Searching out the hydrogen absorption/desorption limiting reaction factors: Strategies allowing to increase kinetics

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Hydrogen gas has become one of the most promising energy carriers. Main breakthrough concerns hydrogen solid storage, specially based on intermetallic material use. Regarding the raw material abundance and cost, the AB type alloy FeTi is an auspicious candidate to store hydrogen. Its absorption/desorption kinetics is a basic hindrance to common use, compared with more usual hydrides.

First, discussions based on literature help us identifying the successive steps leading to metal hydriding, and allow to introduce the physical parameters which drive or limit the reaction. This analysis leads us to suggest strategies in order to increase absorption/desorption kinetics.

Attention is then paid to a thermofluidodynamic model, allowing to describe a macroscopic solid storage reactor. Thus, we can achieve a simulation which describes the overall reaction inside the hydrogen reactor and, by varying the sub-mentioned parameters (thermal conductivity, the powder granularity, environment heat exchange...), we attempt to hierarchy the reaction limiting factors. These simulations are correlated to absorption/desorption experiments for which pressure, temperature and hydrogen flow are recorded.

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1. Introduction

Solid storage coupled with intermetallic is one of the most promising technologies that can provide an efficient and secure holding of the hydrogen gas comparing with the traditional ways such as gas and liquid storage. The solid storage method can be accomplished with a variety of structural type of intermetallic like (AB, AB_2, AB_5, AB_3 and A_2B_7). By inspecting deeply the different structural types, the FeTi AB intermetallic [1] has received a special attention because of the plenty in raw material and the reversible characteristic of the hydride reaction, in other word: absorption and desorption processes. However, in order to ensure that the hydride reaction meets engineering requirements, this alloy still need to be characterized to overcome all challenges such as a harsh activation behavior or a slow reaction kinetics. A pure FeTi needs an applied pressure in the range of 30 bar and a temperature in the range of 670 K [2] to be activated, and it was reported that kinetics are very slow (an absorption stage of a fully activated sample can take over than 10 h to reach the maximum of storage capacity ~1.8 wt.%). Focusing on the hydride reaction of FeTi alloy, this reaction is described according to the following chemical

equation: nFeTi + H_2 ↔ nFeTiH$_{2/n}$ ∓ ΔH, where ΔH is the heat generated or needed during absorption and desorption respectively, because as well known, while the absorption stage the chemical reaction is exothermic, contrariwise the reaction is endothermic for the desorption stage.

All physics phenomena should be described mathematically by using concrete equations which allow to find the system response based on initial conditions, i.e. input variables and material properties for the hydrogen absorption/desorption process. A thermofluidodynamic model is developed based on several physics principles: it describes the reaction from a macro-scale point of view. One of the most relevant issues on the reaction rate is the thermal management and specially the overall heat transfer coefficient. It has been reported that the thermal conductivity of the powders decrease in correlation with the number of repeating cycle to reach a very low value in the range of 0.1 W/m K. The thermal conductivity can be mended by several ways such as powders compacting or/and the intercalation of some materials that have an important thermal conductivity. Those metals can be copper wire, porous graphite, aluminum foam, etc. Kim et al. [3] used the porous graphite with powders compacting to enhance thermal conductivity and have reported that λ is increased to reach 3 W/m K. Also several works have been reported on material doping, as an example Mandal and Srivastava [4] have worked on the FeTi

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(Mn) which have 46% Fe, 50% Ti, and 4% Mn, the alloy is mixed with Mg according to the following composition 40% (FeTi Mn) and 60% Mg. They have shown that 80% of the total amount of hydrogen is desorbed within 10 min. In the other hand, fabrication methods can be listed as one of the pre-treatment ways to increase kinetics. Aoyagi et al. [5] have monitored the behavior of a FeTi sample, and as a result from the performed mechanical treatment, it was seen a formation of new activated surfaces and an improvement in the absorption/desorption reaction rate. Another example of fabrication method is the SICS (self-ignition combustion synthesis). It was proposed by Yasuda et al. [6] for the following interests: purifying the product, hydriding an alloy directly and reduction of the hydrogenation time. It was seen also from literature that powder morphology or grain size is one of the major parameters that can be monitored in order to increase kinetics.

2. Hydriding modeling and experimental comparison

The present section is devoted to the thermofluidodynamic model description. The model aims to describe the (de)hydriding reactions occurring inside a reactor containing a defined amount of hydride powders, fully activated and ready to start an absorption/desorption cycle. The hydride tank has a cylindrical shape which is coupled with a heat exchange (water flow on the outside surface). Based on the principles of energy balance, mass balance and ideal gas law equation, equations for both the absorption and desorption stage are proposed by Talaganis et al. [7]. These equations are listed in Table 1. The simulation is carried out assuming a set of assumptions: constant applied pressure during absorption and desorption, constant cooling or heating fluid temperature, uniform distribution of temperature inside the tank. The finite difference method is employed, i.e. all equations are discretized in time only, alloying to determine according to time: tank temperature, reaction rate, and hydride mass formed during reaction.

In Table 2, all input parameters are listed with their values [8–10].

In this study, attention is paid on the behavior of the FeTi-X (X is a light element of the periodic table) when 100 g of this intermetallic powder is filled into the cylindrical tank and subjected to 10 bar of constant hydrogen pressure. The external heat exchange is natural convection. Fig. 1 shows hydride reaction rate and temperature response during absorption.

Same profile is observed for both temperature and absorption rate evolution. Simulations predict an extremely fast response of the system. Maximum temperature and absorption are reached before 100 s, then both quantities decrease rapidly and reaction ends after 10 min. The pick of absorption rate occurs a bit earlier, after less than 1 min.

Having a simulating tool to predict numerically the FeTi-X alloy response during hydriding, turns out to be really advantageous, in order to understand the various steps of the reaction. However, in order to make it efficient, it is required to have a comparison with experimental results. To do so, a 100 g of FeTi-X is filled into a cylindrical hydrogen reactor coupled with a thermocouple of K-type, and putted under the following thermal conditions: cooling and heating is done under room temperature (natural convection with a coefficient of convection of 10 W/m K). Fig. 2 presents schematically all the components of the bench test that has been used to perform this investigation.

The cylindrical tank has the following dimensions: radius of 2.5 cm and 8 cm in length; and it is coupled with a valve to ensure hydrogen flow, and of course a pressure sensor. The thermocouple is connected to a computer via NI Daq (National instrument), and the real time temperature acquisition is ensured by a LabVIEW application.

The FeTi-X sample is first subjected to a pressure of 20 bar (constant according to time). It is observed a small increase in temperature after 3000 min. Then the powder is subjected to vacuum, and again a pressure of 60 bar is applied in order to force the activation mechanism. In this stage, a higher amplitude temperature pick is observed but still requires 1350 min to occur. The powder is subjected once again to vacuum, and finally a pressure of 10 bar is applied twice, allowing to guaranty the complete activation of the sample and to ensure repeatability.

Table 2
Input variables and their values.

Variables	Definition	FeTi-X
Cp_{H_2}	Heat capacity of H_2	14.3 J/g K
m_s	Solid mass	100 g
m_{H_2}	Hydrogen mass g	
Cp_s	Heat capacity of solid	0.468 J/g K
U	Over all heat transfer coefficient	240 W/m K
T_{in}	H_2 inlet temperature	296 K
T_{wa}	Cooling water temperature	296 K
ΔH_a	Formation enthalpy of absorption	−27.5 kJ/mol
C_a	Pre-exponential factor	16.4 1/s
E_a	Activation energy of absorption	23.8 kJ/mol
P_a	Applied absorption pressure	10 bar
P_0	Atmospheric pressure	101,325 Pa
ΔS_a	Formation entropy of absorption	−104 J/mol K
T_{at}	Atmospheric temperature	298 K
T_{wd}	Heating water temperature	296 K
ΔH_d	Formation enthalpy of desorption	27.6 kJ/mol
sc	Stoichiometric coefficient	1
C_d	Pre-exponential factor	2.6 1/s
E_d	Activation energy of desorption	19.87 kJ/mol
ΔS_d	Formation entropy of desorption	103.04 kJ/mol
MW_{MH}	Molar mass of formed hydride	103.7 g/mol
P_d	Applied desorption pressure	0.068 bar
f_{in}	Inlet hydrogen flux during absorption	
f_{out}	Outlet hydrogen flux during desorption	
A	Heat exchange area (outer surface of the cylindrical tank)	
r_a, r_d	Reaction rates during : absorption/desorption	

Table 1
Absorption/desorption equations.

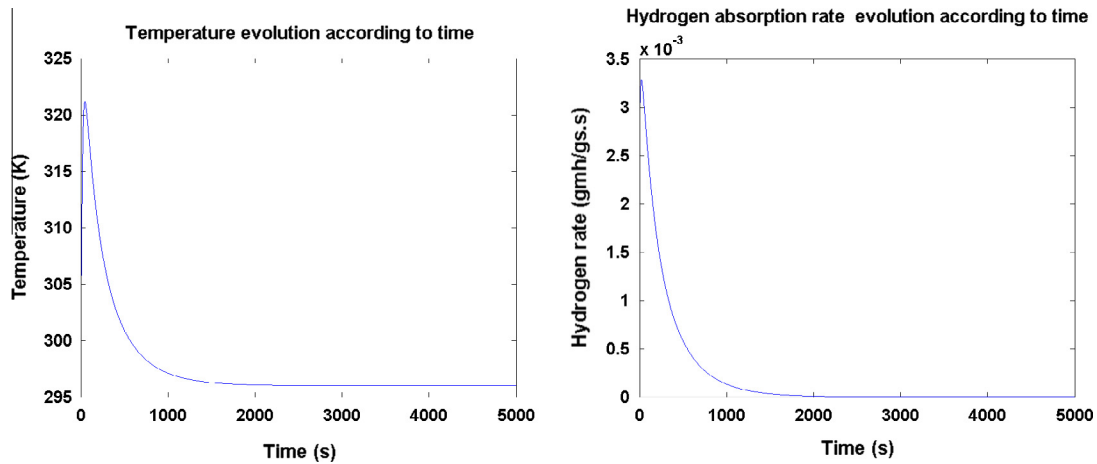|	Absorption		Desorption	
Energy balance	$(m_{H_2}Cp_{H_2} + m_sCp_s)\frac{dT}{dt} = f_{in}Cp_{H_2}(T_{in} - T) + AU(T_{wa} - T) - \Delta H_a r m_s \frac{sc}{MW_{MH}}$	(1)	$(m_{H_2}Cp_{H_2} + m_sCp_s)\frac{dT}{dt} = f_{out}Cp_{H_2}(T - T_{at}) + AU(T_{wd} - T) + \Delta H_d r m_s \frac{sc}{MW_{MH}}$	(6)
Rate reaction	$r_a = C_a e^{\frac{-E_a}{RT}} \ln\left(\frac{P_a}{P_{eq}}\right)\left(1 - \frac{m_{MH}}{m_s}\right)$	(2)	$r_d = C_d e^{\frac{-E_d}{RT}}\left(\frac{P_d - P_{eq}}{P_{eq}}\right)\left(\frac{m_{MH}}{m_s}\right)$	(7)
Ideal gas law	$P_a = \frac{m_{H_2}RT}{MW_{H_2}\cdot V}$	(3)	$P_d = \frac{m_{H_2}RT}{MW_{H_2}\cdot V}$	(8)
Equilibrium pressure	$p_{eq_a} = e^{\left(\frac{\Delta H_a}{RT} - \frac{\Delta S_a}{R}\right)}P_0$	(4)	$p_{eq_d} = e^{\left(-\frac{\Delta H_d}{RT} + \frac{\Delta S_d}{R}\right)}P_0$	(9)
Hydride mass	$\frac{dm_{MH_a}}{dt} = r_a m_s$	(5)	$\frac{dm_{MH_d}}{dt} = r_d m_s$	(10)

Fig. 1. Simulation results (reaction rate and temperature evolution according to time of FeTi-X).
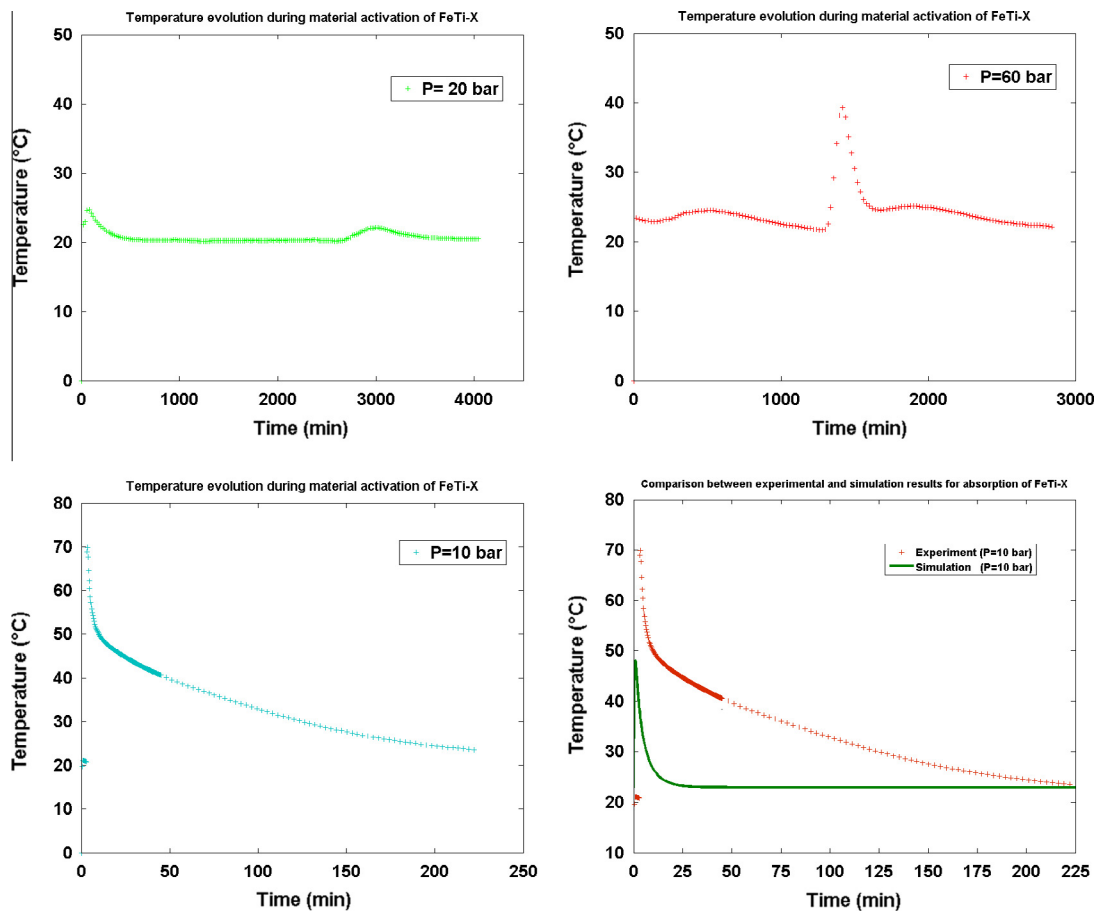

Fig. 2. Temperature evolution according to time during the activation mechanism of FeTi-X, and comparison between simulation and experiment for the first cycle.

Fig. 2 shows the experimental curves of the activation process, and a comparison between experimental and simulation results.

The two temperature curves beneath in Fig. 2 show a comparison between experimental result and simulation results. Simulation result confirms the overall tendency, i.e. a fast increase of temperature with comparable maximum value, followed with a slow cooling till ambient temperature. Retrieving the accurate properties of FeTi-X in order to improve the good correlation between the model and the experimental results will require to describe more precisely physical phenomena and to lighten hypothesis.

3. Sensibility analysis of the thermofluidodynamic model

Regarding mathematical models, they are most of the time of complex form and involve a huge numbers of input parameters. It is so important to classify input parameters by order of their impact on the output data. The prioritization allows to define on what input parameters attention is to be paid. This classification is here obtained using a sensibility study based on screen design methods. Doing so, all input factors are ranked in order of influence, but from a qualitative point of view. In this paper, Morris
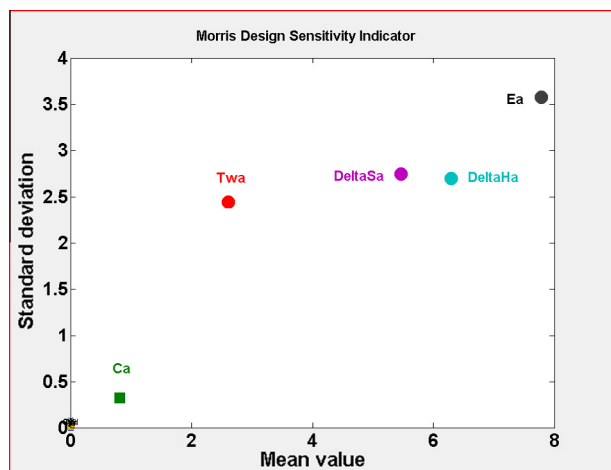
Fig. 3. Morris design sensitivity indicator.

design method is used to manage the sensibility analysis on the theoretical model. This method imposes variation of one input factor at a time. Sensitivity is related to two factor indicators, proposed by Morris method [11]: μ that evaluates the overall effect of the input on the output and σ that gives the coupling effect between input factors. In order to perform a global sensitivity approach, elementary effect of each input must be identified as follow:

$$E_i = \left| \frac{f(x + \xi e_i) - f(x)}{\xi} \right| \qquad (11)$$

$$\mu = \text{mean}\,(E_i) \qquad (12)$$

$$\sigma = \text{Std}\,(E_i) \qquad (13)$$

where ξe_i is a small perturbation induced to an input in the direction of the unit e_i vector.

Calculation of the sensibility analysis is done using dedicated in-house Matlab® software, called SIMBAD. Here after, all input and output parameters used in this study are listed:

1. Input parameters: T_{in}, A, T_{wa}, ΔH_a, ΔS_a, m_s, E_a, P_a, C_a, U, Cp_{H_2}, V.
2. Output parameter: $r_a(t)$ (represented by the root mean square value).

In Fig. 3, all input variables are ranked according their elementary effect mean value and standard deviation. This analysis leads to the conclusion that activation energy E_a has the most important nonlinear effect, i.e. it is coupled with other input parameters. Then, ΔH_a, ΔS_a come after and their effect is also nonlinear. As a general explanation, variables that have the greatest mean value are the most sensible parameters and depending on the standard deviation value, effect can be linear or nonlinear: the more $\text{Std}(E_i)$ is great, the more non linearity effect increases. From Fig. 3, we can rank input parameters by order of importance as follow: $E_a > \Delta S_a > \Delta H_a > T_{wa} > C_a$ and other inputs have negligible effects. Consequently, improving the accuracy of predicted hydride tank responses requires determining with care values of these parameters but also their evolution and dependence according to temperature and time during the hydrogenation process.

4. Conclusion

The present paper aims to contribute at developing strategies in order to increase absorption/desorption of FeTi based alloys. We present a macro scale thermofluidodynamic model, that simulates the response of a FeTi-X hydride tank, and in parallel we introduce a bench test which is employed to establish a comparison between experimental and numerical results. It has been clearly seen that material properties have to be more precisely identified in so far to ensure more accurate fitting between experiments and simulation results. Finally, a sensibility analysis is performed to evidence the most influent input variables, i.e. variables that change widely output results, such as reaction rate. In order to get a robust model and excellent fitting between simulation and experiment, a model calibration must be performed and lighter hypothesis introduced.

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