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STORING HYDROGEN IN THE FORM OF LIGHT ALLOY HYDRIDES

E. Freund and C. Gillerm

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16. Abstract

Different hydrides are investigated to find a system with a sufficiently high storage density (at least 3%). The formation of hydrides with light alloys is examined. Reaction kinetics for hydride formation were defined and applied to the systems Mg-Al-H, Mg-Al-Cu-H, Ti-Al-H, Ti-Al-Cu-H, and Ti-Al-Ni-H. Results indicate that the addition of Al destabilizes MgH2 and TiH2 hydrides while having only a limited effect on the storage density.

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ABSTRACT

The initial purpose was to find a system with a sufficiently high storage density (at least 3%) and which is unstable (PH_2 about 1 bar below 100°C). To accomplish this, the formation of hydrides with light alloys was investigated. The formation of hydrides from an alloy is defined and applied to the systems examined: Mg-Al-H, Mg-Al-Cu-H, Ti-Al-H, Ti-Al-Cu-H and Ti-Al-Ni-H. Results showed that the addition of aluminum destabilizes MgH_2 and TiH_2 hydrides while having only a limited effect on the storage density. The only hydride formed for magnesium alloys is MgH_2. Mixed hydrides are obtained from titanium-aluminum alloys. The reaction kinetics for hydride formation or decomposition are slow, especially with magnesium alloys.

TABLE OF CONTENTS

STORING HYDROGEN IN THE FORM OF LIGHT ALLOY HYDRIDES

E. Freund, C. Gillerm

A) INTRODUCTION /3*

The original purpose of the research program was essentially one of application: perfecting a method of storing hydrogen in conjunction with the hydrogen cell developed at the I.F.P. and capable of being used on light weight vehicles.

Accordingly, a basic condition is that the fuel cell + hydrogen equipment be approximately equal to currently used power equipment (gasoline powered engine + tank). Considering the higher energy efficiency of the fuel cell, the amount of hydrogen needed for storage is about 5 kg (50% instead of 20% for the gasoline powered engine). The characteristics of the tank must fit the following criteria (for this amount of hydrogen):

- volume of about 100 liters (40 liters for a gasoline tank),
- total weight of about 100 kg (about 50 kg for the gasoline tank).

The effectiveness of currently conceivable means of storage is subject to limitations:

- Light weight materials (reinforced resins) must be used to manufacture containers holding the compressed hydrogen solution, making it possible to achieve a holding capacity of 4-5% by weight (100 kg tank), at a minimum pressure of 500 bars (tank volume: 120 liters). At the present time, such containers are very costly and present safety problems;

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*Numbers in the margin indicate pagination in the foreign text.

- liquid hydrogen, obviously of great interest with respect to its mass, can amount to large volumes (about 100 liters). It is not a permanent method of storage and is costly on the basis of energy considerations (the energy consumed in the liquefaction process being approximately equal to 30% of the potential chemical energy of hydrogen);

- chemical storage presents advantages for storage density and compactness. In the case of the catalytic conversion of methanol to water vapor, 5 kg of hydrogen can be obtained from 40 kg of a mixture /4 of $CH_3OH + H_2O$ out of a volume of 50 liters: the energy production is fairly high due to the low heat of reaction (5 kcal/H_2 gram-molecule). This type of storage is not reversible and it requires extensive auxiliary equipment (decomposition reactor and hydrogen separator). This method has been conditionally adopted for electric generators using the I.F.P. cell;

- reversible type MH_x metallic hydrides, where M is a metal or metallic alloy. Without reviewing the different groups of hydrides and the ways in which they are classified, it can be said that while the known compounds are generally compact (volume of about 30 to 50 liters), the storage density is, nevertheless, low (1 to 1.5% by weight) This is the case, at least, for unstable hydrides (dissociation pressure is about one bar at ordinary temperatures), which require the use of prohibitively heavy storage vessels (350 to 500 kg). Other groups of hydrides, especially magnesium hydrides or hydrides of magnesium based alloys $(Mg_2Ni, MG_2 Cu)_1$ have a sufficient storage density (7.6% for MgH_2), but their thermodynamic stability is too great for the intended use (the normal decomposition pressure is more then 300°C and the enthalpy of the decomposition process is high, with the result that the excess heat from the cell cannot be used*).

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*The I.F.P. cell operates at a temperature of 80°C.

Storage in the form of hydrides is, thus, of interest only if a storage density equal to or greater than 3% is obtained for an unstable hydride (PH_2 congruent to 1 bar below 100°C). Considering that the H/M ratio is less than 2% for most alloys (usually close to 1%), the mean atomic mass of the alloy must be at least equal to 50. Applications are, therefore, limited to the use of light metals and to their alloyages with transition metals in the first line on the periodic table (the remaining metals can occur in the alloys only as minor constituents). /5

These requirements led us to investigate the following alloys:

- magnesium alloys with aluminum and transition metals,
- titanium alloys with the preceding metals.

The present report gives the preliminary* results concerning the reactivity of these alloys to hydrogen.

B) EXECUTION OF THE INVESTIGATION /6

Three phases were planned in the research program:

- exploratory investigation consisting of, first, the preparation and treatment of the alloys and, second, the formation of hydrides from the alloy,

- physico-chemical characterization of formed hydrides, changes in alloys following a cycle of hydride formation - decomposition.

The following methods were taken into consideration: structure using X diffraction, morphological investigation (scanning microscope),

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* A request was made in November 1977 to renew financial assistance for the same subject; the present report should be considered as an interim report.

pressurized thermogravimetry;

- testing hydrides in a vessel seemed to be of interest.

As emphasis was placed on the exploratory aspect of the investigation, the third study was not conducted*.

The development of research efforts is detailed in appendix I. We shall examine successively: 1) the experimental methods used and the experimental process itself (technical details are provided in the appendix), 2) the theoretical criteria used to select the systems under consideration.

1) EXPERIMENTAL TECHNIQUES AND CONDUCTING THE EXPERIMENTS

a) Preparation of Alloys

Several techniques were originally considered: melting in a refractory pot in an induction furnace (equipment available in the laboratory), casting in a plasma furnace on cooled melting pot. Finally, only the technique** of melting in the induction furnace with levitation was adopted.

This technique presents the following advantages: /7

- extremely reduced pollution;
- homogeneous alloys which do not require melting;
- few problems of volatility or of obtaining the desired stoichiometry,
- obtaining hardened alloys.

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*Until now, vessel testing has been limited to a few well-known hydrides (MgH_2, ***MG_2NiH_4, $FeTiH_{1.5}$, $LaNi_5H_6$).

**Developed by the Centre d'Etudes de Chimie Métallurgique de Vitry (Metallurgical Chemistry Research Center of Vitry).

***Illegible in translator's copy of original text.

Most alloys were prepared by the Centre d'Etudes de Chimie Métallurgique with which there has been a Research Agreement since 1976 (i.e. before the present research program started).

Annealing treatments in inert air (helium) or embrittlement treatments in hydrogen were subject to limitations because of the considerable pollution caused (melting pots, air), especially in the case of titanium based alloys.

b) Formation of Alloys

Alloys were broken apart under controlled atmospheric conditions (glove box). Three cases may be distinguished:

- brittle intermetallic compounds (example: Mg_2Ni). Standard grinding techniques are suitable;
- soft metals (example: magnesium, magnesium-aluminum solids). They are broken apart by turnings;
- metals which are both hard and unbrittle (example: titanium, titanium-aluminum solids). In this case, a general solution to the problem of grinding was not found. As a result, some of these alloys were studied without breaking them apart, negative results (lack of hydrogen absorption) must, therefore, be interpreted cautiously.

c) Hydrogenation of Alloys /8

Hydrogenation was performed in an agitated autoclave making it possible to reach 650°C under 150 bars (see equipment description in appendix II). All hydrides studied in detail were subjected to several cycles of formation: decomposition, heating to 450-550°C for 10 h, under 140 bars; slow cooling until reaching air temperature under 100 bars; decomposition of any hydride which may have been formed at 400-600°C under 1 bar; hydrogenation at lowest possible temperature. A computer program makes it possible to follow the H/M ratio of the sample through various operations.

This set-up proved to be inadequate to investigate hydrides which are stable, but not very reactive. For reasons of kinetics, it is necessary to operate above 300°C, at least for the first activation. The dissociation pressure must, therefore, be greater than the maximum pressure which can be obtained in the equipment (if PH_2 is approximately equal to 1 bar at 100°C, PH_2 is approximately equal to 1,000 bars at 400°C). A high pressure autoclave (2,000 bars at 600°C) is currently being set up (see appendix II for detailed description). High pressures have been used in other laboratories for the hydrogenation of alloys with little reactivity (for example, references (8) and (12), Appendix IV).

d) Physico-Chemical Characterization of Alloys and Hydrides

Raw alloys were identified by means of X diffraction; only monophasic alloys or basic mixtures were subjected to hydrogenation. The hydrides formed were examined before and after decomposition of the hydride, in order to bring to light any possible irreversible changes in the raw alloy. For unstable hydrides (FeTI or $LaNi_5$ type), Lindeman tubes filled inside a glove box were used.

Various samples were systematically examined under a scanning microscope (study of texture) and under a Castaing microprobe to determine the composition and distribution of the various phases and to identify any possible segregations. /9

Use of a pressurized thermogravimetry was planned during the design stage of the research program in order to investigate the thermodynamic properties and kinetics of formed products (especially absorption isotherms, formation and decomposition kinetics). The pressurized thermobalance installed at the beginning of the contract was never operational and was returned to the manufacturer in May 1978. The study of isotherms was, therefore, performed by volumetry, using hydrogenation equipment; its use was restricted to a limited number of hydrides. Only desorption curves were generally determined. This method is not very accurate, especially for metals with little reactivity (case of magnesium or aluminum magnesium alloys). The decomposition kinetics can also be approximated by volumetry.

e) Investigation of Catalytic Properties

The reactivity of hydrides can be easily approximated by measuring their hydrogenating properties. Preliminary tests of hydrogenation in the liquid phase were performed; the tests adopted were for the hydrogenation of benzene and cyclohexene.

2) SELECTING THE SYSTEMS TO BE INVESTIGATED

The conditions described in the introduction led to the adoption of MM'_x type alloys, where M is a light element forming a stable hydride and M' is a metal (or an alloy) of low atomic mass, which does not form hydrides or which forms unstable hydrides.

For metal M., the study was focussed on magnesium and titanium, /10 although other metals are of considerable interest (especially lithium, sodium, calcium*). The first series of transition metals may be considered for M': Cr, Mn, Fe, Co, Ni, Cu), which are already being employed in ternary hydrides, such as TiM' or REM'_5 (RE: rare earth); another metal of prime interest is aluminum, the AlH_3 hydride of which can be formed only by indirect means and is unstable ($PH_2 = 10^5$ bars at 20°C (1)).

At the present time, there are no well developed theoretical guides making it possible to determine 1) if a hydride will form from a given alloy; 2) what the stability of a formed hydride will be. We were, nevertheless, able to base our research on a few rules borrowed from Van Mal (2) and from Pous and Lutz (3):

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*With the exception of calcium, these metals are discarded on the basis of the following considerations. Calcium is less interesting than magnesium with regard to mass.

- thermodynamic criterion: the hydride formed from an intermetallic compound decreases in stability as the intermetallic compound itself increases in stability (2). This rule is applicable only to alloys belonging to one group (for example RE $(M', M'')_5$, M', M'', which are metals belonging to group VII);

- electronic criterion: the nature and stability of the hydride in an intermetallic compound may be related to the mean number of electrons (ne) contributing to the metal-metal bond in the raw alloy (3). If ne is less than 2, an ionic type hydride is obtained. When ne is greater than 5.5 - 6, the presence of hydrogen in the tetrahedral sites of the network is not compatible with the metal nature of the structure. For unstable hydrides (FeTi, $LaNi_5$), ne is equal to approximately 5 - 5.5.

Wh[illegible] is less than or equal to ne and ne is less than 5, hydrides of intermediate stability are obtained (Mg_2Ni: ne is approximately /11
3.33). This criterion has been systematically used to select systems and compounds within a system (the values are not the same as those proposed in (3));

- structural criteria: for each type of structure, there is a range in which the crystalline parameters must be found in order to form a hydride of appropriate stability. The latter criterion is often applicable, especially for most binary intermetallic compounds.

From the preceding criteria, we may deduce, for example:

- that the addition of aluminum will destabilize magnesium hydrides, because aluminum is both more compact and has a higher number than magnesium;
- that in the Mg-Al-Cu and Mg-Al-Ni systems, the ternaries which have a high aluminum + transition metal content must lead to unstable hydrides. In figure 1, we have shown the region of the Mg-Al-Ni ternary in which ne is greater than or equal to 4;

- that in the Ti-Al system, two effects are contradictory (compactness increases, but does not decrease);

- that it must be possible to obtain hydrides of intermediate stability in the Ti-Al-Ni system.

Before presenting the analysis of results, it should be pointed out that appendix IV provides a recent bibliography on hydrides of light metals.

C) ANALYSIS AND INTERPRETATION OF RESULTS /12

We shall examine successively: the preliminary tests of known systems, the study of alloys and magnesium or titanium based hydrides.

PRELIMINARY TESTS

They were conducted on pure metals: vanadium, titanium, magnesium and $LaNi_5$, Ti-Ni, Mg_2Ni and Mg_2Cu alloys. A more thorough study was conducted on magnesium and its alloyage with nickel and copper.

a) Miscellaneous Testing

The initiation and kinetics of hydrogenation are rapid only for vanadium (98%) and the alloy $LaNi_5$ (99.5%), as the latter reacts at 60°C. The very pure titanium used* reacts under 50 bars only at temperatures exceeding 500°C, because the reaction is very rapid once it initiates. For less pure titanium, the reaction starts at 300°C. Impurities, therefore, seem to have a prime influence on reaction kinetics. For the Ti-NiH system, we have checked that the ternary hydride Ti_2NiH is obtained only at low temperatures; at 300°C, TiH_2 is formed.

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* Sample prepared by CECM of Vitry.

b) Magnesium Hydride

Even though this hydride has been studied with regard to both thermodynamics (1) and kinetics (appendix IV, references (1) (2)), the available data are relatively contradictory, especially with regard to formation kinetics: the maximum hydrogenation rate obtained by direct synthesis and the deactivation process.

Formation kinetics was studied between 350 and 450°C under high /13
pressure (P = 120 bars). The reaction is slow, the hydrogenation time is still 8 h at 450°C. The maximum rate of hydrogenation depends on the granulometry of the sample, as rates exceeding 90% could be reached only with particles with diameters of less than 100 microns. If we begin with massive samples (for example, wire with a diameter of 1 mm), the reaction stops at very slow development rates. This behavior may be interpreted well according to the mechanism proposed by Stander (Appendix IV, reference (1)): there are diffusion limitations following an initial phase consisting of a superficial reaction. The kinetics law proposed by Stander, consisting of an instantaneous germination and a two dimensional growth of seeds, seems to be confirmed by the appearance of hydrides under the scanning microscope (figure 2 and 3): the initial turnings (diameter of 30 to 100 microns) are transformed into a stack of then plates a few microns thick. Similar morpholgies were observed for $LaNi_5H_6$.

We tried to obtain isotherms between 300 and 450° by reacting in desorption. According to (4), the isotherms present well defined pressure levels practically extending from Mg to MgH_2, at least until reaching 500°C. An example of a desorption isotherm curve is given in figure 4.

There was no indication of a pressure plateau. It was observed experimentally that the decomposition reaction which was rapid at first when the pressure of system P is very different from the dissociation pressure of hydride Pe slows down when P approached Pe.

According to pressure measurements as a function of time; the pause at equilibrium requires a reaction time of more than 24 h, for each experimental point. A thermogravimetric investigation, therefore, seems to be preferable. This problem, related to the low reactivity /14 of magnesium hydride, should occur for other hydrides (investigated below). Accordingly, the shape of the experimental isotherm curves is not necessarily characteristic of the thermodynamics of hydride desorption.

During loading-unloading cycles, the maximum absorption capacity increases, as the complete conversion of magnesium into a hydride is obtained in 3 or 4 cycles. Deactivations observed in a few cases could be due to the presence of impurities (oxygen, water). The final hydride is only moderately broken apart (fine X diffraction rays); the initial morphology of the sample is partially preserved (see microphotographies in figures 5 and 6).

c) Mg-Cu-H and Mg-Ni-H Systems

First, for the Mg-Cu system, the results of Reilly and Wiswall for Mg_2Cu (5) are confirmed. Hydrogenation is somewhat easier for pure magnesium and the reaction is complete even with an unbroken up sample, it corresponds correctly to the overall stoechiometer.

$$2Mg_2Cu + 3H_2 \longrightarrow 3\ MgH_2 + MgCu_2$$

The initial alloy Mg_2Cu disappears completely. The preceding reaction, however, does not seem to be perfectly reversible; Mg_2Cu is not formed again stoechimetrically by decomposition of the MgH_2 + $MgCu_2$ mixture. In this system, the second intermetallic compound $MgCu_2$ of structure C_{15}, with parameter a = 7.02 - 7.05 Å necessarily leads to an unstable hydride. The negative results obtained by Reilly and Wiswall under low pressure (30 bars, 300°C), therefore, do not exclude the existence of a hydride. The reaction can be brought to light only at high pressures, while the low reactivity of the Mg-Cu system results in sufficiently high activation temperatures.

For the Ng Mg-Ni-H system, we have examined in detail the constituents ranging from Mg to $MgNi_2$. For the compound Mg_2Ni, the raw alloy is practically monophasic, with less than 3% $MgNi_2$. The reaction initiates at 200°C. The diffraction spectrum of this compound is discussed in appendix V; the diagram cannot be established from the structural data proposed by Reilly and Wiswall. The reaction is reversible between 200 and 500°C. However, the raw alloy Mg_2Ni varies throughout successive loading-unloading cycles: the X diffraction rays become enlarged (decrease in the size of crystallites or appearance of flaws) and the crystalline parameters increase. The compound $MgNi_2$, of structure C_{36} with $a = 4.815$ Å, $c = 15,80$ Å and $ne = 4.9$ should lead to an unstable hydride, such as $MgCu_2$. There was no visible reaction between 100 and 500°C, under 140 bars, possibly due to kinetics, as was the case previously.

2) INVESTIGATION OF SYSTEMS: Mg-Al-M'-H (M' = Cu or Ni)

A) Mg-Al-H System

The phase diagram (figure 7) brings to light a solid solution saturated at ambient temperature for 1.5% aluminum, a solid solution γ of structure A12 theoretically corresponding to $Mg_{17}Al_{12}$ and based on compound Mg_3Al_2, and a solid solution β practically corresponding to Mg_2Al_3. A fourth phase would appear only below 390°C, for 43% magnesium. The entire range of 0-70% aluminum composition was explored. Three phases δ, γ and β were obtained pure, the other phases β and γ were obtained for various compositions.

Phase ε, of unknown structure, was probably combined with the solid solution γ which has a low magnesium content. Solid solutions β are poorly crystallized (enlargement of X diffraction rays). /16

The overall results for the hydrogenation of these alloys are summarized in Table II. Generally speaking, the addition of aluminum lowers the hydrogen storage, from 7.6% for MgH_2 to about 1.8% for Mg_2Al_3 under our experimental conditions. Reactions observed during hydrogenation are complex.

Beginning with phase $\gamma(Mg_3Al_2)$ MgH_2 is formed and phase β diminishes progressively, because the magnesium content and phase γ have not reacted. The reaction may, therefore, be expressed:

$$3Mg_3Al_2(\gamma) + 5H_2 \longrightarrow 5MgH_2 + 2Mg_2Al_3\ (\beta)$$

which should correspond to a hydrogen content of 2.46% by weight for a complete reaction. This value is virtually reached for this composition; only a small quantity of phase γ is visible after reaction. For compound $Mg_{17}Al_{12}$, there is a similar reaction:

$$Mg_{17}Al_{12}\ (\gamma) + 9H_2 \longrightarrow 9MgH_2 + 4Mg_2Al_3\ (\beta)$$

giving a theoretical content of 2.29%. The experimental content is slightly higher, which should correspond to the formation of a phase β with a high aluminum content ($Mg_{0.35}Al_{0.05}$ instead of $Mg_{0.4}Al_{0.6}$), or a partial hydrogenation of Mg_2Al_3. The desorption isotherm obtained at 480°C for $Mg_3Al_2H_{3.6}$ (figure 8) does not present a pressure plateau. The mean decomposition pressure is higher than for magnesium hydride, even though there was no ternary hydride formation. The absence of pressure plateaus may be partially due to kinetics as the reaction speeds are comparable to those observed for pure magnesium. Actually, the hydride formation reaction from phase * is more complex than that /17 observed for Mg_2Cu. In the latter case, the reaction $2Mg_2Cu + 3H_2 \longrightarrow 3MgH_2 + MgCu_2$ involves only defined compounds, whereas we have here:

$$\text{solution } \gamma + H_2 \longrightarrow MgH_2 + \text{solution } \beta,$$

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* Illegible in translator's copy of original French text.

The composition of solutions γ and β are variable, resulting in a variation in free reaction energy (by gram-molecules of hydrogen) as the reaction progresses and, consequently, a variation in the dissociation pressure along an isotherm. The hydride formation reaction seems reversible; after decomposition (400°C, $PH_2 = 1$ bar), a new phase γ is obtained. The decompositon of magnesium hydride is complete only at temperatures exceeding 350°C.

With phase β ($\sim Mg_2Al_3$), we should have the reaction:

$$Mg_2Al_3 + 2H_2 \longrightarrow 2MgH_2 + 3Al$$

this stoechiometry corresponds to a fairly interesting content of 2.9% by weight. The lower experimental value (1.77%) indicates an incomplete reaction in which a mixture of magnesium hydride, aluminum hydride and phase β with low magnesium content ($Mg_{0.37}Al_{0.63}$ instead of $Mg_{0.4}Al_{0.6}$) is obtained. The reaction is reversible, at least within the temperature range explored (350-450°C). The desorption isotherms obtained between 350 and 400°C do not represent a well defined pressure plateau (figure 9). We may see a considerable destabilization relative to pure magnesium ($((PH_2Al_3Hx/(PH_2)$ MgH_2 is congruent to 3 to 4 at a given temperature; this corresponds, for a given pressure, to an increase of at least 60-80°C for the decomposition temperature). The absence of a pressure plateau is probably related to factors of kinetics as the reaction of hydride formation involves only well defined compounds and solid solution β, the composition of which can vary only within a very narrow range.

Alloys of compounds with higher aluminum contents than phase β are diphasic (Al + phase β) and we may observe the exclusive formation of MgH_2 with decomposition of phase β. . The reactivity of this /18
type of alloy decreases as the aluminum content increases.

b) Mg-Al-Cu-H System

The Mg-Al-Cu system is not very well known. Among the ternary compounds described in this system, we were able to detect 3 ternary compounds Mg_4Al_6Cu, MgAlCu and Mg_2Al_5Cu. Two other stoechimetries published: $Mg_6Al_7Cu_3$ and $MgAl_2Cu$ result in mixtures of MgAlCu and two unknown ternaries (or binaries). Only the alloy with the highest magnesium content (Mg_4Al_6Cu) hydrogenates (130 bars, 430°C) with formation of MgH_2, free aluminum and an unknown ternary ($MgAl_2Cu$?). Heat treatment in hydrogen provokes a change in other alloys, but without noticeable absorption (table II). These alloys seem to be of little interest: low storage, poor reactivity, highly complex reactions. Several new phases were brought to light. Indexation of their diffraction diagram would require a much more detailed study of the diagram of phase Mg-Al-Cu.

c) Mg-Al-Ni-H System

The Mg-Al-Ni ternary diagram is not known in detail. High aluminum contents should lead to unstable hydrides. With the melting technique used, it was not possible to prepare homogeneous ternary alloys, even though several methods were attempted (combining magnesium with alloys Ni-Al: difficult because of the high melting points of alloys Ni-Al; combining aluminum with binaries Ni-Mg: difficult because of the highly exothermic characteristic of the reaction). Other techniques will be used (progressive addition of nickel to alloy Mg-Al).

3) INVESTIGATION OF SYSTEMS: Ti-Al-M'-H (M' = Cu or Ni) /19

a) Ti-Al-H System

A simplified phase diagram of the Ti-Al system is provided in figure 10. The range corresponding to phase α is actually complex; two phases α_1, α_2 appear (see appendix IV, reference (14)). For the temperatures taken into consideration in this study, it is possible to distinguish 3 ranges:

- α type solid solutions of hexagonal structure, the parameters decrease as the aluminum content increases. The composition of these solutions includes pure titanium for a composition close to Ti_2Al ($Ti_{0.635}Al_{0.365}$).

- γ type solid solutions of centered face tetragonal structure (Cu Au type). For the compound TiAl the parameters are a = 3.99 Å, b = 4.07 Å and they meet the conditions required for the formation of hydrides. The composition of these solutions actually includes TiAl ($Ti_{0.51}Al_{0.49}$) to $Ti_{0.42}Al_{0.58}$ (similar to Ti_2Al_3).

- $TiAl_3$ compound (solid solution of definite composition) in the form of a tetragonal structure (DO_{22}) with a = 5.4.3.5 Å, c = 8.591 Å. A stable hydride does not have to be formed for this compound.

We have examined the ranges corresponding to solid solutions $\alpha(Ti_xAl\ x<2)$, $\gamma(TiAl_x \cdot 1 \leq x \leq 1.38)$, as well as the compound $TiAl_3$. Part of the results is summarized in table 3. It should be pointed out that some of these alloys were examined without being broken apart.

For compound Ti_3Al (phase α), if we assume that there is a formation of titanium hydride, we should have:

$$Ti_3Al + 3H_2 \longrightarrow 3TiH_2 + Al$$

which is a stoechimetry corresponding to 3.4% hydrogen. The content observed is lower and remains constant after reaction of phase , which has not reacted (composition of this residual phase: Ti_2Al /20 according to the value of crystalline parameters). A poorly crystallized titanium is formed, but there is no detection of aluminum. We may, therefore, conclude that a hydride with a high titanium content is formed. The characterization of this system currently being established.

For the compound Ti_2Al (phase α), the formation of a titanium hydride could be represented by equation:

$$Ti_2Al + 2H_2 \longrightarrow 2TiH_2 + Al$$

which gives a theoretical hydrogen content of 3.6%. This value is almost reached (3.2%), but aluminum is not detected when X diffraction is used. The spectrum obtained after hydrogenation is remarkable in that the titanium hydride obtained results in extremely enlarged diffraction rays corresponding to a very small mean crystallite dimension (about 50 Å) (figure 11). For this composition, it is also possible to form a ternary hydride, but use of X diffraction is not conclusive. The investigation of desorption isotherms is currently being conducted. Synthesis of the hydride will also be tested at moderate temperatures (100-200°C instead of 400-450°C).

Phase γ could not be obtained in pure form ($\alpha + \gamma$ or $\gamma + TiAl_3$ mixtures). The combinations obtained were examined without breaking them apart. No reaction was obtained. Any hydride formed is unstable. The reaction:

$$TiAl + H_2 \longrightarrow TiH_2 + Al$$

is not expected to lead to well defined pressure plateaus because of the stoechimetry of phase γ ; the hydrogen content should remain sufficient (2.6%).

Finally, compound $TiAl_3$ does not produce any reaction. The reaction $TiAl_3 + H_2 \longrightarrow TiH_2 + 3Al$ would not be of interest /21 on the basis of mass considerations (1.6 by weight) if it was produced.

b) <u>Ti-Al-Cu-H System</u>

The Ti-Al-Cu ternary diagram is not known and has not been ex-

explored from the theoretical point of view. We have studied systems TiAlCu and $TiAl_2Cu_2$, presented as ternary compounds in publications. The system TiAlCu actually constitutes a ternary compound, which does not hydrogenate. The second system leads to a mixture of $Ti(Al, Cu)_2$, titanium and a third unidentified phase (ternary?). This mixture does not react either. Exploration of this system has not been renewed.

c) Ti-Al-Ni-H System

We have used the theoretical diagrams proposed by Spencer (6) and Ansara (7) (see figure 12). These diagrams bring to light several ternary compounds: $TiAl_2Ni$, $TiAlNi_2$.

Exploration of this system is still very incomplete. One remarkable characteristic of the ternary alloys Ti-Ni-Al obtained in the region of high titanium concentration is that they are insufficiently crystallized (considerable enlargement of diffraction rays) after hydrogenation, because the hydrides obtained are TiH_2 and mixed hydrides Ti-Ni-H (especially $TiNiH_{0.5}$). Figure 13 gives an example of the diffraction spectrum (raw alloy $Ti_{0.6}Al_{0.1}Ni_{0.3}$). In the region of high nickel or aluminum contents (Al + Ni is at being at least equal 22 Ti), no reaction was visible. The TiAlNi system actually corresponds to a mixture of phase ($TiAlNi_2$ + $TiAl_3$ (?) + ?).

This system is currently being explored to investigate pseudobinaries TiNi - Ti_2Al and Ti_2Ni-TiAl.

CONCLUSION

/22

Two alloy groups were studied: magnesium alloys and particularly titanium alloys. Results show that the addition of aluminum to basic metals, such as magnesium and titanium seems to have an interesting effect:

- it destabilizes hydrides in the case of magnesium. This may be interpreted by the formation of compounds or stable magnesium-aluminum solids (producing unstable hydrides), by the decrease in intermetallic differences and by the increase in the electric density ne;

- it should lead to the formation of mixed hydrides in the case of titanium. These hydrides should not be nearly as stable at TiH_2, because of the decrease in intermetallic differences. According to Rudman et al. (appendix IV, reference (14), unstable hydrides can be obtained from the Ti_3Al system;

- it decreases the storage density, but because of the low atomic mass of aluminum, the residual storage is still considerable in some cases (between 2.5 and 3.5% by weight).

On the other hand, it generally does not improve reaction kinetics; the reactivity of magnesium-aluminum alloys remains comparable to that of pure magnesium. The high temperatures required to activiate the alloys is not conducive to the formation of ternary hydrides. These temperatures even make it impossible to obtain unstable hydrides (the dissociation pressure is higher at these temperatures than the maximum obtainable pressure in the plant). The investigation of such systems will, therefore, be resumed using extreme conditions of hydrogenation (very high pressure permitting unstable hydrides to be formed at temperatures of 200-250°C). 12

Several ternary systems have also been explored: magnesium, aluminum, copper or nickel, copper or nickel titanium aluminum. Systems using copper do not seem to have interesting effects: poor reactivity, low storage density, no formation of mixed hydrides. The addition of nickel, which produces interesting effects in the case of the binaries Mg-Ni and Ti-Ni (formation of reactive hydrides, destabilization), has still not produced new compounds in ternary systems: M-Al-Ni. A more systematic and extensive investigation of these systems is necessary. Before such an investigation is initiated, an approximate phase diagram for raw alloys should at least be established.

The practical target which we have originally set has, therefore, not been reached at this stage of the research program. An exploratory investigation must continue within the ranges we have now precisely defined: Mg-Al and Ti-Al binaries, for high aluminum contents; Mg-Al-Ni and Ti-Al-Ni ternaries. Another system also seems to be interesting: Ti-Mg-Al in regions of high aluminum contents.

In the remainder of the program which was defined in the petition to renew research assistance for the same subject, the range of obtainable experimental conditions will be extended by using a very high pressure autoclave and a pressurized thermobalance set-up on the model perfected at the laboratory for reactivity of Solids at the University of Dijon (Mr. Gerard). It is, thus, hopeful that all hydrides which can be formed will be found (including those found in the systems already explored: case of $MgNi_2$, $MgCu_2$, etc.). /24 The thermodynamic properties will also be accurately studied together with the kinetics of variations occurring in the products obtained.

Another aspect of the program will be to improve the characteristics of the kinetics of the formed products. Even though the basic problem is concerned with thermodynamics, this aspect should not be left out, particularly since the systems under consideration (light alloys containing aluminum) will basically have insufficient reactivity. An attractive and relatively general solution was suggested by the team of Professor Hagunmuller (appendix IV, reference (4)). In order to perfect an optimal procedure requiring the use of a minimum catalytic content, it seemed interesting to study the hydrogenating properties of a certain number of hydrides, together with the variations of these properties as a function of various treatments. Variations through successive loading-unloading cycles will effect the rate of hydrogenation, the final composition of the metal alloy and the various impurities occurring in the initial phase or resulting from the gaseous phase. Accordingly, a limited number of products will be tested for hydrogenating reactions (hydrogenation of ethylene or benzene in the gaseous phase; hydrogenation of cyclohexene or benzene in the liquid phase). Some hydrides ($LaNi_5H_6$, $FiTiH_{1.5}$), moreover, seem to have interesting catalytic effects.

The second important consequence of this research is that, indirectly, it resulted in the perfection of a new method to store hydrogen without using hydrides. A French patent is being applied for. The characteristics of this method of storage are:

- temporary storage (storage on a light weight vehicle for one week without hydrogen losses);
- weight of hydrogen tank: adsorbing alone 15 to 25 kg, tank and equipment 10 to 15 kg per kg of hydrogen. For the typical tank described in the introduction (5 kg hydrogen), we should be able to obtain a storage density of 4%;

- tank volume 30 to 50l/kg.

This type of storage would, therefore, be considerably less compact than for existing hydrides, but more efficient on the basis of mass considerations (with the exception of magnesium hydrides).

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TABLE I

Mg-Al-H SYSTEM SUMMARY OF RESULTS

ALLOY	X STRUCTURE	H/M	% WT	X STRUCTURE AFTER HYDROGENATION
$MgAl_{0,05}$		1,45	5,03	MgH_2
$MgAl_{0,1}$		1.30	4.33	MgH_2
Mg_3Al_2	γ	0,61	2,26	$MgH_2 + \beta$ + -phase γ -a- Mg
$Mg_{17}Al_{12}$	γ	0,65	2,40	id.
Mg_2Al_3	β	0,48	1,77	MgH_2 + Al + β

TABLE II

Mg-Al-Cu-H SYSTEM

ALLOY	X STRUCTURE	H/M	% WT	X STRUCTURE IN H_2
Mg_4Al_6Cu	$Mg_{32}(AlCu)_{49}$*	0.4	1.3	MgH_2, $Mg_{32}(AlCu)_{49}$* Al + -b-
MgAlCu	MgAlCu	0	0	MgAlCu + Mg_2Al_6Cu5
Mg_2Al6Cu_5	$Mg_2Al_6Cu_5$ + -c- $MgCu_2$	0	0	$Mg_2Al_5Cu_5$ + $MgCu_2$ + Al_2Cu + -b-
$MgAl_2Cu$	MgAlCu + 2 phases ?	0	0	?
$Mg_6Al_7Cu_3$	MgAlCu + 2 phases ?	0	0	?

Key: a-Low content in Mg; b-Ternary;
*Phase described in ASTM record.

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TABLE III

Ti-Al-H SYSTEM

ALLOY	X STRUCTURE	H/M	% WT	X STRUCTURE IN H_2
Ti_3Al	α	1.31	2.2	$TiH_2 + \alpha$
Ti_2Al	α	0.95	2.3	TiH_2 (t.m. cryst) + α
$TiAl_3$ -b-	Ti_9Al_{23} ($\sim TiAl_3$) + TiAl	0	0	-a-

Key: a-No change; b-(massive)

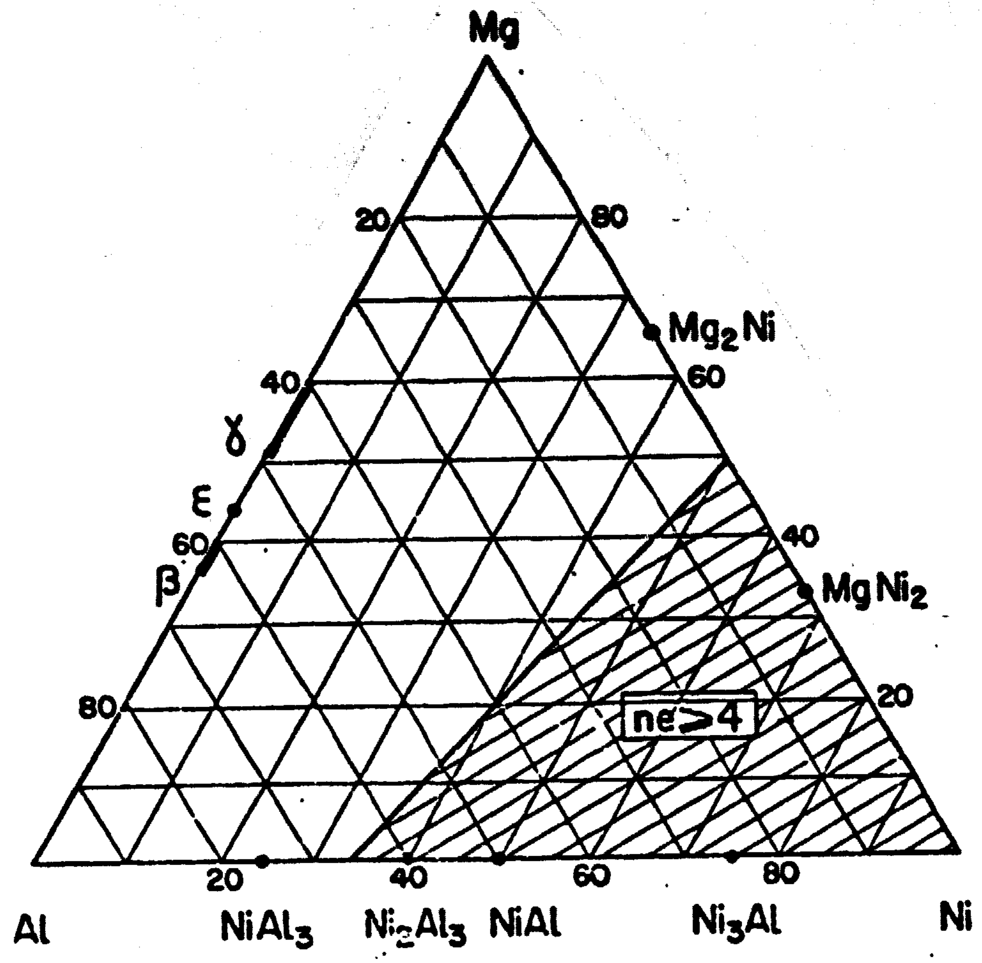

Fig.1

Range of Mg-Al-Ni ternary diagram in which ne is equal to at least 4 (composition: atomic %)

Figure 2: Magnesium hydride obtained from turnings of 100 microns. First hydrogenation. General view 1 mm = 10 microns.

Figure 3: Details of preceding sample. 1 mm = 1 micron.

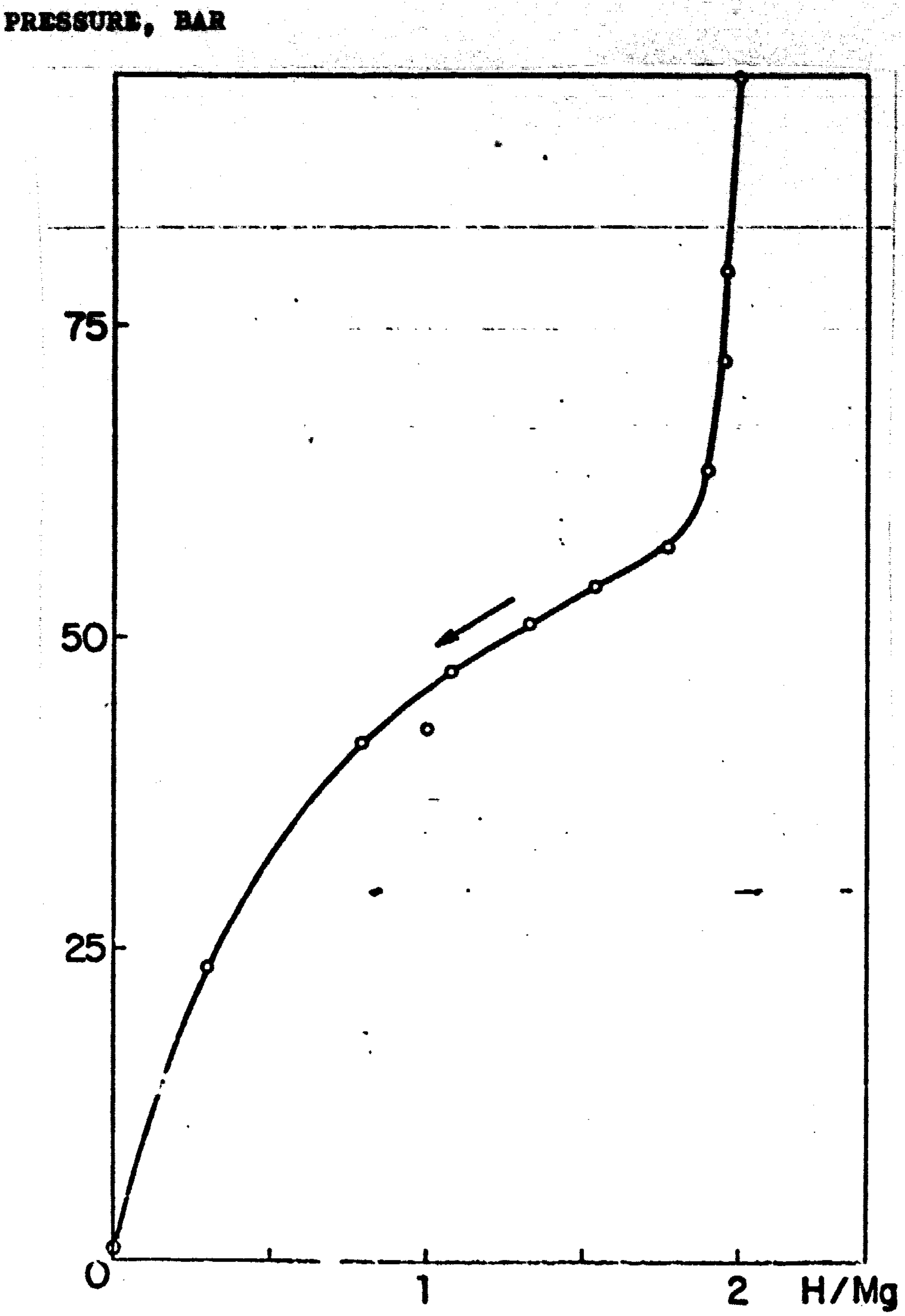

Fig. 4

Desorption curve of magnesium hydride at 490°C.

Figure 5: Magnesium hydride obtained from turnings of 100 microns (specimen of figure 3). 4 hydrogenation + decomposition cycles. General view, 1 mm = 10 microns.

Figure 6: Preceding sample, details - 1 mm = 2 microns.

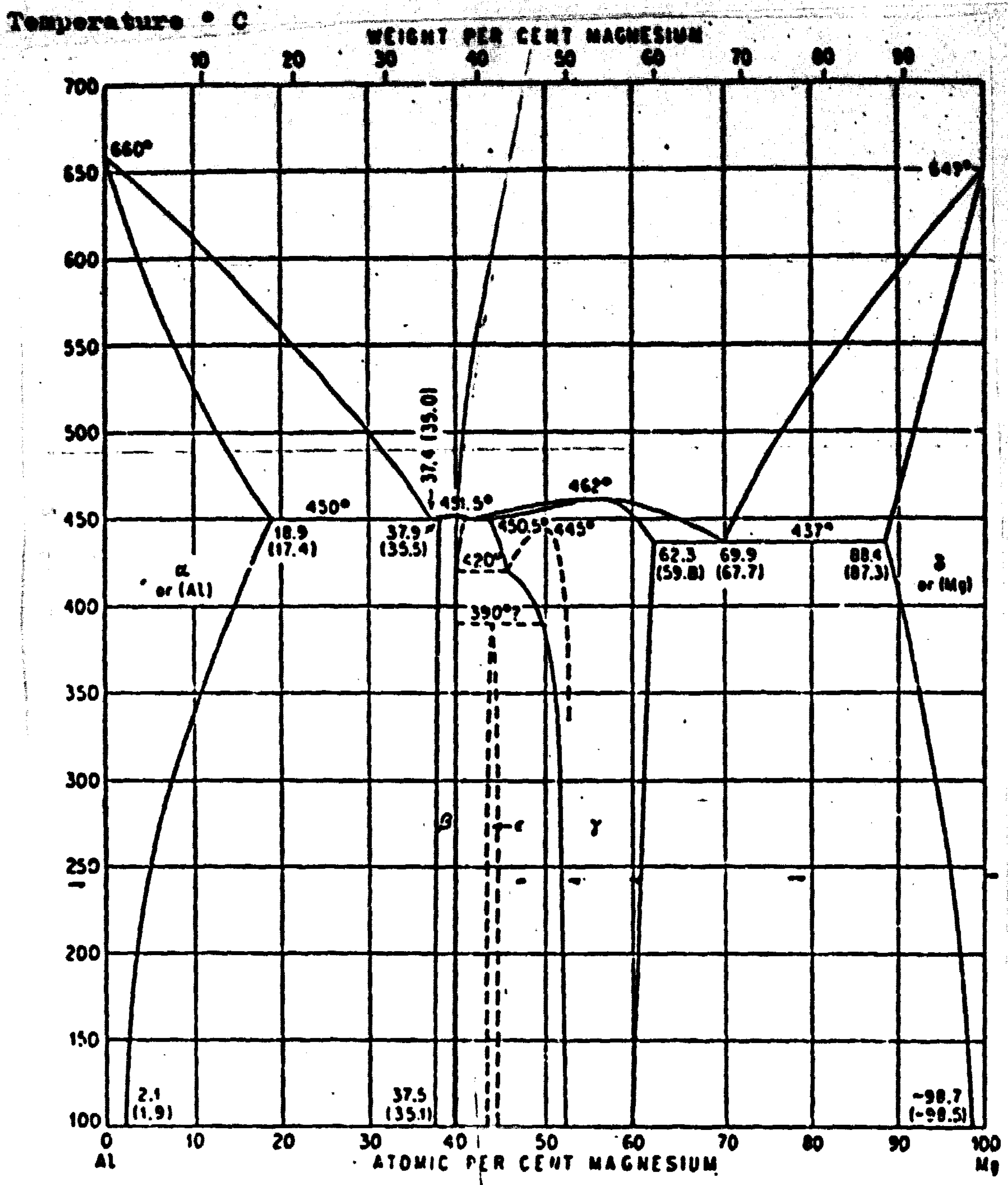

FIG. 7

Phase diagram of Mg-Al system (taken from Constitution of binary alloys, M. Hansen, Mc Graw Hill, 1958).

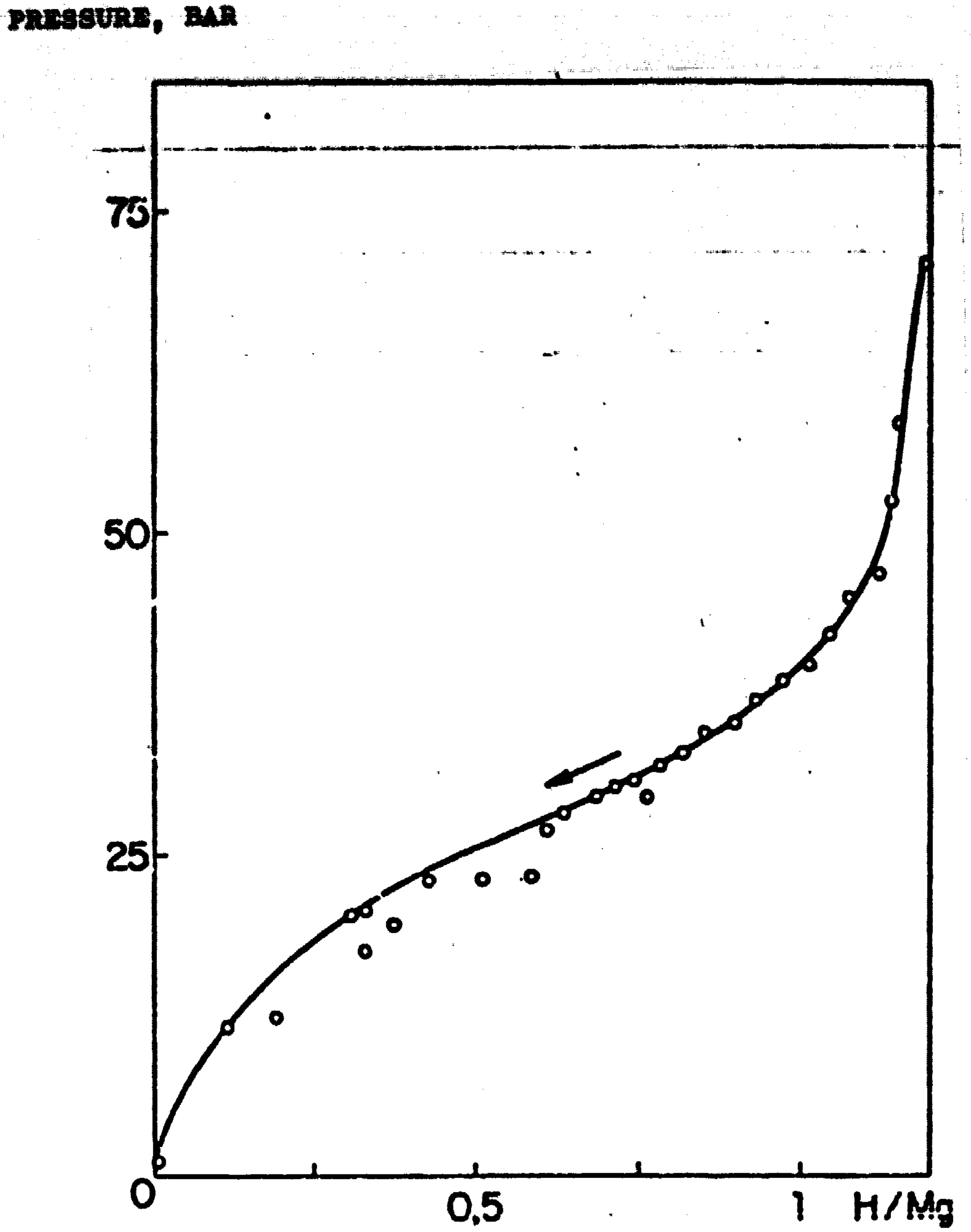

Fig.8

Desorption curve of Mg_3, Al_2 $H_{3.6}$ at 420°C.

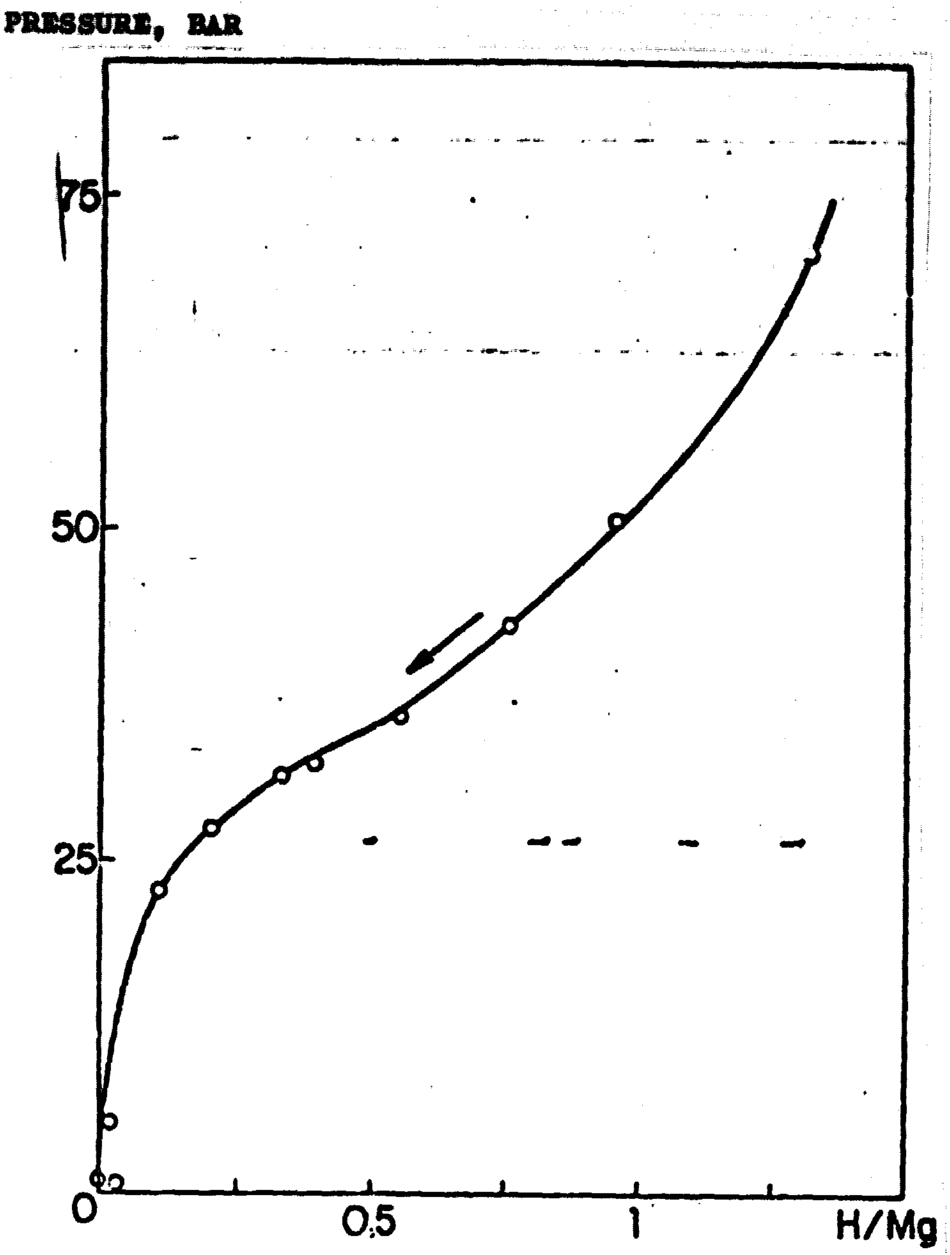

Fig.9

Desorption curve of system $Mg_2Al_3H_{3.1}$ at 410°C.

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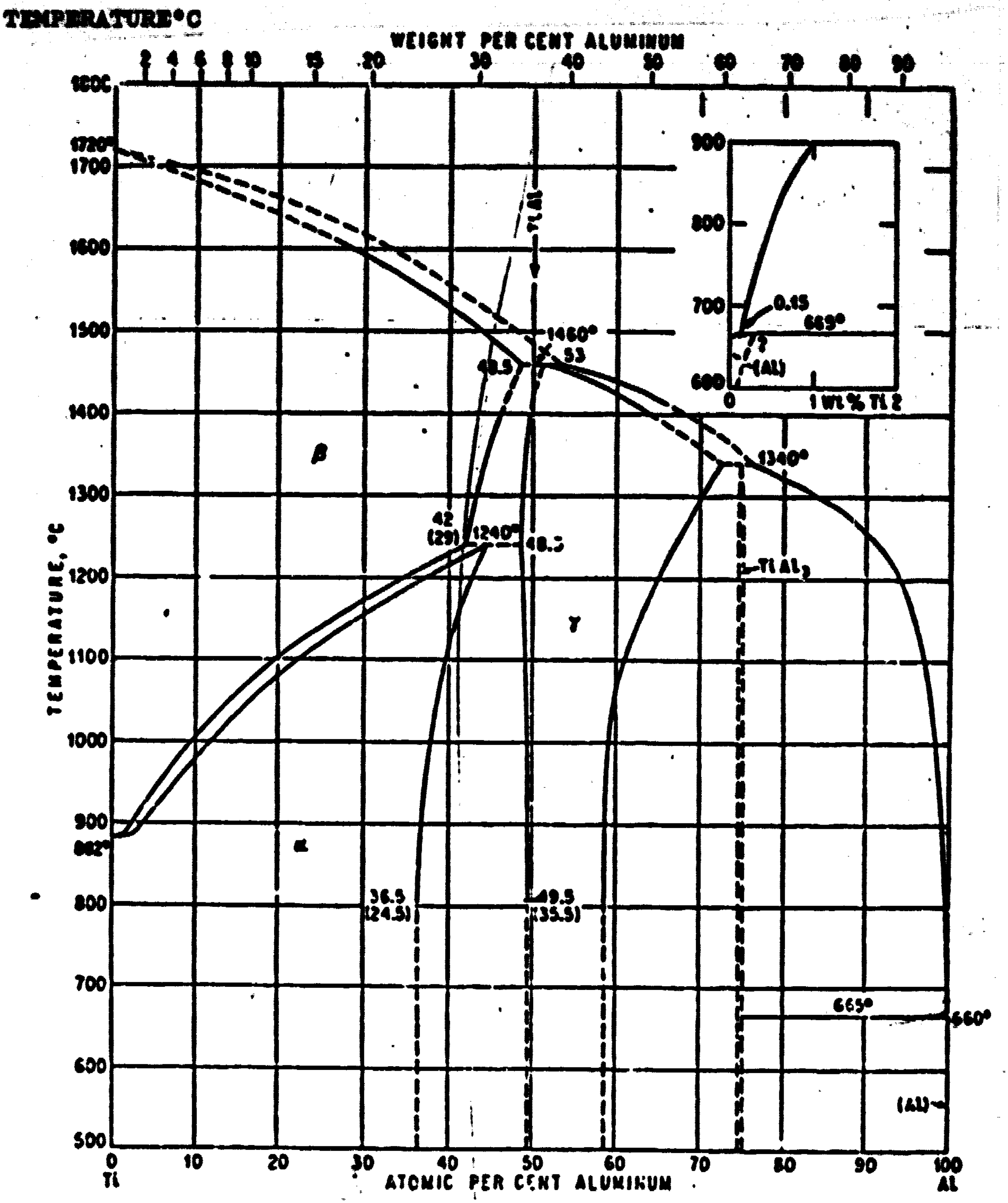

FIG. 10

Phase diagram of system Ti-Al (source: see fig. 7).

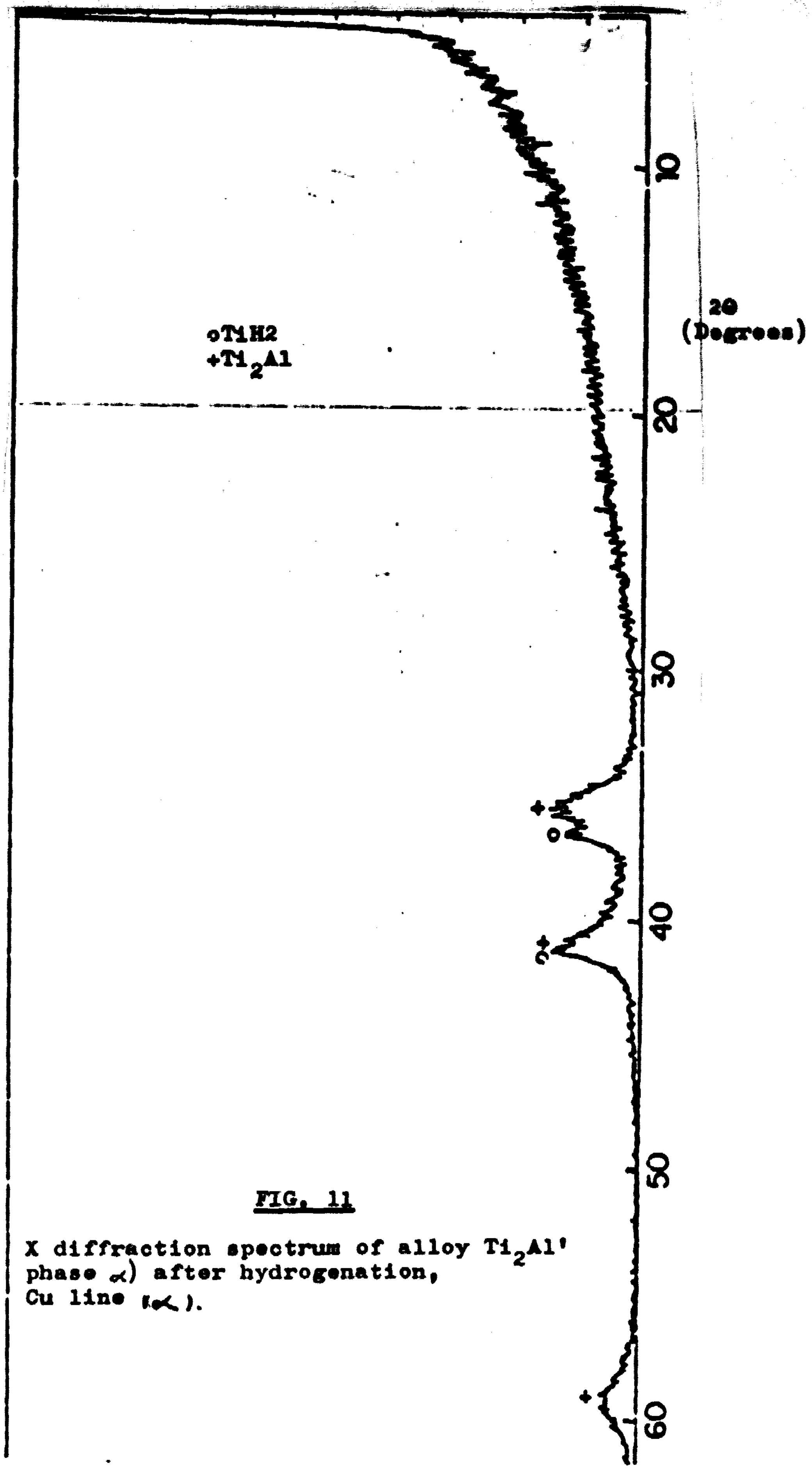

FIG. 11

X diffraction spectrum of alloy Ti$_2$Al' phase α) after hydrogenation, Cu line (α).

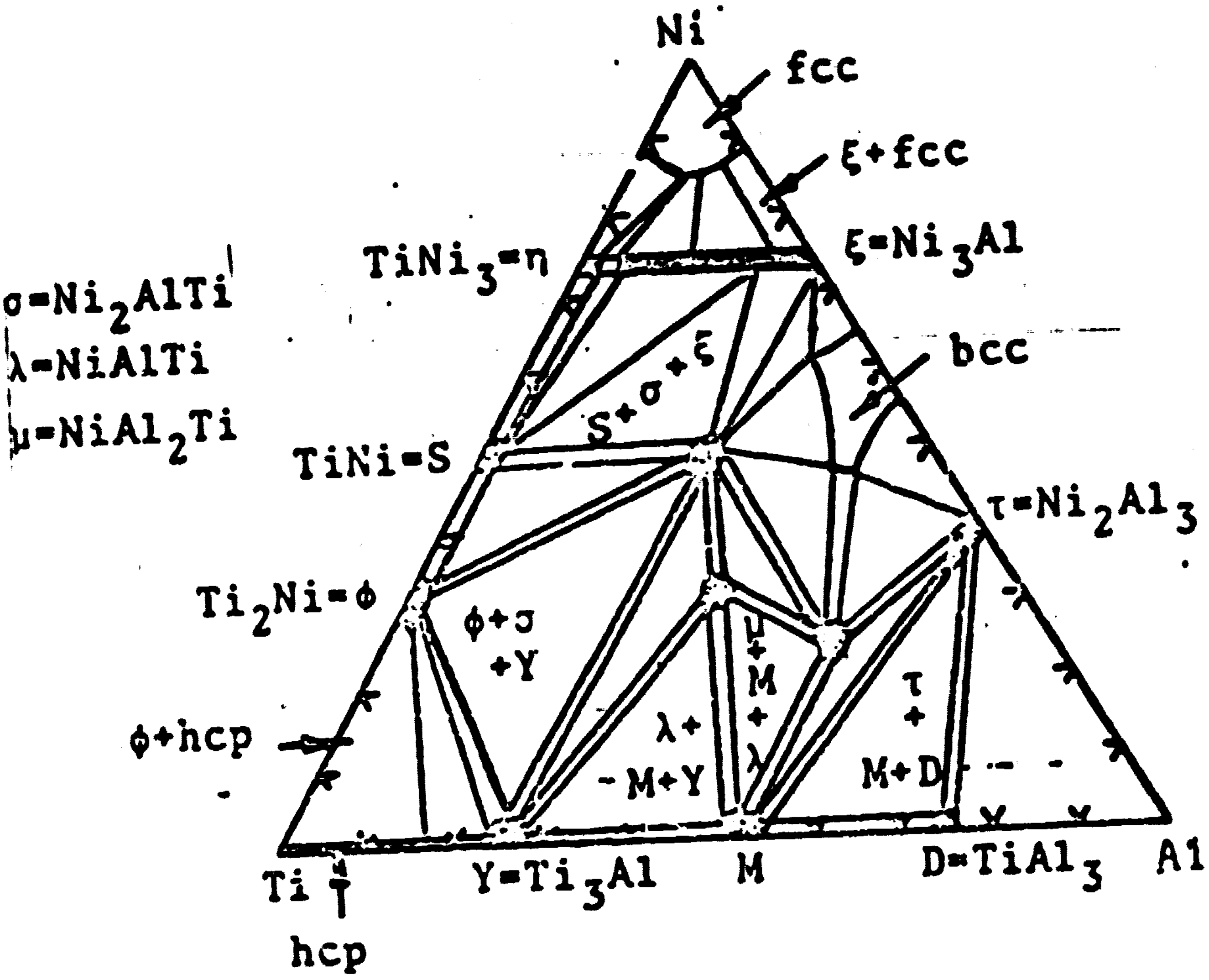

FIG. 12

Phase diagram of system Ti-Al-Ni, according to (6) (T = 750°C).

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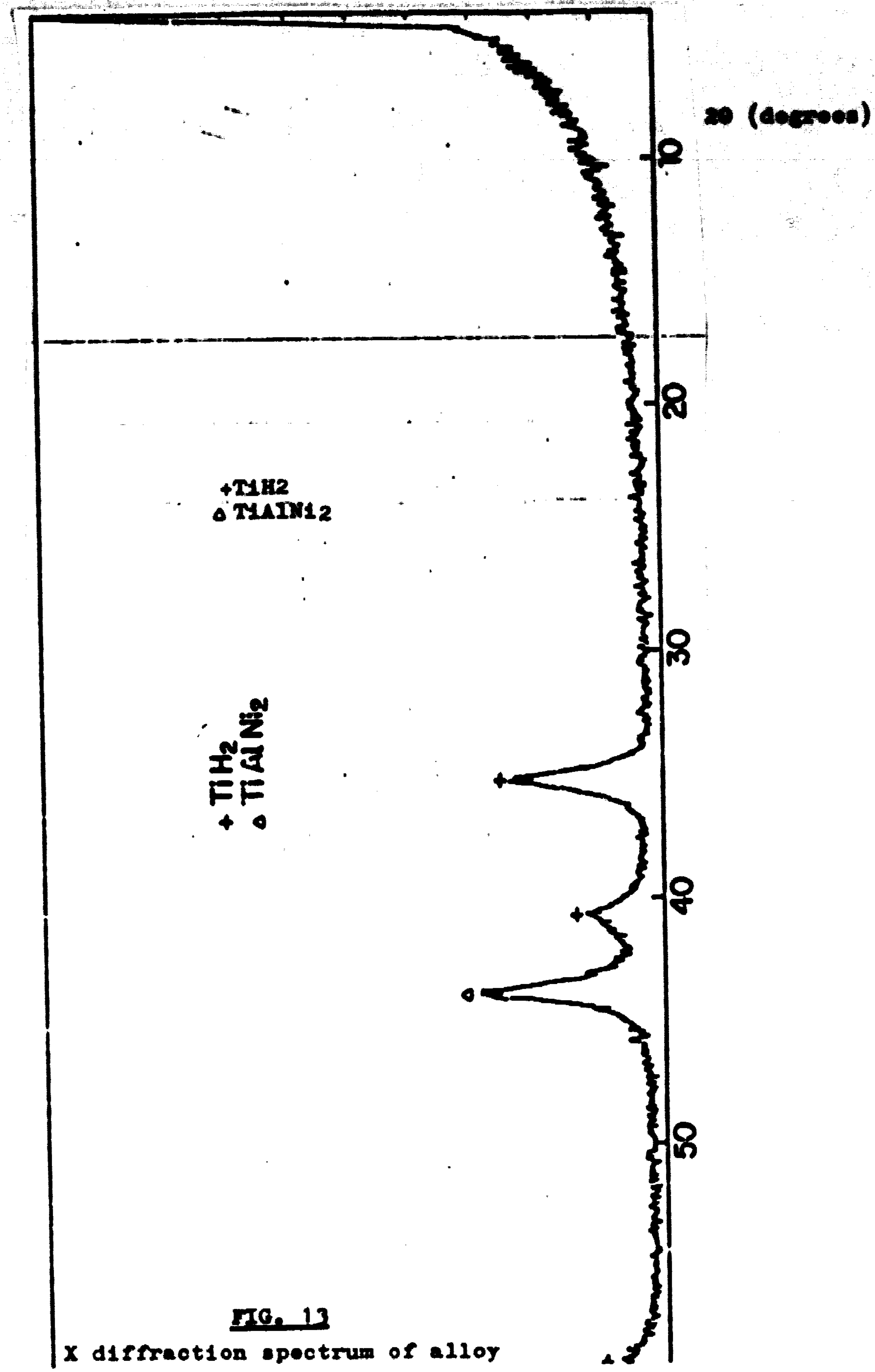

FIG. 13

X diffraction spectrum of alloy

Ti$_{0.6}$Al$_{0.1}$Hi$_{0.3}$ after hydrogenation.

APPENDIX I /40

Development of research studies from November 1976 to March 1977:

- reception of Sartorius pressurized thermobalence (this balance makes it possible to operate up to 150 bars, 600°C), set-up of auxiliary equipment for gas circulation);
- automation of the hydrogenation bench;
- hydrogenation tests of pure metals: magnesium, titanium, vanadium,
- preparation and characterization of magnesium alloys (Mg-Ni, Mg-Cu and Mg-Al systems);
- hydrogenation study of Mg_2Ni and Mg_2Cu;
- testing the Sartorius balance in helium. Large leaks were detected; the device was, thus, sent back to the manufacturer.

From April to June 1976:

- preparation of ternary alloys Mg-Al-Cu;
- preparation of titanium alloys: Ti-Ni, Ti-Al and Ti-Al-Ni;
- characterization of ternary alloys obtained in system Ti-Al-Ni;
- hydrogenation of the preceding alloys;
- unsuccessful testing of the preparation of ternary alloys Mg-Al-Ni;
- new test of the Sartorius balance. At 150 bars in helium, one of the laboratory tubes exploded and destroyed the mechanical part of the balance which was then sent back to the manufacturer.

July - September, October - December 1977: /41

- tests of the preparation of alloys Mg-Ni-Al beginning with binaries Mg-Ni and Mg-Al:
- setting up an annealing furnace in helium or hydrogen;
- construction of a very high pressure autoclave (2,000 bars at 700°C) used for the study of alloys with high aluminum content;

---

*Most alloys listed were prepared at the Centre d'Etudes de Chimie Métallurgique at Vitry in the laboratory of Mr. Bicot.

- beginning of the adsorption study on alloys Mg_2Ni, Mg_3Ni, on alloys Mg-Al, Ti-Al and Ti-Al-Ni by means of volumetry.

Jan - June 1978:

- study of decomposition kinetics for MgH_2 and for hydrides Mg-Al-H,
- physico-chemical characterization of interesting alloys (especially: logging and analysis of X diffraction spectra);
- study of hydrogenating properties in the liquid phase of commercial hydrides ($LaNi_5$),
- setting up a microreactor for catalytic testing in the gaseous phase;
- adjustment of the pressure autoclave;
- adjustment of a Setaram thermobalance for pressurized operation.

APPENDIX II

Low pressure hydrogenation equipment

A general scheme is provided in figure A II. The equipment consists of 3 parts:

- supply and purification of hydrogen. Hydrogen (Air Liquide quality hydrogen) passes into a Deoxo catalyst, then into a trap filled with 13 X zeolite and held at the temperature of liquid nitrogen. Purified hydrogen is stored at 170 bars in an auxiliary tank;

- middle section for pressure measurements. The pressure is read directly on a high-precision manometer and is recorded by means of a DJ instrument type IP pressure transducer, the linearity of which is guaranteed at 0.1%. The volumes introduced may be calculated by using diagrams. The volumes obtained are measured in the water tank. All high pressure valves are SS4UWTFE Nupro valves making it possible to perform a secondary discharge;
- hydrogenation autoclave. It is made of 800 incoloy. Imperviousness is ensured by an "S" SPG metal joint which can operate at 650°C under 150 bars. The rate of leakage of the set of equipment is extremely low (at 500°C, 150 bars, loss of less than 1 bar at the end of one week). The autoclave is placed in an oscillating furnace with adjustable agitation and cyclical programming.

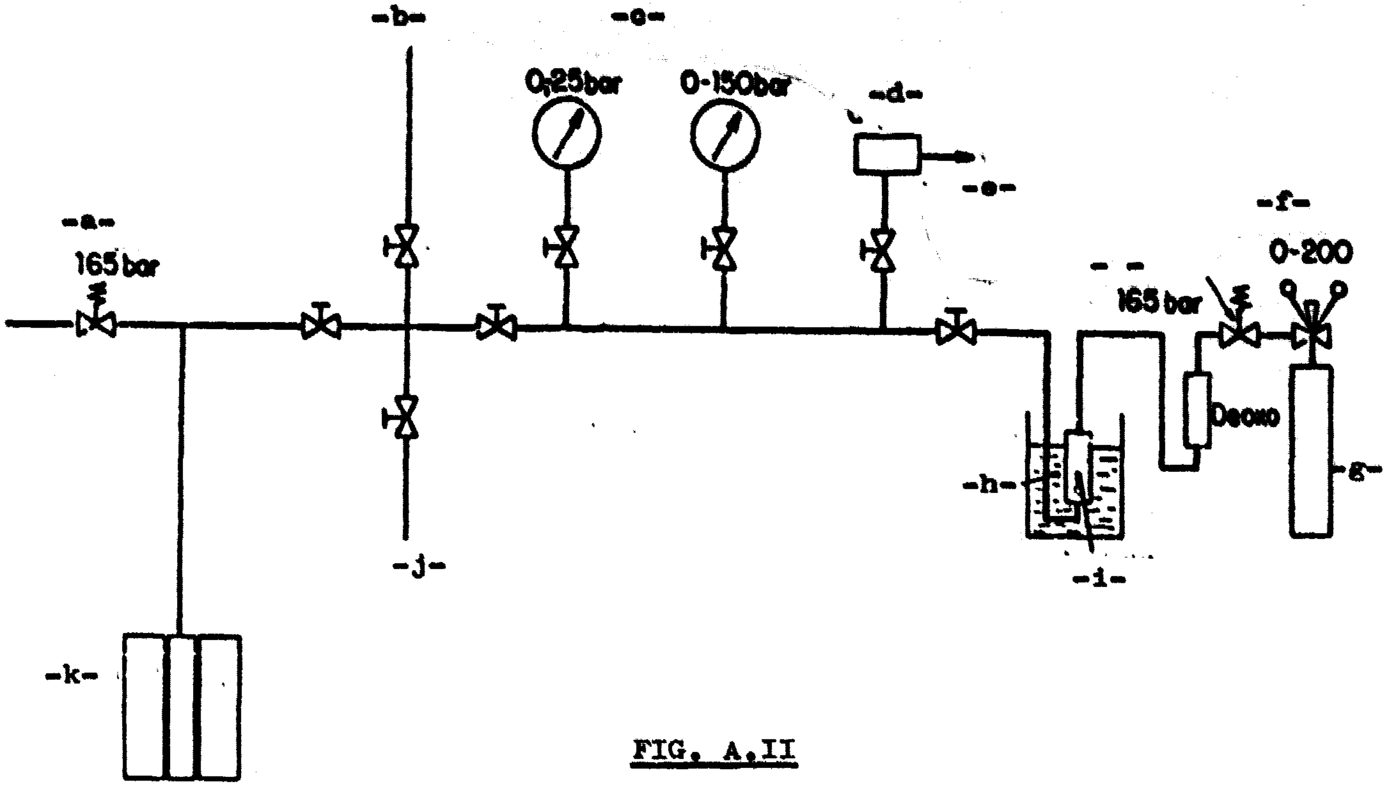

FIG. A.II

Low pressure hydrogenation equipment.

Key: a-Safety insert; b-To vacuum pump; c-manometers; d-Transducer; e-Recorder; f-Pressure reducer; g-H_2 tank; h-Liquid nitrogen; i-Zeolite trap; j-Drain; k-Hydrogenation cell and furnace mounted on agitator.

APPENDIX III

High pressure hydrogenation equipment /44

A general scheme is provided in figure A III. In addition the supply of purified hydrogen, as in Appendix II, the equipment includes:

- high pressure autoclave (2,000 bars at 600°C). Imperviousness is also ensured by an SPB metal joint. The joint is located outside the furnace and is thus not subjected to temperatures exceeding 400°C. Several thermocouples at the level of the samples ensure homogeneous temperatures along the hydrogen supply conduit (passing through the top of the autoclave), thus making it possible to determine the temperature profile (which is necessary in order to calculate amount of hydrogen absorbed by the sample);

- a cryogenic compressor. Hydrogen under 200 bars is supplied into an intermediate tank cooled with liquid nitrogen. The tank is then brought back to normal temperature and to a pressure of more than 750 bars. The autoclave is then connected to the tank. Pressure in the autoclave is controlled by the law P is congruent to 700 $\frac{T}{293}$, i.e. 2,000 bars at 560°C. A series of cryogenic compressors generally make it possible to obtain pressures of about 2,000 bars at atmospheric temperature.

The pressure is measured using a linear pressure transducer at about 0.1%. The valves used are AE30VM 4 071 Engineer autoclaves.

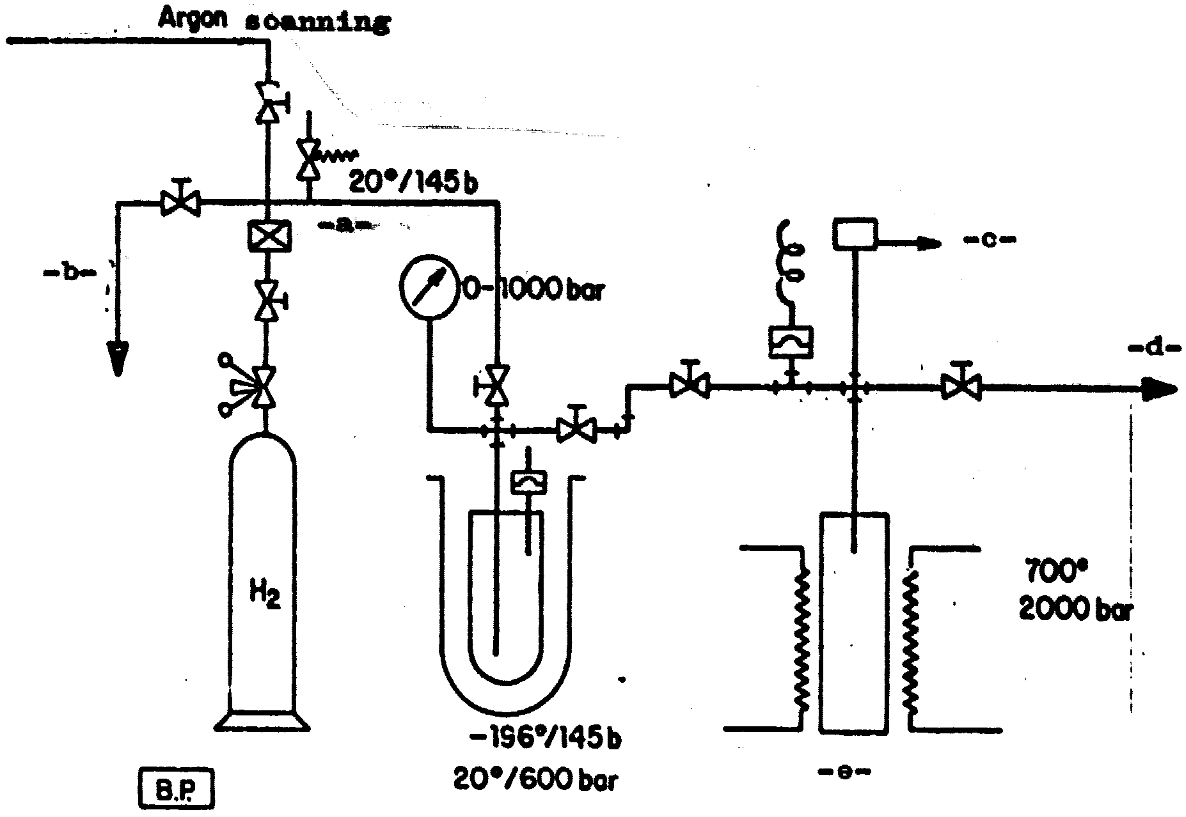

FIG. A.III

Low pressure hydrogenation equipment

Key: a-Purifier; b-Drain or vacuum;
c-Transducer to recorder; d-Vacuum;
e-High pressure cell;

APPENDIX IV

/46

Recent Bibliography on Light Alloy Hydrides

1) Magnesium Alloys

The formation and decomposition kinetics of magnesium hydride was studied by Stander (1) (2). The initial superficial reaction corresponds to a two-dimensional growth of the seeds, the reaction then becomes limited by the diffusion. The diffusion coefficient decreases as the reaction and hydrogen pressure increase. This is why it is difficult to obtain a complete conversion of magnesium. The decomposition of hydrides is limited by the rate of displacement of the reactional interface, while germination has no effect. The rate of reaction is determined by deriving the difference between the applied pressure and the dissociation pressure of hydrides. The decomposition should be complete (for PH_2 congruent to 0) only at temperatures exceeding 330°C, according to Stander (2), and 380°C, according to Nametal (3). The decomposition kinetics of magnesium hydrides can be improved by introducing various additives which serve both as catalysts and as a reserve of hydrogen available at atmospheric temperatures (4).

The system Mg-Al-H was studied by Douglass (5) (6), Reilly and Wiswall (7) (8), Nam et al. (3). The addition of aluminum leads to considerable destabilization. The most thorough study is (8) on a series of Mg-Al alloys with compositions ranging from Mg to Mg_2Al_3. Only phase β (Mg_2Al_3) should lead to isotherms presenting well-defined plateaus. The dissociation pressure at a given temperature is higher for this ternary hydride than for MgH_2 (factor approximately 3). In this work, hydrogenations are performed at high pressure (700 bars). This study, nevertheless, remains fragmentary. The addition of /4 aluminum should improve formation and decomposition kinetics, at least for low contents (5) (6).

Other binary alloys are also studied: $Mg_{17}LA_2$(9); they form an unstable hydride, but have limited storage (1.5%), Mg_9Ce and Mg_9Mm

(Mm = Mischmetall) (8). Also investigated were compounds $R_2Mg_{15}Hi_5$, R_2Mg_{17}, RMg, RMg_3, and alloys where Mg is partially replaced by Ni (RE: rare earth) (10).

2) TITANIUM ALLOYS

YAMANAKA et al. (4) have brought to light a significant fact concerning the system TiNi-H. At 270°C, under 130 bars of hydrogen, the formation of the ternary hydride $TiNiH_{1.4}$ is observed; on the other hand, at 500°C, under the same pressure, TiH_2 is formed:

$$3\ TiNi + 2\ H_2 \longrightarrow 2\ TiH_2 + TiNi_3$$

The formed hydride will be decomposed, depending on the case, at 200°C ($TiNiH_{1.4}$) or at 500°C ($TiH_2 + 0.5\ TiNi_3$); the final state will be the same in both cases (TiNi).

Investigation of the system Ti-Al was conducted by Lundin et al (12) and by Rudman et al (13), (14). Ti_3Al (phase α) should lead to a general formula for hydrides: Ti_3AlH_4. Isotherms do not present defined pressure plateaus (P varies by 10^{-2} at 10^2 bars at 25°C). The thermodynamic properties of the system Ti_3Al-H were studied with low hydrogen contents. The role of aluminum is to block the tetrahedral sites and to increase the dissociation pressure. For higher hydrogen contents, three phases are obtained below 200°C. A pressure plateau of about 1 bar at 100°C should exist for H/M, between 0.4 and 1.5, approximately. The isotherms observed do not present pressure plateaus. /48 Above 200°C, the ternary hydride decomposes with formation of Tl TiH_2. This system, thus, seems interesting for the storage of hydrogen on light vehicles. It should be pointed out that contrary to the compound TiFe, H/Ti ratios of more than 2 are obtained.

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APPENDIX V

Structure of the mixed hydride Mg_2NiH_4.

According to Reilly and Wiswall (Inorg Chem. 1968, 7 (11), 2,254), hydride Mg_2NiH_4 has a tetragonal structure with a = 6.464 Å, c = 7.033 Å. Table A V gives the list for D_{hkl} computed from these values for experimental d's. It is observed that several intense rays are not indexed. Furthermore, the agreement is only approximative for other intense rays. Intensity ratios remain constant for several tests performed on the basis of various samples of alloy Mg_2Ni, which was, therefore, probably not a mixture. Accordingly, the structure proposed for Mg_2NiH_4 was discarded.

TABLE A5

COMPARISON BETWEEN THEORETICAL SPECTRA AND EXPERIMENTAL SPECTRA FOR $Mg_2N_1H_4$.

COMPUTED SPECTRUM		EXPERIMENTAL SPECTRUM	
hkl	d_{hkl}	d_{hkl}	I
001	7.033		
100	6.464		
		5.79	5
101	4.759		
110	4.571	4.55	20
111	3.833	3.82	80
		3.69	70
002	3.517		
200	3.232	3.23	2
102	3.089		
201	2.937		
210	2.891		
		2,849	5
112	2.787	2,797	5
		2,730	5
211	2,674		
		2,475	2
202	2,380	2,380	20
003	2,344		
220	2,285	2.298	100
		2.281	80
		2.251	20
212	2,233		
103	2,204	2.194	10
221	2,174		
300	2.155		
		2.132	2
103	2,086		
301	2,060		
310	2,044	2.049	8
		2.019	10
		2,014	10
311	1.963		

RECORD OF CONCLUSIONS

Enclosed with the Final Report /53

Supplementary coordinated research action: Hydrogen

Financial assistance granted to: Institut Francais du Petrole

Grant No.: 76-7-1 507

Laboratory: Recherches Chimiques de Base

The grant became effective on November 5 1976

Scientific Director: Mr. FREUND

Duration (*): 18 months

Telephone: 749-02-14, X 2, 453

Number of researchers(**): 2

Cost (*): 299,950 F

Purpose of grant: to assist the investigation of hydrogen in the form of light alloys, especially aluminum and magnesium.

Original Objectives: to find an alloy leading to an unstable hydride (PH_2 similar to 1 bar above 100°C) and storage capacity of at least 3%.

Were these objectives reaches? If not, why?

(We were able to examine hydrides with storage and stability levels between those of magnesium hydride and unstable $FeTiH_{1.5}$ hydrides.)

Were results obtained for other objectives than those originally defined? If so, what were these objectives?

A new method of storing hydrogen was brought to light without the use of hydrides.

(*) For the contract with any modification with or without financial assistance.

(**) Including those in the laboratory who did not receive D.G.R.S.T financial assistance.

Should this final report be kept confidential?

NO

If so, why and for how long?

Has your research project been reported in any scientific publications?

NO

If so, attach a list to the record of conclusions in the appendix.

Have any patents been taken out relating to this project?

No, but a patent is being applied for at present.

If so, attach a description to the record of conclusion in the appendix

Can or should this research project be continued?

The investigation should be continued at two levels: more thorough exploration (especially of complex systems) with improved experimental techniques (high pressure), detailed description of products obtained.

Would you like to receive any D.G.R.S.T assistance for the purpose of applying the results obtained.

Another petition for financial assistance has been submitted to DGRST.

General Conclusion of the Research Project

The practical objective originally defined seems obtainable (storage density of hydrides of 3 to 4%, decomposition at the same temperature). With this objective obtained, it must now be determined whether the solution presented can compete with other methods of storage (particularly, newer and lighter containers). Basically, the criteria making it possible to obtain the formation of hydrides on the basis of physico-chemical data (composition, stability, structure) seem to be well defined.

This project has made it possible to use metallurgical techniques in the laboratory which could be used in other areas, particularly for catalysis on other metallic alloys.