Towards the increase of the desorption kinetics in ferrotitanium alloy

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ABSTRACT:

Hydrogen gas aims to become one of the main alternative energy carriers. Ones of the major utilities of the hydrogen gas is the fuel cell, internal combustion engine, chemical industry... Quite apart from these advantages, a big challenge appears concerning the ways of storing hydrogen with the maximum safety warranty.
Storing hydrogen may be solved using various phases of the element: gaseous, liquid but also solid if coupled with intermetallic materials. The last listed method can ensure a large security factor when compared to gas or liquid storage.
Regarding the abundance of the raw materials, the AB type FeTi alloy are promising candidates for which main drawback is the absorption/desorption kinetics when balanced with more usual hydrides.
Based on literature, we first discuss the different strategies we could think of, in order to increase significantly the rate of hydrogen desorption (alloy doping, powder morphology, heat exchange…).
Emphasis is then put on a macro thermodynamic model, which aims to describe the absorption and desorption mechanisms and will be helpful to identify the restricting mechanism.

KEYWORDS: Hydrogen storage, metals hydrides, absorption/desorption kinetics, alloy doping, heat exchange, powder morphology.

INTRODUCTION:

Walking in the direction of producing and using sustainable energy, hydrogen gas can be classified as the first green energy vector, because of the zero polluting emission; the combustion of the hydrogen gas will produce only the water vapor (H_2O). But in order to ensure a practical use of this source of energy, the whole application must be coupled with an efficient storage method, such as the solid storage method. This method can be accomplished with many types of intermetallic compounds from different structural types (AB, AB_2, AB_5, AB_3, and A_2B_7).
The AB type FeTi alloy has been paid a particular attention due to the profusion in raw materials, and reversible hydrogenation behavior (absorption/desorption). It can be certified that after a decade of research, the hydrogen storage capacity of this intermetallic can reach 1.8% ($g(H_2)/g(FeTi)$), with a stable hydrides species. FeTi is also studied because of the moderate kinetic, and the relatively high equilibrium pressure (5 bar). Another characteristics of this alloy is the high temperature of activation that can reach 670 K under a pressure of 29.2 bar.
In the hydrogen absorption process, the following equation: $nFeTi + H_2 \leftrightarrow nFeTiH_{2/n}$ predicts the resulting product. As well known, the absorption reaction is exothermic, the amount of the generated heat is about 30KJ/mole H_2 for a concentration c: 0.05<c<0.5 (c: atomic ratio = H atoms / metal atoms) as mentioned by M.A.Pick and H.Wenzl [1], contrariwise, during the desorption stage the reaction is endothermic.
In front of above listed characteristics, many strategies can be accosted in order to upgrade the hydrogenation/dehydrogenation behavior of the FeTi (Mn) alloy. In this paper, the work will mainly focus on the hydrogen absorption/desorption kinetics. These strategies can be related to the thermal management of the reaction, material doping that affects kinetics and activation behavior, powder morphology, and different methods of production. In parallel a macro thermodynamic model is developed. It presents a physics based set of equations that which link some macro parameters and variables such as: inside temperature reactor, reaction rate, mass of transformed metal, and so many others.

MATERIAL DOPING:

Doping a material is by definition the addition of certain catalysts to hydride powders by different manners such as the mechano-synthesis (accompanied with heat treatment/or not). Based on literature a variety of dopant materials can be used like: Carbon nano-tube, activated carbon, Ti, Pd, Mn, Mg, Zr, Hf, Ni…

Some works and processes related to material doping are dedicated to the improvement of the desorption characteristics of the FeTi alloy. As an illustration the method of synthesis by substitutions through a set of transition metals such as: Zr, Sn, Mm, Ni... is achievable. B.K.Singh et al.[2] found that by substituting Fe by Ni, the as made alloy having the following composition $(Fe_{1-x}Ti_{1+y}Ni_x$, with x=0.2 and y=0.3), showed that about 80% of hydrogen amount is desorped within 3 min, and the total quantity of hydrogen is desorbed within 7 min under the same temperature of desorption that's applied to FeTi.

Proceeding this way, FeTi (Mn) doped with Mg, is also investigated by P.Mandal and O.N.Srivastava [3]. The method of synthesis is unclouded as the following: preparing the FeTi(Mn) through a solid state diffusion, heating up to the melting point the stoichiometric composition of each element (46% Fe, 50% Ti, 4% Mn) and pressing to form a wad (1 x 0.5 cm). The initially prepared alloy is then melted about 5 to 6 times to ensure its homogeneity. After that and by using the encapsulation method, a stoichiometric amount of the (x%- FeTi (Mn)) was taken to surrounds the (100-x) % Mg pellets in order to mainly avoid their sublimation. The resulting alloy (Mg-x% FeTi (Mn)) has showed an enhanced behavior, where 80% of the total amount of hydrogen is absorbed within 10 min, and the total time required to reach the saturation is about 40 min. Another effect of adding Mg to FeTi (Mn) is detected, it increases the hydrogen storage capacity, this capacity reach the maximum of its value (3~3.6%) when x is equal to 40%. However, when inspecting the dehydrogenation behavior, it was found that the rate of dehydrogenation is nearly the same of FeTi.

For the following composition of the ferrotitanium alloy $(FeTi_{1.3})$, Jianxin Ma et al. [4] adopt another dopant material, and a series of experimental procedures were carried out in order to identify the hydrogenation properties of the new alloy, the dopant material is a Mischmetal (Mm) which have the following composition in weight: 51.75 % Ce, 24.26 % La, 18.11% Nd, 6.08% Pr, and 2.26% Fe.

It was observed that the Mm content is an important factor that affects the hydrogen storage characteristics. It appears from experimental results that the Mm-doped $FeTi_{1.3}$ alloy absorbs hydrogen at room temperature, preceded by a heating up to 100°C in vacuum. The hydrogen storage capacity is also increased to reach 177.8 ml/g at 333 K for the 6% Mm-doped $FeTi_{1.3}$. (Several desorption process were conducted under the following temperature 298, 318, 333 K). From a kinetic approach, the addition of Mm to the $FeTi_{1.3}$ in several proportions has increased the absorption kinetics to reach the value of saturation within 30 minutes as maximum, up to the tenth cycle.

MANUFACTURING METHODS:

Latterly, so as to improve the activation energy of the FeTi alloy, the use of hydriding combustion synthesis (HCS) was suggested by Dolukhanyan et al. [5]. This method has many appeals such as the reduction of the hydrogenation time, purifying the product and directly hydriding an alloy.

Based on this method NaotoYasuda et al. [6] proposed the self-ignition combustion synthesis (SICS). This method as explained below has an important effect on the activation behavior of any alloy and especially for the FeTi because of its harsh activation procedure that requires a cyclic heating up to 670 K in vacuum atmosphere, and then cooling down to room temperature under a hydrogen pressure of 4 Mpa.

The self-ignition combustion synthesis (SICS) of the hydrogen storage alloy $TiFe_{1-x}Mn_x$ (x = 0, 0.1, 0.2, 0.3 and 0.5) is described as follow : the homogeneous mixed powders of Ti and Fe and Mn in the molar ratio 1:1-x: x, is uniformly heated up to 1473K, and then is cooled naturally in pressurized hydrogen atmosphere of 0.9 Mpa. All SCISed products absorb hydrogen smoothly at 298 K and an initial pressure of 4.1 Mpa.

As a result from adopting this method of manufacturing: it can be seen that the product softly absorbs hydrogen under a pressure of 4.1 Mpa, and the activation was remarkably facilitated because the increase of the hydrogen permeability into FeTi. This method has no effect on hydrogen absorption/desorption kinetics.

HEAT EXHANGE:

The thermal exchange of the hydriding chemical reaction is to be considered as the limiting step factor. The absorption reaction is an exothermic reaction, it generates heat when the metal is charged with hydrogen. Contrariwise, the desorption reaction shows an endothermic behavior.

The management of the thermal behavior is quite important for ensuring the control of both reactions. During the absorption reaction, heat is generated leading to an increase of the reactor temperature. As a direct consequence the equilibrium pressure is increased and tends stopping the reaction because its driving force is proportional to the differential of pressure. The same analysis may be conducted for the desorption reaction. The endothermic behavior leads to a simultaneous decrease of the inside temperature and of the equilibrium pressure. As previously, in case the thermal management is not optimized, the reaction kinetics can drastically be slow down.

The problem of heat is practically solved for hydrogen reactor by incorporating a cooling/heating system, the system is integrated inside the hydrogen reactor or located outside, and can take several shapes such as straight or helicoidally tubes, but also plate heat exchangers.

The thermal efficiency is strongly affected by the thermal conductivity of the metal hydride. Analyzing the thermal behavior of the metal hydride leads to the understanding that the effective thermal conductivity decreases with the hydrogen cycling, it can reach 0.1 W/m K, whereas the bulk material shows a thermal conductivity of 10 W/m K.

To improve the effective thermal conductivity of the powdered metal hydride, various techniques are proposed such as the insertion of copper wire, aluminum foam…

K wang J. *et al.* [7] suggest to compact powdered metal hydride with porous expanded graphite so as to improve effective thermal conductivity. Porous graphite is used for two essentials reasons: increasing thermal conductivity and ensuring an efficient hydrogen mass transfer. After being compacted, samples are expected to have an effective thermal conductivity greater than 3 W/mK.

POWDER MORPHOLOGY:

The powder morphology is defined as the grain size of the powder. It affects very largely the kinetic behavior of the alloy. During absorption/desorption cycling, the powder granularity decreases and finally shows a dispersion centered on an average value which depends on the hydride composition. For a FeTi alloy, this value is around 50 micrometers. This limit seems to be correlated to mechanical considerations. Going further in this dimensions decrease, i.e. increasing surfaces of exchanges requires to employ mechanical milling. The alloy is to be milled in an inert atmosphere and then exposed under hydrogen pressure.

H. Aoyagi *et al.* [8] investigate the behavior of FeTi ball milled alloy. A FeTi sample is crushed out using a mortar without any special precautions, and then the powder is introduced in a SUS 316 container with stainless steel balls (0.95 cm in diameter) with a ball to sample ratio of 13/1. Ball milling of the sample is achieved with high energy planetary ball mill, and at a speed of rotation of 150 rpm. This mechano-treatment leads to the formation of new activated surfaces, which can improve the hydrogen absorption/desorption rate.

THERMODYNAMIC DESCRIPTION OF A HYDROGEN REACTOR:

Developing a thermodynamic model allowing to describe the overall reaction from a macroscopic point of view is a quite complex task. At the same time, this is of peculiar interest so as to understand and investigate the role of all variables and parameters implied in the hydrogenation/dehydrogenation process.

Here is presented a simplify model, based on strong hypotheses. Nevertheless, the obtained result are already rich of knowledge all the more we study a long cylindrical type tank.

The thermodynamic model takes into account a cylindrical reactor which contains a powdered metal hydride, the temperature is assumed to be homogeneous inside the reactor, what really simplifies differentials equations. Figure 1 shows a longitudinal section of the reactor: the hydrogen reactor is thermally controlled by incorporating a heat exchanger to allow cooling and heating during absorption and desorption respectively. The flowing fluid inside the heat exchanger is water, and it is selected due to its high thermal capacity (14.185 KJ/mole). Besides in order to guarantee the heat transfer from hydride powder to water, water temperature is considered to be constant (water is coming from an open source with high thermal inertia).
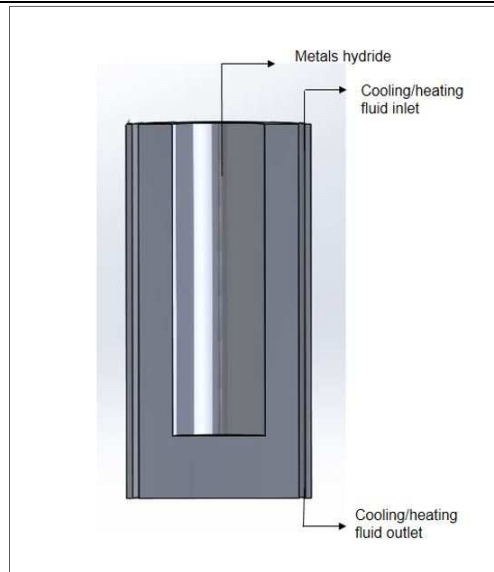
Figure 1- A simplified schematic cross section of a hydrogen reactor system

For the present study, it is decided to have a comparison between FeTi (Mn) and LaNi5 metal hydride type. Table 1 gives the input material data used in the developed model and found in literature [10, 11].

Table 1- Parameters used in simulation

Property	Value and unit (FeTi)	Value and unit (laNi$_5$)
Hydrogen molar mass (*MWH*)	2 g/mol	2 g/mol
Powder molar mass (*MWMH*)	103.7123 g/mol	432 g/mol
Stoichiometric coefficient (*SC*)	1	2.76
Absorption enthalpy (*ΔHa*)	-27.5 kJ/mol	-30.478 kJ/mol
Absorption entropy (*ΔSa*)	-104.32 J/mol.K	-108 J/mol.K
Absorption activation energy (*Ea*)	23..8 kJ/mol	21.170 kJ/mol
Desorption activation energy (*Ed*)	19.87 kJ/mol	16.420 kJ/mol
Desorption enthalpy (*ΔHd*)	27.60 kJ/mol	30.800 KJ/mol
Desorption entropy (*ΔSd*)	103.04 kJ/mol	108 J/mol.K
Absorption kinetic constant (*Ca*)	16.4 1/s	59.2 1/s
Desorption kinetic constant (*Cd*)	2.6 1/s	9.6 1/s
Hydrogen thermal capacity (*Cp_{H2}*)	14.3 J/g.K	14.3 J/g.K
Powder thermal capacity (*Cp_{ms}*)	0.468 J/g.K	0.355 J/g.K
Over all heat transfer coefficient(*U*)	80 W/mK	80 W/mK
Atmospheric temperature T_{at}	298 K	298 K

The mathematical write-up of the reaction requires considering the energy balance, the mass balance and ideal gas law equation. When combining all these equations for absorption and desorption, the resulting equations are differential equations of first order, that can be solved by using the finite difference (explicit method-discretization in time).

The thermodynamic equations may be written as follow, first for absorption, then for desorption:

Absorption:

1-energy balance:
$$\left(m_{H_2}Cp_{H_2} + m_s Cp_s\right)\frac{dT}{dt} = (f_{in}Cp_{H_2}(T_{in} - T) + AU(T_{wa} - T) - \Delta H_a\, rm_s\, \frac{sc}{MWMH}) \tag{1}$$

2- Rate equation:
$$r = Cae^{\frac{-Ea}{RT}}\ln(\frac{Pa}{peq})(1 - \frac{m_{MH}}{m_s}) \tag{2}$$

3- Ideal gas law:
$$Pa = \frac{m_{H2}RT}{MWH.V} \tag{3}$$

4- Equilibrium pressure:
$$p_{eq} = e^{(\frac{\Delta Ha}{RT} - \frac{\Delta Sa}{R})}Po \tag{4}$$

5- Hydride mass variation:
$$\frac{dm_{MH}}{dt} = rm_s \tag{5}$$

Desorption:

1-energy equation:
$$\left(m_{H_2}Cp_{H_2} + m_s Cp_s\right)\frac{dT}{dt} = (f_{out}Cp_{H_2}(T - T_{at}) + AU(T_{wd} - T) + \Delta H_d\, rm_s\, \frac{sc}{MWMH}) \tag{6}$$

2-Rate equation:
$$r = Cde^{\frac{-Ea}{RT}}(\frac{Pd-peq}{peq})(\frac{m_{MH}}{m_s}) \tag{7}$$

3-Ideal gas law:
$$Pd = \frac{m_{H2}RT}{MWH.V} \tag{8}$$

4-Equilibrium pressure:
$$p_{eq} = e^{(-\frac{\Delta Hd}{RT} + \frac{\Delta Sd}{R})}Po \tag{9}$$

5-Hydride mass variation:
$$\frac{dm_{MH}}{dt} = rm_s \tag{10}$$

The following simulation describes the absorption/desorption process for fixed pressures. Experimentally, maintaining these pressures constant during the reaction involves to control the inlet and outlet flow of hydrogen, it means f_{in} and f_{out} parameters in equations 1 and 6, that is to say to monitor these parameters.
The initial inlet hydrogen pressure for the absorption stage is 15 bar, the inlet hydrogen temperature T_{in} is 290K, while the cooling water temperature is 296K.
For the desorption stage, the reactor temperature is equal to the final absorption temperature, and the hydrogen desorption pressure is 0.068 bar.

The hydrogen reactor is subjected to the hydrogen absorption/desorption cycling. The following results describe the cyclic behavior of powder metal hydride for two compounds (FeTi (Mn), LaNi5). This comparison is made in order to show the kinetic differences in time between FeTi and LaNi5 to complete a hydrogen cycle.
Fig 1, 2 show the cyclic behavior of the two compounds, when the initial hydride mass is 0.2 g and the final is 0.835 g. Total mass of metal alloy is 1g.
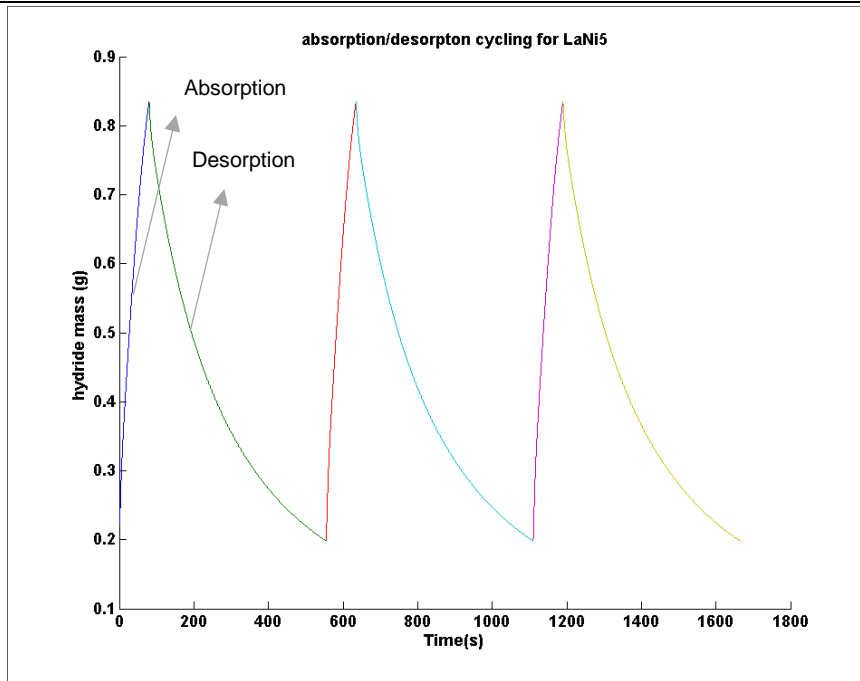
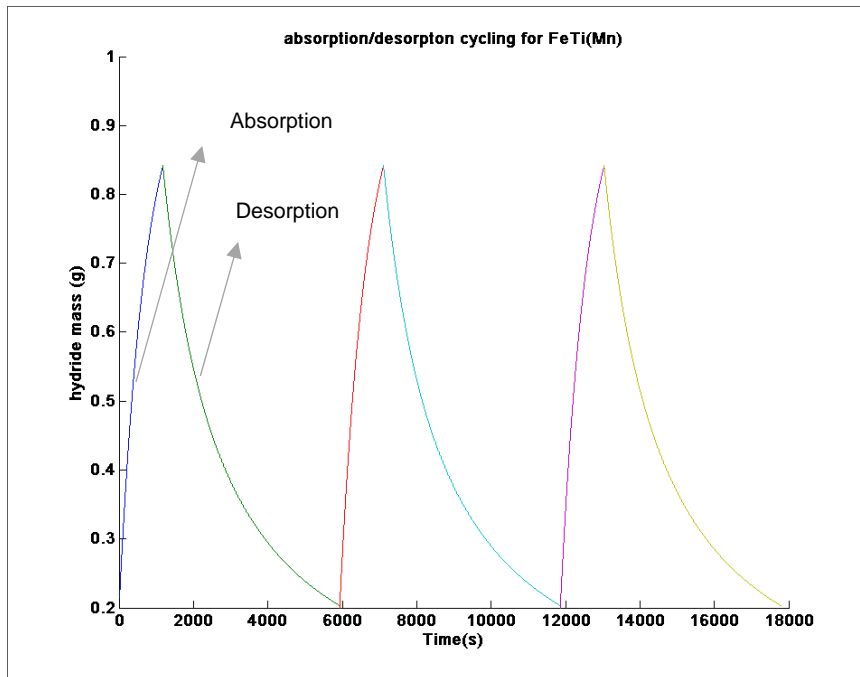**Figure 2: Hydride mass evolution according to time for LaNi5**

Figure 3: Hydride mass evolution according to time for FeTi (Mn)

Remarkably, there is approximately a factor of 10 between time for absorption and desorption for LaNi$_5$ and FeTi (Mn).

For the absorption stage of LaNi5 powder, the time required to go from 0.2 g to 0.835 g of metal hydride is about 80 s, while FeTi (Mn) powder hydride needs 1180 s.
For the desorption stage of LaNi5, the reversible reaction needs 475 s to reach 0.2 g of metal hydride, when this time is 4750 s for FeTi (Mn).

The same tendency is repeated for hydrogen cycling. This similar shape is due to simplified assumptions. These assumptions do not take into account evolution according to time of grain size, volume change, porosity, thermal conductivity…

Fig 4, 5 exhibit a superposition between the hydrogen cycle, and the corresponding temperature behavior for each cycle stage (absorption/desorption).
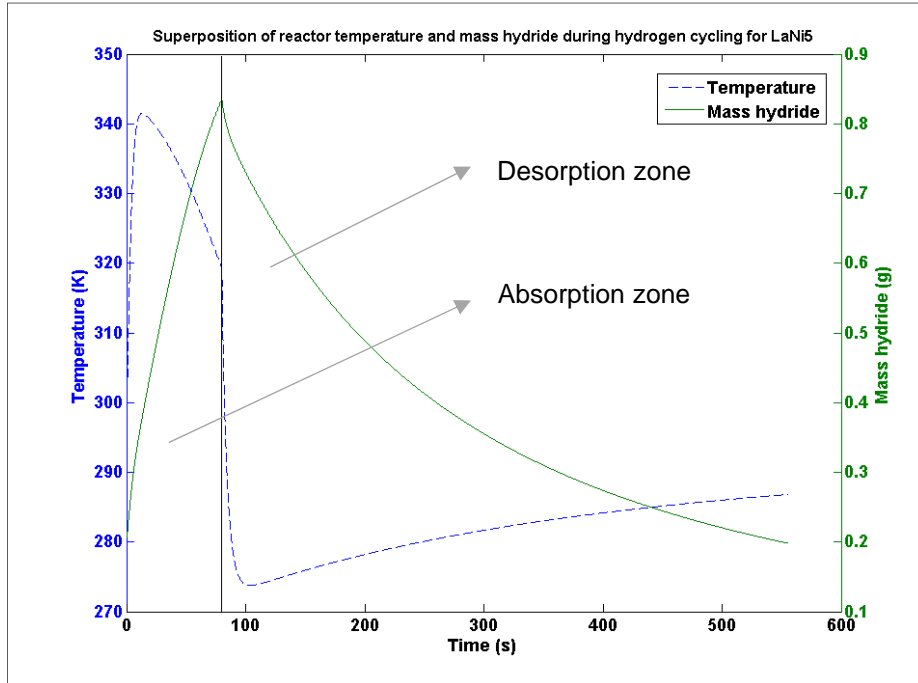

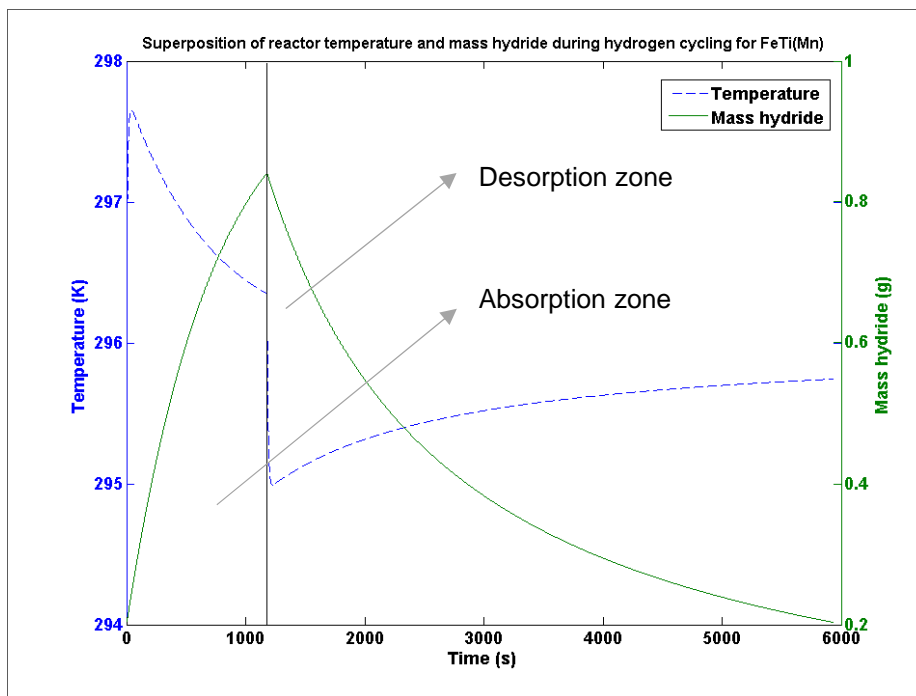**Figure 4: Hydride mass and temperature evolution according to time for LaNi5**

Figure 5: Hydride mass and temperature evolution according to time for FeTi (Mn)

The temperature inside the reactor which contains LaNi$_5$ rises very fast. This sharp increase is due to the high absorption kinetic implying a fast phase change and heat generation. The temperature rise up to 340 K in approximately 35 seconds, and then it decreases as a result of the water cooling system.

After the powder is charged with hydrogen, and when the reactor is subjected to desorption stage, the temperature decreases to reach 273 K, and begins to increase asymptotically to reach the initial water temperature.

The FeTi (Mn) shows the same tendency of temperature, the temperature increases initially to reach 297.6 K within 100 seconds, and then it begins to decrease down to 296.5 K after 1200 seconds, this slow variation in temperature is related to the slow absorption kinetic and then to the low level of heat generation.

Other two variables to be investigated with this modelling are the absorption/desorption rate of both FeTi (Mn), and LaNi5 as illustrated in Fig 6, 7.
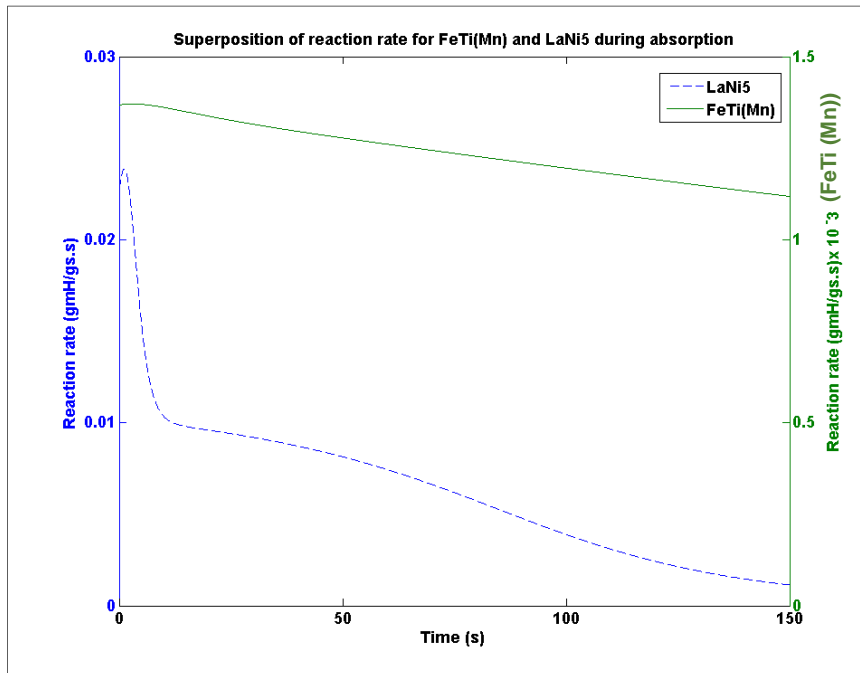

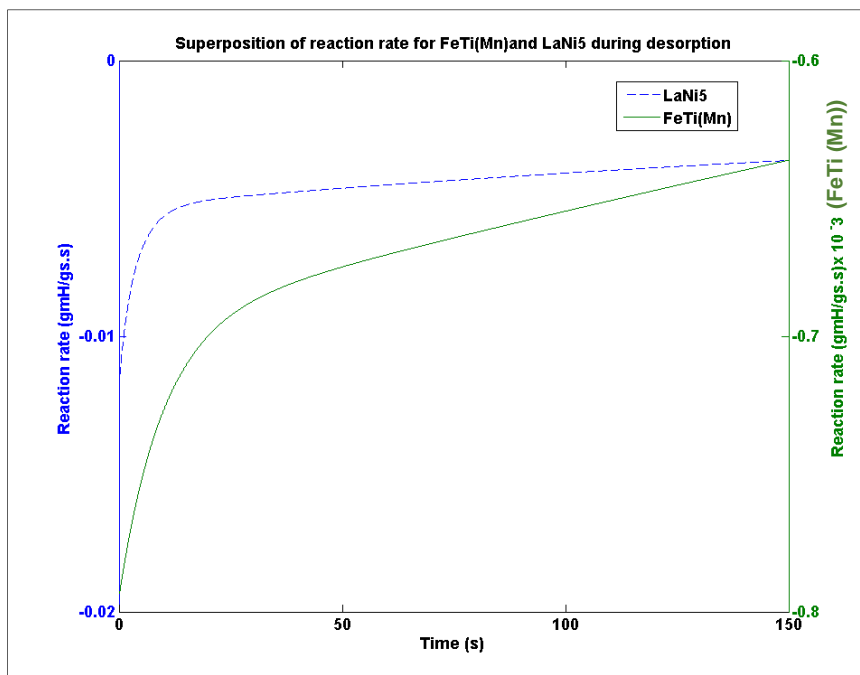**Figure 6: absorption reaction rate evolution according to time for FeTi (Mn) and LaNi5**

Figure 7: absorption reaction rate evolution according to time for FeTi (Mn) and LaNi5

These thermodynamic simulations allow to predict the elsewhere experimentally observed difference between hydrogenation/dehydrogenation behavior of LaNi5 and FeTi (Mn). This difference is mainly due to the large distinction in the pre exponential factor (Ca and Cd), i.e. the parameters driving the reaction kinetic. These two parameters are responsible of this slow kinetic of FeTi, and have to be investigated deeply, to understand what changes are needed to have them evolved such as kinetics of FeTi (Mn) alloys are improved.

CONCLUSION:

This paper makes part of a full study which aims to improve the kinetics of absorption and desorption of FeTi type alloys. These alloys are known to have kinetics up to 10 times less than LaNi$_5$ alloys, what involves they are less commonly employed for metal hydride hydrogen storage. However, the raw materials required to manufacture these FeTi alloys are more readily available.

For the FeTi (Mn) alloys dedicated for hydrogen storage, different strategies for improving absorption/desorption kinetics are listed, such as material doping, powder morphology, fabrication methods, management of heat.

A macroscopic thermodynamic modelling allowing to describe the entire reaction is then introduced. This highlights parameters on which one should play so as to increase the kinetic of those reversible reactions.

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