

Mg₂NiH: A NEW HYDRIDE PHASE IN THE Mg₂Ni-H₂ SYSTEM

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Abstract—A new hydride phase apart from Mg₂NiH₄ has been identified in the Mg₂Ni-H₂ system by pressure-composition-temperature relationships, thermal analyses and X-ray diffraction measurements. The new phase has an approximate composition Mg₂NiH and is considered to be the intermediate phase in the Mg₂Ni-H₂ reaction. The additional hydride phase, Mg₂NiH (named as β -hydride) and the full hydride phase, Mg₂NiH₄ (named as γ -hydride) have been shown to crystallize in monoclinic structure. The β -phase (Mg₂NiH) also exhibits a phase transition from monoclinic to cubic structure similar to the γ -phase (Mg₂NiH₄).

INTRODUCTION

Among the Mg-based alloy hydrides [1], a well known compound is the ternary hydride, Mg₂NiH₄ which has received considerable attention because of its unique absorption-desorption behaviour towards H₂ [2]. Since Mg₂NiH₄ is one of the well characterized metal-H₂ systems, a number of reports are available dealing with various properties of the material. It is generally accepted that the Mg₂Ni-H₂ system has a fairly long plateau region in the pressure-composition-temperature (p - c - T) diagram and there exists a single hydride phase of Mg₂NiH₄ under normal experimental conditions [2-4].

However, the formation of two or more distinct hydride phases excluding the solid solution phase under usual experimental conditions is a normal phenomenon among almost all known alloy-H₂ systems [5-15]. For example, LaNi₅-[5], Th₂Fe₇-[6], GdCo₃-[7], ZrMn_{2.4}-[8] and TiCr_{1.8}-[9] H₂ systems show two different hydride phases, CaNi₅-[10, 11], ErFe₂-[12] and FeTi-[13] H₂ systems give three hydride phases each whereas the LaCo₅-H₂ reaction shows only two hydride phases under normal working conditions [14], but however exhibits two additional phases at very high pressures [15]. Thus, the presence of various hydride phases appear to be a common feature in many alloy-H₂ reactions which could possibly be due to the occupation of H₂ at different interstitial sites available, as has been demonstrated in the case of AB₅-systems [15].

Hence the existence of a second or third hydride phase in most alloy-H₂ systems raises the question of whether this is also the case in Mg₂Ni-H₂ system. Thermal analysis on Mg₂NiH₄ [16-18] at different experimental conditions indicated a two-step decomposition process

which provided support for the existence of a different hydride phase in Mg₂Ni-H₂ reaction. Hence, in the present investigation an attempt has been made to develop on this observation based on TG-DTA, p - c - T and XRD measurements. A preliminary account of the results presented in this article has appeared elsewhere [17].

EXPERIMENTAL PROCEDURES

Starting materials

The alloys, Mg₂Ni used in the present study were commercial and laboratory prepared ones. The commercial sample was supplied by MPD Technology Corporation, New Jersey, U.S.A., as their commercially available hydrogen storage alloy Hystor-301. The intermetallic compound was also prepared in the laboratory as per the procedure described elsewhere [16-19]. The laboratory prepared alloy differed significantly from the commercial one with respect to the impurities, mainly Mg. The commercial sample contains excess of free Mg as the main impurity. It was estimated to be about 7.0-7.5% [20].

The hydrides, Mg₂NiH₄ (synthesized from both commercial and laboratory prepared Mg₂Ni alloys) were the same as has been used in our earlier investigation [16-19]. Samples of Mg₂NiH were prepared either by decomposing the Mg₂NiH₄ phase alone cautiously in a flow reactor and by means of a static reactor system where hydrogen gas was withdrawn from Mg₂NiH₄ sample in aliquots until the approximate desired composition was obtained or by partially and/or completely decomposing the Mg₂NiH₄ phase in a reactor tube of standard design [16]. Hydrogen was flushed through the reactor packed with Mg₂NiH₄ sample in the middle. Then the reactor was heated by passing hydrogen at a flow rate of 40 cm³ min⁻¹ (1 atm) up to 550 K under different time intervals in order to decompose Mg₂NiH₄

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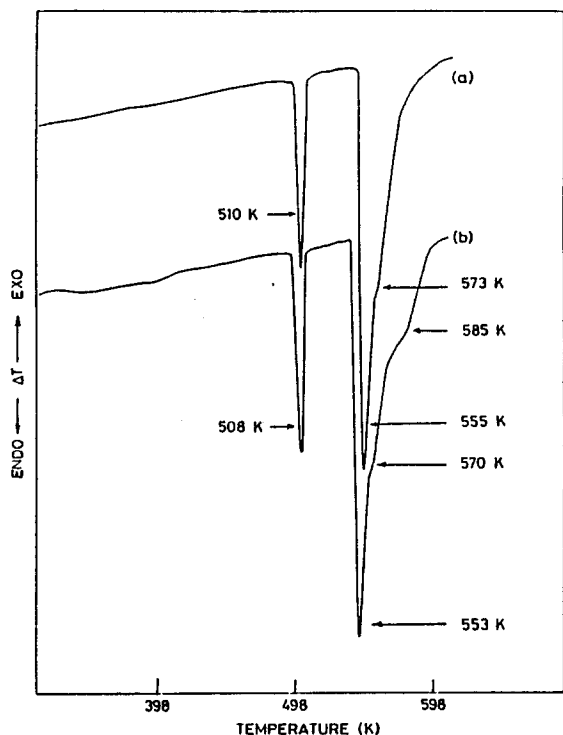


Fig. 1. DTA patterns of Mg_2NiH_4 sample at a constant heating rate of 10 K min^{-1} under 1 atm hydrogen pressure: (a) Synthesized. (b) Commercial.

phase [16]. Unless stated as commercial alloys the samples used are synthesized ones.

Characterization

X-Ray diffractograms of the laboratory prepared samples of Mg_2Ni and Mg_2NiH_4 do not show the presence of either Mg and/or MgH_2 . However, the commercial samples indicate the existence of such impurities, as evidenced from their diffraction lines as contaminants. Thermal analysis results also reveal such information on the hydrided samples thus supporting the earlier observations. This suggests that the commercial alloy results in the formation of a mixture of the main phase, Mg_2NiH_4 and the contaminant phase, MgH_2 upon hydriding. Unlike the commercial alloy, the prepared samples were free from either Mg or MgH_2 respectively, in Mg_2Ni and Mg_2NiH_4 . Even though the exact composition of the different phases vary slightly with temperature and pressure conditions, for the sake of convenience we use a standard single composition for all these phases.

Physico-chemical measurements

Simultaneous Thermogravimetry and Differential Thermal Analysis (TG-DTA). TG-DTA measurements for Mg_2NiH_4 samples were carried out at various heating rates according to the procedure described elsewhere [16-19]. A new hydride phase was identified and was isolated *in situ* by decomposition of Mg_2NiH_4 phase in the thermal analysis unit itself. Subsequently, thermal analysis was carried out on the new hydride phase also. Heating and cooling runs were recorded for the phases in the phase transition as well as in the decomposition regions of the hydrides.

Pressure-composition isotherm (p - c - T). Equilibrium H_2 desorption isotherms were determined for Mg_2NiH_{24} sample in a volumetric apparatus of constant volume, as described earlier in this section. Since the decomposition reaction is sluggish under these temperature and pressure conditions employed in the present study, in practice, it took more than 12 h period to obtain a single complete isotherm to assure thermal equilibrium at each measurement [16].

X-Ray diffraction (XRD). XRD patterns were recorded for the intermediate and full hydride phases under 1 atm H_2 pressure at temperatures below and above the phase transition regions as also at room temperature in a Philips diffractometer as per the procedure outlined previously [16-19].

RESULTS AND DISCUSSION

Thermal studies

Decomposition of Mg_2NiH_4 . The DTA patterns for Mg_2NiH_4 prepared from the commercial alloy (Hystor-301) as well as for that obtained from the Mg_2Ni prepared in this laboratory are presented in Fig. 1. It will be seen from the figure that four endothermic peaks are obtained in the case of the commercial sample (Fig. 1b). The endotherm at 508 K is attributed to a reversible phase transition and the one at 553 K to the decomposition of Mg_2NiH_4 . It is interesting to note that on the high temperature side (next to 553 K), two shoulders appear at 570 and 585 K. The shoulder at 570 K could be ascribed to the decomposition of another hydride phase, Mg_2NiH and the shoulder at 585 K could be due to the decomposition of MgH_2 . The latter would arise due to the hydriding of excess of Mg metal present as a contaminant in the commercial sample. XRD patterns also show the presence of this contamination phase. This is also supported by the observations of Reilly and Wiswall [2], who have shown that two plateaux are observed in the p - c - T diagram of hydrided Mg_2Ni containing excess Mg metal and have ascribed the second plateau to the decomposition of MgH_2 .

In the case of the laboratory prepared sample, the

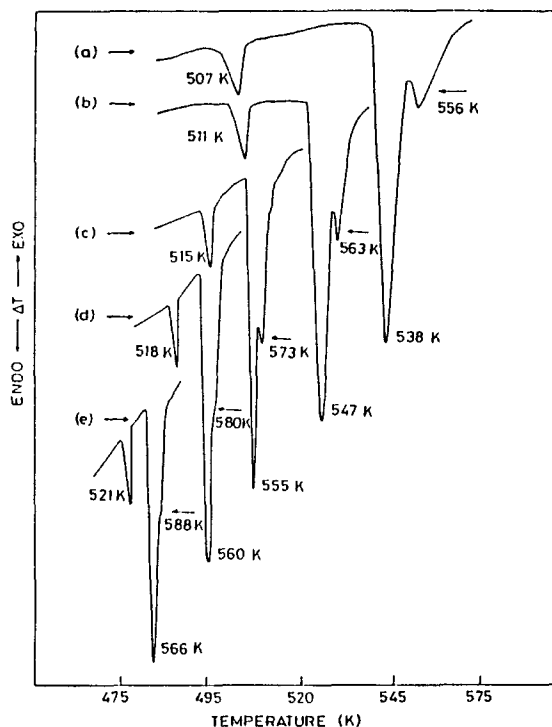


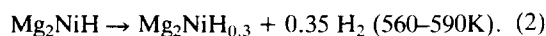
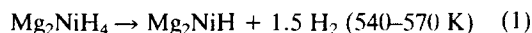
Fig. 2. DTA patterns of Mg₂NiH₄ at different heating rates (K min⁻¹) under 1 atm hydrogen pressure: (a) 2.5 (b) 5.0 (c) 10.0 (d) 15.0 and (e) 20.0. Curve (a) is correctly positioned on the temperature scale while the others are shifted to avoid peak overlap. However, the exact peak maximum temperature values are indicated.

figure shows the appearance of only three endotherms (Fig. 1a). The endotherm at 510 K is due to the reversible phase transition of Mg₂NiH₄ and the one at 553 K is due to the decomposition of Mg₂NiH₄ phase itself. The endotherm at 573 K could be attributed to the decomposition of an additional hydride phase, Mg₂NiH. The latter cannot be due to the decomposition of MgH₂ as the comparison with the results obtained on the commercial sample would show. Moreover, the XRD pattern does not show the presence of the MgH₂ phase as shown by the commercial sample. This is understandable since the laboratory prepared sample does not contain excess Mg. It is relevant to quote that pure MgH₂ shows a decomposition around 590 K [16, 18, 19]. TG results also support the above observations, i.e. it shows a step-wise weight change corresponding to the DTA peaks. A detailed account of the observed weight changes for the commercial and synthesized samples are given in the subsequent section.

Figure 2 shows the DTA curves for the decomposition of Mg₂NiH₄ for the laboratory prepared sample at

different heating rates between 2.5 and 20.0 K min⁻¹. The appearance of a diffuse peak at higher heating rates say 15.0 and 20.0 K min⁻¹ and a clear peak at slower heating rates such as 2.5, 5.0 and 10.0 K min⁻¹ should be noted. The existence of the additional small transition on the high temperature side may be due to the decomposition of another hydride phase and is well separated in the DTA traces obtained with a heating rate of 2.5 K min⁻¹ (Fig. 2a). From the DTA peak areas and the weight loss measurements for the multi-stage decomposition process, it has been derived that the two phases have approximate compositions, Mg₂NiH₄ and Mg₂NiH respectively.

Hence, it is deduced that a clear two-step desorption process is taking place between the heating rates 2.5 and 20.0 K min⁻¹ according to the following schemes:



These results suggest an additional hydride phase in Mg₂Ni-H₂ system.

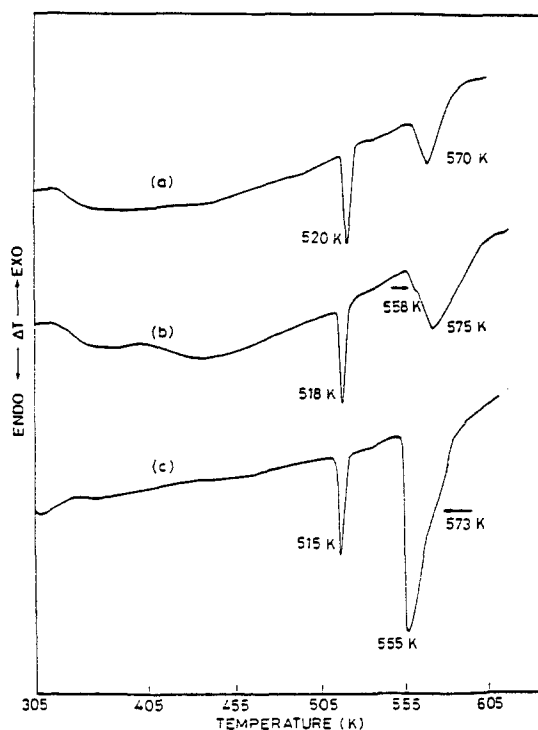


Fig. 3. DTA patterns for the hydrides of Mg₂Ni at a constant heating rate of 10.0 K min⁻¹ under a hydrogen pressure of 1 atm: (a) Mg₂NiH phase (Mg₂NiH₄ phase alone decomposed fully) (b) Mixture of Mg₂NiH and Mg₂NiH₄ phases (Mg₂NiH₄ phase partially decomposed) and (c) Fresh Mg₂NiH₄ (untreated sample).

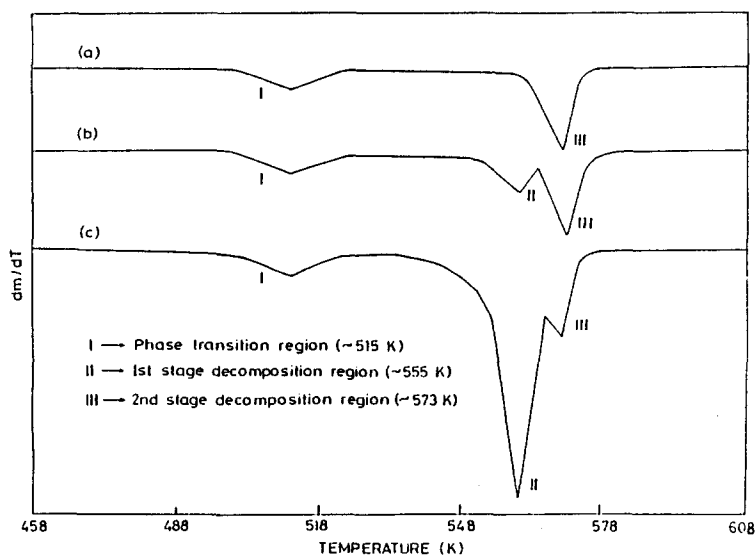


Fig. 4. DTG plots for the hydrides of Mg_2Ni under similar conditions for the samples shown in Fig. 3.

Partial and/or complete elimination of Mg_2NiH_4 phase alone. In order to substantiate the above findings, partial and/or complete decomposition of Mg_2NiH_4 phase alone was carried out in a flow reactor at a heating rate of 10 K min^{-1} . The reddish-brown coloured Mg_2NiH_4 changed to brownish-black on decomposition at 555 K corresponding to Mg_2NiH . On further heating, at 573 K the sample changed to black corresponding to $\text{Mg}_2\text{NiH}_{0.3}$. The samples were subjected to TG-DTA measurements and the thermograms were compared with that of fresh Mg_2NiH_4 .

It is clear from Fig. 3 that the completely decomposed sample (Mg_2NiH_4 phase alone) shows only one endotherm (curve a at 570 K corresponding to the decomposition of Mg_2NiH phase as shown for the fresh Mg_2NiH_4 sample (curve c). However, partially decomposed Mg_2NiH_4 , which is a mixture of Mg_2NiH_4 and Mg_2NiH phases shows a small endotherm at 558 K which corresponds to the decomposition of Mg_2NiH_4 phase in addition to the endotherm at 575 K due to the decomposition of Mg_2NiH phase (curve b). Similar results are also observed in the TG traces. Figure 4 gives the differential thermogravimetry (DTG) plots for the above mentioned samples under identical conditions employed for obtaining Fig. 3. The weight loss regions shown in Fig. 4c correspond to the endothermic processes taking place during the decomposition of Mg_2NiH_4 (Fig. 3c). The small peak observed in the phase transition region (around 510 K) suggests a different composition of Mg_2NiH_4 , i.e. the LT-monoclinic phase changes to HT-cubic phase with a small loss in H_2 content [19]. The weight loss in this region is less than 5%. The

subsequent weight changes at higher temperatures corresponding to the step-wise desorption is found to be about 70 and 25% at 555 and 573 K, respectively, for the first and second stages of decomposition. In addition to the small weight loss at the phase transition region, the commercial sample showed the weight loss of 68, 23 and 4% corresponding to the three decomposition stages, (Fig. 1b) namely Mg_2NiH_4 (553 K), Mg_2NiH (570 K) and MgH_2 (585 K), respectively.

In situ preparation and decomposition of Mg_2NiH . Since the decomposition of Mg_2NiH_4 at lower heating rates show a clear separation of the endotherms due to the multi-step process, the thermograms were carefully recorded at a heating rate of 2.5 K min^{-1} . A typical DTA pattern is presented in Fig. 5a. In order to isolate the new hydride phase, Mg_2NiH , attempts were made to prepare this phase *in situ* by decomposing the Mg_2NiH_4 phase alone as indicated in Fig. 5b. The resulting Mg_2NiH phase is subjected to thermal analysis subsequently. The latter part of the curve (b) gives interesting information. The decomposition of the isolated Mg_2NiH phase occurs at 556 K and is in agreement with the results obtained from simultaneous decomposition of both the phases as shown by the thermogram (a).

Several heating-cooling runs were recorded in order to check the reversibility of the phase transitions observed for both the phases as indicated in Fig. 5. From the figure, it is obvious that the new phase, Mg_2NiH , also exhibits a reversible phase transition at a slightly lower temperature (502 K) than that of the phase transition due to Mg_2NiH_4 (507 K) and is probably also associated

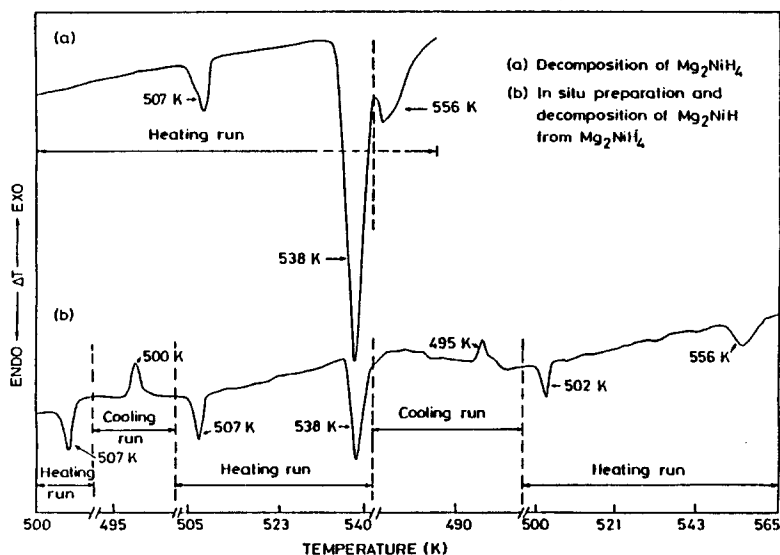


Fig. 5. DTA curves for the Mg₂Ni-H₂ system under a hydrogen pressure of 1 atm with a heating rate of 2.5 K min⁻¹. Curve (a) represents a single heating run and curve (b) is subjected to several thermal cycles (see text).

with a small change in H₂ concentration as observed for Mg₂NiH₄ phase from TG measurements. The thermodynamic parameters for the different phases were calculated from DTA data [16-19] and are summarized in Table 1 along with the decomposition temperatures at 1 atm H₂ pressure.

p-c-T Measurements

The sorption properties of metal-H₂ systems are conveniently represented by *p-c-T* relationships as shown schematically in Fig. 6. This figure shows a series

of isotherms obtained at the various temperatures, namely 515, 523 and 532 K below atmospheric pressure. Each isotherm of Fig. 6 shows two distinct plateaux and it should be emphasized that a clear gap of only 50-100 torr is observed between the hydride phases. The presence of multi-pressure plateaux in the isotherms should be attributed to the decomposition of the different phases. At low H₂ concentration side of the diagram, a second plateau (lower plateau) appears indicating the existence of an additional hydride phase apart from Mg₂NiH₄ (upper plateau) with a composition of Mg₂NiH. The shape of the isotherm also suggests the

Table 1. Desorption temperature (T_m , K), enthalpy (ΔH_f° , kJ mol⁻¹H₂) and entropy (ΔS_f° , JK⁻¹ mol⁻¹H₂) of formation of different hydride phases of the Mg₂Ni-H₂ system

Parameters	Mg ₂ NiH ₄ *		Mg ₂ NiH†	
	DTA	<i>p-c-T</i>	DTA	<i>p-c-T</i>
T_m	555‡	542§	573‡	559§
$-\Delta H_f^\circ$	65.8	64.4	68.4	68.0
$-\Delta S_f^\circ$	118.6	118.8	119.4	120.2

*. † Corresponds to upper and lower plateaux respectively in Fig. 6.

‡ Values at a constant heating rate of 10.0 K min⁻¹ under a H₂ pressure of 1 atm.

§ Values deduced at a H₂ pressure of 1 atm.

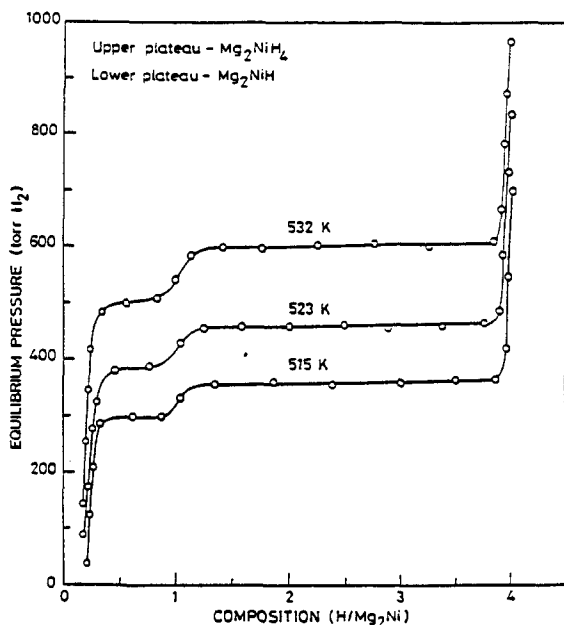


Fig. 6. Desorption isotherms for the $\text{Mg}_2\text{Ni}-\text{H}_2$ system.

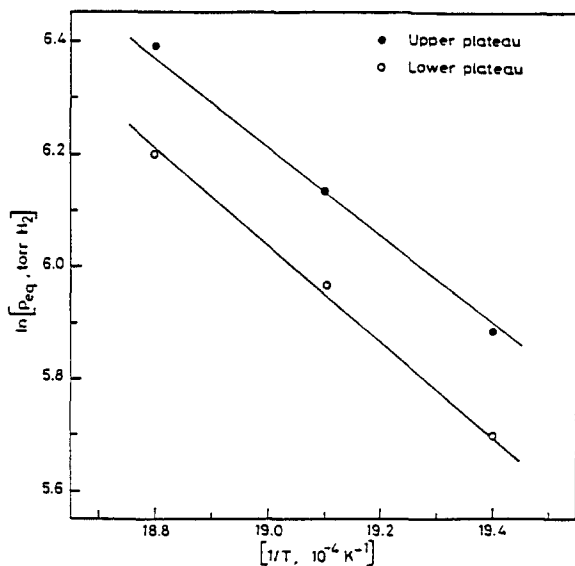


Fig. 7. van't Hoff plots (desorption) for the $\text{Mg}_2\text{Ni}-\text{H}_2$ system (see also Fig. 6).

presence of a hydrogen poor phase with an average composition, $\text{Mg}_2\text{NiH}_{0.3}$.

Thus, $\text{Mg}_2\text{Ni}-\text{H}_2$ system exhibits three distinct hydride phases of the compositions: $\text{Mg}_2\text{NiH}_{0.3}$, Mg_2NiH and Mg_2NiH_4 denoted here as α -, β - and γ -hydrides respectively. The full hydride phase (Mg_2NiH_4) which has been usually called as β -hydride elsewhere [3, 4] has been designated here as γ -hydride, since the intermediate phase (Mg_2NiH) is named as β -hydride. From a series of isotherms as illustrated in Fig. 6, van't Hoff plots were made (see Fig. 7). In the limited pressure-temperature regions where the isotherms have been measured, the plots are straight lines and the thermodynamic functions evaluated from the slopes of these lines are summarized in Table 1 along with the decomposition temperatures at 1 atm H_2 pressure for both the phases.

XRD Analysis

Figure 8 displays the XRD patterns obtained for the different hydride phases and for the parent alloy at room temperature. It is to be noted that the diffraction patterns obtained between the angles 22 and 25° , and 38 and 41° contain pertinent information on Mg_2NiH and Mg_2NiH_4 . The X-ray patterns in Fig. 8a and d are characteristic of the starting alloy (Mg_2Ni) and the solid solution phase ($\text{Mg}_2\text{NiH}_{0.3}$) respectively. $\text{Mg}_2\text{NiH}_{0.3}$ is simply the dissolved H_2 in the hexagonal Mg_2Ni alloy matrix with minor expansions of the unit cell dimensions primarily along the c -axis (Table 2). Analysis of Fig. 8b and c suggests that the XRD patterns are almost similar, however, the diffraction peaks for Mg_2NiH are shifted slightly to lower angles than those of Mg_2NiH_4 indicating that Mg_2NiH would also exhibit a similar metal atom substructure to that of Mg_2NiH_4 with a small deviation in the cell dimensions. This is supported by the report of Noreus and Werner [21], who have pointed out that the hydrogen-deficient phases (Mg_2NiH_x ; $x \sim 2$) exhibit diffraction patterns and structures identical with Mg_2NiH_4 but with a lower symmetry.

In Table 2, the lattice parameters of the different hydride phases are listed. An interesting feature of Mg_2NiH is the occurrence of the structural phase transition from LT-monoclinic to HT-cubic structure at 502 K as observed in the case of Mg_2NiH_4 at 507 K (see Fig. 5). The cell dimensions for the HT-hydride phases are also included in Table 2 along with the X-ray densities. The differences in the values of the densities of the LT- and HT-forms suggest that there may be a small loss in the H_2 content in the HT-phases and is in agreement with the results of thermal analysis. The volume expansion and the calculated densities for Mg_2NiH and Mg_2NiH_4 are not proportional to the H_2 content, since a small or no change in the a -, b - and c -axes is observed. However, a small contraction in the angle β is noticed (93.1 to 92.9°) for Mg_2NiH . Hence, it was not possible to get the dependence of unit cell parameters on H_2 concentration.

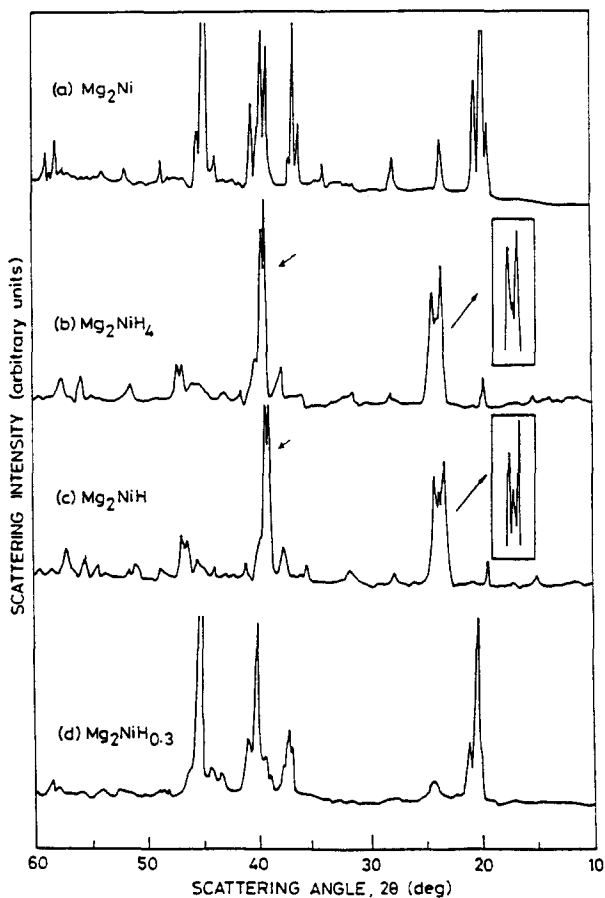


Fig. 8. X-Ray diffraction patterns for the various phases in the Mg₂Ni-H₂ system.

Table 2. XRD Results for the different hydride phases of the Mg₂Ni-H₂ system

Material	Structure	Cell dimensions				Density (g cm ⁻³)
		a(Å)	b(Å)	c(Å)	β (deg)	
Mg ₂ Ni	Hexagonal	5.20	—	13.25	—	3.45
Mg ₂ NiH _{0.3}	Hexagonal	5.22	—	13.38	—	3.40
Mg ₂ NiH	Monoclinic*	6.60	6.42	6.45	92.90	2.71
	Cubic†	6.50	—	—	—	2.69
Mg ₂ NiH ₄	Monoclinic*	6.58	6.40	6.50	93.10	2.70
	Cubic†	6.52	—	—	—	2.67

* Low temperature (LT) form (298 K).

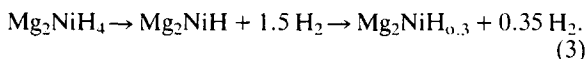
† High temperature (HT) form (510 K).

It seems that the diffraction lines for the full hydride phase at room temperature (Fig. 8b) arises due to the splitting of the lines of the HT-hydride. Interestingly, the peaks are composed of a number of lines (between 22 and 25°, and 38 and 41°) indicating that the LT-phase is simply the distorted form of the cubic phase. In a similar way, in the case of the intermediate phase (Fig. 8c) also, the splittings are observed in the region 22–25° and 38–41°. However, an additional residual central peak at 23.4° is also noticed and the doublet intensity at 38–41° is changed, relative to that for the main hydride phase. The distortion from cubic symmetry decreases slightly in the case of less hydrogen containing phase. In other words, this phase exhibits a monoclinic structure possibly of higher symmetry compared to the full hydride phase. Both the samples, namely Mg₂NiH and Mg₂NiH₄ have been analysed for the hydrogen content before and after XRD measurements by TG-DTA and no change in the composition due to XRD measurements have been observed.

New hydride phase

The two plateau regions in the *p-c*-isotherms are clearly discernable (Fig. 6) and a multi-step desorption process is exhibited by TG-DTA patterns (Figs 1–5). This indicates the existence of two hydride phases which is supported by XRD studies. Therefore, it has been considered that the desorption of H₂ from Mg₂NiH₄ may proceed via an intermediate phase at lower heating rates (< 10 K min⁻¹) or directly at higher heating rates (> 10 K min⁻¹) according to the following schemes:

At lower heating rates:



At higher heating rates:



Lupa *et al.* [22, 23] reported multi-pressure plateau regions for the desorption isotherms for the hydrides of Be- and Fe-substituted Mg₂Ni alloys. It is observed that the plateau regions are well separated and suggests the existence of more than one hydride phase. This has been attributed in terms of H atom site location in the metal lattice, i.e. H atom occupies different types of interstices which are constituted by different metal atoms. In a similar way, one can expect that Mg₂Ni-H₂ system may also exhibit multi-plateau regions. However, it has not been recognised in the desorption isotherms reported earlier in literature [2, 3]. This may be because of the fact that the plateau regions might overlap and show only a single plateau region under high temperature and pressure conditions normally employed, wherein a separation of 50–100 torr may not be discernable. In the present instance, the second plateau could not be due to MgH₂, since the separation between the two observed plateaux (Fig. 6) is very small unlike what has been observed by

Reilly and Wiswall [2] for the excess Mg containing Mg₂Ni.

The occupation of various sites by H atoms has been reported by Zolliker *et al.* [24] from neutron diffraction studies on Mg₂NiH₄. According to which the D atoms are surrounded by the Ni' atoms in nearly tetrahedral configuration and each D atom is bonded to one Ni atom and three or four Mg atom neighbours. Since different types of sites are available for the H atom occupation in Mg₂Ni alloy, this could account for the presence of different hydride phases in this system. The DSC study on the hydriding of Mg₂Ni alloy by Hirata [25] showed two exothermic transitions suggesting that hydriding occurs in two separate temperature ranges. This could be interpreted as being due to the formation of multi-hydride phases, as observed in the present study.

Furthermore, the results can be corroborated by considering the behaviour of LaNi₅-H₂ system. Since the discovery of the H₂ sorption processes in LaNi₅ by van Vucht *et al.* [26], it has been reported to have only one hydride phase (LaNi₅H₆) until Ono *et al.* [5], who have observed an additional hydride phase (LaNi₅H₃) recently. This has been discussed in terms of interstitial site occupancies by H atoms from neutron diffraction data as well as from geometric models proposed by several research groups [27, 28]. By taking into account the different H atom sites available in LaNi₅ alloy, Ono *et al.* [5] have convincingly shown the possibility of different hydride phases. However, it has been established that Y- and Zr-substituted LaNi₅-H₂ systems exhibit distinct multi-hydride phases [29], which indirectly suggest the possibility of the existence of an intermediate phase in the LaNi₅-H₂ system also.

Therefore, it is probable from the foregoing arguments that Mg₂Ni-H₂ system also exhibits a narrow multi-phase region while the Be- and Fe-substituted Mg₂Ni-H₂ systems [22, 23] have rather extended multi-phase regions in an identical fashion to that of the substituted [29] and unsubstituted [5] LaNi₅-H₂ systems respectively. However, the differences in the behaviour of the substituted and unsubstituted systems could be attributed to both electronic and geometric factors, i.e. in the case of substituted alloys, the incorporation of a third element affects the size and shape of the interstices as well as the electronic interaction between the elements and H atoms and hence, the gaps between the different hydride phases in the isotherms either get reduced or increased accordingly.

Contamination phase

From the structural and thermal behaviours of Mg₂NiH, two crystallographic forms were identified similar to that of Mg₂NiH₄ with the same structural characteristics (see Table 2). A monoclinic form at room temperature transforms to cubic structure at 495–502 K with a small difference in compositions as that found in Mg₂NiH₄, discussed earlier elsewhere [19]. It seems

obvious from the XRD patterns (Fig. 8) that there are rather small differences between Mg₂NiH and Mg₂NiH₄ and hence it is difficult to differentiate the diffraction patterns if both the phases were present.

The difficulty with the structural analysis of LT-Mg₂NiH₄ is that its X-ray patterns obtained at room temperature always showed that it contained an unknown phase in most of the samples [21, 30–35]. The amount of unknown coexisting phases, however, change from sample to sample and cannot be controlled. Moreover, the diffraction patterns coincide with that of the LT-form and the pattern for the resulting mixture becoming slightly complicated. Hence, there has been some controversy regarding the existence and nature of these additional hydride phases in the samples. Conflicting results on the possibility of different LT-modifications have been reported [21, 30–35]. According to these reports, there exist at least two different phases, one (called the main phase) of monoclinic structure [16–19] and another (called the intermediate phase) of orthorhombic structure [30, 31, 33, 34] or of cubic symmetry [32] or of a hydrogen-deficient phase with monoclinic structure possibly of lower symmetry [21].

It has been previously shown that a further splitting of 22–25° peaks in Mg₂NiH₄, namely the extra is coming from microtwins introduced in the lattice [36]. In the vicinity of these stacking faults the surrounding is orthorhombic in some sense. Since the stacking faults are rather regularly repeated by lattice vectors, however, diffuse peaks will appear in the diffraction pattern [36, 37]. Thus the new diffuse diffraction patterns can be indexed by orthorhombic unit cell related to monoclinic basal unit cell. This is the reason for the appearance of a third peak between the components of the monoclinically split peak at 23°, and hence the assumed orthorhombic phase. Similarly, this behaviour may also be invoked for the Mg₂NiH phase, though it is predominant in this case, as can be observed from the intensity of the extra peak. However, the details of micro-twinning is slightly complicated [36, 37]. Different sample histories will give different amounts of twinning. But these observations could also be interpreted as being due to the existence of small compositional change, which might be responsible for the different phases. It is to be noted that the composition of the ternary phase is varied considerably, for example, Mg₂NiH_{3.8–4.2}, showing small inhomogeneity regions [2, 21, 38]. This may also affect the results.

It is however not possible to attribute the occurrence of this line to the presence of contamination in the HT-phase as reported in the case of full hydride phase [33], since on account of the lack of a number of other lines of almost equal intensities from the HT-phase. However, the splitting of the other peaks cannot be explained in terms of orthorhombic cell proposed earlier [30, 31, 33, 34] because of the absence of other lines. It cannot be explained satisfactorily in terms of the microtwinning alone [35–37]. Since the intensity variations at

38–41° was not accounted. Noreus and Werner [39] have also noticed differences in the neutron diffraction patterns of the different LT-phases (designated as LT-I and LT-II), however, it cannot be attributed to HT-phase. Earlier, they have reported [32] the possibility of small amount of less H₂ containing phase and it is understood that this may complicate the XRD patterns. It has also been shown that the low temperature preparation (below 483 K) resulted in a two phase hydride mixture consisting of stoichiometric and hydrogen-deficient sub-stoichiometric phases [34, 35].

The variations of stoichiometry of these materials may be accommodated by the existence of planar faults at which there is local variation of cation/anion ratio. Such faults may take the form of sheer planes, microtwins or more complicated configurations and may occur in disordered, partially ordered or well ordered arrays. That is, a disordered sequence of two types of structure having small differences in composition, unit cell dimensions and axial orientations. Streaking in diffraction patterns has frequently been observed and attributed to such faults [40]. However, the sample Mg₂NiH might contain a twinning probability sufficiently higher than Mg₂NiH₄ as deduced from the broadening and the intensity variation of the XRD patterns. It could also be assumed of a second phase similar to that observed for the LT-Mg₂NiH₄.

The XRD patterns of LT- and HT-forms of Mg₂NiH are similar to those of Mg₂NiH₄. The diffraction pattern of the LT-forms exhibit splitting of the peaks, corresponding to the cubic reflection at 23°. Mg₂NiH shows a clear triplet whereas in the case of Mg₂NiH₄, only a doublet, possibly a diffuse peak, was observed. Hence the sample Mg₂NiH₄ presumably contains only a small amount of twinning. Its probability of twinning is not negligible because the reflections are broadened. On the other hand, the new hydride phase contains a significant amount of microtwinning. The existence of Mg₂NiH could also be ascertained from the alteration of the intensity of the doublet in the range 38–41°. Moreover, the diffraction pattern of Mg₂NiH is shifted to the lower angle compared to Mg₂NiH₄. The appearance of a diffuse peak in the doublet in the case of LT-form of Mg₂NiH₄ is usually attributed to the simultaneous presence of a contamination phase either in cubic or orthorhombic form [30–34], and more recently it was analysed in terms of microtwinning [35–37]. The MgNiH phase also shows an identical behaviour to that of Mg₂NiH₄ indicating a triplet in the region 22–25°, containing either stacking faults or the contamination phase.

The difficulties are aggravated by the fact that the diffraction patterns at room temperature are not independent of the manner of the preparation of the samples. As the present investigation implies the possibility of an intermediate or hydrogen-deficient phase in the Mg₂Ni–H₂ system, it is probable that one such hydrogen containing phase, Mg₂NiH_x (1 ≤ x ≤ 4) may be the coexisting phase along with the main phase,

Mg_2NiH_4 and/or microtwinning may be the cause or these phases might facilitate the microtwinning. Analysis of the published data shows that small amount of a second hydride phase normally observed along with the LT-modification of Mg_2NiH_4 may arise because of the experimental conditions such as pressure, temperature and the thermal cycling of hydriding–dehydriding processes employed for the preparation of the hydrides. Hence, one cannot exclude the possibility of the existence of a hydrogen-deficient phase as one of the additional phases. However, definite conclusions should await the outcome of further study of the phase diagram of the Mg_2Ni-H_2 system.

CONCLUSION

The main points that emerge from this study include:

- There exists an additional hydride phase, Mg_2NiH , besides the main hydride phase, Mg_2NiH_4 , in the Mg_2Ni-H_2 system.
- The existence of a new hydride phase, Mg_2NiH , indicates that the Mg_2Ni-H_2 system is not an exception to the general observation of multi-hydride phases that has been exhibited by many alloy- H_2 systems.
- Mg_2Ni-H_2 system has three hydride phases including the H_2 solid solution phase with approximate compositions, $Mg_2NiH_{0.3}$, Mg_2NiH and Mg_2NiH_4 designated as α -, β - and γ -hydrides respectively.
- The β - and γ -hydride phases are shown to be isostructural with small changes in the unit cell dimensions.
- Both the hydride phases exhibit a structural transformation from the LT-form to HT-form at about 500–515 K, the LT-phases having a monoclinic structure and the corresponding HT-phases having a cubic structure.
- The phase transition could arise from a small composition difference between the monoclinic and cubic structures. This transition is presumably due to an order–disorder transition involving the H_2 sublattice.
- The possibility of the existence of hydrogen-deficient phase and/or microtwinning have been suggested as a contamination phase along with the LT-modification of Mg_2NiH and/or Mg_2NiH_4 indicating the LT-modifications of the hydrides are slightly inhomogeneous.
- It is possible to state that in general, intermetallic compounds will exhibit two or more hydride phases, excluding the α -phase upon hydriding.

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REFERENCES

1. P. Selvam, B. Viswanathan, C. S. Swamy and V. Srinivasan, *Int. J. Hydrogen Energy* **11**, 169 (1986).
2. J. J. Reilly and R. H. Wiswall, *Inorg. Chem.* **7**, 2254 (1968).
3. J. Schefer, P. Fischer, W. Halg, F. Stucki, L. Schlapbach, J. J. Didisheim, K. Yvon and A. F. Andresen, *J. Less-Common Metals* **74**, 65 (1980).
4. S. Hayashi, K. Hayamizu and O. Yamamoto, *J. Chem. Phys.* **79**, 5572 (1983).
5. S. Ono, K. Nomura, E. Akiba and H. Uruno, *J. Less-Common Metals* **113**, 113 (1985).
6. H. H. van Mal, *Philips Res. Repts. suppl.* **1**, 57 (1976).
7. C. A. Bechman, A. Goudy, T. Takeshita, W. E. Wallace and R. S. Craig, *Inorg. Chem.* **15**, 2184 (1976).
8. R. M. van Essen and K. H. J. Buschow, *Mater. Res. Bull.* **15**, 1149 (1980).
9. J. R. Johnson and J. J. Reilly, *Inorg. Chem.* **17**, 3103 (1978).
10. A. Yoshikawa and T. Matsumoto, *J. Less-Common Metals* **84**, 263 (1982).
11. G. D. Sandroock, J. J. Murray, M. L. Post and J. B. Taylor, *Mater. Res. Bull.* **17**, 887 (1982).
12. H. A. Kierstead, *J. Less-Common Metals* **70**, 199 (1980).
13. F. Reidinger, J. F. Lynch and J. J. Reilly, *J. Phys. F.* **12**, L49 (1982).
14. F. A. Kuijpers, *J. Less-Common Metals* **27**, 27 (1972).
15. J. F. Lakner, F. S. Uribe and S. A. Steward, *J. Less-Common Metals* **72**, 87 (1980).
16. P. Selvam, Ph.D. Thesis, Indian Institute of Technology, Madras (1987).
17. P. Selvam, B. Viswanathan, C. S. Swamy and V. Srinivasan, *Thermochim. Acta* **125**, 1 (1988).
18. P. Selvam, B. Viswanathan, C. S. Swamy and V. Srinivasan, *Int. J. Hydrogen Energy* **13**, 87 (1988).
19. P. Selvam, B. Viswanathan, C. S. Swamy and V. Srinivasan, *Bull. Mater. Sci.* **9**, 21 (1987).
20. D. Noreus and L. G. Olsson, *J. Chem. Phys.* **78**, 2419 (1983).
21. D. Noreus and P. E. Werner, *Mater. Res. Bull.* **16**, 199 (1981).
22. D. Lupu, A. Biris and E. Indrea, *Int. J. Hydrogen Energy* **7**, 783 (1982).
23. D. Lupu, A. Biris, E. Indrea, N. Aldea and R. V. Bucur, *Int. J. Hydrogen Energy* **8**, 797 (1982).
24. P. Zolliker, K. Yvon, J. D. Jorgensen and F. J. Rotella, *Inorg. Chem.* **25**, 3590 (1986).
25. T. Hirata, *Int. J. Hydrogen Energy* **9**, 855 (1984).
26. J. N. N. van Vucht, F. A. Kuijpers and H. C. A. M. Burning, *Philips Res. Repts.* **25**, 133 (1970).
27. A. F. Andresen, *J. Less-Common Metals* **88**, 1 (1982); and references cited therein.
28. D. G. Westlake, *J. Less-Common Metals* **91**, 275 (1983); and references cited therein.
29. H. H. van Mal, K. H. J. Buschow and A. R. Miedema, *J. Less-Common Metals* **35**, 65 (1974).
30. J. P. Darnaudery, M. Pezat, B. Darriet and P. Hagenmuller, *Mater. Res. Bull.* **16**, 1237 (1981).

31. T. Hirata, T. Matsumoto, M. Amano and Y. Sasaki, *J. Phys. F.* **11**, 521 (1981).
32. S. Ono, H. Hayakawa, A. Suzuki, K. Nomura, N. Nishimiya and T. Tabata, *J. Less-Common Metals* **88**, 63 (1982).
33. H. Hayakawa, Y. Ishido, K. Nomura, H. Uruno and S. Ono, *J. Less-Common Metals* **103**, 277 (1984).
34. Z. Gavra, G. Kimmel, Y. Gefen and M. H. Mintz, *J. Appl. Phys.* **57**, 4548 (1985).
35. D. Noreus, K. Jansson and M. Nygren, *Z. Phys. Chem., N.F.* **146**, 191 (1985).
36. P. Zolliker, K. Yvon and Ch. Baerlocher, *J. Less-Common Metals* **115**, 65 (1986).
37. D. Noreus and L. Kihlborg, *J. Less-Common Metals* **123**, 233 (1986).
38. K. C. Hoffman, J. J. Reilly, F. J. Salzano, C. H. Waide, R. H. Wiswall and W. E. Winche, *Int. J. Hydrogen Energy* **3**, 133 (1976).
39. D. Noreus and P. E. Werner, *J. Less-Common Metals* **97**, 215 (1984).
40. J. M. Cowley and A. Y. Au, *Acta Crystall.* **A34**, 738 (1978).