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NASA TECHNICAL MEMORANDUM

NASA TM-75723

USE OF REVERSIBLE HYDRIDES FOR HYDROGEN STORAGE

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Translation of "Utilisation d'hydrures
reversibles pour le stockage de l'hydrogene".
In: Seminar on Hydrogen as an Energy Vector:
Its Production, Use and Transportation.
Brussels, Belgium, October 3-4, 1978.
Proceedings. Luxembourg, Commission of the
European Communities, 1978, pp 392-406

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, DC 20546   DECEMBER 1980

1. Report No. NASA TM-75723	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle Use of Reversible Hydrides for Hydrogen Storage		**5. Report Date** December 1980
		6. Performing Organization Code
7. Author(s) B. Darriet, M. Pezat, and P. Hagenmuller		**8. Performing Organization Report No.**
		10. Work Unit No.
9. Performing Organization Name and Address .SCITRAN Box 5456 Santa Barbara, CA 93108		**11. Contract or Grant No.** NASW-3198
		13. Type of Report and Period Covered Translation
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		**14. Sponsoring Agency Code**

15. Supplementary Notes

16. Abstract

The addition of metals or alloys whose hydrides have a high dissociation pressure allows a considerable increase in the hydrogenation rate of magnesium. The influence of temperature and hydrogen pressure on the reaction rate have been carefully studied.

The first results concerning the hydriding of magnesium rich alloys such as Mg_2Ca, La_2Mg_{17} and $CeMg_{12}$ are presented.

The hydriding mechanism of La_2Mg_{17} and $CeMg_{12}$ alloys is given.

17. Key Words (Selected by Author(s))	18. Distribution Statement Unclassified - Unlimited		
19. Security Classif. (of this report) Unclassified	**20. Security Classif. (of this page)** Unclassified	**21. No. of Pages** 18	**22.**

USE OF REVERSIBLE HYDRIDES FOR HYDROGEN STORAGE*

B. Darriet, M. Pezat and P. Hagenmuller**

1. INTRODUCTION

For a long time it has been known that many metals react with hydrogen in order to form binary hydrides. Out of all the known binary hydrides, only magnesium hydride has the particular characteristics required for utilization. All of the other binary hydrides can be eliminated for various considerations, either because they are too expensive or they have the wrong characteristics for use as a hydrogen storage agent.

The absorption of hydrogen by intermetallic compounds results in the formation of ternary hydrides and this was studied in a less systematic way. The best known ternary hydrides and the most interesting ones are the following:
- $LaNi_5H_6$ and the derived phases   (1)
- $FeTiH_2$ and the derived phases   (2)

They are characterized by a small mass capacity. In addition, the high cost of $LaNi_5H_6$ and the slow formation rate of $FeTiH_2$ means that they are less interesting than Mg_2NiH_4, and especially more interesting than MgH_2.

This compound has attracted special attention because it has a very high mass capacity, a very low cost   and the magnesium is available in large quantities in nature.

The question which poses itself is to find and then select hydrides which are best suited for storing hydrogen. Various criteria have to be taken into consideration for this, and their importance varies depending on the use to which the hydrides are put.

In order of priority, we will consider the following essential characteristics:
- large hydrogen mass capacities,
- rapid hydride formation rate and high dissociation rate,
- moderate dissociation temperature,
- low storage pressure,
- reduced cost.   /394

Even though it is very difficult to simultaneously improve all of its properties, in practice, the goal to be reached is to optimize them as much as possible.

In this study we will consider magnesium and magnesium alloys with special consideration of two essential criteria, which are a high hydrogen mass capacity and a very low cost price.

In our first analysis, we were forced to improve the synthesis conditions for magnesium hydrides.

After this, we studied magnesium alloys in order to satisfy

in a more satisfactory way a large number of essential criteria for storing hydrogen. It should be realized that the studies on this latter point have only started. We believe that research in this area will result in alloys which can bring about better performance.

2. EXPERIMENTAL PROCEDURES

We used commercial products whose concentration varied between 97 and 99%, looking forward to industrial applications. The magnesium utilized is a 98% powder product.

The intermetallic compounds or alloys used are prepared in a laboratory.

a) Production of alloys

In the case of the alloys, which do not have elements with a high vapor pressure, the preparation is made by fusion in an arc furnace.

Fusion in a sealed molybdenum tube in an argon atmosphere is usually done with magnesium alloys.
- by fusion in an arc furnace:

After mixing the elements in appropriate proportions in a glove box in an argon atmosphere, pellets are made under 5 T/cm^2:

After fusion in the arc furnace in argon, the product is then possibly reheated.   /395
- by fusion in a sealed molybdenum tube:

The magnesium alloys cannot be prepared by the previous method because of the high vapor pressure of the magnesium.

The procedure is identical with the preceding one as far as the preparation of the melting mixtures is concerned. The procedure

3

only differs in the fusion locality, which is performed in a sealed molybdenum tube in an argon atmosphere. In all these cases, fusion is followed by reheating over several hours at a temperature which is suitable for each alloy.

b) Characterization

After each preparation is made, there is a radio-crystallographic check which is carried out in order to identify the phase or the phases which are present.

It is possible that a precise determination of the crystallographic parameters will be made by adding an internal standard in the sample.

c) Activation of alloys used as adjuvants

As we will see later on, certain alloys such as $LaNi_5$ for example, are mixed in the form of powder with magnesium in order to improve synthesis conditions of the latter.

The preparation of these alloys in an arc furnace in general, leads to a compact metallic block. In order to reduce this block to the powder state, it is necessary to carry out several absorption-desorption cycles of the hydrogen, which alloys the alloy to be made fragile and to obtain a very fine powder.

In the case of $LaNi_5$, this operation is carried out at ambient temperature under a pressure of 150 bars.

d) Determination of the absorption and desorption rates

The amounts of absorbed or desorbed hydrogen as a function of time are determined by a manometric method.

Table I shows the main characteristics of magnesium hydride.

TABLE I

molar mass	26.336
density at 25°C	1.45
mass capacity for H_2	7.65%
formation heat	-17.8 kcal/mole H_2
decomposition temperature at 1 atmosphere of H_2	287°C

Out of all the known binary hydrides, MgH_2 is the most promising because of its high mass capacity for hydrogen (7.65%) and its very low cost.

The essential factor which is not favorable for MgH_2 is the difficulty associated with its direct preparation by means of the action of hydrogen on magnesium.

For strong hydrogen pressures (on the order of 150 bar) and at a temperature close to 500°C, the reaction rate is still very slow.

Considering the properties of MgH_2, we found it interesting to improve its synthesis conditions. For this purpose, we added an adjuvant to the magnesium (metal or alloy) which easily reacts with hydrogen but whose hydrides are thermally less stable than MgH_2.

a) Mg adjuvant system

- Hydride formation

We successively examined the influence on the absorption rate of hydrogen by magnesium of each of the following parameters:

. the characteristics of the adjuvant
. the proportion of adjuvant
. the temperature
. the hydrogen pressure.

In all of these cases the amounts of hydrogen which were absorbed are expressed in percentages of hydrogen fixed by the magnesium.   This corresponds to the proportion of hydrized mag-   nesium with respect to the total mass of magnesium which can react.

Figure 1 shows the absorption of the hydrogen as a function of time for various mixtures (Mg-adjuvant) at 345°C at 30 bars for a weighted percentage of 80% of magnesium and 20% adjuvant.   It shows that in all cases, the addition of the adjuvant increases the hydride formation rate of the magnesium.   The system Mg-LaNi$_5$ seems to be the one with the highest performance.

One could believe that the presence of the adjuvant catalyzes the reaction by producing atomic hydrogen in situ which is much more reactive with respect to magnesium.

For the same structural type of adjuvant (that of LaNi$_5$), we wanted to see whether the relative stability and the stoichiometry of the corresponding hydride could influence the hydride formation rate of the magnesium.   The experimental results obtained for the various alloys such as LaCo$_5$, CeCo$_5$, LaNi$_5$ and SmNi$_5$ show that they have a behavior which is comparable, no matter what the corresponding hydride characteristics are.   The hydride formation rates are or even slightly less than in the case of SmNi$_5$, which gives the least stable hydride and the hydride with the smallest hydrogen concentration.

Considering the relatively high cost of these various adjuvants, we considered a system in which one uses the

6

mixed metal $Ni_5(MNi_5)$ as an adjuvant. The results obtained show
that the action of MNi_5 on the hydride formation rate is similar.
The amount of stored hydrogen is of the same order of magnitude as
that which is fixed by $LaNi_5$. Thus, it follows that the performances
which were obtained with an alloy such as $LaNi_5$ are essentially
the same if one uses MNi_5, but the use of the latter is more advan-
tageous because it has a cost   which is substantially below that
of $LaNi_5$.

For 345°C and for 30 bars, Figure 2 gives the result for
various proportions of $LaNi_5$ in the mixture $Mg-LaNi_5$.

The amount of absorbed hydrogen increases with the amount of
$LaNi_5$. Also the increase in the percentage of adjuvant brings
about a reduction in the theoretical mass capacity, as shown by
Table II.

TABLE II

% $LaNi_5$ in the mixture	theoretical mass capa-city at 25°C	% H_2 fixed at the end of 1 hour	experimental mass capacity at the end of 1 hour
20	6.4	87.2	5.62
10	7.0	69.1	4.89

From the economic point of view, and considering these results,
only the costs   of the various mixtures will allow the select-
ion of the most interesting proportion.

The curves given in Figure 3 show that the hydride formation
rate of the magnesium increases with temperature. For a given time,
this increase varies in a linear fashion as a function of temperature.

The increase in the hydrogen pressure influences primarily the
hydride formation rate at the beginning of the reaction (Figure 4).
At the end of one hour, the influence of this factor seems to be

negligible for pressures between 10 and 60 bar.

- Desorption:

The curves of dissociation of MgH_2 (Figure 5) show that the desorption rate at 2 bars depends strongly on temperature. By judiciously selecting this parameter, one can desorb the same amount of hydrogen for a time which varies at a ratio of between 1 to 10.

- pressure-composition isotherms:

Because of the improvement in the synthesis condition MgH_2, smaller pressures and lower temperatures, it is possible to draw pressure-composition isotherms for temperatures between 280°C and 360°C. The results obtained in Figure 6 show a hysteresis phenomenon.

b) <u>Magnesium alloys</u>

We wanted to keep a large mass capacity and, therefore, decided to find alloys which are rich in magnesium and which could react with hydrogen, and whose hydrides would be easier to dissociate than magnesium hydrides. /399

- Mg_2Ca

In the system Mg-Ca, the only defined component found is Mg_2Ca. The theoretical mass capacity of the hydride Mg_2CaH_6 which can be formed is 6.3%.

Mg_2Ca is prepared by fusion in an argon atmosphere in a sealed molybdenum tube. The stoichiometric mixture in the proportions of the two Mg atoms and one atom of Ca is heated to 700°C for about 15 hours. This thermal treatment is followed by a reheating at

600°C for two days.

The curves of Figure 7 show that the hydride formation rate of Mg_2Ca is relatively slow. At 400°C under 50 bars, the percentage of fixed hydrogen is 46% at the end of 40 hours of reaction.

By adding $LaNi_5$ to Mg_2Ca (90% Mg_2Ca - 10% $LaNi_5$), this increases substantially the reaction rate but does not result in a high performance of the system (62% of fixed hydrogen at the end of 40 hours).
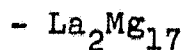
- La_2Mg_{17}

The structure of La_2Mg_{17} derived directly from that of $LaNi_5$ by replacement of a lanthanum atom by two magnesium atoms. The structure of $LaNi_5$ is a host structure for the hydrogen, and we, therefore, believe that La_2Mg_{17} could be of interest for storing hydrogen.

The alloy La_2Mg_{17} is obtained by fusion of a mixture at appropriate proportions of the different constituents. The preparation is prepared in a sealed molybdenum crucible in a dry argon atmosphere and is deoxygenized. After heating to 700°C for one hour, the alloy is reheated for 10 hours at 500°C. Either the alloys are used directly in the form of metallic blocks, or are reduced to the powder state which could possibly be in tablet form.

The high magnesium content of this alloy allows one to predict a high theoretical mass capacity: 5.5% for the formula $La_2Mg_{17}H_{40}$.

The first results show that at 350°C and at a pressure of 30 bars, the percentage of absorbed hydrogen is on the order of 100% at the end of 10 hours. In addition, the hydride formation rate /400 is very rapid: 75% of absorbed hydrogen at the end of five minutes.

A more detailed study shows that in the study temperature and pressure range, the action of hydrogen on La_2Mg_{17} occurs in two stages:

- in the first cycle, the hydride formation results in irreversible decomposition of the alloy and formation of hydrides corresponding to each of the elements:

$$La_2Mg_{17} \quad + \quad 20H_2 \quad \rightarrow \quad 2LaH_3 \quad + \quad 17MgH_2$$

- starting at the second cycle, the reaction is carried out in a reversible manner according to the following reaction diagram:

$$2LaH_3 \quad + \quad 17MgH_2 \underset{2}{\overset{1}{\rightleftarrows}} 2LaH_{2.5} \quad + \quad 17Mg \quad + \quad \frac{35}{2}H_2.$$
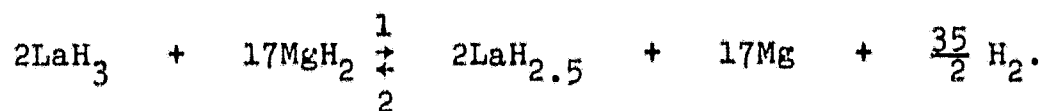
Desorption has characteristics which are very close to those observed for the Mg-adjuvant mixture.

- $CeMg_{12}$

Just like the compound La_2Mg_{17}, the compound $CeMg_{12}$ is derived from a structure of the type $LaNi_5$ by replacement of an atom of Ce by two magnesium atoms.

The procedure for preparing the $CeMg_{12}$ is similar to that for La_2Mg_{17}.

The first results obtained with $CeMg_{12}$ show that they are comparable with those for La_2Mg_{17}.

The hydride formation mechanism occurs in two stages as for the La_2Mg_{17}.

We compared the behavior of a mixture with the proportions (Ce + 12Mg) to the behavior of the alloy $CeMg_{12}$.

10

Figure 9 shows how interesting the $CeMg_{12}$ is for the mixture (Ce + 12Mg). In the two cases, we can see the catalytic role which is played by the cerium. We can explain the higher hydride formation rate of the Mg by not using $CeMg_{12}$ due to the fact that hydride formation results in a more homogeneous distribution of the various elements and in a much finer particle formation.   /401

From these first results which are very encouraging, we will carry out a systematic study of this compound as a function of various parameters (pressure, temperature, etc.) which could influence the condition for preparation and utilization of this hydride.

4. CONCLUSIONS

The results obtained show that the hydride formation rate of magnesium is considerably improved by the presence of another metal or alloy which forms a hydride which is thermodynamically less stable than the MgH_2.

We made a detailed study of the influences of the various parameters on the synthesis conditions and on the hydride formation rate of magnesium for various Mg-adjuvant systems. The study of each of these parameters allowed us to show that the system $Mg-LaNi_5$ has the highest performance, and we were able to formulate the optimum utilization conditions.

From an economic point of view, it seems to be of interest to substitute the mischmetal Ni_5 for the $LaNi_5$ in the systems.

We became interested in magnesium alloys which were rich in magnesium for which encouraging results were obtained.

The study of La_2Mg_{17} which was carried out shows that the compound has characteristics which would be of interest for storing hydrogen. The results obtained allowed us to show that the first

11

hydride formation leads to the formation of a hydride mixture
(LaH_3 + MgH_2).

Starting with the second cycle, the system is reversible and has characteristics which are of interest for storing hydrogen.

In the case of $CeMg_{12}$ we were able to show that the performances obtained with this compound were greater than those obtained with the mixture Ce + 12 Mg.

At the present time we are carrying out a study about alloys of the same family as La_2Mg_{17} and $CeMg_{12}$ in order to increase the number of reversible hydrides which could be used for storing hydrogen. /402

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(3) J. J. REILLY and R. H. WISWALL, Jr., Inorg. Chem., 7 (11) 2254, 1968.
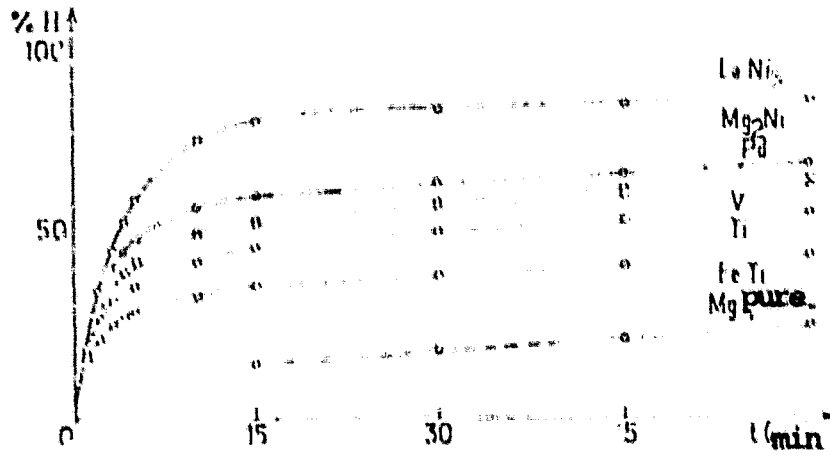
Figure 1.   Hydride formation at 345°C and at a pressure of
30 bars of various magnesium-adjuvant mixtures
(20% mass)
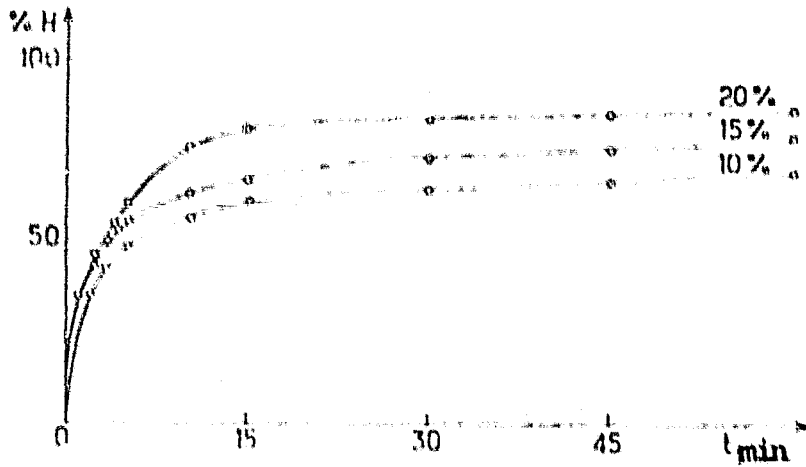
Figure 2.   Hydride formation at 345°C and at a pressure of
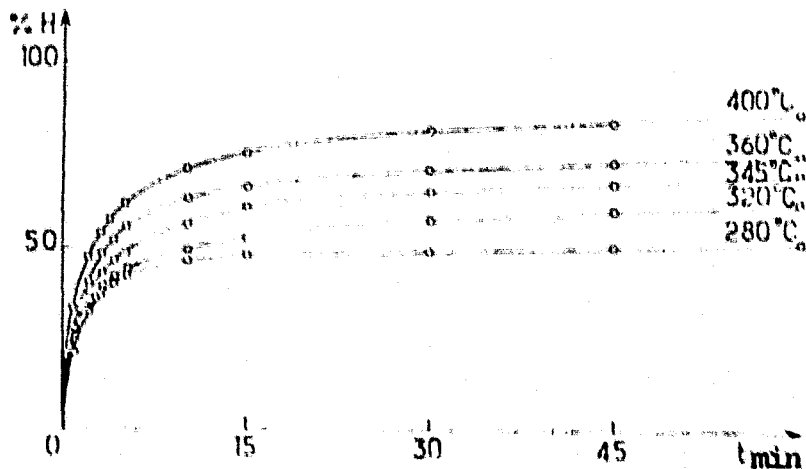30 bars of the mixtures (Mg + LaNi$_5$) for various
proportions of LaNi$_5$

Figure 3.   Hydride formation at a pressure of 30 bars of the
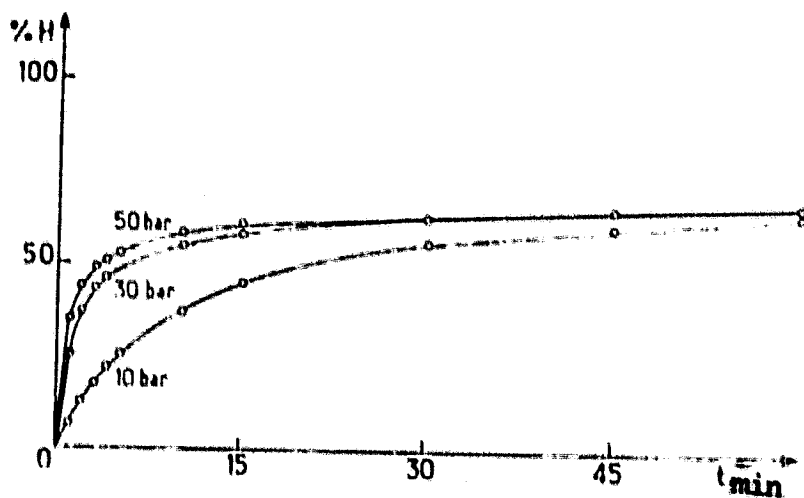mixture (Mg + LaNi$_5$) (10%) at various temperatures

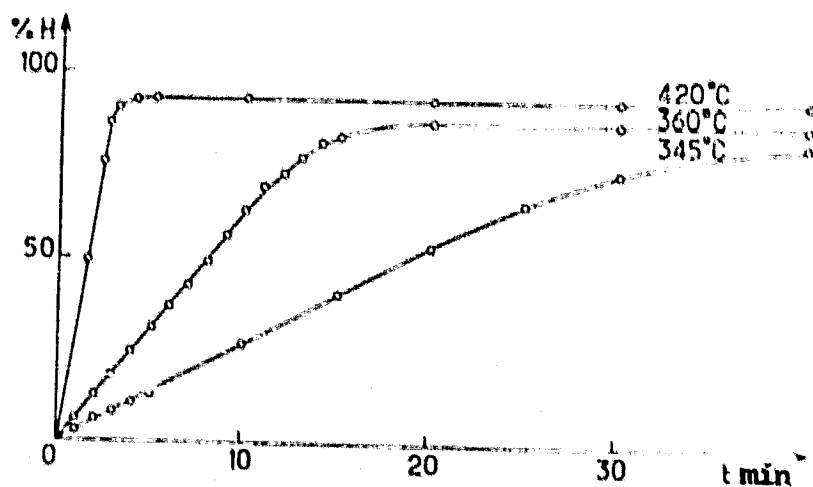Figure 4. Hydride formation at 345°C of the mixture (Mg + LaNi$_5$) (10%) at various hydrogen pressures

Figure 5. Decomposition at various temperatures and at a pressure of two bars of the hydride form from the initial mixture (Mg-LaNi$_5$) (10%).

14
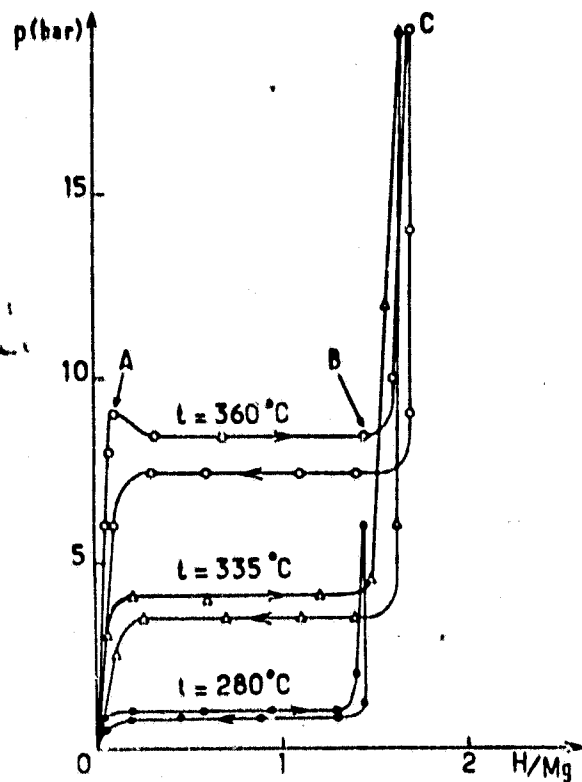
Figure 6.   Pressure-composition isotherms of the system
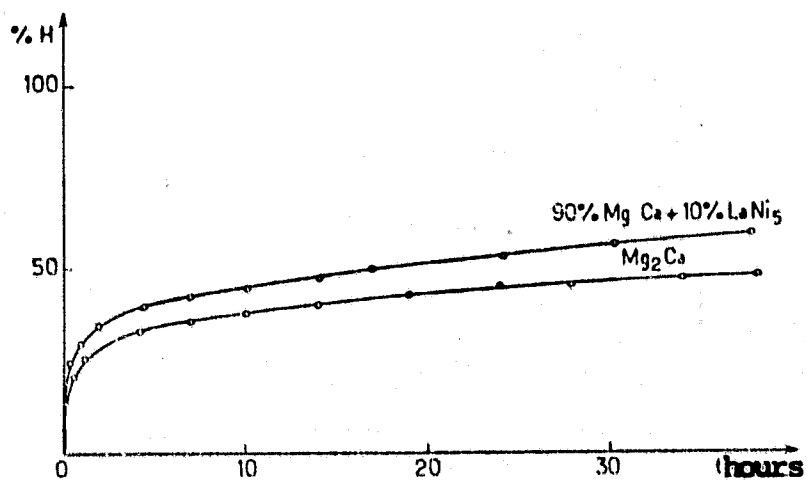 $(Mg + LaNi_5) - H_2$

Figure 7.   Hydride formation at 400°C and at p_{H_2} = 50 bar
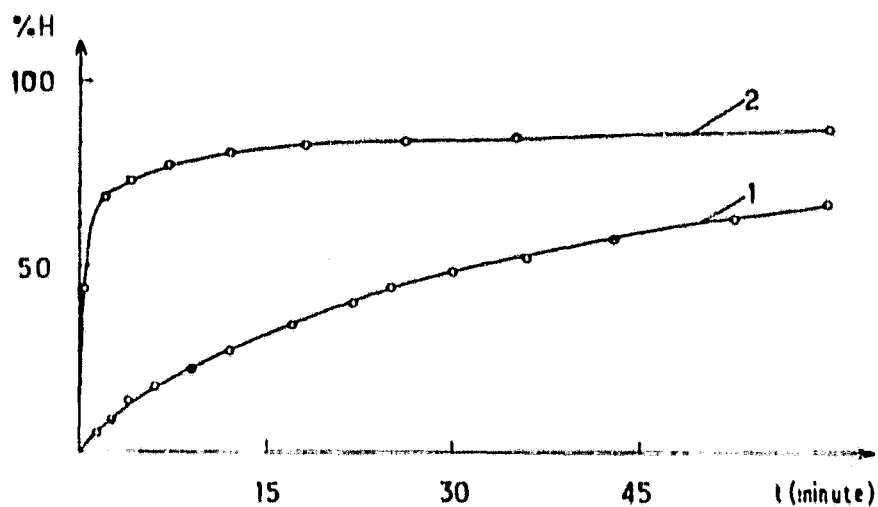   of Mg_2Ca and of 90% Mg_2Ca + 10% $LaNi_5$
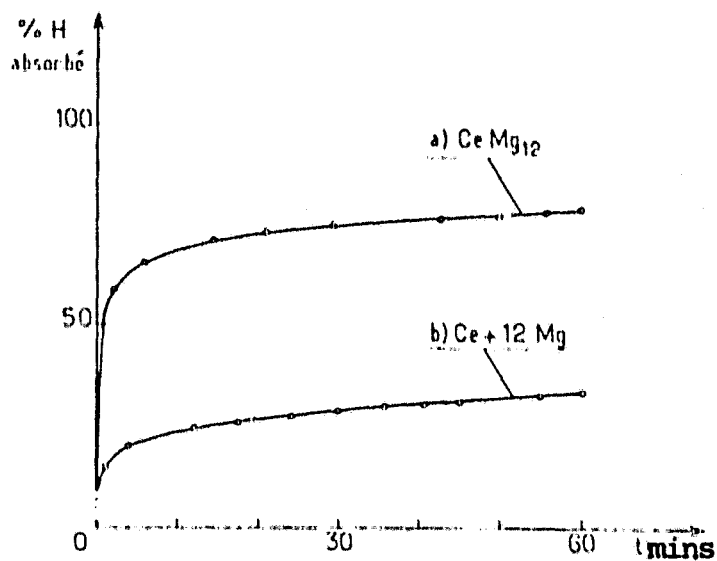
Figure 8.   Hydride formation of La_2Mg_{17} at 325°C at a pressure of 30 bars

Figure 9.   Hydride formation at 325°C and at p_{H_2} = 30 bar
a) of $CeMg_{12}$ (second cycle)
b) of a mixture of Ce + 12 Mg

16