

SAFE PROCESSING ROUTE FOR THE SYNTHESIS OF Mg BASED METALLIC HYDRIDES

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ABSTRACT

Metallic hydrides represent a safe way of storing hydrogen, minimising explosion and flammability risks. Nowadays there are several methods for the storage of hydrogen and the more conventional techniques are high-pressure tanks for gaseous hydrogen and cryogenic vessels for liquid hydrogen. However, there are two main drawbacks in the storage of gaseous and liquid hydrogen. First, as a fuel, hydrogen in the gaseous and liquid states is very combustible and the related law imposes strict regulations on its utilization, storage and transportation. Secondly, even under a high pressure, hydrogen gas is not dense enough for compact storage. Moreover, the gas storage at high pressure involves significant safety risks. Hydrogen storage in the metal hydrides does not have such deficiencies. Metal hydrides are safe and can be easily store and transported. For that reason, it should be stressed that metallic hydrides represent a safe way of storing hydrogen, minimising explosion and flammability risks. Among metallic hydrides, one of the most promising hydrides in terms of absorbed hydrogen content is Mg₂NiH₄. However, it is difficult to obtain Mg₂Ni by the conventional melting method because of the large difference in vapour pressure and melting point between magnesium and nickel. This paper presents an alternative and safe method for obtaining such hydride: HCS (Hydriding Combustion Synthesis). This method presents some interesting advantages over its conventional counterpart: the process is carried out at lower reaction process, which means safer process and the alloy stoichiometry is closer to the nominal (Mg₂Ni) which allow better hydrogen absorption behaviour. The aim of this work is to investigate the formation mechanism of this compound and to study some parameters of the process.

1. INTRODUCTION

Hydrogen storage is a key technology for the implementation of the hydrogen and fuel cell power technologies in mobile, stationary and portable applications. There are several methods for the storage of hydrogen including high-pressure tanks for gaseous hydrogen, cryogenic vessels for liquid hydrogen and metal hydride (solid state) storage systems. There are two main drawbacks in the storage of gaseous and liquid hydrogen. First, as a fuel, hydrogen in the gaseous and liquid states is very combustible and the related law imposes strict regulations on its utilisation, storage and transportation. Secondly, even under a high pressure, hydrogen gas is not dense enough for compact storage. Hydrogen storage in the metal hydrides does not have such deficiencies. Metal hydrides are safe and can be easily store and transported.

Magnesium-based hydrides are promising materials for solid state hydrogen storage because of their lightweight, high specific storage capacity and abundant raw materials. Nevertheless, these materials present high desorption temperature (about 300 °C) to provide the required hydrogen output and have slow hydrogen absorption and desorption kinetics. In the last decade, many efforts were made to overcome these disadvantages, such as element additions [1-4] and different production methods [5-6].

Among magnesium-based alloys, Mg₂Ni intermetallic compound is well known to form Mg₂NiH₄ hydride with a hydrogen storage capacity of 3,6 wt% and interesting absorption/desorption properties. However, it is difficult to obtain Mg₂Ni by the conventional melting method because of the large difference in vapour pressure and melting point between magnesium and nickel. Re-melting processes

(Mg addition) is needed; besides, the produced intermetallic can not absorb hydrogen without several cycles of absorption and desorption. Another possibility to obtain this material is mechanical alloying [7-9], this technique usually takes a long time to prepare alloys and it is easy for the sample to be polluted during milling process.

An innovative method to produce Mg_2NiH_4 is hydrogen combustion synthesis (HCS) [10-12]. The synthesis temperature of the HCS process is much lower than that of ingot process, and a full hydride can be obtained by only one thermal treatment, which combines both processes: the synthesis of the intermetallic and the hydrogenation of the alloy. Mg_2NiH_4 produced by HCS has excellent hydrogen storage properties in comparison with the commercially available ingot metallurgy product [13]. It is not necessary activation process and presents higher hydriding kinetics and higher hydrogen storage capacity.

It is worth noting that Mg_2NiH_4 requires lower synthesis hydrogen pressure than other metallic hydrides. This fact is directly linked with the process safety: the lower the hydrogen pressure during the process the safer the process is. In addition, Mg_2Ni material is not pyrophoric unlike La or other rare earths based alloys used for metallic hydride synthesis. This fact increases the safety during material handling and hydride utilization.

Recently, some efforts have been done in order to explain the high activity of this hydride, and the effects of microstructure [14] and surface characteristics [15] have been studied.

The hydride formation process was proposed [10-14] but it will be necessary more studies to explain this phenomenon. For that reason, the objective of this work has been to study the hydrogenation process of Mg_2NiH_4 produced by HCS. The exothermic reaction between Mg and Ni was detected and the absorption process was studied. Moreover, the influence of some parameters, like holding time, absorption/desorption cycles and cooling rate, were considered. The study of these parameters is very interesting for the development of practical applications.

2. EXPERIMENTAL DETAILS

2.1. Safety Issues

It is well known that working with hydrogen and some hydrogen storing systems have safety concerns. These safety issues have been especially tackled during the study from two different points of view: from the view point of the processing route and from the point of view of the obtained material.

- Safety issues in the processing route: The used facility was designed and built according to the European hydrogen safety standard (ATEX Directive 94/9/EC). In addition the selected processing technology (Hydriding Combustion Synthesis) allows obtaining metallic hydrides using considerably lower synthesis hydrogen pressures. Thanks to the combustion front characteristics, the required hydrogen pressure to allow its diffusion into the metallic alloy is lower than the one used in its counterparts.
- The selected hydride has the following safety advantages compared to other metallic hydrides:
 - The selected material, Mg_2NiH_4 , is not pyrophoric in contrast to other conventional metallic hydrides $LaNi_5$ and, for that reason, its manufacturing, utilization and recycling is safer.
 - Low synthesis pressure: Absorption and desorption pressures of the selected metallic hydride are lower compared to other metallic hydrides: The formation of Mg_2NiH_4 takes place at pressures around 10 bar, in contrast to the 30 bar needed for $LaNi_5$ and

the 50 bar of FeTi. This reduction in pressure reduces importantly the risks in the processing and utilization steps: charge and discharge of the hydrides

Therefore, this work presents, not only the synthesis of an attractive metallic hydride by means of a novel technique, but also the minimization of the risks when working with hydrogen and thus increase safety of the product and of the manufacturing method.

2.2. Synthesis reactor

The experimental installation can be observed in figure 1. The reactor is a stainless steel cylinder with inside length of 175 mm and inner diameter of 130 mm. In the reactor vessel there is an oven with inner diameter of 25 mm. The system has two thermocouples. One of them is S type and is used to control the temperature of the oven. The other one is K type and is in contact with the sample.

The hydrogen pressure inside of the reactor was controlled with an electrovalve and a digital flowmeter. Moreover, with this equipment, it is possible to know the approximate amount of hydrogen absorbed by the material. When the material absorbs hydrogen, the valve maintains the pressure at a constant value and the flowmeter measures the amount of gas introduced into the reactor. This value of the hydrogen content is only a reference to compare different tests, in order to calculate the real amount of absorbed hydrogen, other analyses are needed.

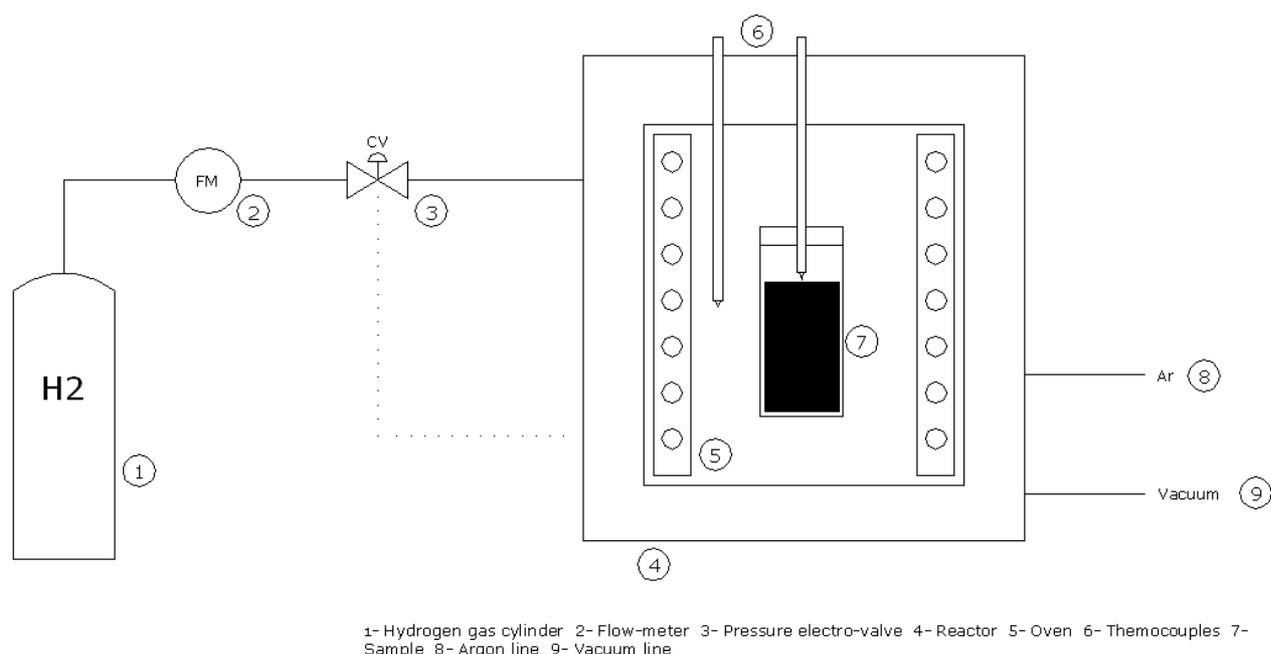


Figure 1. Schematic diagram of the experimental installation.

2.3. Sample preparation

Samples were prepared from commercially available magnesium and nickel powders. The magnesium powder was 99,9 wt% in purity and <100 μm in size and the nickel powder was 99,8 wt% in purity and <2-7 μm in size. Powders were weighed with a molar ratio of 2:1, and the mixing process was carried out in a shake mixer.

Green mixture was introduced into the reactor as loose powder. Before heating, the reactor was evacuated by means of a rotary pump. Then 0.2MPa of Argon were introduced into the vessel and the evacuation procedure was repeated three times in order to remove oxygen completely. After this evacuation process, a pressure of 1 MPa of hydrogen was introduced into the reactor.

The operating parameters of the thermal treatment were selected according to the bibliography [10-11] and preliminary tests. The sample was heated to 600 °C at a heating rate of 20 °C/s.

In table 1 are listed the synthesis conditions of tests performed during this study, due to the fact that not only the reaction mechanism of Mg_2NiH_4 was investigated, but also the effect of several parameters on the process.

- To study the formation of the intermetallic Mg_2Ni , a preliminary test under Argon atmosphere was carried out (test 1).
- In test 2, hydride formation was studied considering thermodynamic aspects.
- In tests 3, 4 and 5, different holding times were chosen in order to explain the effect of this parameter on the product phases and composition.
- Moreover, with the objective of studying the influence of the cooling process, in test 6, a controlled cooling rate of 0.083 °C/s was selected.
- The number of cycles affects the absorption/desorption process, so in test 7 several absorption/desorption cycles were carried out.

Table 1. Experimental conditions

Test N°	Gas (atmosphere)	Holding time (s)	Cooling process	Number of cycles
1	Ar	120	Free cooling	1
2	H ₂	3600	Free cooling	1
3	H ₂	120	Free cooling	1
4	H ₃	550	Free cooling	1
5	H ₂	1770	Free cooling	1
6	H ₂	3600	Controlled (0,083 °C/s)	1
7	H ₂	15	Free cooling	6

Phase analysis: X-ray diffraction (XRD) was conducted to analyse the crystallographic phases. A Siemens D500, working with a copper anode with a wavelength of 0.154 nanometers (monochromatic radiation) was used. This diffractometer can scan 2-theta angles from 10 degrees to 90 degrees, at 40 Kv and 30 mA. Steps were in increments of 0.1 degrees, and counts were collected for 4 seconds at each step.

Microstructure and semi-quantitative chemical composition were analysed using light microscopy and a Jeol JSM 5910 LV Scanning Electron Microscope (SEM) with associated Oxford Inca 300 energy dispersive spectroscopy probe (EDS).

In order to measure the hydrogen content in the products, the following method was used. Samples were heated up in an oven; hydrogen was released from the metallic hydride and this flow of hydrogen was mixed with a flow of oxygen. Both gases reacted to produce water. The amount of water can be measured with a detector and with this value it is possible to calculate hydrogen content.

3. RESULTS AND DISCUSSION

3.1. Hydride formation and holding time effect

As described in section 2.2, a preliminary test under argon atmosphere was carried out (test 1). The results show that with a cycle at 600°C for 120 s, the obtained material was pure Mg_2Ni . It seems that the exothermic reaction between Mg and Ni is fast and there is no necessary holding time to obtain the pure intermetallic.

Afterwards, a new test was carried out in order to study the formation of the metallic hydride Mg_2NiH_4 . According to table 1, test 2 was performed at 600°C for 1 hour (these parameters were selected according to literature [10-11]). Temperature was measured by means of a thermocouple in contact with the sample and in figure 2 it can be observed the thermogram of the process.

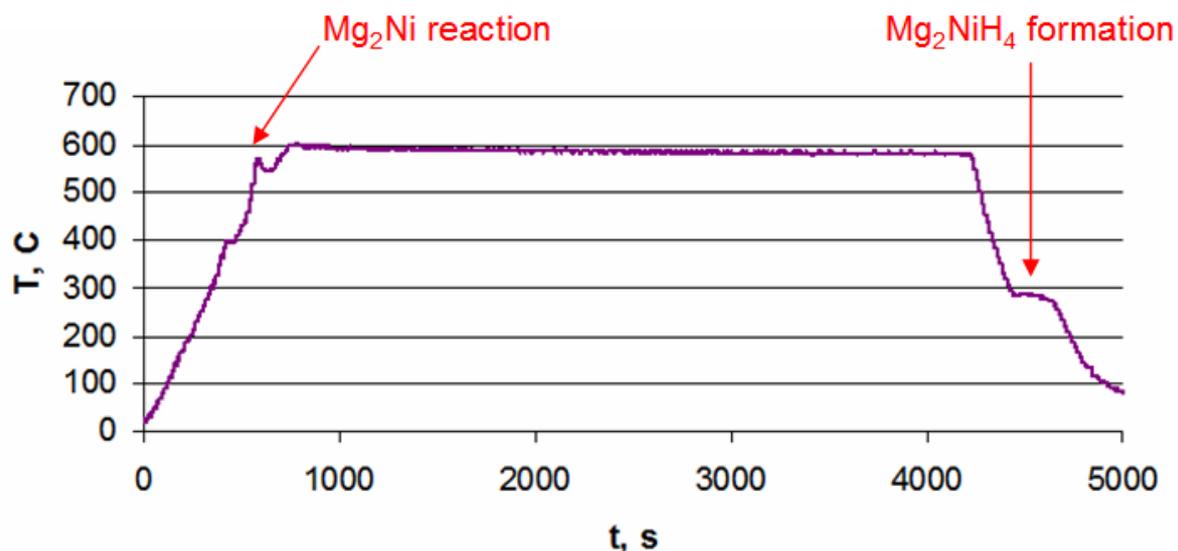


Figure 2. Thermogram of the Mg_2NiH_4 synthesis (free cooling)

During the heating process, it can be observed an exothermic peak. It corresponds with the reaction between Mg and Ni. Moreover, it is very interesting to observe a plateau (isothermal zone) during the cooling process. It is believed that this plateau is related to the hydride formation.

In the test under argon atmosphere (test 1) was demonstrated that is not necessary a long holding time to obtain the intermetallic Mg_2Ni . However, it is interesting to know if this period is necessary for the hydride formation. For that reason, three tests were performed with different holding times (tests 3, 4 and 5).

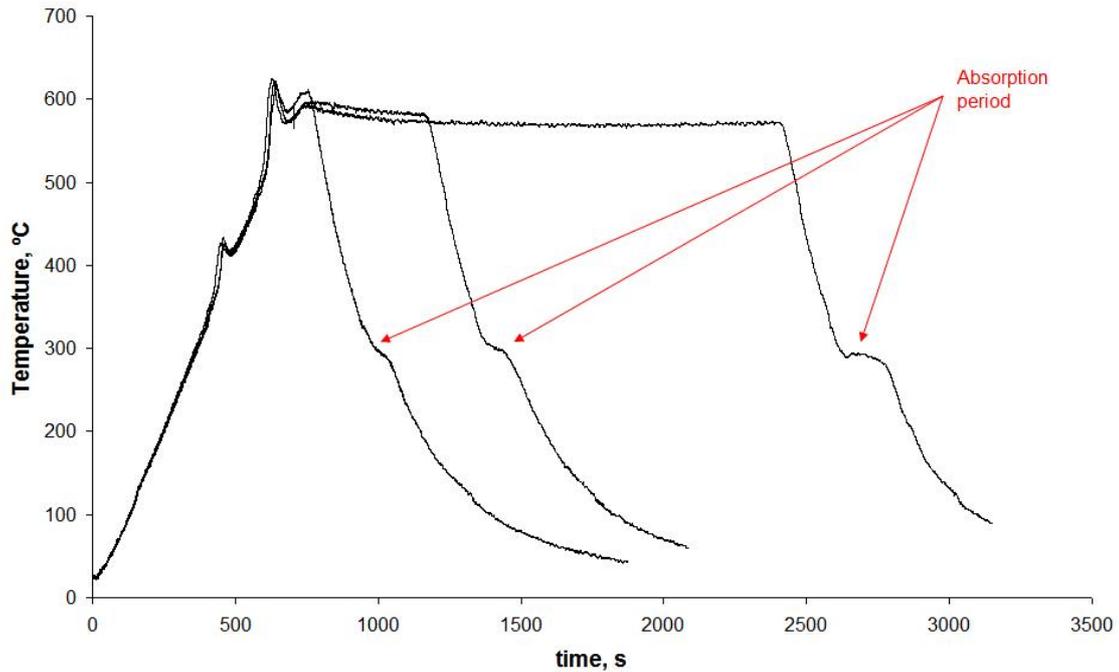


Figure 3. Effect of the holding time

Figure 3 presents the thermograms of the three tests with different holding times. In all of them, the reaction between Mg and Ni can be observed during the heating process. However, the plateau of the cooling process is different in each test. The longer the holding time is, the longer the isothermal stage is. As was described, it is believed that this plateau is related to the hydride formation, and the holding time affects the length of the plateau. However, to obtain more information is necessary to know the hydrogen content absorbed in each sample.

Hydrogen content was calculated by means of chemical analysis, as described in section 2.2. In table 2, results of this characterization are presented. The sample 3 (test 3) with a holding time of two minutes absorbs around 0,9 wt% of hydrogen., whereas with a holding time of 10 min, the hydrogen content is around 1,2 wt%. With the longer holding time (45 minutes), the hydrogen content reaches the 3wt%. The theoretical value for Mg_2NiH_4 is 3,6 %, therefore it seems that there are some impurities in the material.

Table 2. Hydrogen amount vs holding time

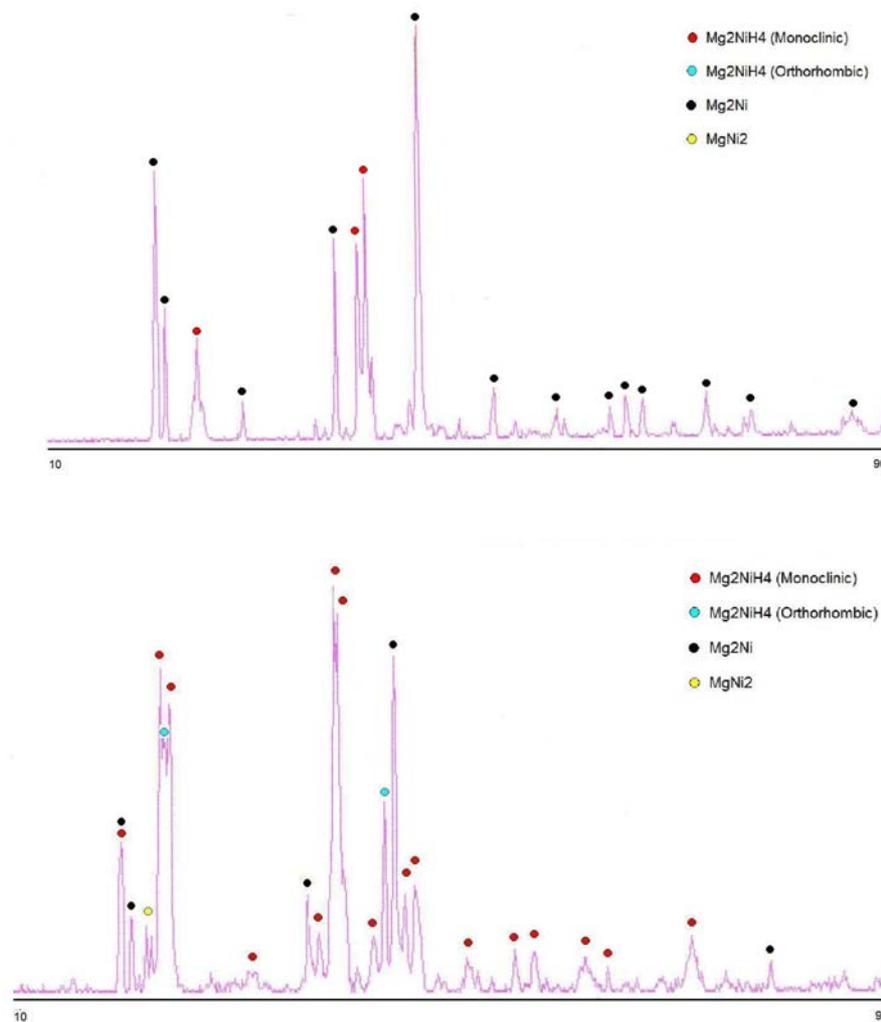
Test	Time	% of hydrogen
Short holding time	2 min	0,92
Medium holding time	10 min	1,18
Long holding time	45 min	3,01

As a consequence of the results, it can be concluded that:

- The longer the holding time is, the higher the hydrogen content absorbed in the material is.
- The longer the holding time is, the longer the plateau of the cooling process is.
- For that reason, it is believed that this plateau is related to hydrogen absorption and it could be a reference of the absorption of the material.

Additionally, in order to study the crystallographic phases of the products, XRD analysis was carried out. Figure 4 shows the XRD patterns of the three samples. Main results were:

- With short holding time (2 min), main phases are Mg_2NiH_4 and Mg_2Ni . However, main phase is Mg_2Ni and secondary phase is Mg_2NiH_4 .
- With medium holding time (10 min): main phases are both: Mg_2NiH_4 and Mg_2Ni .
- With long holding time, only Mg_2NiH_4 is obtained.



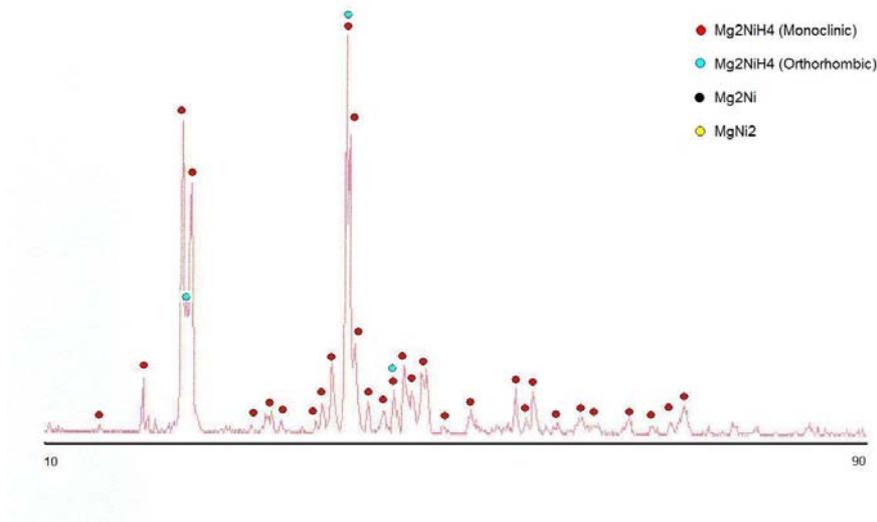


Figure 4. XRD patterns: short holding time (up), medium holding (medium) time and long holding time (down)

XRD patterns are in agreement with chemical analyses. With a short holding time, after the reaction, only the intermetallic Mg_2Ni compound is present, it is necessary to increase the holding time to obtain the hydride.

A deeper study is needed to explain the reaction mechanism in more detail. However, it seems that an increment of the holding time changes the structure of Mg_2Ni . This fact allows hydrogen absorption during the cooling process.

3.2. Effect of cooling rate

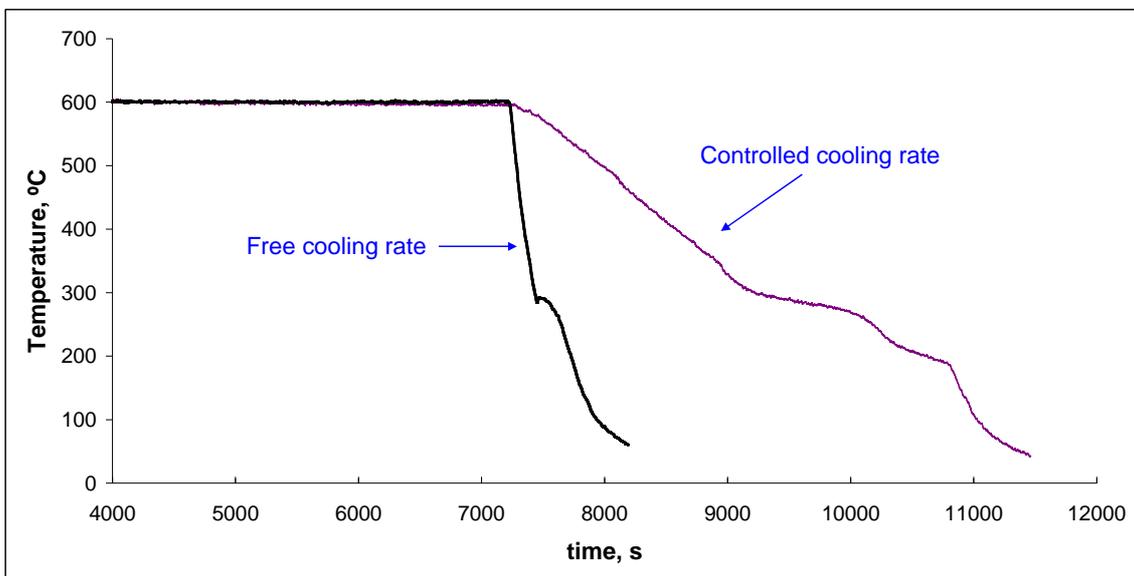


Figure 5. Thermogram of the Mg_2NiH_4 synthesis: controlled cooling (blue line) and free cooling (black line)

Figure 5 presents two cooling curves. In one of them, the cooling process was not controlled (corresponds to test 2), however, in the other curve (test 6) the cooling process was controlled and the cooling rate was maintained at a constant value (5°C/min).

In the previous section 3.2 it was reported that the isothermal stage during the cooling process was related to the formation of the hydride. In this case, it seems that the modification of the cooling rate affects the length and form of this plateau. The isothermal stage, in both samples, started at the same temperature (around 300°C). Nevertheless, in the controlled process, the plateau was longer and finished at lower temperature.

In preliminary analyses, it seems that cooling rate affects not only the purity of the product but also the distribution of the crystallographic phases (Mg_2NiH_4 presents two crystallographic phases: monoclinic and orthorhombic). However, a more complete study will be necessary in order to explain this phenomenon.

3.3. Effect of several absorption/desorption cycles

Other important parameter is the effect of the number of cycles in the absorption/desorption process.

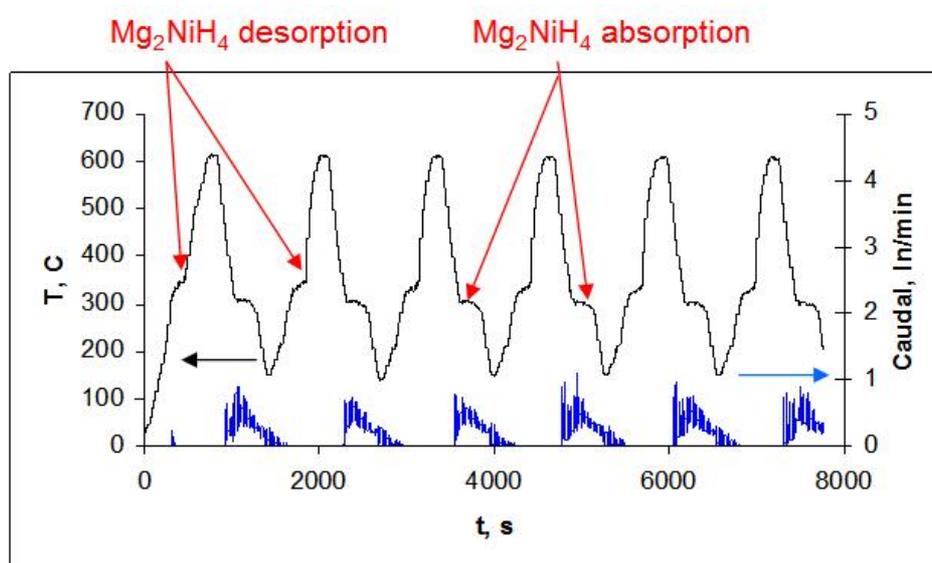
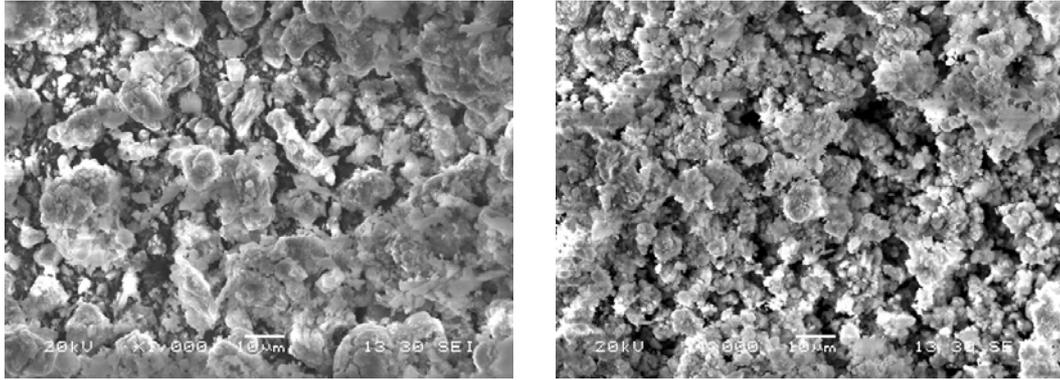


Figure 6. Several absorption cycles

In test 7, the material was introduced into the reactor and several absorption/desorption cycles were carried out. It is important to note that the starting material was Mg_2NiH_4 produced in a previous test (for that reason the material desorbs hydrogen in the first heating process).

Figure 6 presents the thermogram of the test. The black line is the temperature and the blue line is the flow of hydrogen absorbed by the material (measured by the flowmeter). The more significant is that the absorption and desorption temperatures can be observed. The absolute value is not totally correct (may be due to the position of the thermocouple), but it is possible to compare these temperatures for consecutive cycles. Absorption and desorption curves are very similar for all cycles and it is believed that there are not important changes in the hydrogenation process.

Figures 7.A and 7.B show scanning electron microscopy (SEM) images of Mg_2NiH_4 samples synthesized with one (A) and several absorption/desorption cycles (B). In both cases, the surfaces of the particles are smooth and for that reason it seems that there is a liquid phase in the combustion synthesis of this material.



A)

B)

Figure 7. A) Mg_2NiH_4 after one cycle

B) Mg_2NiH_4 after several cycles

It can be observed that after several cycles, particle size is smaller. Absorption/desorption processes can break the particles because; when hydrogen is released can generate fissures in the grains, leading to a particle size reduction.

4. CONCLUSIONS

Main conclusions of this work are:

- Studying the thermograms of the process and the characterization of the samples, it is believed that the formation of the intermetallic Mg_2Ni is produced during the heating process, by means of an exothermic reaction between Mg and Ni. However, the formation of the hydride takes place during the cooling process so that an isothermal stage (a plateau) can be observed.
- The effect of the holding time has been studied and the longer the holding time is, the higher the hydrogen content in the material is. It seems that the cooling process is necessary to deform the crystallographic structure of the intermetallic and to allow hydrogen absorption. XRD analysis shows that after a short holding time, only Mg_2Ni is obtained, however, with a holding time of more than 45 min, only Mg_2NiH_4 appears in the XRD pattern.
- The maximum hydrogen content obtained by chemical analysis was 3,01 wt%. The theoretical absorption capacity is around 3,6 wt%, so that it seems that some impurities remain in the material.
- As a consequence of the results, it seems that the cooling rate has an influence on the absorption process. Preliminary studies show that this parameter not only affects the purity of the product but also the distribution of the crystallographic phases of the hydride (monoclinic and orthorhombic).
- After several cycles, it is believed the absorption/desorption temperatures do not present important changes. However, a particle size reduction is produced. Absorption/desorption processes can generate fissures in particles and this is the likely reason for this phenomenon.
- As a main conclusion, it can be stated that the metallic hydrides developed in this work constitute a safe method of storing hydrogen as energy carrier.

5. REFERENCES

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