

French Project PLUSPAC : development of a hydrogen storage unit for an optimisation of stationary fuel cell systems - safety of metal hybrides

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French Project PLUSPAC:
Development of a hydrogen storage unit for an optimisation of stationary FC systems
SAFETY OF METAL HYDRIDES

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One of the objectives of the French project PLUSPAC (Local Production and hydrogen Storage Unit for an optimisation of Fuel Cell stationary systems), coordinated by the Energy Research Centre of Veolia Environment is to evaluate the performances of hydrogen storage in metal hydrides for the energetic optimisation of a stationary fuel cell system.

INERIS was in charge to assess the safety of metal hydrides as a storage mean. As very few information is available regarding the safety of intermetallic compounds developed within PLUSPAC project, experimental tests have been performed so as to get information about the reactivity of the powder (reaction with air, with water, thermal decomposition). Tests have been performed on activated (15 and 30 cycles) and no activated powders, and also on an other intermetallic compound, which is supposed to be reactive. Nevertheless, none of the tests have shown any adverse reaction, neither with air, nor with water, nor when exposed to high temperatures. Today, it appears that metal hydrides tested have a safe behaviour when exposed to air, water and high temperatures. Further tests would be necessary to investigate other materials.

Keywords : *Metal hydrides, safety, reactivity*

1 The French PLUSPAC Project

Current CHP¹ systems based on fuel cell technology usually consist of a fuel cell stack combined to a hydrogen generator, mostly a reformer of natural gas. Besides, such systems also include all the thermal management sub-systems such as heat exchangers, coolant circuits and their management tools. So, the energy optimisation of such a CHP system is one of the major concerns during its design phase.

Within this context Axane, the French Atomic Energy Commission (CEA) – Hydrogen Technologies Department, National Centre for Scientific Research (CNRS) – Metallurgical Chemistry laboratory of Rare Earth, National Institute of Risks and Industrial Environment (INERIS), Schneider Electric, and the Energy Research Centre of Veolia Environment gathered their efforts within PLUSPAC project.

PLUSPAC project (which stands for Local Production and hydrogen Storage Unit for an optimisation of Fuel Cell stationary systems) aims at developing a hydrogen production-storage system which,

¹ Combined Heat and Power

associated with a fuel cell, would meet both the power and thermal energy variable requirements of a stationary site.

One of the project objectives was to show the feasibility of a hydrogen buffer tank within this kind of CHP unit, and then to develop and test this storage under laboratory conditions.

A constant hydrogen production would allow the reformer to run in an optimal way. However, the hydrogen consumption of the fuel cell is variable according to the energy demands of the user. A buffer tank flattens out the energy loads, thus improving the performances of the system.

Metal hydrides have been selected as hydrogen storage materials for the buffer tank for several reasons. First, they allow to store hydrogen safely (due to low equilibrium pressures at room temperature), with reliability and energy profitability (with no compression and a temperature close to the ambient one). On the other hand, these metal hydrides can also absorb most of the hydrogen at constant pressure, which enables the storage of a significant amount of hydrogen for a given low-pressure range.

Furthermore, due to their volume capacities, metal hydrides have a very good compactness in comparison with other storage technologies (liquid hydrogen, gaseous hydrogen under very high pressure).

As a first step of the project, specifications were determined by Schneider Electric and the Energy Research Centre of Veolia Environment on the basis of an analysis of the thermal and power needs of a representative site. On this basis, CEA has worked on a model of the thermal and mechanical behaviour of the hydrogen solid storage. Simultaneously, CNRS developed a metallic powder, which matches up to the defined specifications. The powder was tested by INERIS under various conditions (reaction to air, water, and coolant on a wide temperature range), with the final objective of filling in a tank developed by CEA with this powder. Then, the fitted tank has been tested on a load under laboratory conditions.

This energy storage would eventually be used for other applications. Currently, the development of a secured and environmentally friendly tank is one of the keys of hydrogen economy breakthrough. Energy storage turns out to be essential for any decentralised hydrogen production system: using intermittent renewable energy sources or fuel cell based emergency power source.

2 The hydride

For this study, LaNi₅ substituted derivatives (AB₅-type compounds) have been chosen as hydrogen storage materials to fulfil the criteria related to the specific application. In order to adapt the thermodynamic properties of LaNi₅ compound, the substitutions of tin for nickel or of mischmetal for lanthanum (Mm stands for mischmetal, a mixture of lanthanum, cerium, neodymium and praseodymium) have been investigated. Several studies report that the substitution of a small amount of tin for nickel in LaNi₅-type intermetallic compounds modifies the thermodynamic properties of the resulting hydride phase (decrease of the plateau pressure, hydrogen storage capacity and hysteresis ratio) [1,2]. In addition, tin significantly improves the cycle life under hydrogen gas cycling [3,4]. Chemical replacement of the La by Mm in order to achieve cost reduction is of interest for a commercial application. For comparison, a Mn substituted compound was also investigated in the present work as Mn substituted sample is expected to be highly reactive.

Two intermetallic compounds (La_{0.9}Ce_{0.05}Nd_{0.04}Pr_{0.01}Ni_{4.63}Sn_{0.32} and LaNi₄Mn) have been synthesised by induction melting of the pure elements under vacuum or argon atmosphere followed by annealing at 1123 K for 7 days. The composition and homogeneity were checked by X-ray diffraction (XRD) with Cu K α radiation, optical metallography and electron probe micro-analysis (EPMA). All samples were found to be single phase with composition very close to the nominal ones.

About 4 to 10 g of sample were ground mechanically under argon and activated by fifteen or thirty solid-gas cycles with a conventional Sievert's type apparatus (volumetric method). Each cycle consists in an absorption under 3.5 MPa of hydrogen gas at 75°C followed by a desorption under primary vacuum. After cycling, all samples were kept under inert atmosphere (Ar or vacuum). The different sample preparations are summarised in Table 1.

Composition	Number of cycles (N)	Weight (g)
$\text{La}_{0.9}\text{Ce}_{0.05}\text{Nd}_{0.04}\text{Pr}_{0.01}\text{Ni}_{4.63}\text{Sn}_{0.32}$	0	3.7
$\text{La}_{0.9}\text{Ce}_{0.05}\text{Nd}_{0.04}\text{Pr}_{0.01}\text{Ni}_{4.63}\text{Sn}_{0.32}$	15	3.8
$\text{La}_{0.9}\text{Ce}_{0.05}\text{Nd}_{0.04}\text{Pr}_{0.01}\text{Ni}_{4.63}\text{Sn}_{0.32}$	30	5
LaNi_4Mn	30	5.5
$\text{La}_{0.9}\text{Ce}_{0.05}\text{Nd}_{0.04}\text{Pr}_{0.01}\text{Ni}_{4.63}\text{Sn}_{0.32}$	30	10.4

Table 1: Characteristic of the different studied samples.

3 The safety tests

3.1 Objectives of the tests

Metal hydrides were considered safer, compared with compressed or liquefied hydrogen storage for the reason that this storage technology did not rely on high pressure or could not be associated with a rapid hydrogen discharge in case of breach for example.

However, there is very few data (poor literature) on metal hydrides (intermetallic powders) behaviour when exposed to air, water, coolant and either thermal stability, though some activated hydrides are known to be pyrophoric.

It is today necessary to get good data on metal hydrides behaviour, otherwise safety analysis of a hydrogen system would be very limited and a public use of these systems could be delayed [5]. Thus, INERIS decided to undertake an experimental program to get a better insight into intermetallic powders safety characteristics.

In this context, in the course of the French project entitled PLUSPAC, which aims at developing and evaluating a metal hydride tank for hydrogen storage, INERIS has performed the following tests:

- intermetallic compound² behaviour when exposed to air,
- intermetallic compound behaviour when exposed to water,
- intermetallic compound behaviour when exposed to coolant,
- and finally, intermetallic compound thermal stability.

3.2 Experimental means

Experiments have been carried out in our Chemical Reaction Safety Lab. This lab is in charge of assessing thermal stability of chemical products and to characterise chemical reactions. It is equipped with various equipment.

The following lab equipment has been used to assess Metal hydrides safety characteristics:

- The DSC (Differential Scanning Calorimeter): it measures the difference of thermal flow between a test sample and a reference sample, when submitted to a thermal cycle (steady temperature increase). The DSC scans exothermic or endothermic reactions and allows to determine the temperature at which the sample becomes unstable as well as the associated enthalpy.

² $\text{La}_{0.9}\text{Ce}_{0.05}\text{Nd}_{0.04}\text{Pr}_{0.01}\text{Ni}_{4.63}\text{Sn}_{0.32}$



Illustration 1: DSC Calorimeter used for tests

All tests were conducted in a Setaram 131 Differential Scanning Calorimeter with the following characteristics :

Temperature range	-170 to 700 °C
Resolution	0.4 μW
Cell volume	30 μl
Cell	Stainless steel – 300 bar
Specific RMS noise	0.008 %W/μl
Time constant	3 seconds
Normal heat rate	5 K/min

3.3 Samples

The samples in the form of a fine powder were provided by the Laboratoire de Chimie Métallurgique des Terres Rares (CNRS) Thiais France in sealed vials under vacuum (see illustration 2).

Once opened in a glove box, the remaining sample was placed in a small closed bottle and stored at ambient temperature.

Samples were of both non-activated and activated types (15 or 30 cycles of charge and discharge). We therefore had to develop new laboratory practices in order not to contaminate samples with air.

Sample code	Sample reference number	Composition	Activation with hydrogen
2R without	04 AZ 209	La _{0,9} Ce _{0,05} Nd _{0,04} Pr _{0,01} Ni _{4,63} Sn _{0,32} (2R)	No activation
2R	04 AZ 210	La _{0,9} Ce _{0,05} Nd _{0,04} Pr _{0,01} Ni _{4,63} Sn _{0,32} (2R)	15 cycles
3R	05 AR 373	La _{0,9} Ce _{0,05} Nd _{0,04} Pr _{0,01} Ni _{4,63} Sn _{0,32} (3R)	30 cycles
4R	06 AE 528	La _{0,9} Ce _{0,05} Nd _{0,04} Pr _{0,01} Ni _{4,63} Sn _{0,32} (4R)	30 cycles
Activated Alloy	05 AS 293	La Ni ₄ Mn	30 cycles

Table 1 : Samples, which were exposed to tests



Illustration 2: Sealed vial containing fine powder

3.4 Main tests results

3.4.1 Preliminary tests

A few milligrams of the metal alloys were exposed to air in the form of a small pile on top of a thermocouple at ambient temperature to see whether the powder would spontaneously ignite. No ignition, incandescence, temperature rise, or change in physical appearance were observed for the five samples.

Other preliminary tests were conducted by exposing a few milligrams of the alloys to air on a balance to determine the weight gain due to oxidation at ambient temperature. No significant weight gain (> 1%) was observed.

For the preliminary compatibility tests between the metal alloys and water and the cooling fluid (Syltherm 800), a few milligrams of alloy was placed in a DSC test cell and a small drop of the liquid was placed on top. The water droplet did not wet the powder samples and no reaction was observed. The Syltherm 800 droplet wetted the powder sample but no exothermic was detected.

3.4.2 DSC tests

DSC tests were carried out on all five metal alloy samples under the following conditions:

Open/Closed cell	Atmosphere	Contact with other substance	Heat rate
Open	Air	None	5 K/min
Open	Air	Water	2 K/min
Open	Air	Syltherm 800	5 K/min
Closed	-	None	5 K/min
Closed	-	Water	5 K/min
Closed	-	Syltherm 800	5 K/min

Table 2: Conditions for DSC experiments of each sample

Samples were introduced in a cell, which was closed or opened, depending on the conditions of tests, as shown in the table above.

Cells are made of stainless steel and contain a very limited quantity of powder (see illustration 3).

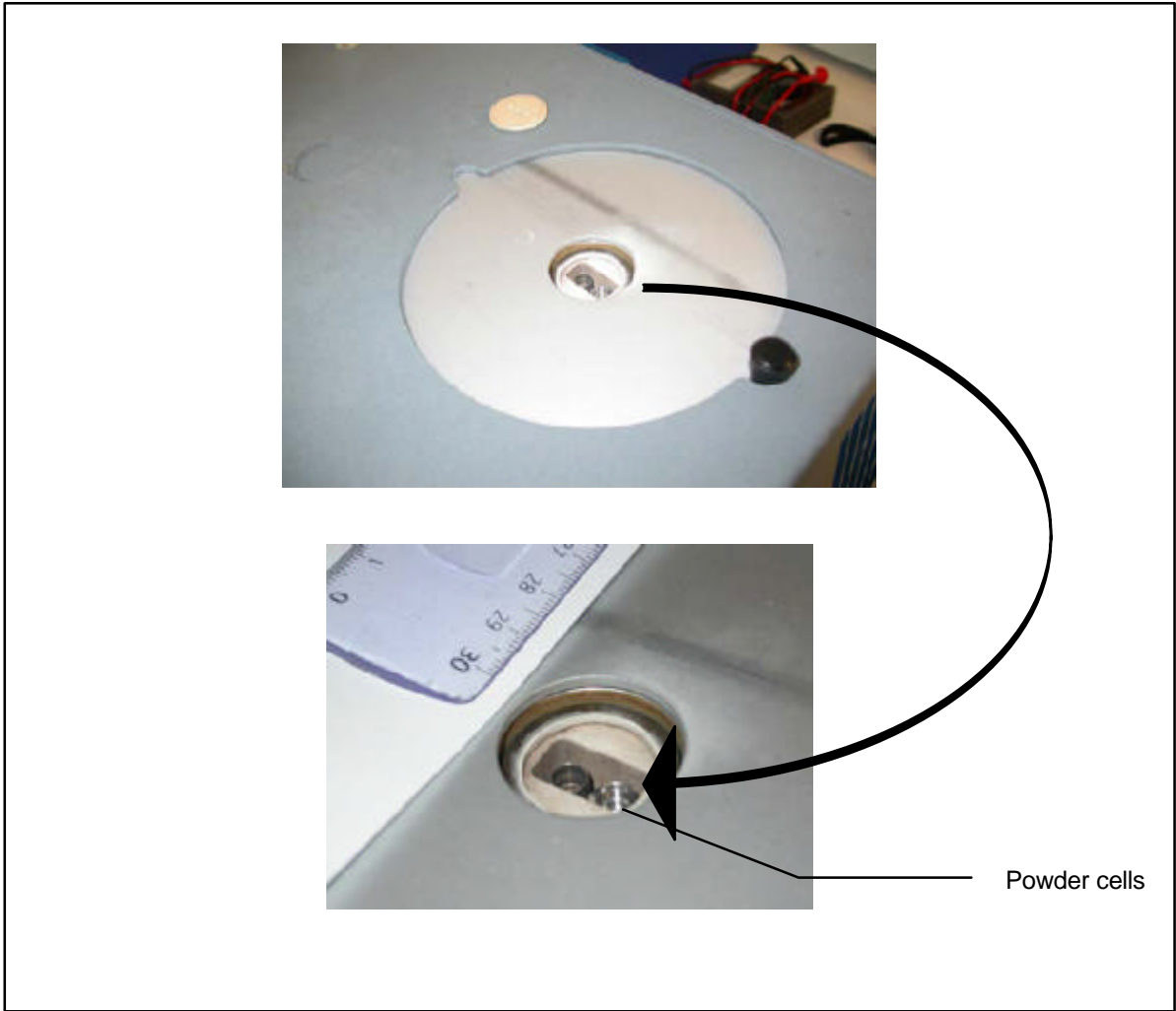


Illustration 3: Illustration of sample cells

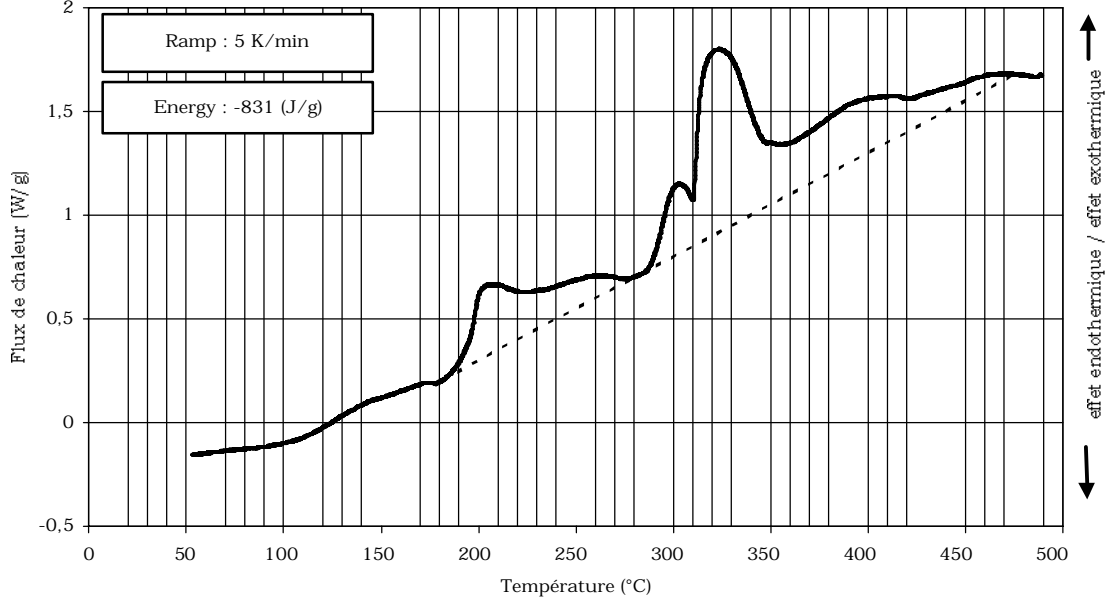
The overall results are reported in the table below.

		2R (04 AZ 209)	2R (04 AZ 210)	3R (05 AR 373)	4R (06 AE 528)	La Ni₄ Mn (05 AS 293)
Number of cycles of adsorption-desorption		none	15	30	30	30
Test summary						
Reaction to air on the balance	Mass gain after 1 hour	+ 0,67 %	No change	+ 0,39 %	- 0,3 %	- 0,75 %
Reaction to air in a pile	Temperature gain	No effect	No effect	No effect	No effect	No effect
Reaction to water droplets on a pile	A drop of water placed on a pile of alloy	The water does not wet the alloy No reaction	The water does not wet the alloy No reaction	The water does not wet the alloy No reaction	The water does not wet the alloy No reaction	The water does not wet the alloy No reaction
Reaction to Syltherm 800	A drop of Syltherm placed on a pile of alloy	The Syltherm wets the powder but no reaction	The Syltherm wets the powder but no reaction	The Syltherm wets the powder but no reaction	The Syltherm wets the powder but no reaction	The Syltherm wets the powder but no reaction
Thermal stability in a closed cell	5 K/min rampe up to 500° C	No reaction	No reaction	No reaction	No reaction	No reaction
Reaction to water in a closed cell	One small drop of water 5 K/min and rampe up to 500° C	Small reaction at 170 °C	Small reaction at 170 °C	Energetic reaction (907 J/g) starting at 165 °C	Energetic reaction (1101 J/g) starting at 160 °C	Energetic and intense reaction (1146 J/g) starting at 140 °C
Reaction to Syltherm in a closed cell	One small drop of Syltherm 5 K/min and rampe up to 500° C	No reaction (same thermogram as Syltherm alone)	No reaction (same thermogram as Syltherm alone)	No reaction (same thermogram as Syltherm alone)	No reaction (same thermogram as Syltherm alone)	No reaction (same thermogram as Syltherm alone)
Reaction to air Open cell	5 K/min rampe up to 500° C	Small reaction (173 J/g) at 270 °C	Reaction at 450 °C Mass gain + 0,001%	Multiple reactions starting at 240 °C Mass gain + 0,001%	Multiple reactions starting at 240 °C Mass gain + 0,002%	Energetic reaction starting at 160 °C (1734 J/g) Mass gain + 0,002%
Reaction to water in an open cell	One small drop of water 2 K/min rampe up to 100° C	No exothermic reaction	No exothermic reaction	No exothermic reaction	No exothermic reaction	No exothermic reaction
Reaction to Syltherm in an open cell	One small drop of Syltherm 5 K/min rampe up to 500° C	-	-	-	Reaction starting at 330 °C	Energetic reaction starting at 320 °C

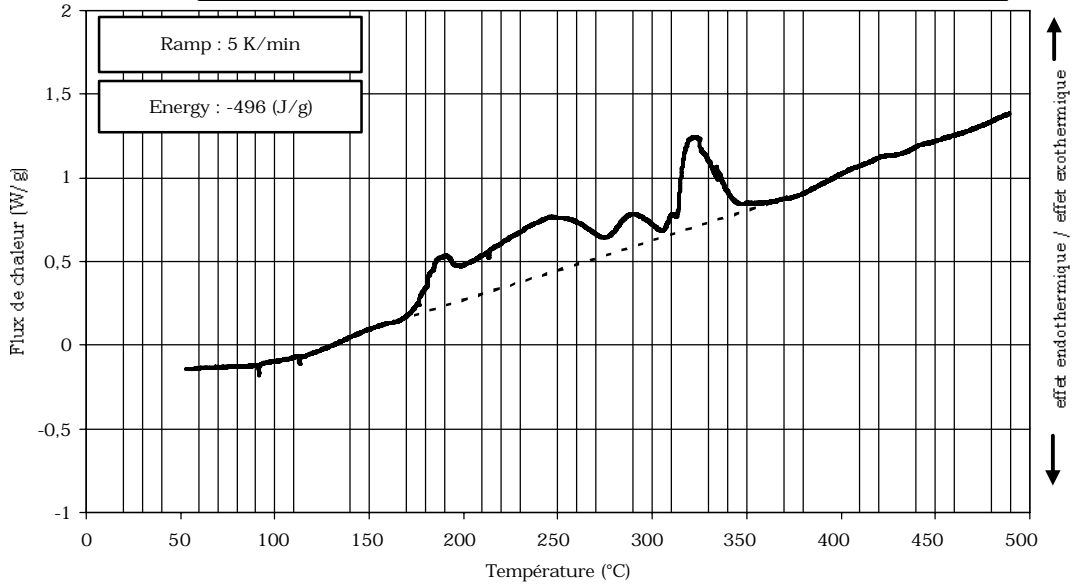
Table 3: Main tests results

- The five metal alloys at various stages of activation did not react to air, water, or the fluid Syltherm 800 at ambient temperature.
- In air, the five samples did not react up to over 400 °C in open cells.
- With water, the activated alloy sample of La Ni₄ Mn reacted energetically in intensely starting at 140 °C in closed cells. The other samples displayed multiple peaks starting at about 170 °C. The thermograms of these tests are presented below. No exothermic reaction was detected with water in the open cell tests up to the boiling point of water.
- No reaction with the fluid Syltherm 800 was detected in the closed cells and in the open cells before 330 °C.

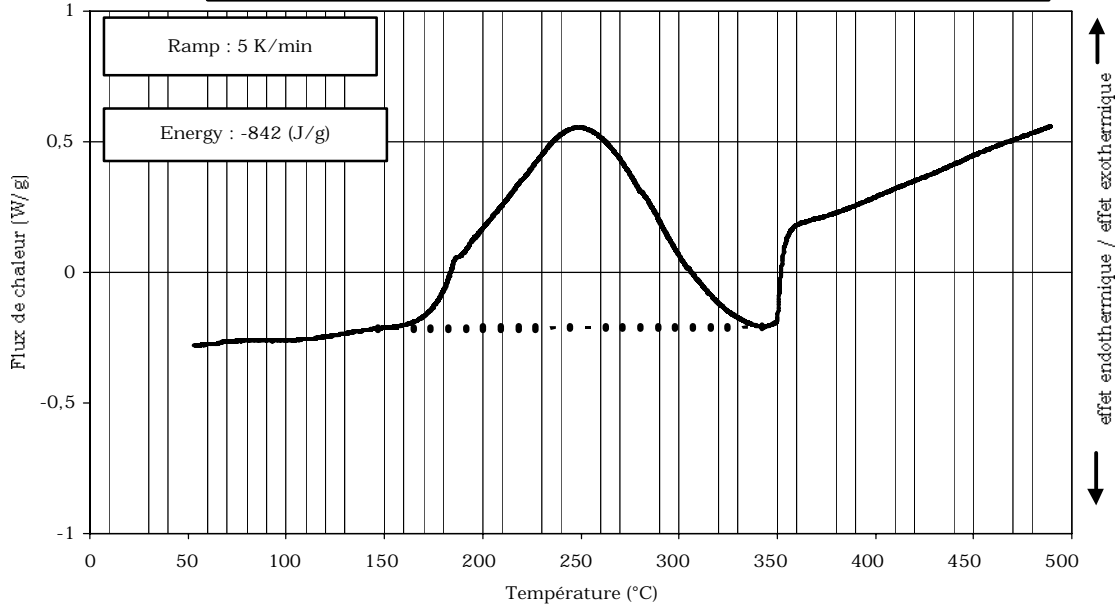
DSC n° 1181 Société : CNRS
Aloy 2R not activated + water (closed cell)
INERIS n° 04 AZ 209



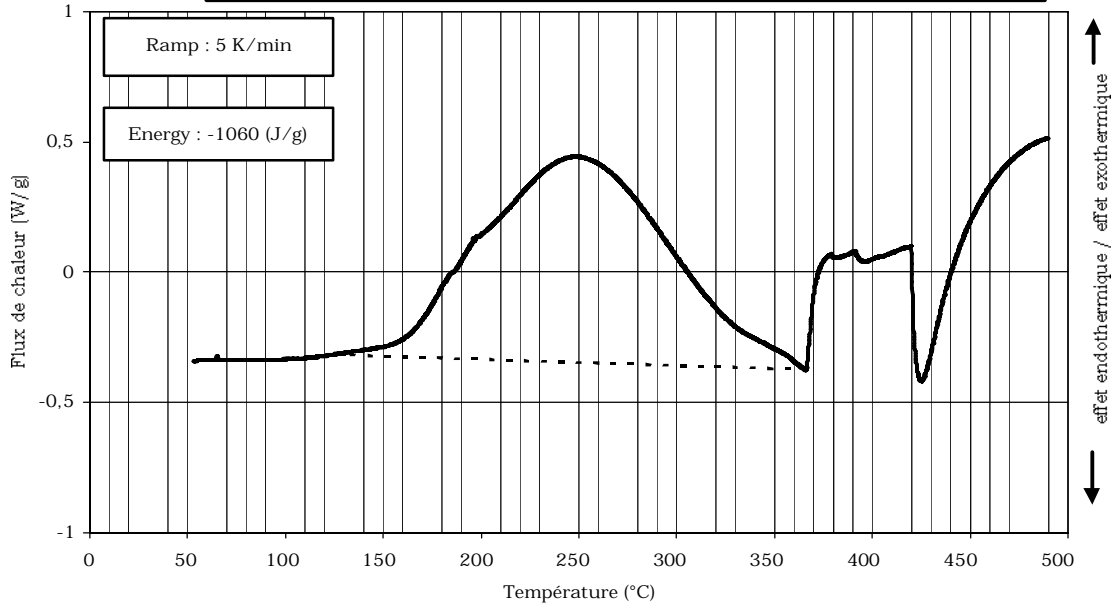
DSC n° 1184 Sample : CNRS
Alloy 2R (15 cycles) + water (closed cell)
INERIS n° 04 AZ 210



DSC n° 1174 Sample : CNRS
 Alloy 3R + water (closed cell)
 INERIS n° 05 AR 373



DSC n° 1169 Sample : CNRS
 Alloy 4R + water (closed cell)
 INERIS n° 06 AE 528



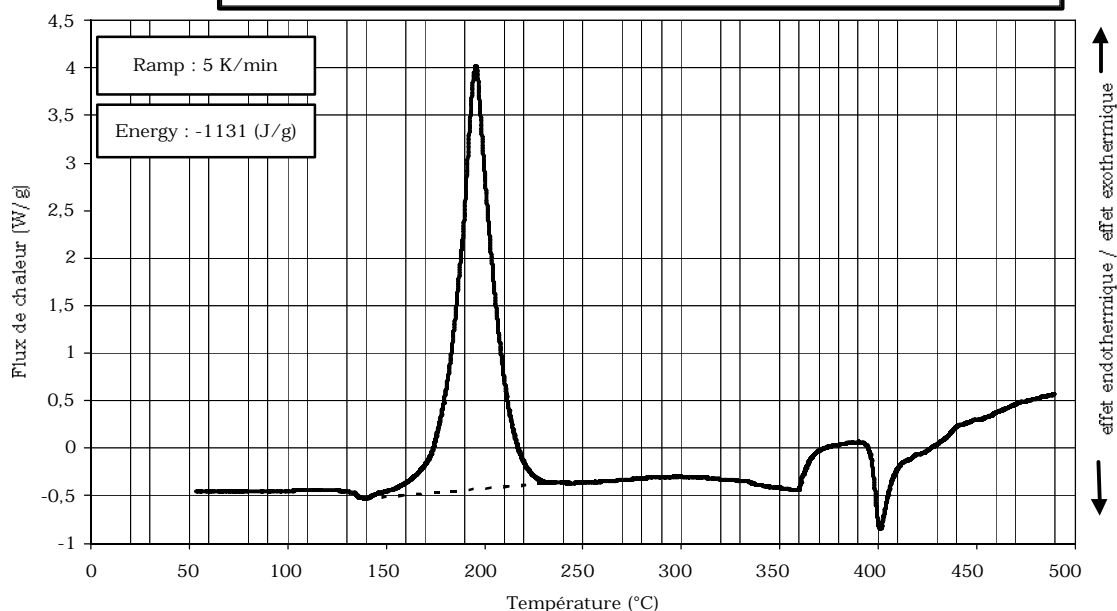


Illustration 4: Thermograms of reaction with water in closed cell for each sample

3.5 Conclusions and perspectives

Experiments undertaken with alloy $\text{La}_{0.9}\text{Ce}_{0.05}\text{Nd}_{0.04}\text{Pr}_{0.01}\text{Ni}_{4.63}\text{Sn}_{0.32}$ show that this metal hydride does react neither with air, nor with water and also remains stable in case of thermal aggression or thermal over-heating. In any case, if there is a reaction, this one is not detectable.

The tiny increase of mass which have been observed at ambient air for activated samples, points out a light oxidation of the alloy.

These conclusions are somehow unexpected, since some of these materials are known to be pyrophoric.

Obviously, all metal hydrides do not have a hazardous behaviour. **Further experiments should be performed** so as to identify those metal alloys which are the most reactive and to identify the cause of their reactivity (composition of the alloy, its state: activated or not, number of activation cycles).

Further steps of the project will consist to study the impact of the presence of hydrogen in the intermetallic compound. Indeed, test have been carried out on intermetallic compounds, for which the last activation cycle was a desorption, so there were hydrogen free. These tests will be performed with the same intermetallic compounds in the Calvet C80 Calorimeter hydride, with circulation of hydrogen.

Moreover, it would be interesting to perform some tests with higher quantities of powder, so as to know if the quantity is not a hazard factor. Scale effect has to be investigated, having in mind that large quantities are handled in laboratories or factories. INERIS has now developed test procedures for metal hydrides safety assessment. These procedures can be shared in the framework of normative work, in order to have a common standard to test and rank metal hydrides hazardous behaviour.

4 Acknowledgements

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5 References

- [1] Luo, S., Luo, W., Clewley, J., Flanagan, T. N., and Bowman, R. C., Jr. Thermodynamic and degradation studies of $\text{LaNi}_{4.8}\text{Sn}_{0.2}\text{-H}$ using isotherms and calorimetry. *Journal of Alloys and Compounds* 1995; 231: 473–478.
- [2] Luo, S., Luo, W., Clewley, J. D., Flanagan, T. B., and Wade, L. A. Thermodynamic studies of the $\text{LaNi}_{5-x}\text{Sn}_x\text{-H}$ system from $x = 0$ to 0.5. *Journal of Alloys and Compounds* 1995; 231: 467–472.
- [3] Lambert, S. W., Chandra, D., Cathey, W. N., Lynch, F. E., and Bowman, R. C., Jr. Investigation of hydriding properties of $\text{LaNi}_{4.8}\text{Sn}_{0.2}$, $\text{LaNi}_{4.27}\text{Sn}_{0.24}$ and $\text{La}_{0.9}\text{Gd}_{0.1}\text{Ni}_5$ after thermal cycling and aging. *Journal of Alloys and Compounds* 1992; 187: 113–135.
- [4] Bowman, R. C., Jr., Luo, C. H., Ahn, C. C., Witham, C. K., and Fultz, B. The effect of tin on the degradation of $\text{LaNi}_{5-y}\text{Sn}_y$ metal hydride during thermal cycling. *Journal of Alloys and Compounds* 1995; 217: 185–192.