STUDIES ON THE THERMAL CHARACTERISTICS OF HYDRIDES OF Mg, Mg_2Ni, Mg_2Cu and $Mg_2Ni_{1-x}M_x$ (M = Fe, Co, Cu or Zn; $0 < x < 1$) ALLOYS

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Abstract—X-ray results on the alloys of the composition $Mg_2Ni_{1-x}M_x$ (M = Fe, Co, Cu or Zn; $0 < x < 1$) suggest a Mg_2Ni-type structure. The alloys, $Mg_2Ni_{0.75}M_{0.25}$ (M = Fe, Co, Cu or Zn) upon hydriding lead to the formation of quarternary hydrides while on dehydriding yield the starting ternary alloys except for copper containing alloys which show multi-phase regions and follow a different path way for the hydriding–dehydriding process. Thermal studies (TG–DTA) on the hydrides indicate the amount of hydrogen evolved as well as the desorption temperatures. The thermodynamic quantities, namely the enthalpies and entropies of formation of the hydrides were deduced from the DTA peak maximum temperature data. The kinetic parameters such as activation energies, reaction rates and orders of the reaction for the decomposition of the hydrides formed from Mg, Mg_2Ni and Mg_2Cu alloys were evaluated from the DTA data. As to the modified Mg_2Ni system, the copper substituted alloys show lower thermal stability and also presents some interesting properties. Hence, it is considered as one of the promising ternary combinations (Mg–Ni–Cu) for hydrogen storage purposes.

INTRODUCTION

Metal hydrides have a number of potential uses and offer a series of interesting technical applications. They have been utilized as viable hydrogen storage media in both mobile and stationary sectors. Of the various metal–hydrogen systems studied, the reversible hydriding–dehydriding of magnesium is considered as a possible storage option, despite its high thermal stability and slow reaction kinetics, primarily because of its high hydrogen density. However, these materials are of great interest in developing new hydrogen storage systems and therefore attention has been focussed in this direction. As the importance of magnesium–hydrogen system has been realised in the recent past, a critical examination and the current status of information in this area was reviewed [1].

Among the magnesium alloys, Mg_2Ni has been proposed as a promising material for hydrogen storage purposes, such as in fuel tanks for hydrogen powered vehicles [2]. The ternary hydride, Mg_2NiH_4 formed from Mg_2Ni alloy has been subjected to thermal studies [3, 4] and the results show a two stage decomposition process, thus suggesting the existence of a new hydride phase, Mg_2NiH in the $Mg_2Ni–H_2$ reaction [4]. There has been considerable interest in the study of kinetic and thermodynamic characteristics of metal hydrides mainly because of their technological importance as well as for the understanding of metal–hydrogen reactions.

It has been suggested [5] that partial substitution of magnesium in Mg_2Ni by an element like calcium, scandium or yttrium may result in the rise of the equilibrium pressure. This would bring the modified Mg_2Ni alloys into the range of reversible room temperature hydrogen sorption systems. In a recent study on Mg_2NiH_4 [6], it has been predicted that the hydrogen concentration in this material could be increased if element like aluminium is partially substituted for magnesium, or nickel is partially replaced by a transition metals such as manganese, iron or cobalt. Hence, attempts [7–15] have been made to prepare such compounds by partial modification of magnesium with metals such as aluminium, calcium, titanium or lanthanum (hydride formers) and nickel by 3d-elements namely iron, cobalt, copper or zinc (non-hydride formers) having the general formula $Mg_{2-x}M_xNi$ and $MgNi_{1-x}M_x$ (M—ternary metal additive), respectively. But the alloys obtained have so far failed to yield the desirable hydrogen content (more than 4 hydrogen atoms per formula unit). However, they show some interesting properties, namely the change in equilibrium pressure–composition–temperature (p–c–T) relationships, favourable kinetic and thermodynamic parameters. Hence, we have prepared a series of substituted Mg_2Ni alloys of the composition $Mg_2Ni_{1-x}M_x$ (M = Fe, Co, Cu or Zn; $0 < x < 1$) and the effect of these ternary metal additives on the hydrogen absorption–desorption properties have been evaluated.

STARTING MATERIALS

The metal powders used for the preparation of various alloys in the present study were supplied by K-light Laboratories, Ltd. U.K. (Magnesium and nickel with 99.9% purity) and Cerac Incorporated, U.S.A. (iron, cobalt, copper and zinc with 99.5% purity). High purity argon and hydrogen gases (Iolar–1 grade) used for the synthesis of the alloys and the corresponding hydrides

respectively were supplied by Indian Oxygen, Ltd, with a maximum oxygen content of 2 ppm as impurity.

EXPERIMENTAL SECTION

Alloys preparation

The binary alloys, Mg_2Ni, Mg_2Cu and ternary alloys of the composition $Mg_2Ni_{1-x}M_x$ (M = Fe, Co, Cu or Zn; $0 < x < 1$) were prepared from the constituent elements according to the following procedure: the pure metal powders were mixed and pressed into pellets in stoichiometric ratios. The pellets were transferred into sintered alumina boats and placed in a tubular furnace. In order to minimize the magnesium evaporation, the pellets were sintered first under an argon atmosphere at 825 K for about 2–3 days. However, a slight excess of magnesium from the stoichiometric compositions were used in order to compensate for the small evaporation losses of magnesium as well as to prevent the formation of $MgNi_2$ during the preparation of the alloys. The sintered pellets were then slowly heated to alloying temperature (950 K) under an argon atm. After fusion it was melted at 1125 K for 30–60 min and then cooled rapidly to room temperature. The ingots were powdered, pressed back into pellets and remelted at 1125 K and the procedure was repeated several times in order to achieve homogeneity. The alloy buttons were then annealed under an argon atm at 850 K for 48 h. The specimens were crushed into powders and used for further studies.

Hydrides synthesis

A stainless steel autoclave set up designed for high temperature (675 K) and high pressure (150 atm) reactions was used for the synthesis of the hydrides. Finely ground alloys were transferred into a nickel crucible and placed in the autoclave. The samples were activated by degassing the reactor and by subsequent hydrogen absorption–desorption processes at 625–675 K under a pressure of 60–80 atm. After several hydriding–dehydriding cycles, well activated samples were obtained. The activated alloys were then hydrided by exposing them to hydrogen at a pressure of 80 atm and a temperature of 625 K to get the final completely hyrided samples.

Physical measurements

The experimental procedures and techniques (XRD and TG–DTA) employed in the present study have been described elsewhere in detail [3, 4]. Kinetic and thermodynamic data of the hydrides were derived from the DTA results by the procedures described earlier [3, 4].

RESULTS AND DISCUSSION

Kinetic studies on Mg-, Mg_2Ni- and Mg_2Cu-hydrides

DTA technique [4] has been used to gain information on the kinetic parameters such as activation energy (E_d), reaction rate (v) and reaction order (n) for the decomposition reactions of the hydrides of Mg, Mg_2Ni and Mg_2Cu samples. The displacement of DTA peak maximum temperature (T_m) as a function of heating rate (φ) was measured and using Kissinger's approach [16], E_d was determined. DTA peak shape analysis was employed for determining the order of the reaction. DTA experiments on these hydrides have been carried out at different heating rates between 2.5 and 20.0 K min^{-1} under a hydrogen pressure of 1 atm. The values of the peak maximum temperatures corresponding to the endothermic decomposition processes for all these samples at various heating rates are given in Table 1. From the values of φ and T_m, the temperature programmed "Arrhenius plots" were made (shown in Fig. 1) from which the values of E_d were calculated and are

Table 1. Reaction rate values from DTA data for the decomposition of various magnesium hydride samples

Heating rate (φ, K min^{-1})	Pure MgH_2		$MgH_2 + MgCu_2$*		Mg_2NiH_4		Mg_2NiH	
	Peak max. temp. (T_m, K)	Rate† (v, s^{-1})	Peak max. temp. (T_m, K)	Rate† (v, s^{-1})	Peak max. temp. (T_m, K)	Rate† (v, s^{-1})	Peak max. temp. (T_m, K)	Rate† (v, s^{-1})
2.5	578	4.34×10^{-3}	526	3.62×10^{-3}	538	3.17×10^{-3}	556	2.69×10^{-3}
5.0	585	8.46×10^{-3}	533	7.06×10^{-3}	547	6.13×10^{-3}	563	5.25×10^{-3}
10.0	590	1.66×10^{-2}	538	1.38×10^{-2}	555	1.19×10^{-2}	573	1.01×10^{-2}
15.0	594	2.46×10^{-2}	545	2.03×10^{-2}	560	1.76×10^{-2}	580	1.48×10^{-2}
20.0	599	3.23×10^{-2}	550	2.65×10^{-2}	566	1.29×10^{-2}	588	1.92×10^{-2}

* The mixture of phases were obtained for the reaction of Mg_2Cu with hydrogen according to equation (4).
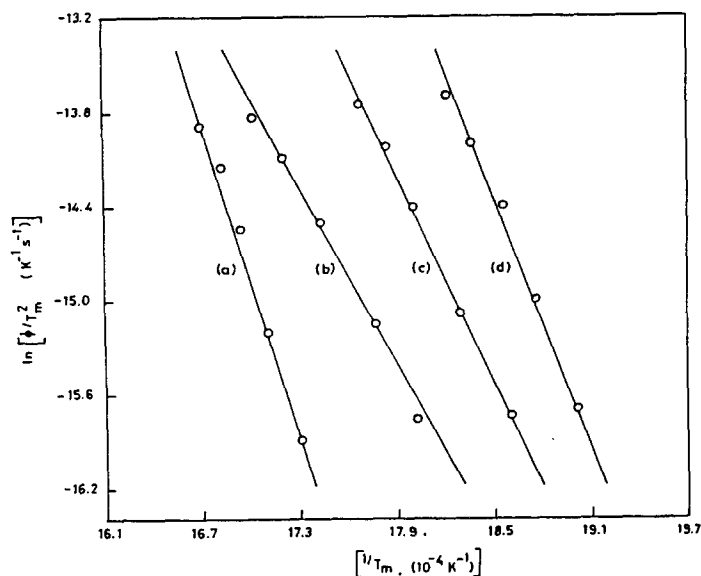† The maximum rate occurs at temperature T_m [16].

Fig. 1. Temperature programmed Arrhenius plots for the decomposition of (a) MgH_2 (b) Mg_2NiH (c) Mg_2NiH_4 and (d) MgH_2 + $MgCu_2$.

given in Table 2 along with the values of shape index and reaction orders.

It is seen from the values given in Table 2 that the activation energies for the decomposition of each hydride follow the sequence:

$$Mg > Mg_2\,Cu > Mg_2Ni. \qquad (1)$$
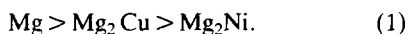
Comparing the values of the activation energies for the decomposition of hydrides such as Mg_2Cu and Mg_2Ni with that of pure Mg reveal undoubted catalytic effect of the addition of copper and nickel to magnesium metal. These observations can be explained by considering the following arguments based on different workers on magnesium- and magnesium based alloy–hydrogen systems. The dehydriding reaction of metal hydrides is considered to be composed of the following elementary steps:

● Chemical reaction at the hydride/alloy interface;
● Diffusion of hydrogen atoms from the bulk to the surface and;
● Associative desorption or recombination of atomic hydrogen into molecular hydrogen on the alloy and/or on the segregated active metal surface.

It is known that surface oxides and adsorbed gases inhibit the hydriding process of magnesium [17] and of most other metals as well [18, 19]. However, it has been reported in literature [20–23] that many 3d-metals are able to adsorb hydrogen dissociatively and desorb hydrogen associatively. The diffusion of hydrogen in

Table 2. Kinetic data from DTA results for the decomposition reactions

Samples	Peak max.* temp. (T_m, K)	Activation energy (E_d, kJ mol^{-1})	Shape index† (s)	Reaction order (n)
Pure MgH_2	575–600	289 ± 5	2.5	2.0
MgH_2+$MgCu_2$‡	525–550	200 ± 5	2.3	1.9
Mg_2NiH_4	540–570	183 ± 4	2.0	1.8
Mg_2NiH	560–590	166 ± 3	2.1	1.8

* At different heating rates between 2.5–20.0 K min^{-1}.
† s is a measure of asymmetry in DTA Peak [16].
‡ The mixture of phases were obtained from the disproportionation of the Mg_2Cu alloy according to reaction (4).

metals especially in transition metals is extremely facile. Phenomenologically this diffusitivity is a consequence of the low value of the activation energy [24].

For unalloyed magnesium, the hydriding–dehydriding rates are affected by a protective magnesium oxide (MgO) layer or even in the absence of the oxide layer, the reaction rates are still considerably slow because the magnesium hydride (MgH_2) formed or pure magnesium (Mg) itself, which function as barriers for hydrogen diffusion. Copper [17, 25] and nickel [26] are known to catalyse the hydriding–dehydriding kinetics of magnesium. Schlapbach and Co-workers [27, 28] have investigated the surface characteristics of Mg_2Ni and Mg_2Cu alloys by means of XPS and AES at room temperature. The intermetallic compounds decomposed at the surface into the component elements. There is also the possibility of the reaction induced segregation of magnesium. In contrast to magnesium, nickel and copper remain largely metallic even after air exposure. They have suggested that the segregation prevents the formation of compact oxide or hydroxide layer of magnesium, leaving behind some amount of metallic nickel or copper, unlike in the case of pure magnesium, thereby enabling dissociation of molecular hydrogen or recombination of atomic hydrogen at the metallic precipitations and/or surface layers. The catalytic effect is thus attributed to surface decomposition and the enrichment in subsurface of the alloys [27, 28]. Indeed, the preferential oxidation of one of the elements of intermetallics have been shown in the cases of $LaNi_5$ [29, 30] and FeTi [31].

Rudman and co-workers [32, 33] studied Mg/Mg_2Cu system at hydrogen pressures when only the magnesium phase was hydrided and dehydrided, so that the Mg_2Cu phase could play a catalytic role. They have concluded from their kinetic results that the external magnesium surface oxidizes and becomes inactive, whereas the interface between the Mg and Mg_2Cu which is not exposed to oxygen or air, does not build-up a barrier. The Mg_2Cu phase provides an external surface that can be reduced, thus eliminating the oxides or surface adsorbed gases for the hydriding–dehydriding reactions. That is, in contrast to the external surface of magnesium, that of Mg_2Cu keeps its ability to dissociate the molecular hydrogen or associate the atomic hydrogen at the surface. It is speculated that the additional catalytic role may be providing of an unhydrided external surface, namely Mg_2Cu or the decomposed copper metal.

Based on the thermodynamic considerations on the formation of metal oxides, it was suggested that under normal hydriding–dehydriding conditions Mg in Mg_2Cu may selectively get oxidized leaving behind a surface that essentially contains metallic copper [33]. As pointed out earlier, the maintaining of an unoxidized external surface is apparently critical for the chemisorption and/or transport of hydrogen atoms to/from the interior. It might analogously be expected that maintaining of an unhydrided external surface would similarly be important. For magnesium-based alloys, there is another

mechanism available for maintaining an unoxidized and unhydrided clean external surface. Because of the high magnesium vapour pressure, magnesium can be preferentially vaporized leaving behind a surface of the second element [33]. However, the relative importance of this mechanism has not yet been established.

It is therefore deduced that the transition metals play a dominant role in the inhibition of oxide formation by providing a clean unoxidized or unhydrided external surface/subsurface (as pure metallic clusters such as nickel and copper or as the respective alloys namely Mg_2Ni and Mg_2Cu), at which the hydrogen gas readily adsorbs, dissociates and then is transported into the bulk where hydride formation occurs; essentially the reverse process occurs in dehydriding.

It should be emphasized that the activation energy values given in literature [34] for the decomposition of MgH_2 is about 300 kJ mol^{-1}, which is close to the value of 289 kJ mol^{-1} obtained in this study. The considerably lower values obtained for Mg_2Ni (186 and 166 kJ mol^{-1} respectively for Mg_2NiH_4 and Mg_2NiH phases) and Mg_2Cu (200 kJ mol^{-1}) hydrides are probably due to the presence of transition metals which activate the desorption. Similar effects were noticed by Mintz *et al.* [35, 36] for magnesium alloys containing aluminium, gallium and indium (167–251 kJ mol^{-1}) and Khrussanova *et al.* [34] have also observed a fall in the activation energy values for La_2Mg_{17} (222 kJ mol^{-1}) and calcium substituted La_2Mg_{17} alloys (201–214 kJ mol^{-1}). The values of rates (v) were calculated from the values of T_m, E_d and φ according to the procedure adopted previously [4] and the computed values for the decomposition of the hydrides are given in Table 1.

The peak maximum temperature values given in Table 1 indicate the relative thermal stabilities (dissociation temperature at 1 atm hydrogen pressure) of the respective hydrides, the stabilities being in the following order:

$$Mg > M_2Ni > Mg_2 Cu. \qquad (2)$$
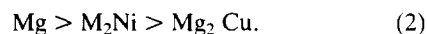
This means, the addition of a second element, namely nickel and copper in this case, decreases the thermal stabilities considerably. Of the two alloys Mg_2Ni and Mg_2Cu, the former shows fast kinetics and higher stability. However, the hydrogen content in Mg_2Cu alloy is low (2.63 Wt%) compared to that for Mg_2Ni alloy (3.62 wt%). Therefore, a ternary composition, Mg–Ni–Cu might be interesting and this forms the subject matter of the next section.

Studies on $Mg_2Ni_{1-x}M_x$ (M = Fe,Co,Cu or Zn; $0 < x < 1$) *alloys*

In order to improve the hydride characteristics of Mg_2Ni alloy further, without substantially decreasing the hydrogen storage capacity, partial substitution of nickel by some other transition metals with composition corresponding to the formation of $Mg_2Ni_{0.75}M_{0.25}$ (M = Fe, Co, Cu or Zn) were prepared and the influence of

the third element on the dehydriding behaviour was systematically investigated. Though the thermal stability of Mg_2Cu-H_2 system is significantly low compared to the ternary hydrides such as Mg_2FeH_6 [37], Mg_2CoH_5 [38], Mg_2NiH_4 [26] and $Mg_{51}Zn_{20}H_{95}$ [39], we have to strike a compromise owing to the rapid kinetics of Mg_2NiH_4 which has led to the study of partial substitution of copper in Mg_2Ni alloy and hence a series of ternary alloys have been prepared with the following composition: $Mg_2Ni_{1-x}Cu_x$ $(0 < x < 1)$. Moreover, these alloys exhibit a large homogeneity range for "x" values up to 0.85 [12]. The cell parameters obtained from the X-ray patterns for the alloys are given in Table 3. The values are in good agreement with literature data [14].

X-ray results on the hydrided samples show essentially the same pattern as that of the parent hydride, Mg_2NiH_4 suggesting the existence of single phase hydrides. The starting ternary alloys were regenerated upon dehydriding, a behaviour similar to the Mg_2Ni-H_2 system [26],
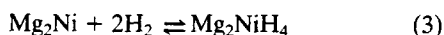
$$Mg_2Ni + 2H_2 \rightleftharpoons Mg_2NiH_4 \qquad (3)$$

except for the copper containing alloys which yield a mixture of phases consisting of MgH_2, Mg_2NiH_4 and $MgCu_2$ as shown in Table 3. The latter behaviour seems to be similar to that of Mg_2Cu due to the decomposition of the alloy during the hydriding reaction [25].

$$Mg_2Cu + 3/2H_2 \rightleftharpoons 3/2MgH_2 + 1/2MgCu_2 \qquad (4)$$

Moreover, only in the copper substituted alloys we could not obtain the starting ternary alloys on dehydriding, instead the diffraction pattern showed a multi-phase corresponding to a mixture of Mg_2Ni and Mg_2Cu phases.

The DTA peak maximum temperatures due to the decomposition of the hydrides corresponding to $Mg_2Ni_{1-x}M_x$ alloys under 1 atm hydrogen and argon are given in Table 3 along with the amount of hydrogen desorbed from the TG measurements. It will be seen that the desorption temperatures under hydrogen atmosphere are greater than those observed under argon atmosphere. One might ascribe this to the suppression of the dissociation due to presence of product hydrogen. It is seen that the alloys Mg_2Ni and $Mg_2Ni_{0.90}Cu_{0.10}$ exhibit the maximum hydrogen desorption capacity. The thermal stabilities (decomposition temperatures at 1 atm hydrogen pressure) of the hydrides of iron and zinc substituted samples are comparable to that of Mg_2NiH_4 (around 555 K) whereas the cobalt containing hydride decomposes around 570 K. The system obtained by partial replacement of nickel by copper in Mg_2Ni gives a hydride which decomposes around 528 K.
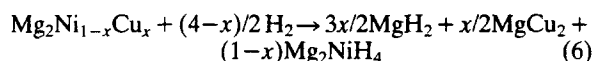
The thermodynamic parameters such as the enthalpies and entropies of formation were calculated from the DTA data [3, 4] based on the expressions proposed by Shilov et al. [40]. Table 3 summarizes the thermodynamic quantities obtained for the binary, ternary and quarternary hydrides of various magnesium alloys investigated under different dehydriding conditions and the

values are comparable with literature data [12, 14]. The differences in the thermodynamic parameters under hydrogen and argon atmospheres is obviously due to the differences in the peak maximum temperatures observed under the two dehydriding conditions.
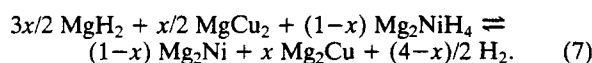
As pointed out earlier, the ternary alloys containing iron, cobalt and zinc form a quarternary hydride according to the following reaction:

$$Mg_2Ni_{0.75}M_{0.25} + (4-x)/2\ H_2 \rightleftharpoons Mg_2Ni_{0.75}M_{0.25}H_{4-x}. \qquad (5)$$
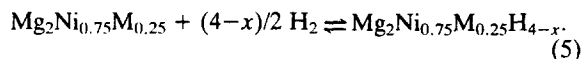
As expected these compounds are, thermally more stable (Table 3), however, their stabilities are not in accordance with those of the ternary hydrides, namely Mg_2FeH_6 [37], Mg_2CoH_5 [38] and $Mg_{51}Zn_{20}G_{95}$ [39]. On the other hand, the copper containing alloys followed a different route. The hydriding–dehydriding mechanism takes place in two consecutive steps. The first hydriding process creates an irreversible disproportionation of the alloy with the formation of MgH_2, Mg_2NiH_4 and $MgCu_2$:

$$Mg_2Ni_{1-x}Cu_x + (4-x)/2\,H_2 \rightarrow 3x/2MgH_2 + x/2MgCu_2 + \\ (1-x)Mg_2NiH_4 \qquad (6)$$

then the absorption–desorption cycles proceed as follows:

$$3x/2\ MgH_2 + x/2\ MgCu_2 + (1-x)\ Mg_2NiH_4 \rightleftharpoons \\ (1-x)\ Mg_2Ni + x\ Mg_2Cu + (4-x)/2\ H_2. \qquad (7)$$

The reaction (7) is simply the combination of reactions (3) and (4).

It is seen that the disproportionation of $Mg_2Ni_{1-x}Cu_x$ alloys during the first hydriding process leads to the formation of three distinct species, namely MgH_2, Mg_2NiH_4 and $MgCu_2$ which may be considered equivalent to a particle breaking up into three particles and would therefore necessarily lead to an increase in the surface area. Hagenmuller and co-workers [41–42] have indicated that the decomposition of $Mg_{12}Ce$ during the first hydrogen absorption, results in a more homogeneous distribution of the components and a finer particle size. Therefore, in the present instance also one might consider that the disproportionation or decomposition of $Mg_2Ni_{1-x}Cu_x$ would lead to a similar result. It has been shown that the specific surface area is the controlling factor in the dehydriding process of MgH_2 [43]. Moreover, the decomposition of the alloy appears to produce a well developed surface contact between the hydrides and the alloy. An important parameter influencing the desorption is the amount of active material in contact with the hydride [44]. The copper addition should also provide more brittle starting alloy similar to Mg_2Cu alloy. Improvements in the absorption-desorption properties could be obtained by changing the mechanical properties of magnesium by alloying it [45, 46].

The presence of copper in these alloys increases the *in situ* surface area, produces an even distribution of the components, creates well developed contacts between the hydrides and the active material and also shows

Table 3. Physico-chemical properties of Mg, Mg$_2$Ni, Mg$_2$Cu and Mg$_2$Ni$_{1-x}$M$_x$ (M = Fe, Co, Cu or Zn; 0 < x < 1) alloys and the corresponding hydrides from XRD and TG-DTA measurements

Materials	Cell parameters (hexagonal) a (Å)	c (Å)	Phases present on hydriding	Hydrogen desorbed (wt. %)	Under hydrogen atmosphere T^*_{des} (K)	Thermodynamic Data $-\Delta H$ (kJ mol^{-1}H$_2$)	$-\Delta S$ (JK^{-1}mol^{-1}H$_2$)	Under argon atmosphere T^*_{des} (K)	Thermodynamic Data $-\Delta H$ (kJ mol^{-1}H$_2$)	$-\Delta S$ (JK^{-1} Mol^{-1} H$_2$)
Pure Mg	3.21	5.21	MgH$_2$	6.95	590	70.7	119.0	560	66.5	118.8
Mg$_2$Ni	5.20	13.25	Mg$_2$NiH$_4$	3.36	555	65.8	118.5	523	61.4	117.4
Mg$_2$Ni$_{0.75}$Fe$_{0.25}$	5.22	13.27	Mg$_2$Ni$_{0.75}$Fe$_{0.25}$H$_x$†	2.94	558	66.3	118.8	534	62.9	117.8
Mg$_2$Ni$_{0.75}$Co$_{0.25}$	5.21	13.20	Mg$_2$Ni$_{0.75}$Co$_{0.25}$H$_x$†	3.08	570	67.7	118.8	545	64.2	117.8
Mg$_2$Ni$_{0.90}$Cu$_{0.10}$	5.20	13.34	MgH$_2$, Mg$_2$NiH$_4$, MgCu$_2$§	3.28	525	61.8 (66.5)¶	117.7	499	57.9 (63.7)¶	116.0
Mg$_2$Ni$_{0.75}$Cu$_{0.25}$	5.21	13.42	MgH$_2$, Mg$_2$NiH$_4$, MgCu$_2$§	3.15	528	62.1 (67.9)¶	117.6	502	58.3 (66.1)¶	116.1
Mg$_2$Ni$_{0.50}$Cu$_{0.50}$	5.22	13.50	MgH$_2$, Mg$_2$NiH$_4$, MgCu$_2$§	2.95	532	62.4 (70.2)¶	117.3	504	58.6 (70.0)¶	116.2
Mg$_2$Ni$_{0.25}$Cu$_{0.75}$	5.23	13.62	MgH$_2$, Mg$_2$NiH$_4$, MgCu$_2$§	2.76	535	62.8 (72.4)¶	117.4	508	59.1 (74.0)¶	116.3
Mg$_2$Ni$_{0.75}$Zn$_{0.25}$	5.24	13.45	Mg$_2$Ni$_{0.75}$Zn$_{0.25}$H$_x$†	3.12	556	65.9	118.5	532	62.7	117.9
Mg$_2$Cu	‡		MgH$_2$, MgCu$_2$§	2.50	538	63.3 (74.7)¶	117.7	515	60.3 (71.5)¶	117.1

* Desorption temperatures at 1 atm pressure under a constant heating rate of 10 K min^{-1}.
† x values corresponds approximately to 4.
‡ Orthorhombic structure with $a = 9.072$Å, $b = 18.242$Å and $c = 5.279$Å.
§ The phases were obtained according to reactions (6) and (4), respectively.
¶ Values in the paranthesis refer to the corrected enthalpy values [3].

Table 4. Dissociation pressure–temperature relationships for various magnesium–hydrogen systems

System	Phases present after hydriding	Dissociation pressure (plateau region) (atm)	Temperature (K)	Ref.
Mg–H$_2$	MgH$_2$	5.8‡	623	[46]
Mg$_{12}$Ce–H$_2$	MgH$_2$, CeH$_3$	9.1‡	623	[48]
Mg$_2$Ni–H$_2$	Mg$_2$NiH$_4$	9.9‡	623	[26]
Mg$_2$Cu–H$_2$	MgH$_2$, MgCu$_2$	21.5‡	623	[25]
Mg–Mg$_2$Ni–H$_2$	MgH$_2$, Mg$_2$Ni	5.5*,‡	623	[26]
Mg–Mg$_2$Cu–H$_2$	MgH$_2$, Mg$_2$Cu	5.4†,‡	623	[25]
Mg–H$_2$	MgH$_2$	1.0	590§	This work
Mg$_2$Ni–H$_2$	Mg$_2$NiH$_4$	1.0	555§	This work
Mg$_2$Cu–H$_2$	MgH$_2$, MgCu$_2$	1.0	538§	This work
Mg$_2$Ni$_{0.90}$Cu$_{0.10}$ –H$_2$	MgH$_2$, Mg$_2$NiH$_4$, MgCu$_2$	1.0	525§	This work

* Plateau region corresponding to the decomposition of MgH$_2$ Phase in the presence of Mg$_2$Ni alloy.
† Plateau region corresponding to the decomposition of MgH$_2$ Phase in the presence of Mg$_2$Cu alloy.
‡ Data based on p–c–T measurements.
§ Data based on DTA measurements.

better mechanical properties during hydriding–dehydriding process, thus accounting for good sorption behaviour of the copper substituted alloys. However, these alloy systems may have different reaction controlled processes as can be expected from different components of the alloy. Therefore, the dehydriding process of Mg$_2$Ni$_{1-x}$Cu$_x$ alloys should be separately investigated.

Table 4 shows the dissociation pressure–temperature relationships for the various magnesium–hydrogen systems. It is seen [25, 26, 47, 48] that the addition of a second metal to magnesium markedly increases the dissociation pressure of the systems, which means that the alloying element plays an important role in increasing the dissociation pressure and it follows the sequence:

$$Mg_2Cu > Mg_2Ni > Mg_{12}\,Ce > Mg. \qquad (8)$$

However, if magnesium is present in the alloy in excess of the composition corresponding to Mg$_2$Ni or Mg$_2$Cu, the decomposition pressure corresponding to the reaction:

$$Mg + H_2 \rightleftharpoons MgH_2 \qquad (9)$$
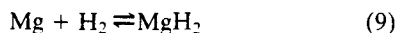
is reduced slightly from 5.8 to 5.5 and 5.4 atm at 623 K (Table 4), respectively, for the Mg$_2$Ni and Mg$_2$Cu alloys containing MgH$_2$ phases [25, 26, 47]. Improvements in the kinetics of the reaction are also observed.

It is however, interesting to note that the presence of a second phase like Mg$_2$Cu, Mg$_2$Ni, MgCu$_2$ or CeH$_3$ along with magnesium, plays an important role in the hydriding and dehydriding reactions [25, 26, 47, 48]. Among the phases, except Mg$_2$Ni and Mg$_2$Cu, the others increase the dissociation pressure to a greater extent (see Table 4). The present work on the stabilities (dissociation temperature at 1 atm pressure) of the hydrides suggest the following order:

$$Mg > Mg_2Ni > Mg_2Cu > Mg_2Ni_{1-x}Cu_x. \qquad (10)$$
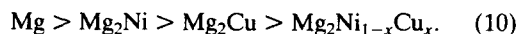
However, it has been shown [12] that the rate of dehydriding of the hydrides of Mg$_2$Ni and Mg$_2$Ni$_{0.90}$Cu$_{0.10}$ are almost the same and it is definitely faster than the Mg$_2$Cu–H$_2$ system.

It is known that Mg$_2$Cu has lower thermal stability and also has a lower reaction rate [25] compared to Mg$_2$Ni [24]. This is also borne out in the present investigation. However, in the present study, it is seen that the composition Mg$_2$Ni$_{0.90}$Cu$_{0.10}$ has a lower thermal stability than Mg$_2$Ni (Table 3). This could be ascribed to the replacement of nickel partially by copper in Mg$_2$Ni. However, it is necessary to note that such replacements affect the thermal stability without practically affecting the hydrogen storage capacity. Thus, considerable decrease in the thermal stabilities and increase in the reaction rates in the hydrides of Mg$_2$Ni$_{0.90}$Cu$_{0.10}$ alloys

could be due to the presence of both nickel and copper metals and hence they play important catalytic role in magnesium–hydrogen reaction.

It is derived from these results that the kinetic and thermodynamic behaviour are dependent upon the active material present or produced in the metal-hydrogen systems. The ternary system Mg–Ni–Cu shows promising results and it is the only system where both the kinetic and thermodynamic characteristics of the hydrides are simultaneously favourable.

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