

(2)

Figure 1. Schematic sketch of metal-hydride reactors a) Reactor I, b) Reactor II

The differential equations governing the hydriding process are mass balance of hydrogen and metal, momentum and energy equations [10].
**Energy Equation**

For the fluid

\[
\rho CG_{pg} \frac{\partial T_g}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( \rho C_{pg} \frac{\partial T_g}{\partial r} \right) + \frac{\partial}{\partial z} \left( \rho C_{pg} \frac{\partial T_g}{\partial z} \right) - \left( \rho G_{pg} u_r \right) \frac{\partial T_g}{\partial t} - \left( \rho G_{pg} u_z \right) \frac{\partial T_g}{\partial z} - h_g \left( T_g - T_s \right) - \max(-m,0) C_{pg} \left( T_g - T_s \right)
\]

(3)

For the solid

\[
(1 - \varepsilon) \rho_s C_{ps} \frac{\partial T_s}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( (1 - \varepsilon) r \lambda_{se} \frac{\partial T_s}{\partial r} \right) + \frac{\partial}{\partial z} \left( (1 - \varepsilon) \lambda_{se} \right) \frac{\partial T_s}{\partial z} + h_g \left( T_g - T_s \right) + \dot{m} \left( \Delta H^r + C_{ps} T_s - C_{pg} T_g \right)
\]

(4)

where \( \varepsilon \) is the porosity, \( u_r \) and \( u_z \) are the velocity components in the \( r \) and \( z \)-direction respectively and \( \rho, C_p, \lambda \) and \( m \) are effective density, specific heat, effective thermal conductivity and rate of hydrogen absorption respectively.

The heat exchange coefficient between solid and gas is written as [7]:

\[
h_g = \frac{\lambda_s}{d_p} \left( 2 + 1.1 \Pr^{1/3} \Re^{0.6} \right)
\]

(5)

where \( \Pr \) and \( \Re \) are Prandtl number and Reynolds number respectively and \( d_p \) is the particle diameter.

**Auxiliary Equations**

The amount of hydrogen absorbed is directly linked to the reaction rate, which is expressed as;

\[
\dot{m} = -C_a \exp \left( -\frac{E_a}{RT} \right) \ln \left( \frac{P_g}{P_{eq}} \right) \left( \rho_{ss} - \rho_s \right)
\]

(6)

where \( C_a \) is material depended constant, \( \rho_{ss} \) is density of the solid phase at saturation and \( P_{eq} \) is equilibrium pressure calculated using the van’t Hoff relationship:

\[
\ln P_{eq} = A - \frac{B}{T}
\]

(7)

where \( A \) and \( B \) are materials constants deduced from the experimental data.

**Initial and Boundary Conditions**

**Initial Conditions**

Hydrogen charge into metal bed and subsequent hydriding processes studied in the reactors shown in Figure 1a and 1b. Initially hydride bed is assumed to have constant temperature and pressure and quiescent. These conditions can be expressed mathematically as;

at \( t=0 \)

\[
P(r,z,0) = P_0, \quad T(r,z,0) = T_0
\]

(8)
Boundary Conditions

Reactor I

The boundary walls are assumed to be impermeable and no slip conditions are valid at the boundary walls. The reaction heat is removed from the boundary walls with a cooling fluid whose temperature is \( T_f \). Hydrogen is charged at \( z = 0 \) with a constant pressure, \( P_0 \) and constant temperature, \( T_0 \). The boundary conditions can be expressed as:

1. \( \frac{\partial T}{\partial r}(0, z, t) = 0 \),
2. \( \lambda \frac{\partial T}{\partial z}(r, 0, t) = h_{gs}(T_0 - T) \),
3. \( \lambda \frac{\partial T}{\partial r}(r_0, z, t) = h_{i}(T - T_a) \),
4. \( \frac{\partial T}{\partial z}(r, H, t) = h_{2}(T - T_a) \),

where \( h_{gs} \) heat transfer coefficient between gas and solid which is calculated from Eq. 8, \( h_i \) and \( h_2 \) are the transfer coefficient between solid/air side and it is value is calculated from standard Churchill and Chu equation and Lloyd and Moran equation [16] respectively.

3 Numerical Method

The partial differential equations are solved numerically with a fully implicit numerical scheme embodied in PHOENICS code [17]. This code solves following general differential equations,

\[
\frac{\partial (\rho \phi)}{\partial t} + \nabla \left( \rho u \phi \right) = \nabla \left( \Gamma \nabla \phi \right) + S_h
\]

where \( \phi \) is a generic variable that representing the variable solved (i.e.,u,v,T), \( \Gamma \) is the exchange coefficient. \( S_h \) represents the source terms. An important advantage of PHOENICS code is that it allows the user to incorporate additional source term that not available in the main program.

A 25x60 grid system is employed after a grid refinement test. A typical run until 5000 sec. takes about 6 hours in a Pentium III. P.C.

4. Experimental Method

Experimental set up for hydrogen absorption is schematically presented in Figure 2. Set up mainly consist of a reactor, a vacuum pump to evacuate the reactor before the experiment, a ball mill to produce fine particles, manometers, thermocouples, a data acquisition system, a tank containing %99.999 pure hydrogen gas and an argon tank to provide working under inert atmosphere environment. The main objective of the study is to see effect of heat transfer rate on hydriding time for the two reactors considered.

The following procedure is followed during the experiments:
• LaNi$_5$ material is grounded for 3 hours. Grinding procedure is conducted by a ball mill which is located in a glow box of 60 mm diameter and 80 mm height. Argon gas is used during the process to prevent possible oxidation. Grinding speed was varied between 500 rpm and 890 rpm. During the grinding process, some graphite at a ratio of 1% of LaNi$_5$ is added as an anti-sticking agent. LaNi$_5$ material is used in the experiments.

• Grounded material is transferred into the reactor in a glove box. This processes carried out at argon atmosphere unless otherwise noted.

• The reactor is heated to almost 200°C for 2 hours under low pressure ($\approx 10^{-4}$ mmHg). After the heating process the reactor is cooled down to room temperature and then hydrogen is charged to the reactor under 10 bar pressure. This heating and cooling process is repeated 5 times for activation of LaNi$_5$ alloy.

• The experimental part was started after activation process had completed. Reactors were then charged with hydrogen at a range of pressure (6-10 bars). Hydriding process is monitored with temperature measurements obtained at several locations on the reactor. The temperature readings are recorded on a computer for further processing and interpretation of hydriding behavior.

5. Results and Discussions

The measured temperature evolution in z-direction under several charging pressures within the reactor I and II are given in Figure 3 and Figure 4, respectively. Experiments are performed under three charge pressures (6 and 10 bars). Temperature changes on the bed are measured at 15, 30, 45, 60, 75 mm from the top of the bed. General characteristic of hydriding process is a sudden increase of bed temperature after charging is initiated. This increase is the result of exothermic hydriding reaction. It is observed that there is a perceivable temperature gradient in the bed within first 500 seconds in both reactors. This difference vanishes with time in both reactors especially under higher charging pressure (see Figure 3 and Figure 4). However, a significant temperature gradient observed in Reactor I (Figure 3). This result may be attributed to the enhanced heat transfer in Reactor II. Since hydriding reaction rate is strongly dependent on temperature.
To study, hydriding process in detail, calculated two dimensional temperature profile and evolution of hydride formation at 100 and 500 seconds, for Reactor I are given in Figure 5 and Figure 6, respectively. It is seen that at around 100 sec a sudden increase of bed temperature all over of the bed is evident due to the exothermic hydriding reaction. Temperature near the cooled wall slightly decreases at 500 sec. It is seen that H/M (amount of hydride formed/amount of metal) ratio is higher at lower temperatures. Generally more hydride is formed near walls in z-direction because of cooling effect. There is a gradual decrease in H/M ratio in the middle part of the reactor. This is also true along the radius. Figure 7 and Figure 8 represent the temperature profile and evolution of hydride formation at same experimental conditions for Reactor II. A similar temperature and H/M distribution is obtained with Reactor II.

Figure 3. Measured temperature evolution in the Reactor I.
   a)6 bar, b)10 bar

Figure 4. Measured temperature evolution in the Reactor II.
   a)6 bar, b)10 bar
Figure 5. Temperature profile in the Reactor I at selected times. a) t=100 s, b) t=500 s.

Figure 6. Evolution of hydride formation in the Reactor I. a) t=100 s, b) t=500 s.

Figure 7. Temperature profile in the Reactor II at selected times. a) t=100 s, b) t=500 s.
Figure 8. Evolution of hydride formation in the Reactor II. a) t=100 s, b) t=500 s.

Experimental data and model predictions are compared in Figures 9 and 10. These figures also reflect the effect of inlet pressure on the hydriding process. The selected inlet hydrogen gas pressures are 6, 8 and 10 bar. There is a slight difference in experimental and theoretical values, which is somehow smaller in Reactor II as compared with Reactor I. It can be seen that evolved temperature values for Reactor II are greater than that of Reactor I. It can be concluded that temperature evolution is very sensitive to hydrogen gas inlet pressure. There is an increase in temperature evolution as increase in inlet hydrogen pressure. This effect is more pronounced between 6 bar and 8 bar in Reactor I. In Reactor II an higher pressure (10 bar) is needed to see this effect.

Figure 9. Influence of the hydrogen gas inlet pressure on the temperature evolution in the Reactor I.
6. Conclusion

Hydrogen absorption in metal hydride reactors experimentally and theoretically investigated. An experimental set up is designed to study main characteristics of hydriding process and effect of bed geometry and heat transfer on the hydriding process.

Hydriding process is characterized by exothermic reaction between LaNi$_5$ and H$_2$ and rapid temperature increase due the heat release. Hydriding time mainly depend on the successful heat removal from the bed. A bed geometry which provides more heat transfer area significantly reduces hydriding time.

A mathematical model is developed to study hydriding process in detail and system optimization. Mathematical model considers coupled heat and mass transfer and fluid flow in the hydride bed. The governing equations are numerically solved and calculated results are compared with experimental data. It is found that mathematical model adequately captures the main physics of the hydriding process and can be employed for a better hydride bed design to reduce hydriding time.

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