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MAGNESIUM AND MAGNESIUM ALLOY HYDRIDES

P. SELVAM, B. VISWANATHAN, C. S. SWAMY and V. SRINIVASAN
Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

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Abstract—This review addresses the question of using magnesium and magnesium-based alloys as "rechargeable hydrogen storage" media. The effect of addition of organic compounds as well as other metals (both transition and non-transition elements) on the sorption characteristics of magnesium is considered in detail. The current status of information in this field is reviewed with a view to evaluating the potential of these materials for use as hydrogen storage media in vehicular applications.

INTRODUCTION

Hydrogen is an attractive and very efficient fuel as well as an excellent medium for energy storage. Given the necessary primary energy (coal, nuclear or solar), hydrogen could become a fuel of inexhaustible nature. According to energy researchers, hydrogen could be one of the possible secondary energy carriers (fuel) at the end of the petroleum era [1, 2]. As a result of diminishing fossil fuel (petroleum, natural gas and coal) supplies, hydrogen technology can be practically advantageous and it can be universally employed for household, industrial and automotive purposes in a similar way to petroleum technology. It was the general consensus of the International Association for Hydrogen Energy (IAHE) and the World Hydrogen Energy Conferences (WHEC) that among the energy options available, hydrogen, being unique and an environmentally compatible fuel, would start replacing the fossil fuels [3]. Therefore, WHEC call for a new urgency to the situation and suggest that this option should be considered soon for the following reasons.

- The acid rains caused by the pollution generated by fossil fuels make the lakes, tanks etc. unsuitable habitats for fish or aquatic plants;
- there is evidence that the mean temperature of the world is increasing with increase of CO_2 (the main combustion product of fossil fuels) build-up in the atmosphere, which will play havoc with the earth's climate;
- a third factor is the ever-growing air pollution. The combustion products CO, CO_2, SO_2, soot and ash are dumped into the environment, the atmosphere, water and land, thus speeding up the degradation and poisoning of the biosphere.

(a) *Hydrogen*

Hydrogen is a clean fuel and the use of it as fuel holds no serious problems. Hydrogen is present in water in practically inexhaustible quantities and it can be generated from readily available and abundant raw materials and energy sources. Burning of hydrogen gives rise to water, a non-depletable material source and it is essentially non-polluting. Hence it is the only system where energy and environment are not adversaries. It produces more energy per unit weight than any other fuel (Table 1) [4]. Hydrogen has been well known as a fuel for internal combustion engines for a long time. In view of the problems of the energy supply and environment protection, the question of the use of hydrogen as an alternative or additional fuel to gasoline has been thoroughly discussed [5]. The hydrogen energy system satisfies all the prerequisites such as abundant availability at low cost, convenient distribution, versatility of usage and societal compatibility. The fact that hydrogen is renewable and compatible with all the primary energy sources makes it the permanent energy system. It can be readily converted to mechanical, electrical or thermal energy with higher efficiencies than the fossil fuels.

Best of all, hydrogen gas can easily substitute for natural gas, diesel and gasoline. So it ideally complements the other clean and versatile secondary energy

Table 1. Energy densities of various fuels [4]

Fuel	Energy density heat of combustion (higher heating value) [MJ kg^{-1}]
Hydrogen	141.90
Methane	55.55
Ethane	51.92
Propane	50.39
Gasoline	47.27
Natural gas	47.21
Kerosene	46.00
Crude oil	45.55
Benzene	42.29
Coal	31.38
Ethanol	29.70
Methanol	22.69
Ammonia	20.54
Wood	17.12

Table 2. Hydrogen content and energy density in various media [6–8]

Medium	Hydrogen content (wt%)	Volumetric density* (H atoms l^{-1}) ($\times 10^{19}$)	Energy density† (MJ kg^{-1})	(mJ l^{-1})
Gaseous H_2 (150 atm)	100.00	0.5	141.90	1.02
Liquid H_2 (−253°C)	100.00	4.2	141.90	9.92
MgH_2	7.65	6.7	9.92	14.32
VH_2	2.10	11.4	—	—
Mg_2NiH_4	3.60	5.9	4.48	11.49
$TiFeH_{1.95}$	1.95	5.5	2.47	13.56
$LaNi_5H_{6.7}$	1.50	7.6	1.94	12.77
$ZrMn_2H_{3.6}$	1.75	6.0	—	—
$ZrMn_2Fe_{0.8}H_{3.4}$	1.38	4.8	—	—

* Does not include container weight or void volumes.
† Refers to the value equivalent to hydrogen in metal hydrides.

carrier, electricity. Unfortunately, despite its unique properties, hydrogen has not yet been widely exploited for use as a fuel. Perhaps the most important factor that limits its use is the difficulty involved in storing it conveniently and economically.

(b) *Hydrogen storage as metal hydrides*

The fact that hydrogen is a gaseous fuel and has a low density poses a problem for its storage. Hydrogen has been traditionally stored, transported and used as compressed gas or cryogenic liquid. But there is an alternative, namely rechargeable metal hydrides. The problems encountered with gas cylinder storage are the high pressure, large volume, high weight and safety risks, whereas with liquid hydrogen the factors are the high consumption of primary energy, extremely low temperatures, high evaporation rates, and safety risks. But the storage of hydrogen as decomposable metal hydrides avoids these extreme limitations. The reversible reaction of hydrogen with metals, alloys or intermetallic compounds is considered as a convenient way for storing hydrogen. Besides these advantages, unit volume of a metal hydride holds more hydrogen than liquid gaseous hydrogen (Table 2) [6–8]. Storage of hydrogen in the form of hydrides requires low pressure, a factor that has safety implications and involves little energy. The hydrides are quite stable below their dissociation temperatures. The disadvantage of hydrides is their cost and weight. However, metal hydrides, besides being attractive means of storing hydrogen, can also be used for accumulating heat, thus serving a dual function [9]. It is this heat/hydrogen coupling which makes it possible for both mobile and stationary applications.

Scientific interest in the behaviour of hydrogen in metals, alloys and intermetallic compounds has increased rapidly in recent years largely because of the realization of many energy-related technological applications for metal hydrides [10–13]. For example, hydrogen has been suggested as a possible long-range successor to petroleum as a heating and motor fuel with hydrogen being stored chemically in a metal alloy in the form of metal hydrides. Many metals have the property of combining directly with hydrogen to form a class of compounds known as metal hydrides [14]. Unfortunately, despite the fact that most elemental metals will react directly and reversibly with hydrogen, only magnesium (MgH_2) could be useful from an energy storage point of view. All the others can be eliminated from consideration because of the expense and unsuitable properties. However, it has been shown that many alloys and intermetallic compounds will react directly and reversibly with hydrogen to form distinct hydride phases which, in many cases, have properties that are quite different from that of the binary hydride of the individual alloy components. The most important characteristics for hydrogen storage are:

- the amount of hydrogen absorbed/desorbed;
- the thermal stability of the hydride;
- the hydriding/dehydriding kinetics.

In addition, the cost of the hydriding material should be cheap. The rechargeable metal hydrides offer a number of practical applications ranging from internal combustion engines to fuel cells [15–25]. The most commonly discussed application of rechargeable hydrides is fuel storage, especially for hydrogen-fuelled internal combustion engine vehicles [26–34].

METAL HYDRIDES FOR VEHICULAR APPLICATIONS

In vehicular applications, a hydride storage tank can be used in many ways, such as for:

- fuel supply;
- air conditioning;
- water condensation;
- storing and recovering waste heat from engine;
- auxiliary heating purposes.

The supplementary functions besides fuel supply do not waste any primary energy [35]. A hydrogen storage material for utilization of hydrogen as a fuel in mobile appliances has to meet stringent requirements in regard to hydrogen capacity, stability of the hydride, the hydrogen exchange rates, economy and safety. Many alloys and intermetallic compounds absorb large quantities of hydrogen. As to the reversible storage system, the best known compounds are $LaNi_5$ [36], TiFe [37], Mg_2Ni [38] and $ZrMn_2Fe_x$ [8]. $LaNi_5$ and TiFe are two familiar materials which absorb and desorb copious amount of hydrogen under mild conditions of temperature and pressure. $LaNi_5$ is a good hydrogen storage material except for its weight and cost. TiFe is also useful, but it is heavy and moreover, requires considerable effort for activation prior to absorbing hydrogen [39]. The hydrogen sorption and physical properties of a large number of AB_2 Laves phase compounds were investigated by various groups [40], but the hydrides formed were too stable to be of practical importance. Recent work on $ZrMn_2Fe_x$ alloys [8] has shown promise. However, these materials also have drawbacks such as the weight and cost of the metals.

Despite many good properties, these compounds suffer from a low-weight fraction of stored hydrogen (Table 2) and none of these hydrides are yet cost competitive. Consequently, there has been attempts to develop better hydrogen storage materials. Light-weight hydrides are suitable for automotive hydrogen fuel storage applications (energy carriers). Considerations based on cost, weight, storage capacity and material availability reveal that reversible hydriding of magnesium according to the reaction:

$$Mg + H_2 \rightleftharpoons MgH_2 \qquad (1)$$

is the most attractive option for hydrogen storage. Magnesium as a hydrogen storage material meets two important storage criteria: (1) it can store large quantities of hydrogen, more than any other metal-hydrogen system (Table 2), and (2) it is relatively inexpensive. So it offers potential for storage of hydrogen for automobile applications [1, 5, 27–29, 41, 42]. As far as the weight and range of operation conditions are concerned Mg is the best choice for mobile applications (Table 3) [5, 43]. However, it has two significant disadvantages, namely: (1) Mg–H_2 reaction has poor kinetics, and (2) the hydride is very stable; a temperature of 286°C is required to reach a dissociation pressure of 1 atm [6, 44, 45].

Hoffman *et al.* [46] suggested that Mg catalyzed by other metals and additives can serve as an alternative automotive hydrogen fuel storage compound. It was proposed that the exhaust gas heat of the engine be used to supply the heat of decomposition. However, the quantity of usable waste heat is not quite sufficient to entirely satisfy the heat of decomposition and would have to be supplemented by burning a portion of the stored hydrogen [47]. Hence, attempts were made to partially eliminate these disadvantages by using Mg compounds modified with organic compounds and metal additives without substantially decreasing the hydrogen storage capacity. This presentation therefore, deals with the various aspects of the progress made on the development of Mg and Mg-based alloy hydrides.

Table 3. Storage data for low- and high-temperature hydrides [5]

Material	Volume (l)	Weight (kg)	H_2 storage capacity (kg)	Range of* operation (km)
		At constant volume		
TiFe	50	200	4.00	150
$LaNi_5$†	50	200	2.75	110
Mg_2Ni	50	100	4.00	150
Mg	50	100	8.00	300
		At constant weight		
TiFe	50	200	4.00	150
$LaNi_5$†	50	200	2.75	110
Mg_2Ni	100	200	8.00	300
Mg	100	200	16.00	600
		At constant range of operation		
TiFe	50	200	4.00	150
$LaNi_5$†	67	270	4.00	150
Mg_2Ni	50	100	4.00	150
Mg	25	50	4.00	150

* Range of operation if a van with 44 kW and 2.4 ton weight is used.

† Data from ref. [43].

HYDROGEN STORAGE SYSTEMS BASED ON MAGNESIUM

(a) *Pure magnesium for hydrogen storage*

MgH_2 is considered as a potentially suitable medium for hydrogen storage because it can contain large amounts of hydrogen, namely, 7.65 wt%. The reaction (1) is generally difficult to nucleate because the surface is usually contaminated by magnesium oxide (MgO), or magnesium hydroxide ($Mg(OH)_2$) which either inhibits the dissociative adsorption of hydrogen or the transfer of hydrogen from the surface to bulk. Once nucleated, MgH_2 then grows slowly, the rate-limiting step being the diffusion of hydrogen through the growing MgH_2 layer [48]. Dissociative adsorption on the MgH_2 surface can also limit the growth rate [49, 50]. Thus, both the nucleation and growth kinetics of MgH_2 can be accelerated by the addition of a catalyst capable of promoting dissociative adsorption of hydrogen. This model for the hydriding and dehydriding mechanism is illustrated schematically in Fig. 1. It has been known that surface oxides and adsorbed gases inhibit the hydriding of Mg [51–53]. Such surface layers also inhibit dehydriding [53, 54]. Unfortunately, even if one eliminates the oxide layer formation, the reaction rates are still considerably low because of the protective layer problem. In hydriding, MgH_2 acts as diffusion barrier for hydrogen, while

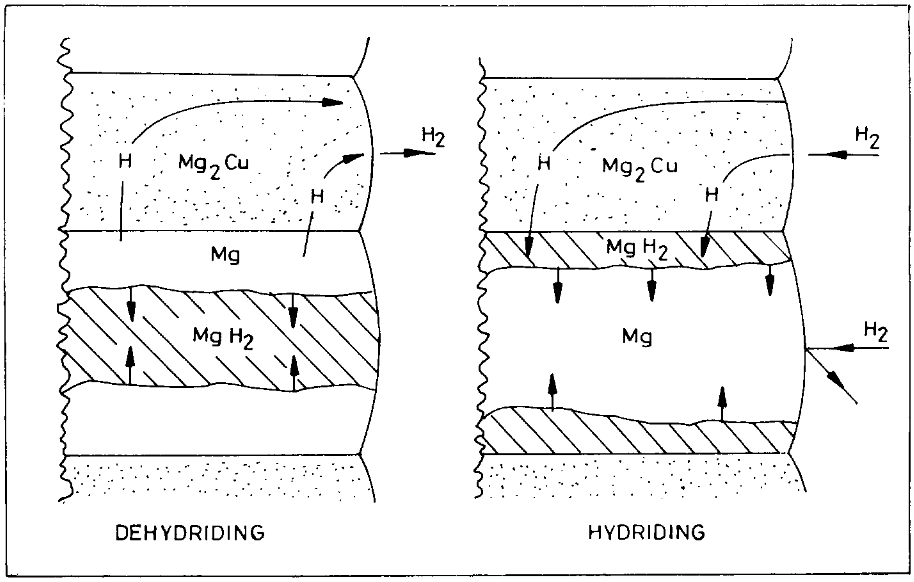

Fig. 1. Hydriding and dehydriding model of Mg_2Cu catalyzed Mg [49, 50].

in dehydriding Mg functions as the diffusion barrier. Hence, pure Mg has received little attention.

In recent years, many investigations on the Mg–H_2 systems have been reported. There are many inconsistencies in the experimental results reported and their interpretation. For example, they show variable kinetics; the hydriding and dehydriding rates are slow [55–58, 35] and incomplete [58–60]. Several hydrogen formation mechanisms have been reported involving the migration of Mg [56, 57, 59], or hydrogen [48, 58, 61, 62], or the diffusion of hydrogen through the metal lattice [63]. Alternatively, it could occur via chemical reaction or hydrogen activation on a contaminated surface layer [49], or by superficial nucleation and growth of the hydride without fragmentation of the sample [43], or the diffusion of hydrogen through an external hydride layer (shrinking core) [49, 64], lattice rearrangement (hcp Mg to bcc MgH_2) [65], the transfer of hydrogen across the metal–hydride interface (nucleation) [66], and the heat transfer limitations. Also they show little agreement on the activation requirements [56], contamination sensitivity [51] and the evaluated thermodynamic values [55, 58, 60–63, 67–69].

As a consequence of this, Vigeholm *et al.* [70–73] have reinvestigated the Mg–H_2 system and found properties quite different from those previously reported. The absorption of hydrogen in Mg (purity 99.8–99.9%) was studied at various pressures (10–50 atm) and temperatures (260–425°C). The desorption was carried out at temperatures in the range 325–400°C against a constant hydrogen pressure of 1.5 atm. The hydrogenation of the sample resulted in the formation of the stoichiometric compound MgH_2. Subsequent desorption at 1.5 atm, however, liberated only 88% of the hydrogen taken up (Figs 2 and 3). The main comments of Vigeholm *et al.* [70–73] are:

- Mg powder of particle size less than approximately 50 μm and with impurity concentrations and com-

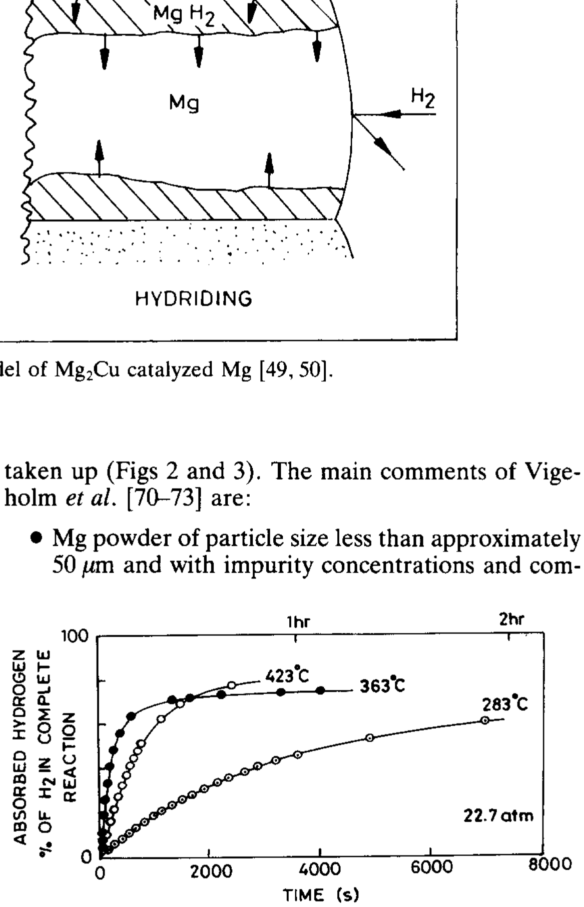

Fig. 2. Hydriding kinetics of pure Mg at various temperatures under a hydrogen pressure of 22.7 atm [72].

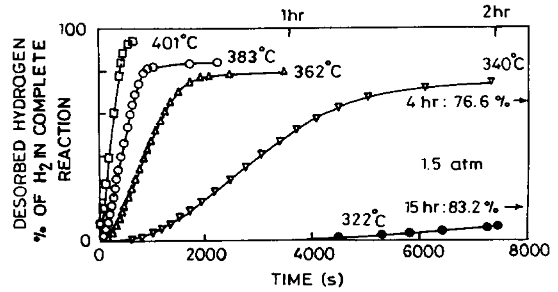

Fig. 3. Dehydriding kinetics of MgH_2 at different temperatures under a hydrogen pressure of 1.5 atm [72].

positions typical of normal Mg products will absorb hydrogen readily above 300°C at pressures exceeding the equilibrium level over a considerable number of cycles;

- the reaction rates are not influenced significantly by the number of cycles within 150 cycles, and only to a small degree up to 500 cycles;
- the amount of hydrogen which may be absorbed and desorbed depends upon the material, ranging from initially 80–96% of the stoichiometric value, dropping to 50–60% up to 500 cycles;
- the fall in storage capacity can be attributed to loss of Mg through formation of MgO and to formation through sintering of agglomerates with bulk regions larger than 50 μm;
- no pre-treatment of the Mg powder is needed unlike as claimed by Stander [56];
- surface oxidation has no adverse effect on the reaction rate. That is, the rather extensive surface oxidation in their materials leads to the formation of crystalline MgO which cracks away from the particle surface exposing the pure metal. This would not be the case with a very thin oxide coating, which should be sufficiently ductile to adhere to the particle, thus hindering the hydrogen access to the metal;
- the optimal reaction rate is reached after one cycle, in disagreement with the findings of Guinet *et al.* [59] and Belkbir *et al.* [43, 69], who claim that the hydrogen capacity is quickly reduced with repeated cycling;
- in small particles the hydride may form simultaneously all through the material. If so the entire process will be governed by hydrogen diffusion and not by slow MgH_2–Mg boundary movement;
- the rate of hydrogenation reaction is fast even at temperatures below 325°C. The rate of reverse reaction however, is somewhat slower at low temperatures and may limit the practical applicability of Mg;
- the hydrogenation cycle runs of pure Mg suggest that this material is well suited and is a promising candidate for hydrogen storage for hundreds of cycles with a useful capacity of approximately 5 wt% hydrogen or more, in contrast to the quite negative results of Guinet *et al.* [59], Tanguy *et al.* [60] and Belkbir *et al.* [43, 69].

Hence, in attempts to eliminate or reduce these disadvantages, several authors have used various catalysts for the direct synthesis of MgH_2 from its elements [35, 51, 60, 63, 66, 74–92]. These catalysts may be classified into two categories. The first class includes those catalysts (iodine, magnesium iodide, mercuric chloride, alkyl halides, condensed ring compounds etc.) which are added to the gas phase, or mixed, or pre-treated, or condensed with Mg, and which will be referred to as heterogeneous catalysts [51, 74–78]. The second kind of catalysts are certain metal additives which are alloyed with Mg and which will be referred to as homogeneous catalysts [35, 51, 59, 60, 63, 66, 79–92]. Improved results were obtained by the addition of catalytic materials to Mg, which not only catalyze the initial synthesis of the hydride, but also have an influence on the kinetics of the reaction. One of the major objectives is to reduce the dissociation temperature of MgH_2 while retaining high hydrogen capacity.

MAGNESIUM AND MAGNESIUM ALLOYS MODIFIED WITH ORGANIC COMPOUNDS

The first direct synthesis of MgH_2 from its elements has been reported by Wiberg *et al.* [74], the necessary conditions being a high temperature (570°C), a high pressure of hydrogen (200 atm) and the presence of MgI_2 or $HgCl_2$ as a catalyst. They obtained a 60% yield of MgH_2. Later Faust *et al.* [75] observed better yields of MgH_2 in the presence of certain other catalysts (iodine, allyl iodide and propargyl bromide) at hydrogen pressures and temperatures substantially lower than those reported previously. For example, at 5 atm hydrogen pressure and at 175°C, a 99.6% yield of MgH_2 was obtained. It was suggested that organo-magnesium halides were formed on the surface of the Mg particles followed by the pyrolysis of the organic compound and the formation of MgH_2 at approximately 175°C [75]. This appears to be in agreement with the reports of Freundlich and Clandel [76] on the preparation of MgH_2 via pyrolysis of alkyl magnesium halide compounds. Dymova *et al.* [51] have found the optimum conditions (380–450°C at an initial hydrogen pressure of 100–200 atm) for the rapid and almost complete reaction of Mg with hydrogen by the addition of catalysts (iodine, alkyl halide and carbon tetrachloride). They obtained a yield of 97–98% of MgH_2. The catalytic additives were mainly certain known Mg activators used for the production of Grignard reagents. Among the Mg activators CCl_4 proved to be effective.

It is known that alkali metals form charge transfer or electron donor–acceptor (EDA) complexes with polynuclear aromatic compounds like naphthalene, anthracene etc. These complexes can activate hydrogen and absorb significant quantities to form metal hydrides [93]. In view of this, Imamura *et al.* [78, 94–96] investigated the behaviour of Mg intermetallics ($SmMg_3$ and Mg_2Ni) and Mg with polynuclear aromatic compounds. They observed that the modified compounds constitute a novel approach to the improvement of the hydrogen sorption properties in terms of a lowering of pressure (below 1 atm) and temperature (room temperature, in the case of the Mg modified system, the hydrogen absorption measurements were carried out at 200–250°C) and enhanced hydrogen absorption and desorption characteristics compared to the untreated $SmMg_3$ [84], Mg_2Ni [38] and Mg [51].

The exceptional ability for hydrogen sorption is presumed to be due to complexation of $SmMg_3$, Mg_2Ni, or Mg with the condensed ring compounds. It was also noticed that in the absence of organic compounds there was no indication of hydrogen absorption by $SmMg_3$,

Table 4. Hydrogen absorption in $SmMg_3$ and Mg_2Ni modified with polynuclear aromatic compounds at room temperature (22°C) by admitting hydrogen at 500 torr [94–96]

Sample*	Hydrogen content ($mmol\ g^{-1}$)
$SmMg_3$–Naphthalene	0.65
$SmMg_3$–Anthracene	0.45
$SmMg_3$–Phenanthrene	0.53
$SmMg_3$–Chrysene	0.83
$SmMg_3$–Perylene	0.80
Mg_2Ni–Phenanthrene	0.32
Mg_2Ni–Chrysene	0.50
Mg_2Ni–Anthracene	0.30
Mg_2Ni–Perylene	0.50
Mg_2Ni–Naphthacene	0.46
Mg_2Ni–Chloranil	0.42
Mg_2Ni–Tetracyanoethylene	0.30 2.27†
Mg_2Ni–Phthalonitrile	1.26 2.97‡
Mg–Tetrahydrofuran	§
Mg–Tetrahydrofuran-perylene	§

* The samples were prepared by reacting 1:1 mixture of $SmMg_3$ or Mg_2Ni and the organic compound.

† Hydrogen absorbed at 100°C.

‡ Hydrogen absorbed at 150°C.

§ No data available on the storage capacity but shows a marked enhancement of the activity towards hydrogen absorption at 200–250°C [78].

Mg_2Ni or Mg under similar conditions. The ability for hydrogen absorption varies considerably with the nature of aromatic compounds (Table 4). This is because of the variation of electronic interaction between the aromatic material and the hydrogen storage materials. It is probable that the modified compounds possess an outer layer of the EDA species [95, 96]. They are probably involved in breaking the bond in hydrogen molecules thereby activating hydrogen and then transferring to the adjoining sites of $SmMg_3$, Mg_2Ni or Mg by a diffusion/spillover process [78, 96]. Hence, the role of the EDA complexes might be similar to those of elemental nickel on the surface of $LaNi_5$ [97].

Co-condensation of Mg atoms with organic compounds (tetrahydrofuran, perylene) leads to the easy formation of MgH_2. The apparent activation energy for hydride formation was calculated as 41.4 $kJ\ mol^{-1}$ [78], which is much smaller than the value of 96.7 $kJ\ mol^{-1}$ [56] and 115.5 $kJ\ mol^{-1}$ [64] for pure Mg. The modification of Mg–THF powder with perylene results in a marked enhancement of the activity of Mg particles. In a series of experiments, the Mg_2Ni–anthracene system exhibited the best recovery of hydrogen with good reproducibility [95, 96], whereas a large increase in the hydrogen absorption capacity of Mg_2Ni treated with tetracyanoethylene and phthalonitrile was observed [96]. The dehydriding process of the hydrided material leads to the starting material, indicating there was no decomposition of the modified systems. These results imply that the alloys treated with aromatic materials led to superior properties, especially for obtaining favourable hydriding and dehydriding kinetics.

METAL CATALYZED MAGNESIUM SYSTEMS

In order to eliminate the limitations of using Mg alone, studies of numerous metal additions to Mg (binary, ternary and multicomponent) were carried out in order to find the optimum alloy for hydrogen storage. Reilly and Wiswall [38, 79] reported a fairly rapid reaction of Mg_2Ni and Mg_2Cu with hydrogen at about 300°C. They concluded that the presence of Ni or Cu has a catalytic effect on the hydrogenation of Mg. They also observed that the addition of 5 wt% Ni to Mg accelerated the formation of MgH_2 [98]. Recently, Rudman and co-workers [48–50] have studied the kinetics of hydrogenation of the eutectic alloy Mg–Mg_2Cu under conditions when only the Mg phase was hydrided and dehydrided, while the Mg_2Cu phase acted only as a catalyst. They concluded from their kinetic results that the external Mg surface oxidizes and becomes inactive, whereas the interface between Mg and Mg_2Cu, which is not exposed to oxygen, does not build up a barrier. Hence, in their model the authors assume that in contrast to the external surface of Mg, that of Mg_2Cu keeps its ability to dissociate hydrogen which is then delivered to the underlying Mg. Thus, the authors suggested through thermodynamic arguments that hydrogen keeps Ni and Cu free from oxidation but not Mg. Mintz *et al.* [62, 64, 85, 99] have investigated the reaction between hydrogen and activated Mg, as well as the activated Mg containing small amounts of group III-A metal additives (aluminium, gallium and indium). They observed considerable difference between the hydriding rate of pure Mg and that of modified Mg. These results suggest that the presence of the metal additives have a catalytic effect. The catalytic effect of these elements is probably due to the formation of oxide-free penetration sites on the surface of Mg particles, as reported for the Mg–Mg_2Cu system [48–50].

The above results and arguments suggest the possibility that selective oxidation due to surface segregation is the cause for the catalytic effect of Mg_2Cu, Mg_2Ni and other Mg alloys. These results were confirmed by XPS and AES experiments on Mg_2Ni, Mg_2Cu, Mg–Mg_2Ni and Mg–Mg_2Cu surfaces [100]. The XPS and AES analyses together with investigations of magnetic properties [101] revealed that, in these alloys at room temperature, as well as at 300°C, Mg diffuses to the surface. The segregated Mg gets oxidized and keeps the Ni and Cu in the metallic state even after exposure to air. This behaviour is similar to that of $LaNi_5$ [102] and TiFe [103]. Thus, at the surface, precipitations of Ni or Cu occur by surface segregation and decomposition. The subsurface and the precipitations are able to dissociate molecular hydrogen. Thus, the metal clusters serve as the dissociative adsorption catalyst. At the elevated temperatures (300°C) even stronger segregation is expected and results in additional metallic active surfaces [48–50, 104]. Hence, the surface segregation prevents the formation of a compact oxide layer. This would explain the better hydrogenation kinetics of Mg alloys. Schlapbach [105] suggested that as long as the segregation and decomposition continue, dissociative chemisorption and associative desorption can occur. According to Vigeholm *et al.* [70–73] the oxide layer presents a barrier only when it is thin and ductile, otherwise it can crack and allow penetration.

Shamir *et al.* [106] have studied the surface characteristics of some Mg–In and Mg–Al alloys by XPS and AES techniques. In the case of Mg–In alloys, it was found that Mg atoms are oxidized at the surface, leaving the In atoms in their metallic state, similar to the behaviour of Mg–Ni and Mg–Cu alloys as reported earlier [100], while in Mg–Al alloys both Mg and Al are oxidized at the surface. Hence the addition of small amounts of In to Mg metal catalyzes the hydrogenation reaction more effectively than the Al additions.

Thus, in alloys, surface segregation and decomposition produce clean subsurfaces. Continuous segregation with cycling accounts for the excellent absorption and desorption kinetics and the catalytic activity of intermetallics. Hence, the addition of small amounts of catalyst to Mg seems to minimize the oxide surface by providing a clean unoxidized external surface at which the hydrogen gas readily adsorbs dissociatively and diffuses into the interior where hydride formation occurs. Essentially the reverse takes place in dehydriding.

(a) *Magnesium–transition metal systems*

The dissociation of molecular hydrogen, the diffusion of hydrogen and the recombination of atomic hydrogen are important steps in the hydrogen storage processes. It has been reported that many transition metals are suitable for these purposes [107]. A number of experimental [108] and theoretical [109] investigations on the qualitative and quantitative aspects of hydrogen chemisorption on various metals have been reported in the literature. The diffusivity of hydrogen in metals (especially in transition metals) is extremely high. Phenomenologically, the high diffusivity is a consequence of the low activation energy for hydrogen diffusion [110]. Hence attempts were made to improve the hydriding and dehydriding behaviour of Mg by suitable alloying with transition metals.

Reilly and Wiswall [38, 79] reported successful hydriding and dehydriding experiments with Mg_2Ni and Mg_2Cu in the sixties. Owing to the relative stability of MgH_2, modifications of $MgMH_x$ (M = transition metal) were made to decrease the dissociation temperature. Alloys of Mg, Ni and Cu showed considerable decrease in the dissociation temperature of the hydride [111]. In this section the available information on the Mg–transition metal systems are summarized.

(i) *Magnesium–nickel alloys.* Light-weight hydrides of relatively low stability are needed for automobile applications and therefore systematic studies on the substituted Mg alloys are desirable to establish general trends in hydride stability. Libowitz *et al.* [112] observed originally that the ternary hydride, $ZrNiH_3$, was more unstable than the binary hydride, ZrH_2. The same idea was followed by Reilly and Wiswall [38, 79] for the stable $Mg–H_2$ systems. They studied the reaction of hydrogen with intermetallic compounds viz. Mg_2Ni and Mg_2Cu. They reported a fairly rapid reaction of the intermetallic compounds with hydrogen at moderate temperatures (300°C) with a lower decomposition temperature than the parent hydride, MgH_2 (250°C, pH_2 = 1 atm).

Mg_2Ni alloys. Mg forms two intermetallic compounds with Ni, viz. Mg_2Ni and $MgNi_2$ [113]. The latter does not react with hydrogen at pressures up to 540 atm in the temperature range −196 to 300°C. However, Mg_2Ni reacts with hydrogen to form a ternary hydride, Mg_2NiH_4,

$$Mg_2Ni + H_2 \rightleftharpoons Mg_2NiH_4 \qquad (2)$$

even at room temperature. At 200°C and a pressure of 14 atm, it will react rapidly [38]. A series of pressure–composition iostherms for this system is shown in Fig. 4. The abrupt termination of the isotherms at a composition corresponding to Mg_2NiH_4 indicates that the hydride has a well-defined stoichiometry. The maximum

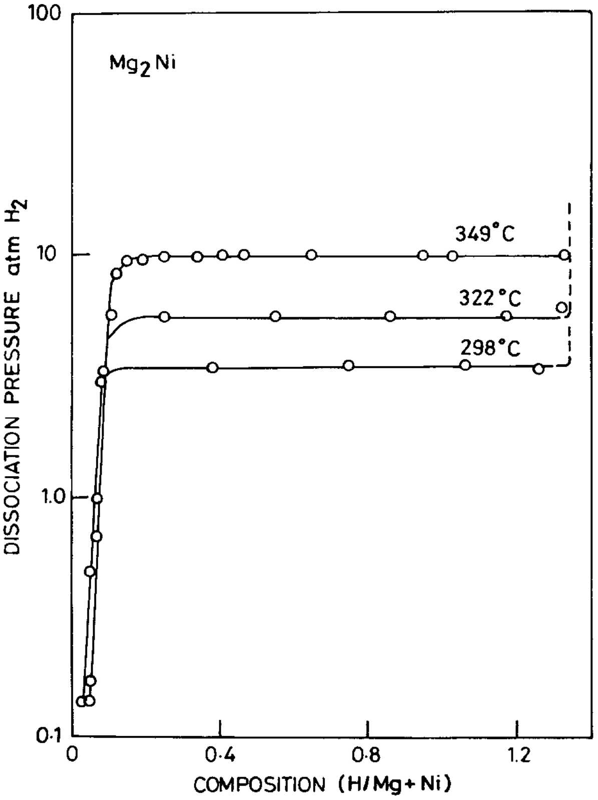

Fig. 4. Desorption isotherms for the $Mg_2Ni–H_2$ system. The initial composition is 45.9 wt% Mg and 54.6 wt% Ni [38].

solubility of hydrogen in the α-phase corresponds to a composition of $Mg_2NiH_{0.3}$. The reaction starting with the hydrogen-saturated alloy may be written as:

$$1.08Mg_2NiH_{0.3} + 2H_2 \rightleftharpoons 1.08Mg_2NiH_4. \quad (3)$$

The hydrogen content in Mg_2NiH_4 is about 3.6 wt%, which is still a better value compared to other hydrogen storage materials, but it is less than one-half the amount, by weight, of hydrogen in MgH_2 (Table 2). The Mg_2Ni–H_2 system is somewhat more unstable thermally than the corresponding Mg–H_2 system. As far as the reaction kinetics are concerned, the absorption process is faster, as mentioned earlier, and the dissociation of the hydride is relatively rapid and has been studied [114]. Buchner *et al.* [35] have also reported a 3.7 wt% hydrogen absorption on Mg_2Ni alloy with a dissociation pressure of 1 atm at about 260°C.

Modified or substituted Mg_2Ni *alloys.* Oesterricher *et al.* [115] have suggested that the partial substitution of Mg in Mg_2Ni by an element of a more exothermic heat of hydride formation, such as Ca, Sc or Y may result in a rise of equilibrium pressure for the substituted Mg_2Ni. This would bring Mg_2Ni into the range of reversible room temperature hydrogen sorption. In a recent study on Mg_2NiH_4, Yvon *et al.* [116] suggested that the maximum hydrogen concentration of this compound is mainly limited by electronic factors and that structurally related compounds (M_2TH_x—where M = alkaline earth or divalent rare-earth metal; T = transition metal of group VIII; $4 \leqslant x \leqslant 6$) [117] having more than four hydrogen atoms per formula unit could possibly be stabilized by partially replacing Ni with a transition metal of lower valency or Mg by a non-transition metal of higher valency.

Attempts have been made to prepare such compounds by partially replacing Ni by 3d elements [62, 118–122], and Mg by non-transition elements [122] in the binary phase of Mg_2Ni. But the alloys obtained have so far failed to yield hydrides having more than four H atoms per formula unit. On the other hand they show some interesting properties with respect to hydriding and dehydriding kinetics as well as the dissociation temperature of the hydride. It was also reported that the partial substitution of Mg by 3d metals on Mg-rich, rare-earth intermetallic compounds resulted in improved dehydriding kinetics [123–126].

In order to achieve partial substitution of Ni atoms in Mg_2Ni by iron or cobalt, some experiments were performed [62]. However, no significant amount of substitution occurred in the $Mg_2Ni_{1-x}M_x$ (M = Fe or Co) systems. The highest substituent concentrations of about 2 atom % were obtained for Co. The effects of these low-concentration additives on the stability of the corresponding hydrides were negligible. The same observation was noticed by Darnaudery *et al.* [119] for the addition of Mn or Ti, but they do observe the substitution of other elements such as V, Cr, Fe, Co, Cu and Zn. On the contrary, Lupu *et al.* [120] reported that there is no substitution in $Mg_2Ni_{1-x}Fe_x$ ($x \leqslant 0.37$) alloys. This was explained on the basis of Extended X-ray Absorption Fine Structure (EXAFS) measurements with Mössbauer spectral results. In this range of composition multiphase alloys were obtained containing Mg_2Ni, Mg and more or less finely dispersed Fe in the form of isolated atoms or small clusters as proved by the EXAFS technique and Mössbauer spectroscopy. Thus they confirmed that there is no significant substitution of Ni by Fe atoms in the Mg_2Ni lattice, which is in agreement with the observation of Mintz *et al.* [62]. Stable hydrides are formed with Fe substituted Mg_2Ni alloys, which is in disagreement with results of Darnaudery *et al.* [119] (Table 5). However, these alloys show higher desorption rates than pure Mg_2Ni, which is similar to the effect of Al in Mg–Ni–Al alloys [127].

Alloys of the type $Mg_2Ni_{1-x}M_x$ (M = V, Cr, Mn, Fe or Co; $0.01 \leqslant x \leqslant 0.05$) have been investigated [128]. It has been reported that the amount of absorbed hydrogen increases for Co and Cr substituted alloys. These results are in disagreement with those of Darnaudery *et al.* [119]. It was also reported that the decomposition rate of $Mg_2Ni_{0.95}Co_{0.05}$–hydride is 17.38% per minute, which is 20% greater than that of Mg_2Ni–hydride. A comparative study of the action of hydrogen on $Mg_2Ni_{1-x}M_x$ (M = V, Cr, Fe, Co, Cu or Zn; $x = 0.25$) alloys has been carried out [119]. Hydriding of the alloys resulted in the formation of quaternary hydrides. The hydriding process leads to the starting ternary alloys, except in the case of Cu-containing alloy. This behaviour of $Mg_2Ni_{0.75}Cu_{0.25}$ seems to be similar to that of Mg_2Cu due to the decomposition of the alloy during the hydriding reaction [79]. The thermal stabilities of these compounds are close to that of Mg_2NiH_4. In each case the hydrogen/alloy mole ratio is lower than the corresponding Mg_2NiH_4 (Table 5).

Interestingly, the replacement of Ni in Mg_2Ni by the 3d elements alters the dissociation temperature markedly (Table 5). For example the dissociation temperature in 1 atm pressure for Cu-containing alloy significantly drops from 250° to 227°C, whereas for the Co-containing alloy this temperature increases to 267°C. The absorption and desorption rates for $Mg_2Ni_{1-x}M_x$ alloys are close to those obtained with Mg_2Ni except for the Co-containing alloy. Because of the encouraging results obtained with the $Mg_2Ni_{1-x}Cu_x$ system, Darnaudery *et al.* [129] continued their work on the same system by varying the x values from 0 to 0.85 in order to optimize the alloy. The absorption and desorption rates for these alloys are close to those obtained with Mg_2Ni. The other properties of these compounds are listed in Table 5.

Lupu *et al.*[121] reported results on Be-substituted Mg_2Ni alloys, $Mg_2Ni_{1-x}Be_x$ ($x = 0.15$ or 0.25). The heat of formation shows an increased stability for the hydrides of the modified alloys compared to that of pure Mg_2Ni. Hirata *et al.* [122] have investigated modified intermetallic compounds of the composition $Mg_{2-x}MNi$ (M = Al or La; $0.05 \leqslant x \leqslant 0.1$). They observed that the stability of the hydride is decreased by partial substitution of Mg by Al. An activation energy of about 84 kJ mol^{-1} was determined for dehydriding. This value

Table 5. The various properties for the $Mg_2Ni_{1-x}M_x$ and $Mg_{2-x}M_xNi$ alloys (M = transition and non-transition metals; $0 \leq x \leq 1$) [24, 38, 55, 79, 119–122]

Alloy composition (atomic ratio)	Cell parameters (Hexagonal structure)		Hydrogen content			Hydride dissociation temp. at $pH_2 = 1$ atm (°C)	Thermodynamic data for the hydride	
	a (A°)	c (A°)	H-atoms per molecule	Expl. wt %	Theo. wt %		ΔH (kJ mol H_2^{-1})	ΔS (kJ mol H_2^{-1})
Magnesium	3.21	5.21	2.00	7.60	7.65	287	−74.5	−135.0
Mg_2Ni	5.19	13.25	4.20	3.60	3.62	250	−64.5	−122.0
Mg_2Ni	5.20	13.25	4.00	3.70	3.62	253	−64.0	−122.5
$Mg_2Ni_{0.75}V_{0.25}$	5.22	13.29	3.17	2.90	3.66	250	−62.2	−119.1
$Mg_2Ni_{0.75}Cr_{0.25}$	5.21	13.26	3.29	3.00	3.65	248	−60.0	−114.9
$Mg_2Ni_{0.75}Fe_{0.25}$	5.22	13.28	3.09	2.80	3.62	253	−63.2	−121.0
$Mg_2Ni_{0.75}Co_{0.25}$	5.21	13.18	3.45	3.10	3.59	279	−64.5	−123.5
$Mg_2Ni_{0.75}Cu_{0.25}$	5.20	13.43	3.30			227	−53.2	−101.9
$Mg_2Ni_{0.90}Cu_{0.10}$	†	†	3.50	—	—	—	—	—
$Mg_2Ni_{0.50}Cu_{0.50}$	†	†	2.80	—	—	223	−63.2	−124.0
$Mg_2Ni_{0.25}Cu_{0.75}$	†	†	2.70	—	—	229	−67.4	−129.9
$Mg_2Ni_{0.75}Zn_{0.25}$	5.24	13.46	3.66	—	—	246	−61.5	−117.8
Mg_2Cu	—	—	2.60	—	—	239	−72.8	−142.1
$Mg_2Ni_{0.75}Fe_{0.25}$	—	—	—	—	—	250	−85.8*	−164.3*
							−82.7	−158.4
$Mg_2Ni_{0.63}Fe_{0.37}$	—	—	—	—	—	250	−77.0*	−147.4*
					—		−81.6	−156.3
							−82.7	−158.4
$Mg_2Ni_{0.85}Be_{0.15}$	5.25	13.33	—	—	—	250	−91.2*	−174.6*
							−70.7	−135.4
$Mg_2Ni_{0.75}Be_{0.25}$	5.28	13.41	—	—	—	250	−79.9	−153.0
$Mg_{1.92}Al_{0.08}Ni$	†	†	—	—	—	—	−70.5	−135.0

* Corresponds to the lower and upper plateau regions.

† The crystal structure and unit cell dimensions are almost the same as those of Mg_2Ni.

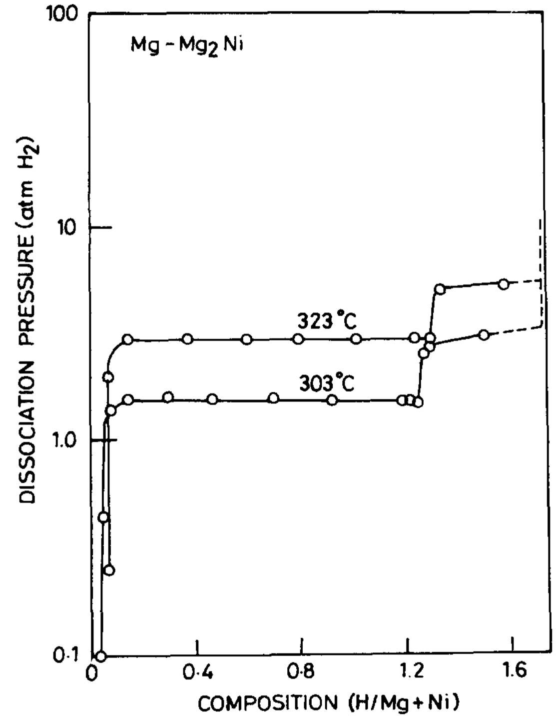

Fig. 5. Desorption isotherms for Mg–Mg_2Ni–H_2 system. The initial composition is 72.9 wt% Mg, and 25.2 wt% Ni [38].

of activation energy is lower than those determined for the formation and decomposition of the hydrides, Mg_2NiH_4 (86.4 kJ mol^{-1}) [57, 114], and MgH_2 (96 kJ mol^{-1}) [52, 56, 66]. These results provide evidence for the improved dehydriding kinetic properties of the hydride of the modified alloys. Simultaneously they prepared compounds such as $Mg_{1.95}La_{0.05}Ni$ and $Mg_2Ni_{0.98}Cu_{0.02}$ [122]. The effect of the additives (La or Cu) on the hydriding and dehydriding kinetics of Mg_2Ni has not been fully evaluated yet. $Mg_{2-x}M_xNi$ (M = Al or Ca; $0.01 \leq x \leq 1.0$) alloys are used as hydrogen storage materials. It has been observed that the average decomposition rate of $Mg_{1.8}Ca_{0.2}Ni$ hydride was 20.33% per minute, against 14.14% per minute for Mg_2NiH_4 [130].

It has been reported that the substituted Mg_2Ni alloys are isostructural with Mg_2Ni, which has a hexagonal symmetry [62, 119, 121, 122]. This is in disagreement with the observations of Lupu *et al.* [120]. Mg_2NiH_4 exhibits a phase transition from the low-temperature (LT) structure to the high-temperature (HT) structure at about 230°C. However, there is still some controversy regarding the crystal structure of the hydride [131]. The hydrides of the modified intermetallic compounds also show allotropic varieties similar to those of Mg_2NiH_4.

Mg–Mg₂Ni alloys. Mg_2NiH_4 is not attractive as an energy storage compound. It contains less than one-half the amount by weight of hydrogen in MgH_2 with only a small decrease in stability; its primary virtue lies in the fact that Mg_2Ni acts as a catalyst for the Mg–H_2 reaction [38]. The presence of excess of Mg produces an isotherm with two plateau pressures. Figure 5 shows typical pressure–composition isotherms for an alloy composition of 72.9 wt% Mg and 25.2 wt% Ni. This alloy contains 5.7 wt% hydrogen. The excess Mg in the alloy forms MgH_2, which corresponds to the lower plateau due to the reaction (1). When all free Mg is exhausted, the second higher plateau appears, which is due to reaction (2) of intermetallic compound, Mg_2Ni with hydrogen.

Thus, the presence of Mg_2Ni has a catalytic effect on the reaction of Mg with H_2 in the Mg-rich alloys. This was confirmed by the XPS and AES results on the Mg–Ni systems [100]. It was found that Mg_2Ni promotes the hydriding of Mg, because of the absence of a compact oxide layer as with pure Mg, and also the presence of catalytically active metal.

Buchner *et al.* [35] have reported that the maximal hydrogen contents in Mg-rich Ni alloys are as given in Table 6. The kinetics of hydriding and dehydriding are faster in these alloys than that of MgH_2. In order to

Table 6. Hydrogen absorption of various magnesium–nickel alloys

System	Alloy composition (wt%)	Hydrogen content (wt%)	Hydriding conditions Pressure (atm)	Temp. (°C)	Ref.
Mg_2Ni	45.3 Mg–54.7 Ni	3.6	25	350	38
		3.7	10	300	35
Mg–Mg_2Ni	74.8 Mg–25.2 Ni	5.7	25	350	38
	75.0 Mg–25.0 Ni	6.0–6.5	21–56	400–500	66
	90.0 Mg–10.0 Ni	5.2	10	300	114
	95.0 Mg–5.0 Ni	7.3	—	—	98
	22 Mg–78 Mg_2Ni	4.8	10	300	35
	67 Mg–33 Mg_2Ni	6.0	10	300	35
	*	7.0	10	300–400	15

* Magnesium with 5 atomic % nickel ($Mg_{0.95}Ni_{0.05}$).

achieve the greatest possible storage capacity, the Ni content must be kept very low. However, doping with Ni ensures sufficiently fast kinetics because of the formation of the Mg_2Ni phase. It is therefore necessary to identify the lowest concentration of Ni at which the mechanism of bypass charging (35) is not impaired. Such investigations have revealed an optimum Ni concentration of approximately 5 atomic %. The maximum hydrogen storage capacity that can be achieved with this composition is approximately 7.0 wt% [15].

The formation and dissociation of Mg–25 wt% Ni hydride was studied by Douglass [66]. The hydriding reaction of the alloy resulted in two hydrides, viz. MgH_2 and Mg_2NiH_4, the former being more stable and forming first by consuming the primary Mg phase of the eutectic structure. The hydride advances into the alloy as a "front", after which the eutectic plates of Mg_2Ni react to form the ternary hydride. Finally, the larger primary plates of Mg_2Ni react. The maximum hydrogen content obtained in this alloy was 6.5 wt%. These values are higher than the theoretical value if one considers that the structure is a hypereutectic one consisting of about 45.3 wt% Mg_2Ni and about 54.7 wt% Mg, the two phases containing 3.6 and 7.65 wt% hydrogen when hydrided to Mg_2NiH_4 and MgH_2, respectively to give a total hydrogen content of 5.63 wt%.

Douglass [66] explained this discrepancy on the basis of the microstructure of the alloy and of the machined particles. Scanning electron micrographs showed the presence of large primary particles of Mg_2Ni that solidify when the temperature is decreased. The remaining liquid at the eutectic temperature solidified to give a eutectic mixture of Mg_2Ni and Mg, the eutectic Mg_2Ni being thin, small white particles. Machining of this alloy caused the brittle intermetallic compound to fracture and drop out wherever it was exposed to the surface. Consequently, the machined chips had very little or no primary Mg_2Ni in them, as seen from the micrograph [66]. In other words, the particles had mainly the eutectic structures. The theoretical hydrogen content of the modified structure was calculated to be 6.0 wt%, which is consistent with the experimental observations. The value of 6.5 wt% is still not explainable unless it is presumed that some surface oxide on the interior of the stainless steel retort is formed which is dislodged and mixes with the hydride.

Mg–10 wt% Ni alloy was hydrided at 300°C under 10 atm of hydrogen as readily as Mg_2Ni [132]. This alloy is more profitable than Mg_2Ni from the point of view of hydrogen content as well as the Ni content by weight. The alloy absorbs 4.7–5.2 wt% hydrogen. Crystallographically, Mg_2Ni is an intermetallic compound but Mg–10 wt% Ni is a mixture of pure Mg and the eutectic of Mg and Mg_2Ni, the rate of decomposition being quite slow at 300°C even in vacuum. According to Rohy *et al.* [133], $Mg_{0.85}Ni_{0.10}Zn_{0.05}H_x$ reaches 1 atm at 260°C, a temperature which is considerably lower than that of 302°C for $Mg_{0.90}Ni_{0.10}H_x$. The hydrogen content in Mg–10 wt% alloy is increased with the increased number of cycles [132]. Exposing the hydrided material to air caused a considerable deactivation of the sample in the dehydriding kinetics. Thus the dehydriding reaction required a somewhat higher reaction temperature than the equilibrium temperature. The absorption capacities of various Mg–Ni alloys are listed in Table 6.

Nachman and Rohy [87] have developed an extensive alloying programme for the Mg-based alloy hydrides suitable for automotive hydrogen fuel storage applications. This involved addition of elements such as Cu, Zn, Sn, Ga, Y, Si, Al, In and rare-earth metals which resulted in the formation of ternary and multicomponent systems. After alloy optimization studies, they found that the alloy $Mg_{0.845}Ni_{0.05}Cu_{0.10}Y_{0.005}$

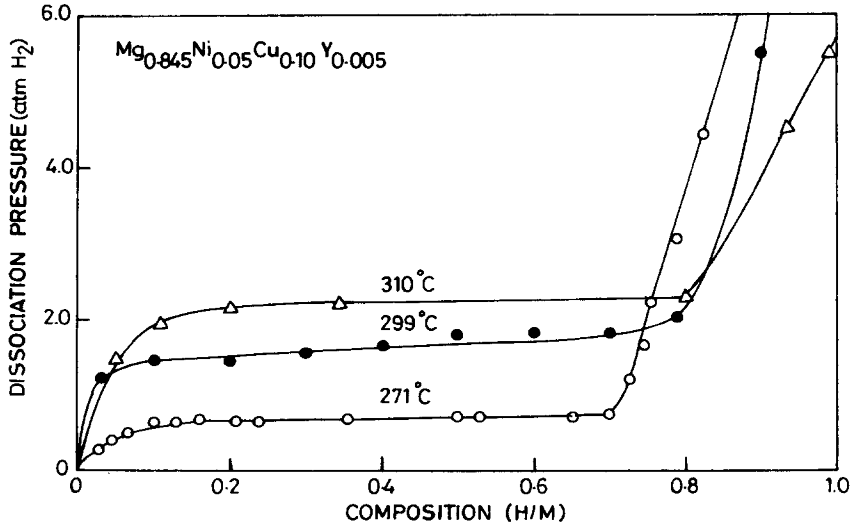

Fig. 6. Desorption isotherms for Mg–Ni–Cu–Y–H_2 system [87].

emerged as representing the best effort for low dissociation temperature combined with low nickel content. The pressure–composition isotherms were determined at various temperatures and are shown in Fig. 6. Comparing Fig. 6 with Fig. 5 one can see that the dissociation pressure of the alloy, $Mg_{0.845}Ni_{0.05}Cu_{0.10}Y_{0.005}$ with 5 wt% Ni is somewhat higher than that of the 25 wt% Ni alloy at the same temperature. Thus the alloy exhibited improved hydride properties over the Mg–25 wt% Ni alloy reported by Reilly and Wiswall [80].

Kinetics of Mg–Ni alloys. Although the studies on the kinetics of the reaction between Mg–Ni alloys and hydrogen were reported [31, 114, 132–136], it has not been studied critically; the results are inconsistent with each other. One of the reasons for this is that powder beds of metal hydrides have poor heat transmissivity and the heat of the reaction can not be effectively transferred [137]. Buchner *et al.* [35] have, however, reported results showing faster desorption kinetics for Mg_2Ni.

Deactivation and reactivation of Mg–Ni alloys. Eisenberg *et al.* [136] studied the effect of Ni plating on the hydriding and dehydriding kinetics of Mg. They found that electroplated Ni on Mg had little effect on the initial activation, hydrogen absorption capacity and kinetics, but however, had considerable effect on desorption kinetics. They have encountered the problem of agglomeration of the surface Ni into larger crystallites, thus reducing the surface Ni dispersion. Because of this sintering of Ni on the Mg surface, the rate of dehydriding is decreased rapidly (Fig. 7). Also the plot of "effective surface Ni content" against specific desorption rate (SDR) data suggests that the surface Ni is the factor controlling desorption rate rather than bulk Ni. Therefore with better surface Ni dispersion, the rate of dehydriding can be increased. The preferred form of Ni is a thin film which would provide the ideal situation (Fig. 7). The agglomeration can be solved either by developing a plating technique that would yield a thin layer of Ni exhibiting a high degree of structural integrity with the Mg surface, or by vapour deposition of Ni on the Mg surface. Thus, a plated Ni catalyst imparts to Mg a desorption rate range required for automotive storage, as seen from Fig. 7.

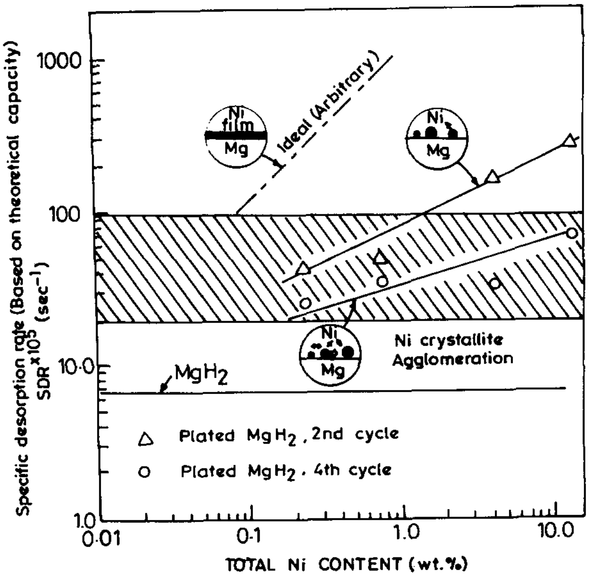

Fig. 7. The effect of Ni content on the Specific Desorption Rate (SDR) for Ni-plated MgH_2. The hatched area represents the approximate range suitable for automotive applications [136].

Mg–Ni alloys containing less than 55 wt% Ni have low melting points (about 500–760°C) which are close to the working temperature. It is important to note the deactivation of the alloy by sintering during the reaction [138]. Akiba *et al.* [138] have investigated Mg–23.3 wt% Ni alloy which has the lowest melting point (507°C) of the Mg–Ni alloys. They found that the reaction rate decreased during the reaction. It is believed that the partially hydrided alloy sinters during the reaction. That is, agglomeration of Ni on the Mg surface occurs as reported by Eisenberg *et al.* [136]. Hence, Akiba *et al.* [138] suggest that cycling the hydrogen content through evacuation and full hydriding enables the alloy to regain its original activity.

(ii) *Magnesium–copper alloys.* Mg forms two intermetallic compounds with Cu, viz. Mg_2Cu and $MgCu_2$ [113]. Only Mg_2Cu alloy reacts readily with hydrogen at 300°C and a hydrogen pressure of 21.5 atm $MgCu_2$ does not react with hydrogen at temperatures up to 350°C and hydrogen pressures of 23.5 atm [79].

Mg_2Cu alloys. Hydriding of the intermetallic compound Mg_2Cu proceeds by the following reaction:

$$2Mg_2Cu + 3H_2 \rightleftharpoons 3MgH_2 + MgCu_2, \qquad (4)$$

where the maximum H/M ratio is approximately 1.0. X-ray analysis showed only the presence of MgH_2 and $MgCu_2$. Since only MgH_2 is present, no ternary hydrides are formed during this reaction. This alloy contains 2.7 wt% hydrogen. This is, however, not commensurate with a marginal decrease in stability obtained.

Modified or substituted Mg_2Cu alloys. The influence of Al on the Mg_2Cu–H_2 system was studied by Biris *et al.* [139]. Melting 4–11 atomic% Al with a mixture of Mg and Cu (atomic ratio Mg/Cu = 2/1) leads to the formation of $MgCu_{2-x}Al_x$ [$Mg(Cu,Al)_2$] alloys ($MgCu_2$ structure) together with Mg_2Cu and Mg excess. The interesting aspect of the desorption isotherms of this system is that there is a considerable amount of hydrogen which cannot be desorbed even by heating the sample for several hours at 470°C. The only component responsible for the absorption of the remaining hydrogen is $Mg(Cu,Al)_2$. Taking into account that pure $MgCu_2$ does not absorb hydrogen [79], the behaviour of $MgCu_{2-x}Al_x$ must be due to Al.

Biris *et al.* [139] reported a compound formation with the composition $MgCu_{1.6}Al_{0.4}$ ($MgCu_2$ structure) separately. It does not absorb hydrogen in the same condition. Thus they concluded that the presence of Mg and/or Mg_2Cu in close contact with the finely dispersed $MgCu_{2-x}Al_x$ in the alloys has a catalytic effect on the hydrogen absorption in the latter. The hydrogen absorbed in this phase is strongly bound as proved by the desorption isotherms (hydrogen is not desorbed even by heating the sample to 470°C) and nuclear magnetic measurements. The NMR measurements show that the hydrogen diffusion is ineffective [139].

Mg–Mg$_2$Cu alloys. When Mg is present in the alloy in excess of the composition corresponding to Mg_2Cu, the pressure–composition isotherm exhibits two plateaus. This situation is similar to Mg–Mg_2Ni system [38]. The alloy (starting composition was 90.5 wt% Mg and 9.5 wt% Cu) reacts quite rapidly with hydrogen below 300°C at a pressure of 30 atm. It has an effective storage capacity in excess of 6.62 wt% of hydrogen. In this case the upper plateau is due to the reaction of the intermetallic compound, Mg_2Cu with hydrogen [79]. However, it is interesting to note that the presence of Mg_2Cu in a two-phase Mg–Mg_2Cu alloy has a catalytic effect for the direct reaction of hydrogen with Mg, whereas higher hydrogen pressures and temperatures are necessary to form MgH_2 from Mg alone [44, 55]. This has been proved by thermodynamic [49, 50] and surface studies [100, 140]. In addition, the decomposition of MgH_2 in the presence of Mg_2Cu is quite rapid, particularly at the higher H/Mg ratios, equilibrium dissociation pressures could be reached even at 275°C.

In order to check on the validity of the proposed hydrogen reactions, Reilly and Wiswall prepared a number of alloys of various compositions, hydrided and dehydrided several times. They found that the hydrogen contents are in good agreement with the predicted values. They also observed that the alloy with 90.5 wt% Mg absorbed more hydrogen (6.62 wt%) compared to the lower wt% Mg content. Guinet *et al.* [59] studied Mg–5 atomic% Cu ($Mg_{0.95}Cu_{0.05}$) and was found to have a good sorption capacity (4 atomic% of hydrogen in 1 h at 350°C), and good hydriding and dehydriding kinetics as previously shown [79].

(iii) *Magnesium–scandium alloys.* The hydrogen absorption and desorption properties of Mg-based Sc alloy was studied by Ogawa *et al.* [88]. They observed that the amount of hydrogen desorbed is much smaller than the amount of absorbed hydrogen under the same conditions (ambient pressure and temperature). MgH_2 has a crystal structure of rutile type [44]. In this structure each hydrogen atom is coordinated to three Mg atoms. They assumed that the hydrides of $Mg_{0.9}Sc_{0.1}$ (Mg–1 atomic% Sc) also have a similar structure by replacing one of the Mg atoms by a Sc atom. It was argued that the sloping plateau arises (Fig. 8) because of the strong bond between the hydrogen atom and the neighbouring Sc atoms. The strong bond is attributed to the outer electron of the Sc atom in the solid solution which has significant "d" character. Supporting evidence for this view was obtained by Ogawa and Aoki [141] from the electronic structure in Mg–Y alloys; the 4d-electron of Y still maintains its "d" character in the alloys. Since Y and Sc are located in the same group, they assumed that the "d" electron of Sc behaves similar to that of Y in the Mg host. Thus, the amount of hydrogen desorbed is much smaller than the amount of absorbed predicted from the formula, (Mg–Sc)H_2 [88].

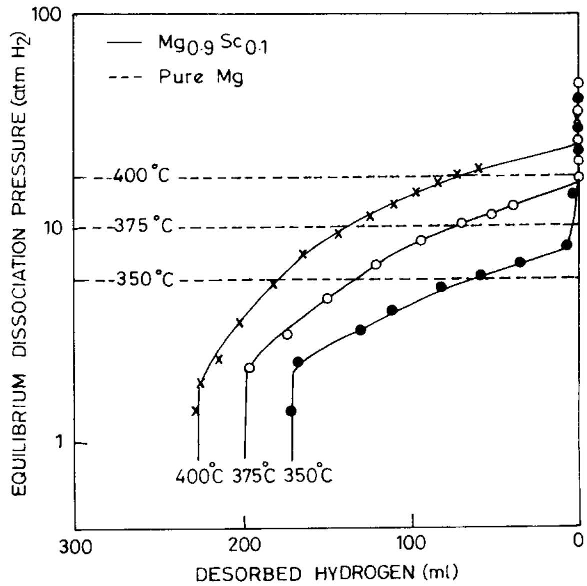

Fig. 8. Desorption isotherms for $Mg_{0.9}Sc_{0.1}$–H_2 systems. The dissociation pressure of MgH_2 (dashed lines) is also plotted for comparison [55, 88].

(iv) *Magnesium–yttrium alloys.* Buchner *et al.* [35] have investigated Mg–$Mg_{17}Y_{13}$ alloys to optimize the storage capacity, absorption and desorption kinetics and dissociation enthalpy with respect to vehicular application. They reported that results similar to that of the Mg_2Ni [35] were obtained in the Mg–Y system. In contrast to Mg–Mg_2Ni systems, the pressure–composition isotherms have only one plateau, the heat of formation is comparable to the heat of formation of MgH_2. The kinetics of hydriding and dehydriding are faster than that of MgH_2. Like the Mg–Mg_2Ni system the Mg–$Mg_{17}Y_{13}$ system shows good hydriding and dehydriding character. Rohy and Nachman [87] have investigated various ternary alloys of Mg with Y as one of the components. Thus, the modification of $Mg_{17}Al_{12}$ and $Mg_{0.9}Al_{0.1}$ (Mg–10 atomic% Al) alloys with the ternary addition of Y resulted in alloys exhibiting rapid kinetics and higher plateau pressures than the binary alloys hydrided under the same condition. The addition of Y to Mg–Cu–Ni alloys also exhibits improved kinetics and plateau pressure over Mg_2Ni (38).

Douglass [34] has investigated binary and ternary alloys of Mg with Y. The Y-containing alloys exhibit the most rapid hydriding and dehydriding kinetics compared to other alloys [34]. The best alloy studied was the ternary alloy, Mg–5Y–5Ni which corresponds to a composition of 71.4, 14.2 and 9.4 wt% of Mg, Y and Ni respectively, which consistently yielded 3.0 wt%

Table 7. Hydrogen absorption and desorption behaviour of various magnesium–transition metal alloys

Alloy composition (atomic percent)	Hydrogen content (wt%)	Hydriding conditions		Hydrogen released (wt%)	Dehydriding conditions		Ref.
		Pr. (atm)	Temp. (°C)		Pr. (atm)	Temp. (°C)	
Mg_2Ni	3.6	25	350	—	—	—	38
$Mg–Mg_2Ni$	5.7	25	350	—	—	—	38
Mg_2Cu	2.7	30	300	—	—	—	79
$Mg–Mg_2Cu$	6.6	30	300	—	—	—	79
Mg_2Fe*	5.4	20–120	450–520	—	—	—	142
$Mg–Mg_{17}Y_{13}$	5.0	10	400–450	4.5	3.0	320	35
Mg–1Y	4.5	56	400	4.0	1.0	300	34
Mg–5Y	7.0	56	400	3.4	1.0	300	34
Mg–5Mn	6.0	56	400	1.5	1.0	300	34
Mg–5Co	2.0	56	400	0.0	1.0	300	34
Mg–1Ag	5.7	56	400	2.0	1.0	300	34
Mg–5Ag	5.3	56	400	0.0	1.0	300	34
Mg–1Al–1Y	6.0	56	400	—	—	—	34
Mg–1Ag–1Y	6.3	56	400	—	—	—	34
Mg–5Ni–5Y	5.2	56	400	3.1	1.0	300	34
Mg–5Al–5Y	5.0	56	400	3.1	1.0	300	34
Mg–10Al–10Y	4.1	43	400	—	1.6	310	87
Mg–34Al–10Y	3.6	43	400	—	2.2 1.0	310 286	87
Mg–10Cu–5Ni–0.5Y	3.7	21	400	—	2.0 1.5	310 299	87

* This alloy is unstable, but forms a stable Mg_2FeH_6.

hydrogen at 250°C in about 3 h. The second best alloy was Mg–5Y, which desorbed 3.4 wt% hydrogen at 300°C in 1 h. However, the total amount of hydrogen released was about one-half of the total amount stored. Unless all of the hydrogen can be released there is no special advantage compared to Mg_2Ni which hydrided to form Mg_2NiH_4 (3.6 wt% H_2), from which 3.0 wt%, or more hydrogen can be recovered at a lower temperature [38]. Because of the high cost of Y, Douglass [34] has suggested that a composition of Mg–1Y–5Ni might be interesting. The results of the hydriding and dehydriding characteristics of various Mg–Y alloys are summarized in Table 7.

(v) *Magnesium–iron alloys.* Welter and Rudman [86] have investigated a two-phase approach which employs iron particles (5 atomic%) as a dissociative adsorption catalyst for hydriding Mg. From their studies they arrived at the following conclusions:

- addition of iron resulted in significantly faster hydriding kinetics, indicating that iron particles have a catalytic effect;
- the preparation of the sample did not succeed in producing an even dispersion of iron particles, and
- the catalytic effect can be increased considerably by the dispersion of finer iron particles.

Though iron does not form intermetallic compounds with Mg, it readily combines with hydrogen and Mg to form a ternary hydride according to the reaction:

$$2Mg + Fe + 3H_2 \rightleftharpoons Mg_2FeH_6, \qquad (5)$$

which was investigated by Didisheim *et al.* [142, 143] recently. The new iron-based ternary hydride, Mg_2FeH_6 belongs to a structural class of ternary metal hydrides having the general composition M_2TH_x (M = alkaline-earth, or divalent rare-earth metal; T = transition element of group VIII; $4 \leq x \leq 6$) [38, 116, 143].

The influence of electronic factors on the stability and hydrogen storage capacity of metal hydrides has been established for the structural series Mg_2NiH_4 [116], Mg_2CoH_5 [144] and Mg_2FeH_6 [142]. This was supported by Gupta [145] from the augmented plane wave band structure calculations. The ternary hydride, Mg_2FeH_6 shows considerably better hydrogen content (5.4 wt%) than Mg_2NiH_4 (3.6 wt%). Also, the hydrogen concentration per unit volume of Mg_2FeH_6 is exceptionally high (9.1×10^{19} atoms l^{-1}), exceeding, for instance, that of MgH_2 (6.5×10^{19} atoms l^{-1}) by about 40%. However, with respect to the theoretical stability, Mg_2FeH_6 appears to be less promising for energy storage applications, mainly because of its high enthalpy of dissociation (98 kJ mol H_2^{-1}). Also, the disproportionation of Mg_2FeH_6 into elemental Mg and Fe upon desorption, and the hydrogen uptake of the sample decreased after four consecutive cycles.

(vi) *Magnesium with other transition elements.* Douglass [34] has studied the reaction between hydrogen and Mg with some transition elements (Mn, Co, Y and Ag) over a concentration range of 1–5 atomic%. The salient points of the hydriding and dehydriding behaviour are given in Table 8. From this table it is

Table 8. Hydriding characteristics of ternary magnesium–lithium alloys [87]

Alloy composition (atomic ratio)	δT* (°C)	Hydrogen absorbed (wt%)	Plateau pressure at 310°C (atm)
$Mg_{0.8}Li_{0.1}Ni_{0.1}$	44	2.04	0.2
$Mg_{0.8}Li_{0.1}Zn_{0.1}$	19	1.63	0.6
$Mg_{0.8}Li_{0.1}Sn_{0.1}$	10	1.70	0.8
$Mg_{0.8}Li_{0.1}Si_{0.1}$	18	1.26	0.8
$Mg_{0.8}Li_{0.1}Cu_{0.1}$	14	0.86	0.6
$Mg_{0.7}Li_{0.1}Ni_{0.1}Sn_{0.1}$	89	2.32	2.4
$Mg_{0.8}Li_{0.05}Ni_{0.1}Sn_{0.05}$	81	2.48	2.0
$Mg_{0.75}Li_{0.1}Ni_{0.1}Cu_{0.05}$	60	1.05	1.6

* The temperature rise observed during hydriding which is found to be a good qualitative measure of hydriding kinetics. The increase in the δT value indicates relatively the rapidity of hydriding kinetics.

clear that the Mg–Co alloy absorbed considerably less amounts of hydrogen, so it was rejected as unacceptable and was not tested further, whereas the alloy Mg–In picked up good amounts of hydrogen, but because of its slow dehydriding kinetics, this alloy was also eliminated from further study. Even though the dehydriding behaviour of Mg–Ag alloy is slow, it was retained for further study because of its rapid hydriding behaviour (Fig. 9). A composition of Mg_3Ag has also been reported [26]. Thus, these data indicate a smaller catalytic effect of Co on the hydriding reaction and of Mn and Ag on the dehydriding reaction compared to the well known systems such as Mg–Ni and Mg–Cu. Alloys containing Ag and Y exhibit rapid hydriding kinetics and pick up more hydrogen. Dehydriding is most rapid for Mg–Y alloys, but it is slow in the case of Mg–Ag alloys. Therefore, a ternary approach was carried out based on the performance of binary alloys so that two relatively good binary additions were combined to give a better alloy.

(b) *Magnesium–non-transition metal systems*

(i) *Magnesium–lithium alloys.* The densities of Mg and Li are very low and the hydride contains substantial quantities of hydrogen viz. 7.65 wt% for MgH_2, and 12.68 wt% for LiH. However, the disadvantage of both hydrides is their relatively high thermodynamic stability, with LiH exhibiting an even higher stability than MgH_2. Thus, the hydrides of Mg and Li alloys also showed a higher stability than the binary hydrides. Hence, Nachman and Rohy [87] have studied ternary, quarternary and multicomponent systems to decrease the thermodynamic stability of the Mg–Li alloy hydrides by the addition of alloying elements such as Zn, Sn, Si, Ni and Cu. The highest hydrogen content in this series was achieved with the alloy $Mg_{0.8}Li_{0.1}Ni_{0.1}$ (2.04 wt% H_2). Since results with the best characteristics were obtained with this ternary hydride, it was used as a base for quarternary alloy hydrides [87]. It was observed that the addition of 10 atomic% Cu or Sn resulted in the increase of dissociation pressure (Table 8). It is interesting to note that the alloy containing 5 atomic% Sn ($Mg_{0.8}Li_{0.05}Ni_{0.1}Sn_{0.05}$) has the highest plateau pressure and is one of the systems with highest hydrogen contents obtainable among the quarternary systems. Addition of a fifth element was made by approximately 5–6 atomic%

Table 9. Hydriding characteristics of various binary and ternary magnesium–aluminium alloys [66, 81, 87]

Alloy composition (atomic ratio)	δT* (°C)	Hydrogen absorbed (wt%)	Plateau pressure at 300°C (atm)
$Mg_{17}Al_{12}$ (γ-phase)	—	3.31	—
Mg_4Al_5 (ε-phase)	—	2.77	—
Mg_2Al_3 (β-phase)	—	3.28	—
MgAl ($\beta + \gamma$-phase)	—	0.38	—
$Mg_{0.62}Al_{0.38}$	19	2.30	1.4
$Mg_{0.59}Al_{0.36}Ni_{0.05}$	28	3.36	1.8
$Mg_{0.59}Al_{0.36}La_{0.05}$	31	3.04	1.9
$Mg_{0.59}Al_{0.36}Y_{0.05}$	30	2.01	2.2
$Mg_{0.56}Al_{0.34}La_{0.10}$	—	2.12	1.7
$Mg_{0.56}Al_{0.34}Y_{0.10}$	40	3.29	2.1–2.6
$Mg_{0.56}Al_{0.34}Ni_{0.05}Y_{0.05}$	—	2.58	1.5
$Mg_{0.56}Al_{0.34}Mm_{0.10}$†	—	2.15	1.8
$Mg_{0.80}Al_{0.01}Y_{0.10}$	65	4.08	1.7
$Mg_{0.80}Al_{0.10}La_{0.10}$	123	4.22	2.1
$Mg_{0.91}Al_{0.09}$	—	7.0	—

* Refer Table 8.
† Mm = Mischmetal

Si, Cu or Zn. It was concluded that there was no particular advantages with these multicomponent systems when compared with quaternary systems.

Thus, Nachman and Rohy [87] have concluded from these results that the thermodynamic stability of LiH is difficult to overcome by decreasing interstitial hole size. Similar conclusions were reached by Air Products and Chemicals, Inc. [146] in their studies of the Mg-5 atomic% Li alloy, in which the structural model predicts an opposite trend to chemical stability.

(ii) *Magnesium–aluminium alloys*. Preliminary results have been reported on the hydrogenation reaction of Mg–Al alloys [65, 66, 80, 87, 147–150]. Data on hydriding characteristics of these alloy systems are summarized in Table 9. It has been found that hydriding of the alloys causes disproportionation into MgH_2 and Al according to the reaction:

$$Mg_2Al_3 + 2H_2 \rightleftharpoons 2MgH_2 + 3Al \tag{6}$$

$$Mg_{17}Al_{12} + 17H_2 \rightleftharpoons 17MgH_2 + 12Al. \tag{7}$$

The reaction rates, however, seem to be very slow thus rendering this system impracticable for most applications. Addition of small amounts of Ni or In to the Mg–Al alloys causes a significant increase in the hydrogenation rate of these compounds [65, 147, 148, 151, 152].

Nachman and Rohy [87] have attempted to decrease the thermodynamic stability of Mg–Al alloy hydrides by single- or multi-additions of alloying elements consisting of Ni, Cu, Zn, Sn, Si, Li and rare-earths. The active elements, particularly rare-earths, may behave as scavengers to prevent oxidation of Al, which is believed to be responsible for the poor hydriding kinetics of the Mg–Al alloys. Among the alloys studied, the $Mg_{17}Al_{12}$ alloy showed a higher hydrogen content. The addition of 5 atomic% Ni to this alloy showed improved hydriding kinetics. The highest plateau pressure was achieved with Y-containing alloy (5 atomic%). The addition of 5 atomic% of Sn, Si and Li appears to provide no benefit to the hydriding behaviour of the basic intermetallic compound, $Mg_{17}Al_{12}$. Alloy of the composition $Mg_{0.56}Al_{0.34}Y_{0.10}$ exhibited the highest dissociation pressure over the entire plateau region (Table 9). The kinetics of hydriding, dehydriding and the hydrogen absorption capacities of $Mg_{17}Al_{12}$ alloys are greatly improved or altered by the addition of rare-earths or Ni or In.

Douglass [66] has reported a maximum hydrogen absorption of 7.0 wt% by Mg–10 wt% Al alloy, which corresponds to 90% of the material being hydrided and was removed completely during dehydriding. The desorption process is significantly fast. However, the system requires higher recharging time. Hence, Nachman and Rohy [87] undertook the task of increasing the hydriding and dehydriding kinetics of Mg–10 wt% Al alloys, without reducing the hydrogen absorption capacity. So the addition of La or Y were given emphasis. Both alloys absorbed substantial quantities of hydrogen after a 12 h period. The hydriding characteristics of these alloys are given in Table 9. Thus, the modifications of $Mg_{17}Al_{12}$ and Mg–10 wt% Al with ternary additions of La and Y resulted in alloys exhibiting rapid kinetics, higher plateau pressures (about one-half times) and higher hydrogen contents (three times) than the binary alloy hydrides under the same conditions.

Table 10. Activation energies for the hydriding of pure magnesium with group III-A metals [85, 153]

Alloys	Concentration of alloying element (atomic percent)	Activation energy, E_a (kJ mol H_2^{-1})
Pure Mg	—	231.0
Mg–Al	0.4	92.0
	1.0	150.6
	1.8	142.4
	4.5	242.8
Mg–Ga	0.1	108.8
	0.7	125.6
	1.2	251.2
	3.4	201.0
	5.2	150.6
Mg–In	0.3	117.2
	0.5	118.8
	0.8	167.4
	1.0	117.2
	2.5	184.2
	8.6	175.8

(iii) *Magnesium with other non-transition elements.* Mintz *et al.* [85, 153] have studied the reaction between hydrogen and activated Mg and Mg with group III-A metals (Al, Ga and In) over a concentration range of 0.1–10.0 atomic%. They noticed a marked difference between the hydriding of the pure Mg and that of Mg alloys. A detailed description of the hydriding characteristics of the various Mg–In alloys has been reported [154]. It was found that the hydriding reaction represents a three-dimensional, diffusion-controlled process. Based on this, the activation energies were calculated and the results are reproduced in Table 10. It is evident from this table that a decrease in activation energy occurs by alloying Mg with small amounts of group III-A elements. These values of activation energies are probably related to diffusion of hydrogen through the MgH_2 product layer. Thus, the addition of group III-A elements accelerates the diffusion of hydrogen in MgH_2 by lowering the activation energy of the process. However, for the alloys containing larger amounts of the group III-A constituents, the activation energy values increase again, and are comparable with, that of pure Mg. Further, it has been noticed that the addition of In to Mg did not affect the rate of decomposition of the hydride [85]. This may be accounted for by supposing that a different mechanism controls the decomposition of MgH_2 [57].

Douglass [34] has carried out a systematic study to develop Mg alloy hydrides. The initial approach was to

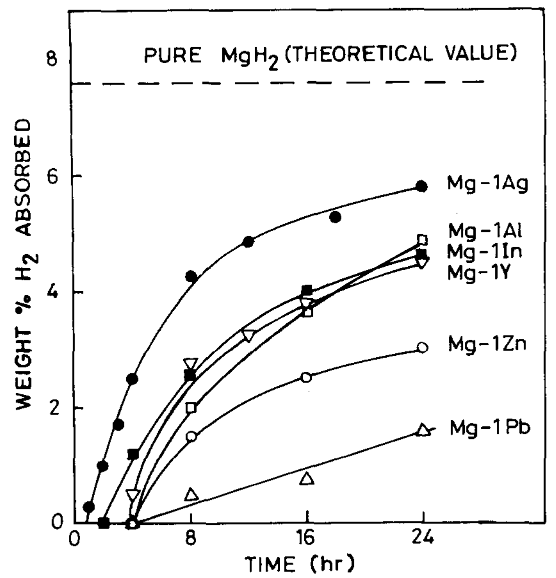

Fig. 9. Hydriding kinetics of Mg containing 1 atomic% various metals at 400°C [34].

study the solid solution of various elements in Mg. Dilute solutions of Mg with 1 atomic% Al, In, Pb, Zn and Cd were hydrided. The alloys Mg–1Zn and Mg–1Pb picked up considerably less hydrogen (Table 11) and the hydriding kinetics are significantly slow (Fig. 9). Thus, these alloys were rejected. The result from the Mg–1Zn alloy is well-supported by Bruzzone *et al.* [89], who found a composition $Mg_{51}Zn_{20}$, which absorbed considerable amounts of hydrogen (3.62 wt%). The alloy Mg–1Cd absorbed 5.0 wt% hydrogen, but because of its slow dehydriding kinetics, this alloy was also eliminated from further study. Alloys containing Al, In exhibited rapid hydriding kinetics and picked up more hydrogen, but because of their poor dehydriding kinetics these alloys were eliminated from further studies. Even though Mg–1Ag alloy showed slow dehydriding kinetics it was retained because of its rapid hydriding behaviour. The next approach was to study two-phase alloys which included the addition of Sn, Ca, Bi, Si and Sb. These elements are relatively cheap, easily available and convenient to alloy. The hydriding and dehydriding characteristics of the solid solution and the two-phase alloy are given in Table 11. It is clear from the table that none of the alloys appear to be useful for hydrogen storage application.

A large number of other Mg alloys have been screened by Reilly, referred in [26]. Among the alloys investigated were $Mg_{17}Ba_2$, Mg_3Cd, Mg_3Sb_2, MgSn and MgZn. Studies on Mg–Al, Mg–Zn, Mg_2Ca, Mg_2Sn, Mg_2Pb, Mg_3Sb_2 and Mg_2Si alloys were carried out by Suzuki and Nishimiya [83]. Several other binary Mg alloys such as Mg_3Cd, Mg_2Sn and MgAl have been suggested by Guinet *et al.* [59]. Information has also been published on the hydriding of alloys of Ca and Mg without results of practical importance [155]. The hydrogen sorption capacity of Mg_2Ca alloy was investigated by Shaltiel [161] and Oesterricher *et al.* [115]. They found that this alloy requires a high activation temperature for the hydriding reaction. The addition of Al [156] and Cu [157] to the parent alloy, Mg_2Ca, considerably reduces the activation energy.

(c) *Magnesium–rare-earth metal systems*

It has been reported that the alloying of Ce with Mg alters the ability to absorb hydrogen at room temperature, but the time required to complete the hydride formation is longer [80, 158, 159]. Mikheeva *et al.* [80] have studied the hydriding of Mg–Ce alloys in detail. Up to a concentration of 50 atomic% Mg, the alloys absorb hydrogen at room temperature without preliminary heat treatment. Increase in Mg content increases the hydriding time. Alloys containing over 50 atomic% Mg, do not absorb hydrogen at room temperature. The room temperature absorption of hydro-

Table 11. Hydriding and dehydriding characteristics of various magnesium–non-transition metal alloys [34]

Alloy composition (atomic percent)	System	Percent hydrogen picked up in 24 h at 400°C	Percent hydrogen liberated in 1 h at 300°C
Mg–1Al	single phase	6.1	2.4
Mg–1In	single phase	4.6	1.8
Mg–1Cd	single phase	5.0	0.6
Mg–1Zn	single phase	3.0	—
Mg–1Pb	single phase	1.6	—
Mg–5Sn	Eutectic: Mg + Mg_2Sn	5.0	2.0
Mg–5Ca	Eutectic: Mg + Mg_2Ca	4.9	0.7
Mg–5Bi	Eutectic: Mg + Mg_3Bi_2	2.0	0.0
Mg–5Si	Eutectic: Mg + Mg_2Si	3.5	0.1
Mg–5Sb	Eutectic: Mg + Mg_3Sb_2	2.4	0.0
Mg–1Al–1Ag	Mg + trace 2nd phase	6.0	0.0

gen on $SmMg_2$ [84], $EuMg_2$ [160] and $LnMg_2$ (Ln = La, Ce or Nd) [161] have also been reported. These alloys picked up considerable amounts of hydrogen. However, no data is available on the hydriding and dehydriding kinetics as well as on the desorption capacities of these alloys. In the search for new hydride materials particularly for automobile applications, Reilly and Wiswall [162] have investigated the hydriding characteristics of La_2Mg_{17} alloy. They found a hydrogen weight content of 5.3% and a dissociation pressure similar to that of MgH_2. Later Reilly *et al.* [81] studied the hydrogen absorption properties of $LnMg_9$ type (Ln = Ce or Mm) compounds. These intermetallics absorbed 4.1 and 4.4 wt% hydrogen respectively. No comments were made by the investigators regarding the activation or kinetics of hydriding and dehydriding of these alloys. Alloys of the type $La_xMm_{1-x}Mg_9$ (Mm = mischmetal; $0.5 \leq x \leq 1$) were also reported [163].

(i) *Magnesium-rich rare-earth alloys.* The intermetallic compounds of the composition $LnMg_{12}$ (Ln = La, Ce or Mm), Ln_2Mg_{17} (Ln = La or Ce) and Ln_5Mg_{41} (Ln = Ce) are reported in the literature [164, 165]. Moreover, the structure type of $LnMg_{12}$ and Ln_2Mg_{17} is derived directly from that of $LaNi_5$ by substitution of Ni by Mg and the replacement of either one-half or one-third of La atoms by two Mg atoms [166]. The structure of $LaNi_5$ is a good host lattice for hydrogen [167], it may be expected that $LnMg_{12}$ and Ln_2Mg_{17} could also be appropriate for hydrogen storage. Tanguy *et al.* [60, 168] have carried out the synthesis of MgH_2 by the addition of small amounts of catalyst ($LaNi_5$, TiFe etc.); the $LaNi_5$ enhance significantly the hydriding rate of Mg without appreciable increase in weight and cost. These alloys react with hydrogen even at room temperature. Rohy *et al.* [111] have reported that small additions of rare-earth elements to Mg resulted in improved dehydriding kinetics, but not to the extent anticipated.

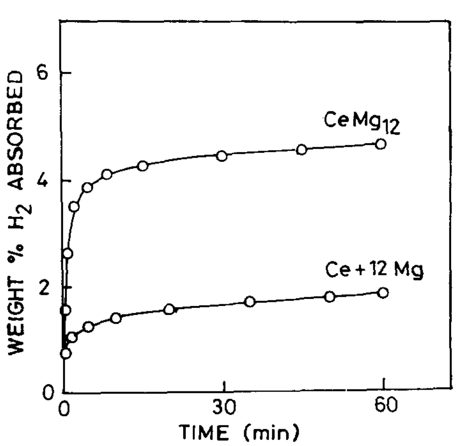

Fig. 10. Hydriding kinetics of $CeMg_{12}$ alloys at 325°C under a hydrogen pressure of 30 atm and of (Ce + 12Mg) sintered mixture with 95% compactness [126].

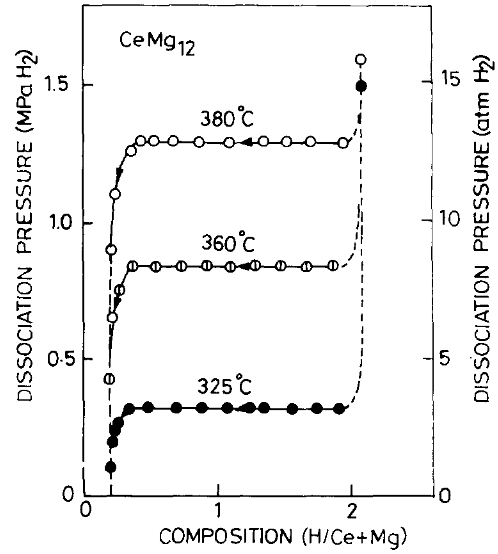

Fig. 11. Desorption isotherms for $CeMg_{12}$–H_2 systems [126].

On the basis of these results Hagenmuller *et al.* [169–171] have suggested the use of Mg-rich rare-earth alloys leading to easily dissociable hydrides instead of sintered mixtures of Mg and metal catalysts (Fig. 10) since the dissociation of the intermetallics during the first hydrogen absorption results in a more homogeneous distribution of the components and a small particle size. Therefore, alloys such as $CeMg_{12}$, La_2Mg_{17} and Ce_5Mg_{41} have been chosen for systematic studies. Hydriding of these intermetallics initially causes an irreversible decomposition of the alloy with the formation of MgH_2 and the corresponding rare-earth hydride.

$$Ln_xMg_y + (m+n)H_2 \rightarrow xLnH_3 + yMgH_{2n-3x} \qquad (8)$$

(when $x = 1$, 2 or 5; $y = 12$, 17 or 41; $m = 11$, 16 or 40 and $n = 5/2$, 4 or 17/2—corresponding to the composition of $CeMg_{12}$, La_2Mg_{17} and Ce_5Mg_{41}). The following reaction takes place during the absorption and desorption cycles.

$$xLnH_3 + yMgH_{2n-3x} \rightleftharpoons xLnH_z + yMg + (m+n-xz)H_2. \qquad (9)$$

It has been shown that the composition of the rare-earth hydride is between $Ln_{2.6}$ to $Ln_{2.9}$ (i.e. z lies between 2.6 and 2.9) whatever the rare-earth used. This is in good agreement with the values deduced from the thermodynamic data for these hydrides [172] and the pressure–composition isotherms obtained for $CeMg_{12}$ alloy (Fig. 11) [124, 170].

The alloys $CeMg_{12}$, La_2Mg_{17} and Ce_5Mg_{41} react easily with hydrogen and have almost the same hydriding rate at 325°C. But at 130°C the hydriding of Ce_5Mg_{41} is faster than that of La_2Mg_{17} or $CeMg_{12}$. Moreover, $CeMg_{12}$ has a lower dehydriding rate than the other two

Table 12. Comparison of some selected Mg-rich rare-earth based alloys [123–125, 169, 170, 174]

Alloys	Hydrogen absorbed at 325°C and 30 atm (wt%)	Time required to desorb 50% H_2 at 325°C and 2 atm (min)
$CeMg_{12}$	6.00	105
$CeMg_{11}V$	4.00	40
$CeMg_{11}Cr$	4.00	40
$CeMg_{11}Mn$	4.00	40
$CeMg_{11}Fe$	4.00	30
$CeMg_{11}Ni$	4.56	15
La_2Mg_{17}	5.50	60
$La_2Mg_{16}Ni$	3.80	45
Ce_5Mg_{41}	5.51	75
$CeMg_9$*	4.10	—
$MnMg_9$*	4.40	—

* Data from Ref. [81]; Mm = Mischmetal.

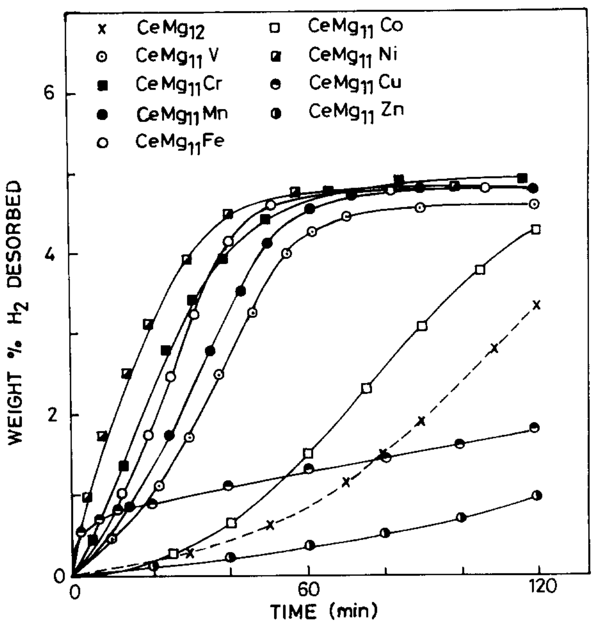

Fig. 12. Dehydriding kinetics of $CeMg_{12}$ and $CeMg_{11}M$ alloys at 325°C under a hydrogen pressure of 2 atm [126].

both at 325°C and 340°C. However, it is able to absorb and desorb greater amounts of hydrogen [124, 126]. Similar results were obtained by Semenenko *et al.* [173] for the $LaMg_{12}$ alloy. The total hydrogen content and the desorption properties of these alloys are shown in Table 12.

(ii) *Modified or substituted magnesium-rich rare-earth alloys.* In order to accelerate the hydriding–dehydriding process of $CeMg_{12}$, partial substitution of Mg in $CeMg_{12}$ by 3d elements (V,Cr,Mn,Fe,Co,Ni,Cu and Zn) has been investigated for the composition $CeMg_{11}M$ [123–126]. X-ray crystallographic and microprobe analysis showed that a two-phase mixture is obtained for each alloy except for the Co and Zn containing alloys. The Co-substituted alloy showed the presence of three phases viz. $CeMg_{13}$, $CeCo_3$ and Mg, whereas the Zn-containing alloy gives a single phase material corresponding to $CeMg_{11}Zn$—the $CeMg_{12}$-type phase. In the case of V,Cr,Mn or Fe-modified alloys, the phases are $CeMg_{11}$ ($CeMg_{12}$-type phase) and the corresponding 3d elements. On the other hand, the partial replacement of Mg by Ni stabilizes a Ce_2Mg_{17}-type phase [165] in addition to the expected Mg_2Ni phase; with Cu a $CeMg_{12}$-type phase containing small amounts of Cu coexists with Mg_2Cu. All these phases form the corresponding hydrides. Hydriding–dehydriding cycles have been established for each alloy and have been compared with those of $CeMg_{12}$ [125–126].

All the alloys have similar hydriding behaviour to that of $CeMg_{12}$. However, $CeMg_{11}Ni$ shows the fastest hydrogen uptake and the slowest uptake is observed for the V-containing alloy. The dehydriding rate is, however, greatly enhanced for V,Cr,Mn,Fe and Ni-containing alloys (Fig. 12). Khrussanova *et al.* [174] partially replaced Mg by Ni in the La_2Mg_{17} alloy. Hydriding of the alloy $La_2Mg_{16}Ni$ leads to the formation of the Mg_2NiH_4 phase in addition to LaH_3 and MgH_2 phases. The results obtained are similar to those noticed for the $CeMg_{11}Ni$ alloy. The absorption characteristics of the substituted Mg-rich rare-earth alloys are also given in Table 12.

In brief, the following conclusions were arrived by the authors [123–126, 169–171, 174]:

- The hydriding and dehydriding rates of Mg were improved when Mg-rich rare-earth based alloys were used;
- the rare-earth based Mg alloys react easily with hydrogen. They have a significant absorption rate even at room temperature;
- these alloys show a high hydrogen content (Table 12);
- the increase in pressure enhances the hydriding rate initially, but after about an hour the absorption appears roughly the same whatever the pressure;
- the alloys decompose during hydriding with the formation of MgH_2 and the corresponding rare-earth hydride which acts as a catalyst in the hydriding of Mg;
- experiments of hydriding and dehydriding cycles with reference to temperature and pressure show that they are based mainly on Mg hydriding using the rare-earth hydride as a catalyst;
- the hydriding rate is not strongly influenced by the presence of 3d elements in $CeMg_{11}M$ and $La_2Mg_{16}Ni$, but the dehydriding rate is enhanced. This increase in the desorption rate may be a catalytic effect due to the 3d elements in addition to the effects due to the rare-earth metal;
- these intermetallic compounds are better hydrogen

storage materials than the sintered mixtures of rare-earth and Mg with the same composition (for example, $CeMg_{12}$ and (Ce + 12Mg)).

(iii) *Kinetics of $CeMg_{12}$ alloys.* The intermetallic compound $CeMg_{12}$ has been well-established [165] and it has been shown that it has a high hydrogen storage capacity. However, the hydrogen absorption and desorption reaction of $CeMg_{12}$ is relatively slow. Understanding of the kinetic mechanism of the hydriding and dehydriding reactions will be essential for practical purposes. Thus, investigations have been carried out regarding the kinetic aspects based on the experimental results [175–177].

Lim and Lee [175] have analysed the hydriding reaction of $CeMg_{12}$ based on a theoretical model developed by Park and Lee [178]. They found that the initial stage of the reaction is controlled by chemisorption of hydrogen on the metal surface. The rate-controlling step at the latter stage is not clearly understood. Presumably, the hydrogen diffusion in the hydride phase or the chemical reaction at the metal/hydride interface may control the reaction. Boulet and Gerard [176] have interpreted from the kinetic curves that the mechanism of formation and decomposition must be similar for all these Mg hydrides regardless of whether they are obtained from pure or alloyed Mg. However, the reaction rates for both formation and decomposition of the alloy hydride ($CeMg_{12}$) are very different from those obtained using pure Mg (10 times faster in the case of $CeMg_{12}$ alloy). The high reactivity with hydrogen is due to effects of morphological parameters such as mechanical stresses and strains, and incoherent grain boundaries which increase hydrogen diffusion and hydride nucleation and which are produced by the formation of finely divided precipitates of CeH_3.

Ivanov *et al.* [177] have studied the hydriding and dehydriding kinetics of Mg in the $CeMg_{12}$ alloy. It was shown that the formation of MgH_2 occurs by a diffusion-controlled process and the hydriding rate is determined through a growing hydride layer of MgH_2. It was also shown that a passivating effect (air oxidation) takes place only on the external surface of the particles and this can be regenerated by subsequent hydrogen cycling. First hydriding of $CeMg_{12}$ leads to irreversible decomposition of this alloy to MgH_2 and CeH_3. This appears to be a way to produce a well-developed surface contact between Mg and Ce. In addition CeH_z supplies hydrogen to the Mg surface, which was deduced from the properties of rare-earth – H_2 systems [179]. That is why the mechanical mixture (Ce + 12Mg) and the eutectic alloy, $CeMg_{25}$ show slower hydriding kinetics than the $CeMg_{12}$ alloy. These results suggest the catalytic effect of CeH_z on the Mg hydriding–dehydriding process. It was also noted that the hydriding rate of $CeMg_{12}$ alloy is increased compared to the pure Mg. This is due to the existence of elastic stress at the hydride–metal boundary which can change the diffusion conditions. These stresses lead to cracking of the storage material during hydriding [180]. Thus, the use of Mg alloys instead of pure Mg, produces a number of cracks and enhances the hydriding speed.

CONCLUSION

The scientific investigations on hydrogen storage by metal alloys have reached a stage of technical development. Although it may not be possible to have all desirable properties in one and the same alloy for automobile applications, the system based on Mg seems to be a promising one. Alloy substitution seems to be a good approach for obtaining storage materials with desirable characteristics. This is substantiated by the studies on the addition of In, Ni, Y or La, to Mg–Al alloys, and the substitution of transition elements to Mg–Ni and Mg-rich rare-earth alloys. Although a number of approaches including modification with polynuclear aromatic compounds have been tried in the past, there are many aspects on which a clear picture has not yet emerged. Generalities on stabilities, stoichiometries and preferred hydrogen sites are not immediately possible. However, a clear understanding of the thermodynamic and electronic properties, crystal structure, surface processes like segregation, carbonization etc. will be forthcoming in the near future which will enable one to formulate an efficient storage medium.

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REFERENCES

1. J. O'M. Bockris, *Science* **176**, 1323 (1972). D. P. Gregory, *Scient. Am.* **228**, 13 (1973). T. N. Veziroglu, *Hydrogen Energy*. Plenum Press, New York (1975).
2. H. Buchner, *Prog. Energy Combustion Sci.* **6**, 331 (1980).
3. T. N. Veziroglu, *Int. J. Hydrogen Energy* **8**, 1 (1983).
4. E. L. Harder, *Fundamentals of Energy Production*. John Wiley, New York (1982).
5. H. Buchner, in *Hydrogen Energy Systems, Proc. 2nd World Hydrogen Energy Conf.*, Zurich, 21–24 August 1978 (T. N. Veziroglu and W. Seifritz eds.), Vol. 4, p. 1749. Pergamon Press, New York (1978).
6. J. J. Reilly, in *Hydrides for Energy Storage, Proc. Int. Symp.*, Geilo, 14–19 August 1977 (A. F. Andresen and A. J. Maeland eds.), p. 301. Pergamon Press, Oxford (1978). Report BNL-23046, New York (1977).
7. K. C. Hoffman, J. J. Reilly, F. J. Salzano, C. H. Waide, R. H. Wiswall and W. E. Winsche, *Int. J. Hydrogen Energy* **1**, 133 (1976).
8. V. K. Sinha, F. Pourarian and W. E. Wallace, *J. Phys. Chem.* **86**, 4952 (1982). F. Pourarian, V. K. Sinha and W. E. Wallace, *J. Phys. Chem.* **86**, 4956 (1982).
9. H. Buchner, *Int. J. Hydrogen Energy* **3**, 385 (1978).
10. D. G. Westlake, C. B. Satterthwaite and J. H. Weaver, *Phys. Today* **31**, 32, (1978).
11. J. J. Reilly and G. D. Sandrock, *Scient. Am.* **242**, 118 (1980).
12. E. Snape and F. E. Lynch, *Chem. Tech.* **10**, 578 (1980).

13. G. D. Sandrock and E. L. Huston, *Chem. Tech.* **11**, 754 (1981).
14. W. M. Mueller, J. P. Blackledge, G. G. Libowitz, *Metal Hydrides*. Academic Press, New York (1968).
15. J. Toepler, O. Bernaure and H. Buchner, *J. Less-Common Metals* **74**, 385 (1980).
16. G. G. Libowitz and Z. Blank, *Solid State Chem.* **19**, 271 (1977).
17. K. Nomura and Y. Ishido, *Energy Conversion* **19**, 49 (1979).
18. F. E. Lynch, *J. Less-Common Metals* **74**, 411 (1980).
19. G. D. Sandrock and E. Snape, *Proc. Joint American Chemical Society/Chemical Society of Japan Symp.* Hawaii, April 1979, p. 293. ACS, Washington D.C. (1980).
20. D. L. Henriksen, D. B. Mackay and V. R. Anderson, *Proc. 1st World Hydrogen Energy Conf.*, Miami Beach, Florida, 1–3 March 1976 (T. N. Veziroglu ed.), Vol. 3, p. 7C-1. The University of Miami, Coral Gables, Florida (1976).
21. E. L. Huston and J. J. Sheridan III, in *American Chemical Society Symp. Series* (K. A. Gschneider, Jr. ed.), Vol. 164, p. 223 (1981).
22. G. L. Holleck, J. R. Driscoll and B. E. Paul, *J. Less-Common Metals* **74**, 379 (1980).
23. H. Buchner, in *Hydrogen Energy Systems, Proc. 2nd World Hydrogen Energy Conf.*, Zurich, 21–24 August 1978 (T. N. Veziroglu and W. Seifritz eds.), Vol. 3, p. 1613. Pergamon Press, New York (1978).
24. J. J. Reilly, *Z. Phys. Chem. N.F.* **117**, 155 (1979).
25. C. Folonari, G. Iemmi, F. Manfredi and A. Rolle, *J. Less-Common Metals* **74**, 371 (1980).
26. R. Wiswall, in *Topics in Applied Physics* (G. Alefeld and J. Volkl eds.), Vol. 29, p. 201. Springer, Berlin (1978).
27. H. Buchner, in *Hydrides for Energy Storage, Proc. Int. Symp.* Geilo, 14–19 August 1977 (A. F. Andresen and A. J. Mealand eds.), p. 569. Pergamon Press, Oxford (1978).
28. F. E. Lynch and E. Snape, in *Hydrogen Energy Systems, Proc. 2nd World Hydrogen Energy Conf.*, Zurich, 21–24 August 1978 (T. N. Veziroglu and W. Seifritz eds.), Vol. 3, p. 1475. Pergamon Press, New York (1978).
29. H. Buchner, *Chemi-Technik* **7**, 371 (1978).
30. H. Buchner and R. Povel, *Int. J. Hydrogen Energy* **7**, 259 (1982).
31. J. J. Reilly, in *Hydrogen. Its Technology and Implications* (K. E. Cox and K. D. Williamson eds.), Vol. 2, Ch. 2. CRC Press, Cleveland, Ohio (1977).
32. R. E. Billings, *Proc. Hydrogen Economy Miami Energy Conf.* (*THEME*), Miami Beach, Florida, 18–20 March 1974, p. S8. Plenum Press, New York (1975); *Int. Symp. on the Properties and Applications of Metal Hydrides*, Colorado Springs, Colorado, 7–11 April 1980.
33. K. Binder and G. Withalm, in *Hydrogen Energy Progress, Proc. 3rd World Hydrogen Energy Conf.*, Tokyo, 22–26 June 1980 (T. N. Veziroglu, K. Fueki and T. Ohta eds.), Vol. 2, p. 1103. Pergamon Press, New York (1980).
34. D. L. Douglass, in *Hydrides for Energy Storage, Proc. Int. Symp.*, Geilo, 14–19 August (A. F. Andresen and A. J. Mealand eds.), p. 151. Pergamon Press, Oxford (1978).
35. H. Buchner, O. Bernauer and W. Straub, in *Hydrogen Energy Systems, Proc. 2nd World Hydrogen Energy Conf.*, Zurich, 21–24 August 1978 (T. N. Veziroglu and W. Seifritz eds.), Vol. 3, p. 1677. Pergamon Press, New York (1978).
36. J. H. N. van Vucht, F. A. Kuijpers and H. C. A. Burning, *Phillips Res. Rep.* **25**, 133 (1970).
37. J. J. Reilly and R. H. Wiswall, Jr., *Inorg. Chem.* **13**, 218 (1974).
38. J. J. Reilly and R. H. Wiswall, Jr., *Inorg. Chem.* **7**, 2254 (1968). R. H. Wiswall, Jr. and J. J. Reilly, *Proc. 7th Intersociety Energy Conversion Engineering Conf.* (*IECEC*), San Diego, p. 1342 (1972). C. H. Waide, J. J. Reilly and R. R. Wiswall, Jr., *Proc. Hydrogen Economy Miami Energy Conf.* (*THEME*), Miami Beach, Florida, 18–20 March 1974, p. 770. Plenum Press, New York (1975).
39. W. E. Wallace, R. S. Craig and U. V. S. Rao, *Adv. Chem. Series* **186**, 207 (1980).
40. A. Pebler and E. A. Galbransen, *Electrochem. Technol.* **4**, 211 (1966); *Trans. Metall. Soc. AIME* **239**, 1593 (1967). J. R. Johnson and J. J. Reilly, *Report BNL-24253*, New York (1978). K. N. Semenenko, V. N. Verberskiin, S. V. M. Trokhin and V. V. Burnagheva, *Russ. J. Inorg. Chem.* **25**, 961 (1980). I. Jacob and D. Shaltiel, in *Hydrogen Energy Systems, Proc. 2nd World Hydrogen Energy Conf.*, Zurich, 21–24 August 1978 (T. N. Veziroglu and W. Seifritz eds.), Vol. 3, p. 1689. Pergamon Press, New York (1978).
41. J. J. Reilly, R. H. Wiswall, Jr., K. C. Hoffman and C. H. Waide, in *Metal Hydrides as Hydrogen Storage Media, 7th Alternative Automotive Power Systems Division Contractors Coordination Meeting*. Ann Arbor, Michigan (1974).
42. D. A. Rohy and J. F. Nachman, *Report on Department of Energy* (*DOE*) *Contract* DE-AC03-7851059, *Highway Vehicle Systems*. Contractor Co-ordination Meeting, Dearborn, Michigan, October 1979.
43. L. Belkbir, E. Joly and N. Gerard, *Int. J. Hydrogen Energy* **6**, 285 (1981).
44. F. H. Ellinger, C. E. Holley, Jr., B. B. McInteer, D. Pavone, R. M. Potter, E. Staritzky and W. H. Zachariasen, *J. Am. Chem. Soc.* **82**, 3504 (1955).
45. J. A. Kenneley, J. W. Varwig and H. W. Myers, *J. Phys. Chem.* **64**, 703 (1960).
46. K. C. Hoffman, W. E. Winsche, R. H. Wiswall, Jr., J. J. Reilly, T. V. Steehan and C. H. Waide, in *Metal Hydrides as a Source of Fuel for Vehicular Propulsion, Int. Automotive Engineering Congress*, Detroit, Paper 690232, SAE Trans. (1969). Referred in Ref. [31].
47. K. C. Hoffman, J. J. Reilly, F. J. Salzano and J. M. King, *Proc. 9th Intersociety Energy Conversion Engineering Conf.* (*IECEC*), *ASME*, Warrendale (1976).
48. Z. Luz, J. Genossar and P. S. Rudman, *J. Less-Common Metals* **73**, 113 (1980); *Scripta Metall.* **14**, 275 (1980).
49. J. Genossar and P. S. Rudman, *Z. Phys. Chem. N.F.* **116**, 215 (1979).
50. A. Karty, J. Genossar and P. S. Rudman, *J. appl. Phys.* **50**, 7200 (1979).
51. T. N. Dymova, Z. K. Sterlyadkina and V. G. Safronov, *Russ. J. Inorg. Chem.* **6**, 389 (1961).
52. P. S. Rudman, *J. appl. Phys.* **50**, 7195 (1979).
53. H. Wenzl and J. M. Welter, in *Current Topics in Materials Science* (E. Kaldis ed.), vol. 1, p. 603. North-Holland, Amsterdam (1978).
54. D. M. Gualtieri, K. S. V. L. Narasimhan and T. Takeshita, *J. appl. Phys.* **47**, 3432 (1976).
55. J. F. Stampfer, Jr., C. E. Holley, Jr. and J. F. Suttle, *J. Am. Chem. Soc.* **82**, 3504 (1960).
56. C. M. Stander, *Z. Phys. Chem. N.F.* **104**, 229 (1977).
57. C. M. Stander, *J. Inorg. Nucl. Chem.* **39**, 221 (1977).

58. J. Isler, Thesis, University of Dijon, May 1979. Referred in Ref. [176].
59. Ph. Guinet, P. Perround and J. Rebiers, in *Hydrogen Energy Systems, Proc. 2nd World Hydrogen Energy Conf.*, Zurich, 21–24 August 1978 (T. N. Veziroglu and W. Seifritz eds.), Vol. 3, p. 1657. Pergamon Press, New York (1978).
60. B. Tanguy, J. L. Soubeyrour, M. Pezat, J. Portier and P. Hagenmuller, *Mat. Res. Bull.* **11**, 1441 (1976).
61. J. Felsteiner and H. Heilper, *Phys. Rev. B.* **23**, 5156 (1981).
62. M. H. Mintz, Z. Gavra, G. Kimmel and Z. Hadari, *J. Less-Common Metals* **74**, 263 (1980).
63. J. Renner and H. J. Grabke, *Z. Metallkd.* **63**, H5 (1972).
64. M. H. Mintz and Z. Hadari, *Israel J. Tech.* **14**, 231 (1976).
65. D. A. Zagnoli, F. G. Eisenberg and J. J. Sheridan III, *Light-Weight Metal Hydrides Materials Development, Air Products/BNL Contract No. 485875-S*, 7 December 1979. Referred in Ref. [136].
66. D. L. Douglass, *Metall. Trans.* **6A**, 2179 (1975).
67. Ch. Nolhier, Thesis, University of Paris XI, December 1979. Referred in Ref. [176].
68. J. Bousquet, J. M. Blanchard, B. Bonnetot and P. Claudy, *Bull. Soc. Chim. Fr.* **6**, 1841 (1969).
69. L. Belkbir, E. Joly and N. Gerard, *Adv. Hydrogen Energy (Hydrogen Energy Progress)*, **4**, 2145 (1981).
70. B. Vigeholm, J. Kjoller and B. Larsen, *Powder Met. Int.* **12**, 136 (1980); *J. Less-Common Metals* **74**, 341 (1980).
71. B. Vigeholm, *Light Metal Age* **39**, Nos. 5 & 6 (1981).
72. B. Vigeholm, J. Kjoller, B. Larsen and A. S. Pedersen, in *Hydrogen Energy Progress IV, Proc. 4th World Hydrogen Energy Conf.*, California, 13–17 June 1982 (T. N. Veziroglu, W. D. Van Vorst and J. H. Kelley eds.), Vol. 3, p. 1227. Pergamon Press, New York (1982); in *Hydrogen as an Energy Carrier, Proc. 3rd Int. Seminar*, Lyon, 25–27 May 1983 (G. Imarisio and A. S. Sturb eds.), p. 442. D. Reidel, Dordrecht (1983); *J. Less-Common Metals* **89**, 135 (1983); *Int. J. Hydrogen Energy* **8**, 809 (1983).
73. A. S. Pedersen, J. Kjoller, B. Larsen and B. Vigeholm, *Int. J. Hydrogen Energy* **8**, 205 (1983); **9**, 799 (1984).
74. E. Wiberg, H. Goeltzer and R. Bauer, *Z. Naturforsch* **6B**, 394 (1951).
75. J. P. Faust, E. D. Whitney, H. D. Batha, T. L. Heying and C. E. Fogle, *J. appl. Chem.* **10**, 187 (1960).
76. W. Freundlich and B. Claudel, *Bull. Soc. Chim. Fr.* **967** (1956).
77. B. Wiberg and R. Bauer, *Chem. Ber.* **85**, 593 (1952); *Z. Naturforsch* **5B**, 369 (1950).
78. H. Imamura, M. Kawahigashi and S. Tsuchiya, *J. Less-Common Metals* **95**, 157 (1983).
79. J. J. Reilly and R. H. Wiswall, Jr. *Inorg. Chem.* **6**, 2220 (1967).
80. V. I. Mikheeva, Z. K. Sterlyadkina, A. I. Konstantinova and O. N. Kryukova, *Russ. J. Inorg. Chem.* **8**, 682 (1963).
81. J. J. Reilly, R. H. Wiswall Jr. and C. H. Waide, *Final Report, GPA Grant R-802579, BNL*, New York (1974).
82. E. Akiba, K. Nomura and S. Ono, in *Hydrogen Energy Progress, Proc. 3rd World Hydrogen Energy Conf.*, Tokyo, 23–26 June 1980 (T. N. Veziroglu *et al.* eds.). Pergamon Press, Oxford, 1980.
83. A. Suzuki and N. Nishimiya, *Japanese Patent Application No. 52 359 06* (1977). Referred in Ref. [132].
84. R. L. Beck, *Summary Report on Contract No. AT (33-3)-3 to the U.S. Atomic Energy Commission* from the University of Denver, 15th October 1962 (available from the Office of Technical Services, Department of Commerce, Washington D.C.). Referred in Refs. [94] and [161].
85. M. H. Mintz, S. Malkiely, Z. Gavra and Z. Hadari, *J. Inorg. Nucl. Chem.* **40**, 1949 (1978).
86. J. M. Welter and P. S. Rudman, *Scripta Metall.* **16**, 285 (1982).
87. J. F. Nachman and D. A. Rohy, *Proc. Miami Int. Symp. on Metal-Hydrogen Systems*, Miami Beach, Florida, 13–15 April 1981 (T. N. Veziroglu ed.), p. 577. Pergamon Press, New York (1982).
88. K. Ogawa, H. Aoki and T. Kobayashi, *J. Less-Common Metals* **88**, 283 (1982).
89. G. Bruzzone, G. Costa, M. Ferretti and G. L. Olcese, *Int. J. Hydrogen Energy* **8**, 459 (1983).
90. M. Pezat, A. Hbika, B. Darriet and P. Hagenmuller, *French Patent No. 78 203 82* (1978). Referred in Ref. [176].
91. S. Ono and Y. Ohsumi, *Ceramics Japan* **14**, 339 (1979).
92. B. Bogdanovic, *German Patent No. 280 444 53* (1978).
93. K. Tamaru, *Advances in Catalysis and Related Subjects*, Vol. 20, p. 327. Academic Press, New York/London, (1969). S. Tanaka, S. Naito, M. Ichkawas, M. Soma, T. Onishi and K. Tamaru, *Trans. Faraday Soc.* **65**, 976 (1970). K. Tamaru, *Catal. Rev.* **4**, 161 (1971). K. Tamaru and M. Ichikawa, *Catalysis by Electron Donor–Acceptor Complexes*. Kodansha, Tokyo (1975).
94. H. Imamura and S. Tsuchiya, *J. Chem. Soc. Chem. Commun.* p. 567 (1981); *J. Catal.* **72**, 383 (1981); *J. Chem. Soc. Faraday Trans. I* **79**, 1461 (1983); *Proc. 6th Japan–Soviet Catalysis Seminar*, Osaka, p. 104, 5–7 October 1981; *China–Japan–U.S. Symp. on Heterogeneous Catalysis*, 1982, Paper A09J.
95. H. Imamura, T. Takahashi and S. Tsuchiya, *J. Catal.* **77**, 289 (1982).
96. H. Imamura, T. Takahashi, T. Galleguillos I and S. Tsuchiya, *Proc. Int. Symp. on the Properties and Applications of Metal Hydrides*—II, 1982; *J. Less-Common Metals* **89**, 251 (1983).
97. W. E. Wallace, R. F. Kalicek Jr, and H. Imamura, *J. Phys. Chem.* **83**, 1708 (1979). W. E. Wallace, A. Elatter, H. Imamura, R. S. Craig and A. G. Moldovan, in The Science and Technology of Rare-Earth Materials (W. E. Wallace and E. C. Subbarao eds.), p. 329. Academic Press, New York (1980).
98. R. H. Wiswall, Jr. and J. J. Reilly, *Proc. 7th Intersociety Energy Conversion Engineering Conf. (IECEC)*, San Diego, p. 1342 (1972). Referred by G. P. Grupta, *Proc. 1st World Hydrogen Energy Conf.*, Miami Beach, Florida, 1–3 March 1976 (T. N. Veziroglu ed.), Vol. 3, P.7C–47. The University of Miami, Coral Gables, Florida (1976).
99. Z. Gavra, Z. Hadari and M. H. Mintz, *J. Inorg. Nucl. Chem.* **43**, 1763 (1981).
100. L. Schlapbach, D. Shaltiel and P. Oelhafen, *Mat. Res. Bull.* **14**, 1235 (1979). Th. von Waldkrich, A. Seiler, P. Zurcher and H. J. Mathieu, *Mat. Res. Bull.* **15**, 353 (1980). A. Seiler, L. Schlapbach, Th. von Waldkirch, D. Shaltiel and F. Stucki, *J. Less-Common Metals* **73**, 193 (1980). L. Schlapbach, Th. von Waldkirch and A. Seiler, in *Hydrogen in Metals, Proc. JIMIS-2*, p. 349 (1980).
101. F. Stucki and L. Schlapbach, in *Proc. Int. Symp. on the Properties and Applications of Metal Hydrides*, Colorado Springs, Colorado, 7–11 April 1980; *J. Less-Common Metals* **74**, 235 (1980).
102. H. C. Siegmann, L. Schlapbach and C. R. Brundle, *Phys. Rev. Lett.* **40**, 972 (1978). L. Schlapbach, A. Seiler, F. Stucki and H. C. Siegmann, *J. Less-Common Metals* **73**,

145 (1980). Th. von Waldkirch and P. Zurcher, *Appl. Phys. Lett.* **33**, 689 (1978). L. Schlapbach, A. Seiler, H. C. Siegmann, Th. von Waldkirch and P. Zurcher, *Int. J. Hydrogen Energy* **4**, 21 (1979).

103. L. Schlapbach, A. Seiler and F. Stucki, *Mat. Res. Bull.* **13**, 697, 1031 (1978). L. Schlapbach, A. Seiler, F. Stucki, P. Zurcher, P. Fischer and J. Schefer, *Z. Phys. Chem.* **117**, 205 (1979). G. Busch, L. Schlapbach, F. Stucki, P. Fischer and A. F. Andresen, *Int. J. Hydrogen Energy* **4**, 29 (1979).
104. J. Genossar and P. S. Rudman, Conference on Hydrogen in Metals, Munster (1979); *Phys. Chem.* **116**, 215 (1979). L. Schlapbach, A. Seiler, F. Stucki, P. Zurcher and P. Fischer, Conference on Hydrogen in Metals, Munster (1979); *Z. Phys. Chem.* **117**, 205 (1979).
105. L. Schlapbach, *J. Less-Common Metals* **73**, 145 (1980).
106. N. Shamir, M. H. Mintz, J. Bloch and U. Atzmony, *J. Less-Common Metals* **92**, 253 (1983).
107. G. C. Bond, *Catalysis by Metals*. Academic Press, New York (1962). R. Speiser, in *Metal Hydrides* (W. M. Mueller, J. P. Blackledge and G. G. Libowitz eds). Academic Press, New York (1968). D. A. Dowden, in *Chemisorption* (W. E. Garner ed.), p. 3. Butterworth, London, (1958). B. M. W. Trapnell and D. O. Hayward, in *Chemisorption* (W. E. Garner ed.), p. 75. Butterworth, London (1964). A. B. Kunz, M. P. Guse and R. J. Blint, *Chem. Phys. Lett.* **37**, 512 (1976). G. Comsa and R. David, *Chem. Phys. Lett.* **49**, 512 (1977).
108. J. J. Lapujoulade and K. S. Neil, *J. Chem. Phys.* **70**, 798 (1973). K. Christmann, O. Schober, G. Ertle and M. Newman, *J. Chem. Phys.* **71**, 4528 (1974). M. Balooch, M. J. Cardillo, D. R. Miller and R. E. Stickhey, *Surf. Sci.* **46**, 358 (1974). H. Conrad, G. Ertle, J. Kuppers and E. E. Latta, *Surf. Sci.* **58**, 578 (1976). J. E. Demuth, *Surf. Sci.* **65**, 369 (1977).
109. R. C. Baetzold, *J. Catal.* **29**, 129 (1973). D. J. M. Fassaert and A. vander Avoind, *Surf. Sci.* **55**, 291, 313 (1976). C. F. Melius, J. W. Moskowitz, A. P. Mortola, M. B. Baillie and M. A. Ratner, *Surf. Sci.* **59**, 279 (1976). D. E. Ellis, H. Adachi and F. W. Averill, *Surf. Sci.* **58**, 497 (1976). P. E. M. Siegbahn and M. R. A. Blomberg and C. W. Bauchilicher, Jr., *J. Chem. Phys.* **81**, 1373, 2103 (1984).
110. K. W. Kehr, in *Hydrogen in Metals I, Topics in Applied Physics* (G. Alefeld and J. Volkl eds.), Vol. 28, p. 197. Springer, Berlin (1978).
111. D. A. Rohy, J. F. Nachman, A. N. Hammer and T. E. Duffy, *Report SAN-1167-1* (1979); *Energy Res. Abst.* **5**, No. 27052 (1980).
112. G. G. Libowitz, *J. Phys. Chem.* **76**, 62 (1958).
113. M. Hangen, *Constitution of Binary Alloys*. McGraw-Hill, New York (1958).
114. J. J. Reilly, R. H. Wiswall Jr. and A. Aronson, *USAEC Report, BNL-50149(S-71)*, Nuclear Engineering Department, Brookhaven National Laboratory, Upton, New York (1968). Referred in Ref. [31].
115. H. Oesterricher, K. Ensslen, A. Kerlin and E. Bucher, *Mat. Res. Bull.* **15**, 275 (1980).
116. K. Yvon, J. Schefer and F. Stucki, *Inorg. Chem.* **20**, 2776 (1981).
117. R. O. Moyer, Jr., C. Stanitski, J. Tanaka, M. I. Kay and R. Kleinberg, *J. Solid State Chem.* **3**, 541 (1971). J. S. Thompson, R. O. Moyer, Jr. and R. Lindsay, *Inorg. Chem.* **14**, 1866 (1975). R. Lindsay, R. O. Moyer, Jr., J. S. Thompson and D. Kuhn, *Inorg. Chem.* **15**, 3050 (1976).
118. S. Ono, K. Nomura, K. Suzuki, S. Higano and K. Kamino, *Trans. Jpn. Inst. Met.* Suppl. **21**, 361 (1980).
119. J. P. Darnaudery, B. Darriet and M. Pezat, *Int. J. Hydrogen Energy* **8**, 705 (1983).
120. D. Lupu, A. Biris, E. Indrea, N. Alden, R. V. Bucur and M. Morariu, *Int. J. Hydrogen Energy* **8**, 797 (1983).
121. D. Lupu, A. Biris and E. Indrea, *Int. J. Hydrogen Energy* **7**, 783 (1982).
122. T. Hirata, T. Matsumoto, M. Amano and Y. Sasaki, *J. Less-Common Metals* **89**, 85 (1983).
123. M. Pezat, A. Hbika and B. Darriet, *Mat. Res. Bull.* **15**, 139 (1980).
124. B. Darriet, A. Hbika and M. Pezat, *J. Less-Common Metals* **75**, 43 (1980).
125. B. Darriet, M. Pezat and P. Hagenmuller, in *Hydrogen as an Energy Vector, C.E.C. Int. Seminar* Bruxelles (A. A. Strub and G. Imarisio eds.), p. 489 (1980).
126. M. Pezat, B. Darriet and P. Hagenmuller, *J. Less-Common Metals* **74**, 427 (1980).
127. A. Biris, D. Lupu, E. Indrea and R. V. Bucur, in *Hydrogen et Materiaux, Int. Symp.*, Paris, 7–11 June 1982 (P. Azou ed.), Vol. 1, p. 383 (1982).
128. *Agency of Industrial Sciences and Technology, Mitsubishi Steel Manufacturing Company Ltd, Appl. 79/111, 422*, 31 August 1979. *Chem. Abst.* **95**, No. 118463t (1981).
129. J. P. Darnaudery, M. Pezat and B. Darriet, *J. Less-Common Metals* **92**, 199 (1983).
130. *Agency of Industrial Sciences and Technology, Mitsubishi Steel Manufacturing Company Ltd. Appl. 79/111, 421*, 31 August 1979. *Chem. Abst.* **95**, No. 118464u (1981).
131. P. Selvam, B. Viswanathan, C. S. Swamy and V. Srinivasan, *Report No. 5(1)/4/81-NES/719*, New Delhi, March (1985).
132. E. Akiba, K. Nomura, S. Ono and S. Suda, Hydrogen Energy Progress (T. N. Veziroglu ed.), p. 881. Pergamon Press, New York (1980). N. Nishimiya, A. Suzuki and S. Ono, *Int. J. Hydrogen Energy* **7**, 741 (1982). K. Nomura, E. Akiba, S. Ono and S. Suda, In *Hydrogen in Metals, Proc. JIMIS-2*, p. 353 (1980).
133. D. A. Rohy, J. F. Nachman, T. E. Duffy and A. N. Hammer, *Energy Research and Development Administration*, Ann Arbor, Michigan (1976). Referred in Ref. [132b].
134. H. M. Lutz and O. De Pous, *Proc. 2nd Int. Congress on Hydrogen in Metals*, Paris, 6–10 June 1977, Vol. 2, Paper-1F5. Pergamon Press, Paris (1978).
135. K. Nomura, E. Akiba and S. Ono, *Int. J. Hydrogen Energy* **6**, 295 (1981). E. Akiba, K. Nomura, S. Ono and S. Suda, *Int. J. Hydrogen Energy* **7**, 787 (1982). E. Akiba, K. Nomura, S. Ono and Y. Mizuno, *J. Less-Common Metals* **83**, L43 (1982). S. Ono, E. Akiba and K. Imanari, *Proc. Miami Int. Symp. on Metal–Hydrogen Systems*, Miami Beach, Florida, 13–15 April 1981 (T. N. Veziroglu, ed.), p. 467. Pergamon Press, New York (1982). S. Ono, H. Hayakawa, A. Suzuki, K. Nomura, N. Nishimiya and T. Tabata, *J. Less-Common Metals* **88**, 63 (1982).
136. F. G. Eisenberg, D. A. Zagnoli and J. J. Sheridan III, *J. Less-Common Metals* **74**, 323 (1980).
137. O. Boser, *J. Less-Common Metals*, **46**, 91 (1976).
138. E. Akiba, K. Nomura, S. Ono and Y. Mizuno, *J. Less-Common Metals* **89**, 145 (1983).
139. A. Biris, D. Lupu, R. V. Bucur, E. Indrea, G. Borodi and M. Bogdan, *Int. J. Hydrogen Energy* **7**, 89 (1982).
140. A. Seiler, *J. Less-Common Metals* **73**, 193 (1980).
141. K. Ogawa and H. Aoki, in *Point Defects and Defect Interactions in Metals* (J. I. Takamura, M. Doyama and M. Kiritani eds.), p. 329. University of Tokyo Press (1982).

142. J. J. Didisheim, P. Zolliker, K. Yvon, P. Fischer, J. Schefer, M. Gubelmann and A. F. Williams, *Inorg. Chem.* **23**, 1953 (1984).
143. J. J. Didisheim, K. Yvon, P. Fischer, J. Schefer, M. Gubelmann and A. F. Williams, *Z. Kristallogr.* **162**, 61 (1983).
144. P. Zolliker and K. Yvon, Unpublished results. Referred by K. Yvon, *J. Less-Common Metals* **103**, 53 (1984).
145. M. Gupta, *J. Less-Common Metals* **103**, 325 (1984).
146. *Air Products and Chemicals, Inc. Final Report on BNL Contract No. 435582-S*, May 1979. Referred in Ref. [87].
147. D. A. Rohy, J. F. Nachman, A. N. Hammer and T. E. Duffy, *Final Report on DOE Contract No. EY-76-C-1167* (1979). Referred in Ref. [87].
148. F. G. Eisenberg and J. J. Sheridan III, *Air Products and Chemicals, Inc., BNL Contract No. 433582-S*, May (1979). Referred in Ref. [136].
149. M. H. Mintz, Z. Gavra and G. Kimmel, in *Proc. Int. Symp. on the Properties and Applications of Metal Hydrides*, Colorado Springs, Colorado, 7–11 April (1980).
150. J. J. Reilly and R. H. Wiswall, Jr., *Report BNL-21322*, May 1974.
151. Z. Gavra, *Report, Nuclear Centre, Negev and Ben-gurion*, University of the Negev. (1980).
152. F. G. Eisenberg, D. A. Zagnoli and J. J. Sheridan III, in *Proc. Int. Symp. on the Properties and Applications of Metal Hydrides*, Colorado Springs, Colorado, 7–11 April 1980.
153. M. H. Mintz, Z. Gavra and Z. Hadari, *J. Inorg. Nucl. Chem.* **40**, 765 (1978).
154. M. H. Mintz, Z. Gavra, S. Malkiely and Z. Hadari, U.S. patent. Referred in Ref. [153].
155. H. H. van Mal, K. H. J. Buschow, A. R. Miedema, *J. Less-Common Metals* **49**, 473 (1976).
156. K. N. Semenenko, V. N. Verbetskii and A. N. Sytnikov, *Russ. J. Inorg. Chem.* **28**, 1673 (1983).
157. V. N. Verbetskii, A. N. Sytnikov and K. N. Semenenko, *Russ. J. Inorg. Chem.* **29**, 360 (1984).
158. V. I. Mikheeva, Z. K. Sterlyadkina, *Dokl. Akad. Nauk SSSR* **141**, 104 (1961).
159. A. Siverts and E. Roell, *Z. Anorg. Chem.* **146**, 149 (1925).
160. F. W. Oliver, K. W. West, R. L. Cohen and K. H. J. Buschow, *J. Phys. F. Metal Phys.* **8**, 701 (1978).
161. D. Shaltiel, *J. Less-Common Metals* **62**, 407 (1978).
162. J. J. Reilly and R. H. Wiswall, Jr., *Report BNL-17136*, New York (1972).
163. *Sanyo Electric Company Ltd, Appl. 79/101,054*, August 1979. *Chem. Abstr.* **95**, No. 190123z (1981).
164. W. H. Wood and E. M. Cramer, *J. Less-Common Metals* **9**, 321 (1965). Q. C. Johnson and G. S. Smith, *Acta Crystallogr.* **23**, 327 (1967). J. E. Pahlman and J. F. Smith, *Met. Trans.* **3**, 2423 (1972).
165. Q. C. Johnson and G. S. Smith, *Acta Crystallogr.* **22**, 360 (1966).
166. J. V. Florio, N. C. Baenziger and R. E. Rundle, *Acta Crystallogr.* **9**, 367 (1956).
167. K. H. J. Buschow and M. M. van Mal, *J. Less-Common Metals* **29**, 203 (1972). M. M. van Mal, *Philips Res. Rep.* Suppl. 1 (1976).
168. B. Tanguy, J. L. Souberyoux, M. Pezat, J. Porties and P. Hagenmuller, *French Patent No. 75 286 46*, September (1975). Referred in Ref. [126].
169. B. Darriet, M. Pezat, A. Hbika and P. Hagenmuller, *Mat. Res. Bull.* **14**, 377 (1979).
170. B. Darriet, M. Pezat, A. Hbika and P. Hagenmuller, *Int. J. Hydrogen Energy* **5**, 173 (1980).
171. B. Darriet, M. Pezat and P. Hagenmuller, Comm. Eur. Communities, Eur 6783 (Fr.) (1980), *Chem. Abst.* **95**, No. 100548q (1981).
172. K. I. Hardcastle and J. C. Ward, *Inorg. Chem.* **5**, 1728 (1966).
173. K. N. Semenenko, V. N. Verbetskii and A. V. Kochukou, *Dokl. Akad. Nauk SSSR* **258**, 362 (1981).
174. M. Khrussanova, M. Pezat, B. Darriet and P. Hagenmuller, *J. Less-Common Metals* **86**, 153 (1982).
175. S. H. Lim and J. Y. Lee, *Int. J. Hydrogen Energy* **8**, 369 (1983).
176. J. M. Boulet and N. Gerard, *J. Less-Common Metals* **89**, 151 (1983).
177. E. I. Ivanov, M. Pezat, B. Darriet and P. Hagenmuller, *Revue de Chimie Minerale* **20**, 60 (1983).
178. C. N. Park and J. Y. Lee, *J. Less-Common Metals* **83**, 39 (1982).
179. W. L. Korst and J. C. Warf., *Inorg. Chem.* **5**, 1719 (1966). W. E. Wallace, in *Hydrogen in Metals, Topics in Applied Physics*, Vol. 28, p. 175. Springer, Berlin (1978).
180. D. Dougherty and P. J. Herley, *J. Less-Common Metals* **73**, 97 (1980).