

NOVEL SAFE METHOD OF MANUFACTURING HYDROGEN METALLIC HYDRIDES

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ABSTRACT

The present work proposes a novel safe method for obtaining metallic hydrides. The method is called SHS (Self-Propagating High temperature synthesis). A novel high pressure gas reactor governed by an electromechanical control device has been designed and built up in order to synthesise metallic hydrides. This system is provided with a control system that allows calculating the amount of gas coming into the reaction vessel at every stage of the process. The main feature of this method is that metallic hydrides can be safely synthesised using low gas reaction pressures. In order to validate the assessing system the main kinetic regularities of SHS in Ti-H₂ system were studied. In addition phase analysis (by means of X ray diffraction) as well as chemical analysis have been performed.

1. INTRODUCTION

1.1 Hydrogen storage options

Hydrogen storage [1-4] is a key enabling technology. None of the current technologies satisfy all of the hydrogen storage attributes sought by manufacturers and end users. Government-industry coordination on research and development is needed to lower costs, improve performance and develop advanced materials. Efforts should focus on improving existing commercial technologies, including compressed hydrogen gas and liquid hydrogen, and exploring new storage technologies involving advanced materials such as metal hydrides.

One of the main drawback for the limited use of hydrogen as fuel, is the safety issue. Hydrogen is flammable when mixed with oxygen in the range from 4% to 75% of hydrogen. This fact generates an important social concern about the use of hydrogen (liquid or gas form). In this sense, it can be said that, hydrogen in the gaseous and liquid states is very combustible and the related law imposes strict regulations on its transportation and utilisation. In addition, although the storage of compressed hydrogen gas in tanks is a mature technology the design has some problems: inefficient use of the space, high weight and volume, low impact resistance and low safety. Liquid hydrogen takes up less storage volume than gas but requires cryogenic containers: the liquefaction of hydrogen is an energy-intensive process and results in large evaporative losses; about one-third of the energy content of the hydrogen is lost in the process.

Metal hydrides offer an alternative way of overcoming this safety problem, presenting the advantages of lower pressure storage, conformable shapes, reasonable volumetric storage efficiency and safe storage (compared to gas and liquid state).

1.2 Metal hydrides

The hydrides of transition metals [5] have arisen considerable interest not only as convenient representatives of phases with variable composition, but also as important materials for engineering protective means against penetrating radiation, convertible hydrogen carriers (hydrogen power engineering), effective catalysts of organic and inorganic synthesis, etc. Relative thermal stability and the ability of hydrogen convertible allocation make a number of hydrides (for example, TiH_2 , ZrH_2 , MgH_2 , $TiFeH_2$, $TiNiH_2$, Mg_2NiH_4 , etc.) good accumulators of hydrogen. In addition, metallic hydrides, although having their drawbacks, are a safer way of storing hydrogen than gas or liquid storage.

Metal hydrides are composed of metal atoms constituting of a host lattice and hydrogen atoms that are trapped in interstitial sites, such as lattice defects. The trap site can be a vacancy or a line defect. In the case of a line defect, a string of hydrogen atoms may accumulate along the defect.

There are several methods for obtaining metallic hydrides:

The most widespread way for obtaining the hydrides of transition metals is the direct absorption of molecular hydrogen by whole mass of solid or liquid metal. Even in 1866 Graham [6] established that palladium can convertible dissolve 900 volumes of hydrogen at heating, and he described this phenomenon as "occlusion". This phenomenon is currently often spoken of as absorption or dissolution.

Considerable attention to the absorption of hydrogen by transition metals has been given by Sieverts [7,8]. The large number of transition metal-hydrogen systems was investigated by Mickeeva and co-workers [9,10].

The hydrides of transition metals can also be obtained due to chemical reactions in solutions such as: reduction of transition metal compounds in the presence of metalorganic compounds, exchange reactions with other hydrides (simple or complex) and with other reducers in the medium of an aqueous or nonaqueous solvent.

Another innovative and cost-effective method for the synthesis of metallic hydrides is Self propagating high temperature synthesis (SHS). The SHS is based on the principle of maximum utilization of chemical energy of reacting substances (exothermicity) for obtaining inorganic compounds, materials, and items of various application purposes and also for organizing highly efficient technological processes. This technique besides obtaining binary hydrides, it also allows obtaining intermetallic hydrides, which can store greater hydrogen quantities. SHS offered good promises when applied to metal hydrogen (M-H) system [11-13]. Preliminary thermodynamic analysis shows that interaction of metals and hydrogen in a number of cases occurs with heat release which should encourage formation and propagation of a synthesis wave. However, hydride formation in this combustion system was doubtful due to the thermodynamic instability of hydride, which leads to its dissociation at comparatively low temperatures. Nevertheless, the combustion reaction in a M-H system is feasible in principle, and the final products are almost stoichiometric hydrides.

Metallic Hydrides obtained by SHS are synthesised at low pressures (starting from 0,3atm). On the other hand, metallic hydrides synthesised by conventional methods are obtained at rather high pressures (in the order of 10atm.), making these processes more risky compared to the proposed technique. This fact makes the SHS very attractive from the safety point of view.

This work aims explaining the new safer way of manufacturing metallic hydrides, by means of SHS technology and the validation of the developed reaction facility.

1.3 Self-propagating High-temperature Synthesis (SHS)

The macroscopic characteristics of SHS [6,7] processes resemble those observed in conventional combustion processes. The reactants, in form of fine powders, are usually dry-mixed and cold-pressed in order to obtain cylindrical pellets. Figure 1 shows the most important steps in the synthesis process.

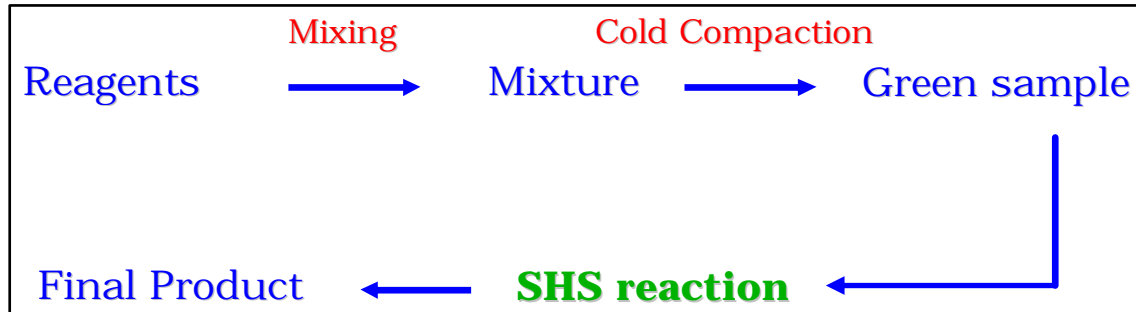


Figure 1: Main steps of a typical SHS process involving only solid reactants

These pellets are then placed in a controlled atmosphere, and ignited by an electrical coil, a laser beam or an electric discharge. A high temperature reaction front is initiated which propagates through the reactants. Figure 2 shows an example of a reaction front propagating through a sample. Note that the process takes place only in four seconds.

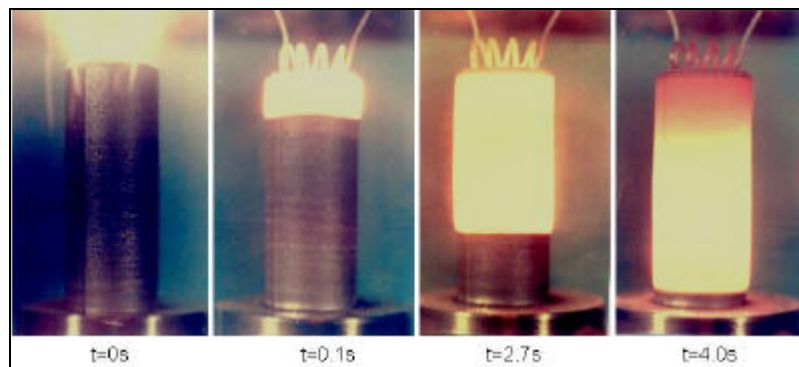


Figure 2: Front propagation in a Ti-C sample.

A variant of this scheme involves one gaseous reactant. This approach allows the synthesis of nitrides, hydrides and oxides.

Main advantages of SHS for the synthesis of metallic hydrides are:

- ❖ Safe way of obtaining metallic hydrides: due to the low reaction pressure required to obtain the hydrides, this methodology is much safer than current conventional manufacturing methods.
- ❖ Low energy consumption.
- ❖ Simple technological equipment.
- ❖ Feasibility of production lines adaptable to production of different materials.
- ❖ Reduced processing time.
- ❖ Environmentally friendly technique.

The combustion of metals in hydrogen proceeds in two stages:

- 1) Propagation of a reaction front through the porous sample.
- 2) Post-reacting, when stoichiometric hydrides are formed due to additional absorption of hydrogen after passing the reaction front.

A distinguishing feature of combustion of metal powders in hydrogen is the fact, that at small gas pressures the amount of gaseous reagent is sufficient to ensure the product formation. Low hydrogen pressures, such as 1 bar, give place to the desired product. This is a great advantage, particularly from the process safety point of view, in comparison to conventional metallic hydride synthesis methods where high hydrogen pressures and long times are required to obtain the product.

2.- EXPERIMENTAL PROCEDURE

2.1.- Facility Description and Fundaments

In order to have an accurate to control the synthesis process and have an accurate estimation of the hydrogen content in the final hydride product, INASMET designed and built up a new facility for the performance of gas phase SHS reactions. The system was designed based on the general SHS reactor requirements and specifically based on gas phase reactions needs. Automatization and parameters control have been key issues in the design and construction.

The system is composed by the following main parts (see figure 3):

- Reaction vessel: reactor (working pressure up to 60atm) of 2.4l, provided with two windows in order to watch and video record the reaction. The reactor top has all the connections for temperature measuring (two thermocouples) and power supply.
- Hydrogen installation: especial hydrogen installation which allows working with this gas in the safest way possible.
- Vacuum pump: able to give a vacuum of 10^{-2} bar. The objective of this pump is to remove the oxygen from the reactor to avoid any contact between hydrogen and oxygen.
- Electrovalve (measuring range: from 1 to 20 atm): this system is provided with an electrovalve controlled by the signal of digital pressure gauge that continuously measures the pressure and enables almost instantaneously to regulate it inside the reactor. Due to the gradual aperture of the valve, the pressure is controlled with high accuracy. The valve has been especially designed to work under hydrogen atmosphere. There is a PLC to control the process.
- Digital Flowmeter (measuring range: from 0 to 15 nl/min): this is a volumetric flowmeter. This device measures the gas volume (in litres under normal conditions: $T=298K$ and $P=1atm$) flow along the hydridation process. It is especially designed to work with hydrogen.
- Control software: control software allows monitoring and storing all the relevant data of the process: temperature (two thermocouples), gas volume flow along the time, reaction pressure during the process, gas consumption during the hydridation process. The process control software allows watching on the screen the hydridation stages, gas volume flow, and temperature at every second; knowing at a real time the absorbed hydrogen content.
- Computer: the control software is installed in the computer. This receives electrical signals from the electro valve, pressure gauge, flowmeter, thermocouples, and power supply device. The computer processes and stores all the date, for further analysis.
- Power supply device (with a changeable voltage from 3 to 12 volts).
- Argon line: there is a system to supply argon to the reactor.
- A safety valve: this valve keeps the system from over-pressure situations opening automatically when the pressures reaches 60 bar.
- There are several high pressure manual valves to close or open the reactor inlets and outlets.

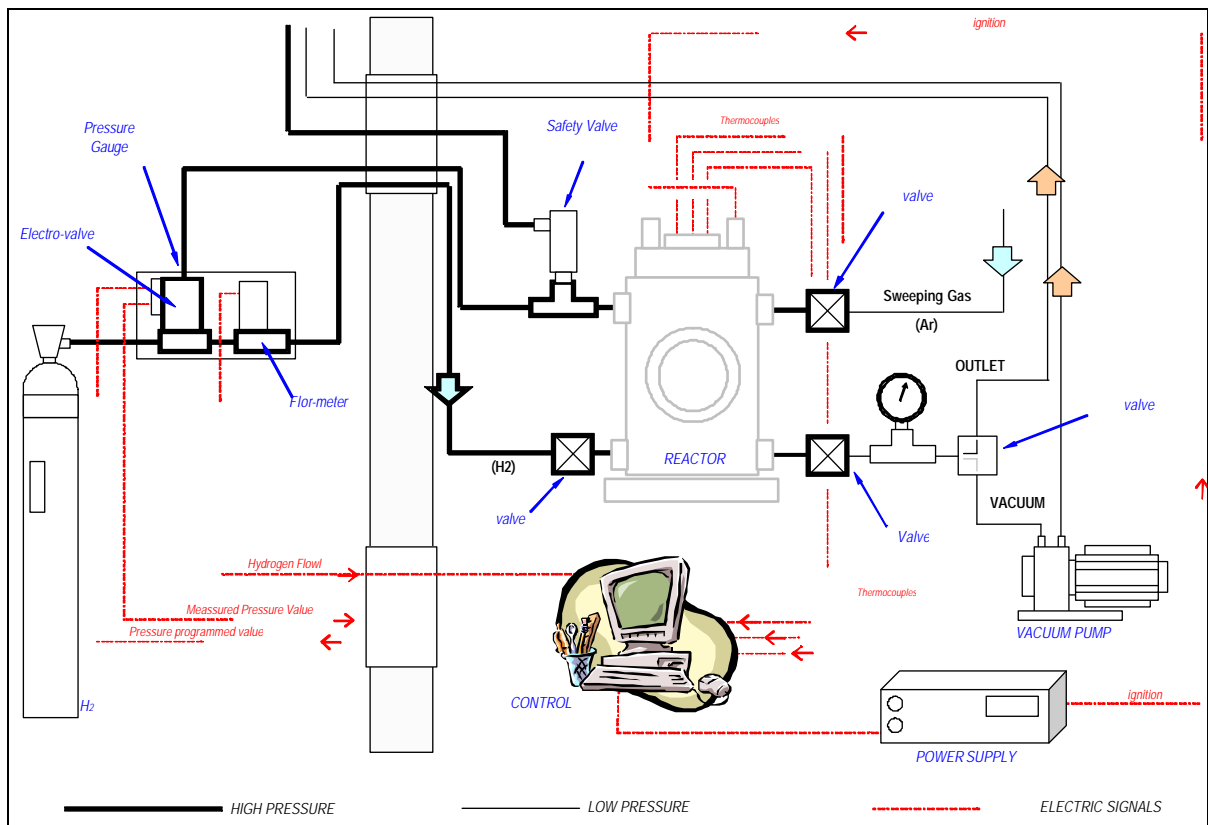


Figure 3: Scheme of the hydride synthesis facility.

The system is based on the flowmeter data acquisition at a constant reaction pressure: the reaction takes place at a constant pressure. This pressure is programmed on the PC and the valve controls the pressure inside the reactor (by means of the pressure gauge). Once the reaction begins, the hydrogen starts filtrating into the sample and reacting with the metallic powder. As a consequence of this, the pressure drops into the reactor. In order to maintain the pressure constant at the programmed value, the valve opens until it reaches the set-up value. As the hydrogen is passing by the pipe, the flowmeter measures the amount of gas introduced into the reactor. This way, it is possible to know the hydridation parameters (temperature of the system, instantaneous gas consumption, product stoichiometry, gas volume flow and reaction pressure), at every stage of the process. Thus, the product formation can be determined by this new system using an analytical procedure derived from flow meter data received. Figure 4 shows a photograph of the reactor.



Figure 4: Metallic Hydrides Synthesis Reactor.

2.2. Experimental Tests:

In order to test and validate the above described installation, trials with titanium powder have been carried out with the aim of studying the hydridation phenomena of Titanium.

Elemental powder of Titanium has been used. Table I shows some physical properties of the used raw materials:

Table I: Raw materials properties.

RAW MATERIAL	PARTICLE SIZE	PURITY
Titanium (Ti)	< 100 μm	> 99%
Hydrogen (H ₂)	-----	> 99,95%

Samples of seven grams of titanium were cold pressed into cylindrical specimens with the dimensions of 13mm in diameter and an average height of 20mm (depending on the green density). The samples were put into the SHS Hydride reactor. The reactor was purged three times: first, vacuum was made with a pump, and then the vessel was filled with argon. Finally, the reactor was filled with hydrogen up to the reaction set-up pressure. The samples were ignited using a tungsten coil. Combustion maximum temperature and thermograms were obtained using Ni/Cr-Ni/Al (K type) thermocouples, and a labview software to monitor and store the data (temperature, reaction pressure, gas volume flow and gas consumption).

Table II shows the sample main features and used reaction parameters.

Table II: Used sample features and reaction parameters.

Parameter	Value
Material	Titanium (Ti)
Sample shape	cylindrical
Sample diameter (cm)	13
Sample mass (g)	7
Green density (%)	45 % of the theoretical density
Sample length	20mm
Reaction pressure (bar)	1-5bar
Purge gas	Argon
Purges number	3

Using the collected data a Macro-kinetic study was performed in order to compare the obtained result with previous works and to validate the developed methodology.

The phase formation study was performed using SIEMENS D-500 X ray diffractometer with a copper anode for the crystalline phase analysis, and the chemical analysis (hydrogen content) was carried out in a CARLO ERBA-1108 analyser. The hydride was dissociated by means of flash combustion method and the measured in a thermal conductivity detector chromatograph.

3. RESULTS AND DISCUSSION

3.1 Data obtention and explanation

The developed system allows obtaining the following data from each experiment: temperature (up to two thermocouples), reaction pressure, gas volume flow and gas consumption. Figure 5 shows an example of the data at combustion of titanium in hydrogen.

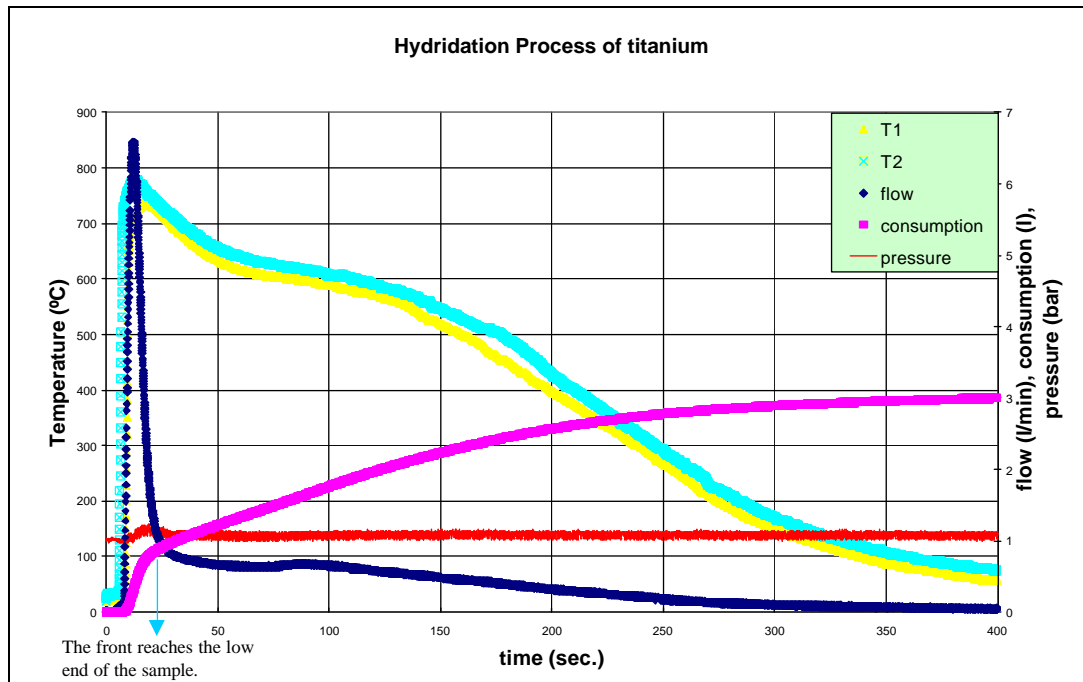


Figure 5: Hydridation process parameters.

Where, the light blue and the yellow lines are the temperature, the dark blue line is the gas volumetric flow during the process, the pink line is the gas consumption and the red line is the reaction pressure. As it can be seen the system monitors all the relevant data related to the hydridation process. Note that according to the pressure curve (red line), the hydridation process takes place at a constant pressure.

The gas flow curve gives a maximum flow rate at the beginning of the reaction (the peak of the dark blue curve). This is caused by the high gas absorption rate during the first moment of the reaction, until the front reaches the end of the sample (see the light blue arrow). At that point the front has already travelled along the whole sample and the gas absorption phenomena begins to take place. As the absorption kinetic is quite slow comparing to the front propagation, a more constant gas flow rate is observed in the second part of the curve. Eventually the gas flow rate becomes zero, when all the hydrogenation has taken place.

The pink line shows a very similar result to the gas flow rate curve. At the beginning of the reaction, as the gas absorption rate is high, the slope of the gas consumption curve is very steep. When the reaction front comes to the end of the sample (light blue arrow) the gas flow rate decreases and thus the consumption curve change the slope, giving place to the hydrogen absorption step. Finally the consumption becomes constant, which means that the gas flow rate is zero. This data is in agreement with the literature where it is described that the process of synthesis of hydrides by combustion proceeds in two stages: the first stage involves the formation of a β -solid solution of hydrogen in the metal and the second involves the formation of the hydride phase. This observation is the consequence of thermodynamic constraints. Hydrides phases are relatively unstable and tend to dissociate at temperatures in the range of 600-700°C. Thus, in the stage of combustion front propagation only solid

solutions of hydrogen in titanium form with $H/Ti < 1$, which was firstly shown in [16,17] by continuous measurement of pressure change (ΔP) in the reactor during combustion wave propagation. With the developed system it is possible to identify this point by the gas consumption curve.

Having a look into the thermocouple data, it can be seen that the maximum temperature almost matches with the end of the maximum of the gas flow curve. However if this zone is amplified, it can be appreciated that the maximum temperature is reached at the same time as the maximum value of the gas flow rate and not after the peak (as logically it could be thought). This is due to the fact that the response time of the flowmeter is slightly slower to the one of the thermocouple. It also can be seen that after the maximum temperature there is a plateau zone where the main part of the absorption process happens.

3.2.- Final Product Stoichiometry Study:

By means of the developed facility is possible to calculate the final product stoichiometry, it is said, the amount of hydrogen that has been absorbed. This calculation is done by an appropriate study of the gas flow and gas volume consumption during the process. In this sense, table III shows the comparison between the data obtained from the flowmeter and the data obtained from the chemical analysis of the sample for 5 different reaction pressures.

Table III: Comparison of the hydrogen content in the product at different reaction pressures.

Reaction pressure	Product Stoichiometry	Theoretical absorbed H ₂	Results of Absorbed H ₂ from flowmeter data wt. % (TiH _x)	Results of Absorbed H ₂ from Chemical analysis data wt. % (TiH _x)
1 bar	TiH ₂	4,00 wt.%	3,95 wt.% (TiH _{1,97})	3,98 wt.% (TiH _{1,99})
2 bar	TiH ₂	4,00 wt.%	3,95 wt.% (TiH _{1,97})	3,98 wt.% (TiH _{1,99})
3 bar	TiH ₂	4,00 wt.%	3,98 wt.% (TiH _{1,98})	3,98 wt.% (TiH _{1,99})
4 bar	TiH ₂	4,00 wt.%	3,95 wt.% (TiH _{1,97})	3,97 wt.% (TiH _{1,98})
5 bar	TiH ₂	4,00 wt.%	3,97 wt.% (TiH _{1,98})	3,98 wt.% (TiH _{1,99})

As it can be seen there is a fairly good agreement between the value obtained from the flowmeter data analysis and the chemical analysis. This, fact confirms that it is possible to calculate the hydrogen content of the metallic hydride at a reasonably accuracy without performing chemical analysis.

Another important data is that the final product stoichiometry is independent to the reaction pressure in the investigated range and always is very close to the theoretical stoichiometry, as it has been already reported

In addition to this hydrogen content study, a phase analysis was carried out by means of an X ray diffractometer. Figure 6 shows the obtained X ray pattern. It can be seen that the obtained product is titanium dihydride. This result also confirms the values obtained in the chemical analysis.

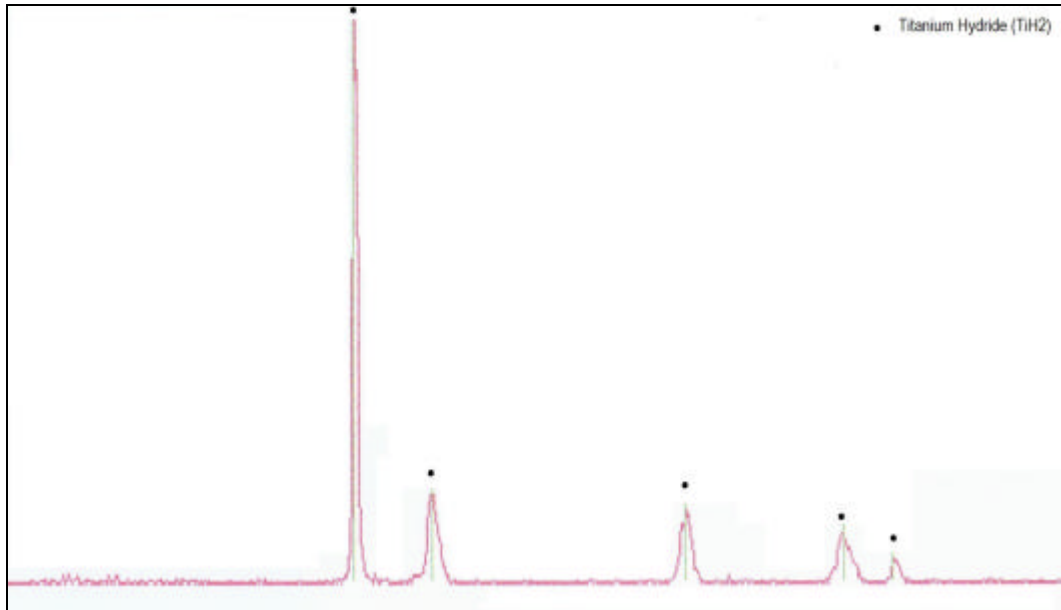


Figure 6: Typical curves of a TiH_x reaction

4. CONCLUSIONS

This work has presented a novel method of metallic hydride synthesis: SHS. This is highly innovative and presents some advantages over their conventional homologues:

- This method is notably safer than their conventional homonyms, since the used hydrogen pressure is much lower, thus reducing the risk associated to high hydrogen pressure.
- It allows obtaining the product with much less energy consumption than conventional processes.
- The developed methodology enables to know the hydride features during the product formation. In addition, it is possible to calculate the product stoichiometry from the stored data, without chemical analysis.

Some other conclusion can be summarized as follows:

- It is possible to control and monitor hydriding combustion reaction and know what the hydrogen content is in the metallic powder during the process without interruption the reaction.
- Finally it is important to note that the developed method is able to detect and study filtration problems in gas phase reactions, therefore being interesting for nitridation combustion processes where the filtration phenomena plays a relevant role.
- The operation pressure is low: As it can be seen, the reaction pressure dos not affect the final product stoichiometry. Compared to conventional methods of manufacturing metallic hydrides, SHS allows obtaining the final stoichiometric hydrides at low pressures (1 bar). This fact increases considerably the manufacturing safety degree.
- The obtained final product is very close to the theoretical stoichiometric product.

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