

X-ray crystallographic and thermal studies on the hydrides of magnesium and its intermetallics

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

MS received 11 August 1986; revised 12 December 1986

Abstract. Magnesium nickel hydride, Mg_2NiH_4 , exists in two crystallographic modifications, the low temperature phase crystallizing in monoclinic structure and the high temperature phase having a cubic structure. The phase transition (~ 510 K) was accompanied by a small composition change. The enthalpies and entropies of formation of these hydrides were calculated from the DTA data and compared with the values obtained by other methods.

Keywords. Magnesium nickel hydride; phase transition; enthalpy; entropy of formation.

1. Introduction

Among the magnesium alloys, Mg_2Ni forms a ternary hydride, Mg_2NiH_4 , with favourable hydrogen content (3.6 wt. %), moderate stability and rapid kinetics (Reilly and Wiswall 1968). Its presence (Mg_2Ni) also improves the hydriding kinetics of the binary hydride, MgH_2 (Reilly and Wiswall 1968; Seiler *et al* 1980). The earliest crystallographic and thermal studies of Mg_2NiH_4 by Gavra *et al* (1979) showed a reversible allotropic phase transition around 485–520 K. There are various reports of crystallographic studies and thermal analyses on this system with a view to elucidate the crystal symmetry of the hydride as well as to identify the phase transformation (Reilly and Wiswall 1968; Gavra *et al* 1979; Mintz *et al* 1980; Schefer *et al* 1980; Hirata *et al* 1981; Darnaudery *et al* 1981; Andresen *et al* 1981; Schefer *et al* 1981; Noreus and Werner 1981, 1984; Genossar and Rudman 1981; Yvon *et al* 1981; Ono *et al* 1982a,b; Darnaudery *et al* 1983a; Noreus and Olsson 1983; Hayakawa *et al* 1984; Soubeyroux *et al* 1984a,b; Carter and Carter 1984; Gavra *et al* 1985; Zolliker *et al* 1986).

There has been a great interest in the thermodynamic properties of metal hydrides because of their importance in various technical purposes as well as in the physical understanding of metal-hydrogen reactions. Numerous experimental (Mueller *et al* 1968; Andresen and Maeland 1978; Alefeld and Volkl 1978; Bambakidis 1981; Wenzl and Labsanft 1983) and theoretical (Switendick 1972; Van Mal *et al* 1974; Lundin *et al* 1977; Gelatt *et al* 1978; Bouten and Miedema 1980) investigations on the thermodynamic aspects of the interaction of hydrogen with metals, alloys and intermetallic compounds have been reported. Experimentally the thermodynamic quantities can be obtained from pressure-composition isotherms (p-c-T) (Buchner 1978; Fischer *et al* 1978; Sandrock and Huston 1981) or from related equivalent approach of electrode potential-composition-temperature relationships or from heat capacity measurements (Flanagan and Oates 1972) or from calorimetric methods (Reilly and Wiswall 1974; Labsanft 1979; Bowerman *et al* 1979, 1980; Murray *et al* 1981, 1983; Pasturel *et al* 1982; Wenzl and Labsanft 1983). Recently Shilov *et al* (1983) suggested

an alternative method based on approximate enthalpy balance equation in conjunction with differential thermal analysis (DTA).

The present investigation was undertaken to obtain information on the conflicting reports on x-ray crystallographic data for the structural modifications of Mg_2NiH_4 and the thermodynamic characteristics of the magnesium and its alloy hydrides using the DTA technique.

2. Starting materials

The sources of the samples used in the present study are BDH-GLAXO Laboratories Ltd., (India) (36 mesh, 99.5% purity) or/and SISCO Research Laboratories Pvt. Ltd. (India) (36 mesh, 99.8% purity) for magnesium, (Koch-Light Laboratories Ltd., U.K.; for nickel (100 mesh, 99.8% purity)) and SISCO Research Laboratories Pvt. Ltd. (India) for Copper (200 mesh, 99.5% purity). Commercial samples of Mg_2Ni and Mg_2Cu alloys used in the present study were supplied by the Ergenics Division of the MPD Technology Corporation, New Jersey (USA) with the designation Hystor-301 and 302 respectively. High purity argon (Iolar-1 grade) and hydrogen (Iolar-1 grade) supplied by M/s Indian Oxygen Limited with a maximum oxygen content of 2 ppm were used for the preparation and hydriding purposes respectively.

3. Experimental procedures

3.1 Preparation of alloys and hydrides

The alloys Mg_2Ni and Mg_2Cu were prepared by heating pure metals in the stoichiometric ratio at 1125 K and annealing it in argon for 48 hr at 825 K. The hydrides were synthesized in an autoclave with a maximum operating temperature of 673 K and a pressure of 150 atm.

3.2 X-ray diffraction and thermal analysis

X-ray powder diffraction measurements were carried out with or without a heating stage facility on a diffractometer (Philips model PW-1140) using CuK_α radiation. Simultaneous differential thermal and thermogravimetric analyses (DTA-TGA) were performed under 1 atm hydrogen/argon pressure using a thermogravimetric and differential thermal analysis combined unit (Stanton Redcroft thermal analyzer, model STA-780) upto 725 K with a heating rate of 10 K per min.

4. Results and discussion

4.1 X-ray diffraction analysis

The hydride, Mg_2NiH_4 was found to have a different crystallographic form at higher temperatures (510 K). This suggests a structural phase transition (Stucki 1983). The x-ray diffraction data of the LT-phase (room temperature) of Mg_2NiH_4 could be

indexed on the basis of a monoclinic unit cell while the HT-phase (above 510 K) could be indexed on the basis of a cubic symmetry. Therefore, the Mg_2NiH_4 sample was found to undergo a structural phase transition from a LT-monoclinic to a HT-cubic phase around 510 K. The values of the least square refined cell parameters for the LT- and HT-phases obtained in the present study are given in table 1. The x-ray diffraction data obtained in the present study favour a monoclinic structure for the LT-phase and a cubic structure for the HT-phase.

Thus, the preparation conditions employed in the present study favour mainly a monoclinic structure which has a distorted cubic symmetry. The x-ray densities of the LT- and HT-forms of the samples 2.71 and 2.67 gm/cm^3 respectively are in reasonable agreement with the experimental values reported (Reilly and Wiswall 1968; Mintz *et al* 1980; Ishido *et al* 1982; Post *et al* 1984) and agree well with the calculated values (Genossar and Rudman 1981; Ono *et al* 1984).

4.2 Differential thermal and thermogravimetric analyses

DTA thermograms were obtained for the hydrides of Mg, Mg_2Ni and Mg_2Cu samples by heating them in the temperature range from room temperature to 725 K under hydrogen/argon atmospheres. The decomposition of the hydrides is seen by the endothermic peaks (see table 2 for the decomposition temperatures). It is seen that the hydrides decompose at lower temperatures for the intermetallic hydrides compared to the binary system MgH_2 .

The decomposition temperatures in argon atmosphere are lower than those observed in the hydrogen atmosphere (refer to data given in table 2) and these values agree with the reported decomposition temperatures from pressure-composition isotherms. Hirata *et al* (1984) observed that the decomposition temperature of the hydride of Mg_2Ni can be as high as 598 K in 0.1 MPa of hydrogen pressure. Gavra *et al* (1979) reported that the decomposition temperature of Mg_2NiH_4 under 700 torr of hydrogen pressure is around 553–573 K. The results of the present study agree with these reports.

The thermal analysis of Mg_2NiH_4 carried out in 1 atm hydrogen pressure showed two endothermic peaks revealing a reversible phase transition and decomposition around 510 K and 555 K respectively (figure 1). The small endothermic peak around

Table 1. X-ray data for the LT- and HT-forms of Mg_2NiH_4 samples.

Source (Mg_2NiH_4 sample)	Structure and cell parameters	
	LT form (monoclinic)	HT form (cubic)
Synthesized	$a = 6.581 \text{ \AA}^c$ $b = 6.400 \text{ \AA}^d$ $c = 6.499 \text{ \AA}^e$ $\beta = 93.10^\circ$	$a = 6.519 \text{ \AA}^e$
Hystor-301	$a = 6.585 \text{ \AA}^f$ $b = 6.406 \text{ \AA}^c$ $c = 6.493 \text{ \AA}^g$ $\beta = 93.10^\circ$	$a = 6.521 \text{ \AA}^e$

Table 2. Hydrogen desorption temperatures at 1 atm (T_{des} , K) and thermodynamic properties (enthalpy, ΔH , kJ mol⁻¹ H₂ and entropy, ΔS , JK⁻¹ mol⁻¹ H₂) for the hydrides of Mg, Mg₂Ni and Mg₂Cu from DTA data. Calorimetric and p-c-T results are given for comparison.

System	Hydride	Differential thermal analysis										Calorimetry
		Under argon atm.		Under hydrogen atm.		Pressure-composition-isotherms				Calorimetry		
		T_{des}	$-\Delta H$	$-\Delta S$	T_{des}	$-\Delta H$	$-\Delta S$	T_{des}	$-\Delta H$		$-\Delta S$	
Mg-H ₂	MgH ₂ (BDH) MgH ₂ (SISCO)	563 560	67.0 66.5	119.0 118.8	593 590	71.2 70.7	120.1 119.8	551-562 (Stampfer <i>et al</i> 1960; Tanguy <i>et al</i> 1976; Pedersen <i>et al</i> 1983; Post <i>et al</i> 1984; Ono <i>et al</i> 1984)	70.0-77.0	126.0-135.0	75.0	(Post <i>et al</i> 1984)
Mg ₂ Ni-H ₂	Mg ₂ NiH ₄ (Synthesized) Mg ₂ NiH ₄ (Hystor-301)	523 528	61.4 62.1	117.4 117.6	555 553	65.8 65.6	118.5 118.6	523-533 (Reilly and Wiswall 1968; Lutz and De Pous 1977; Akiba <i>et al</i> 1982; Buchner <i>et al</i> 1978; Ono <i>et al</i> 1984; Darmaudery <i>et al</i> 1983b; Post <i>et al</i> 1984)	60.7-67.0	117.2-116.0	63.1	(Post <i>et al</i> 1984)
Mg ₂ Cu-H ₂ *	Mg H ₂ (Synthesized) Mg H ₂ (Hystor-302)	518 513	71.9 71.3	134.7 134.9	541 538	75.1 74.7	138.8 138.9	512 (Reilly and Wiswall 1967; Darmaudery <i>et al</i> 1983b)	72.8	142.1	—	—

* In this case no ternary hydride is formed but a binary hydride is formed according to the reaction (Reilly and Wiswall 1967). Enthalpy correction for the formation of Mg₂Cu alloy was made in view of the decomposition of the hydride and subsequent reaction of Mg with MgCu₂.

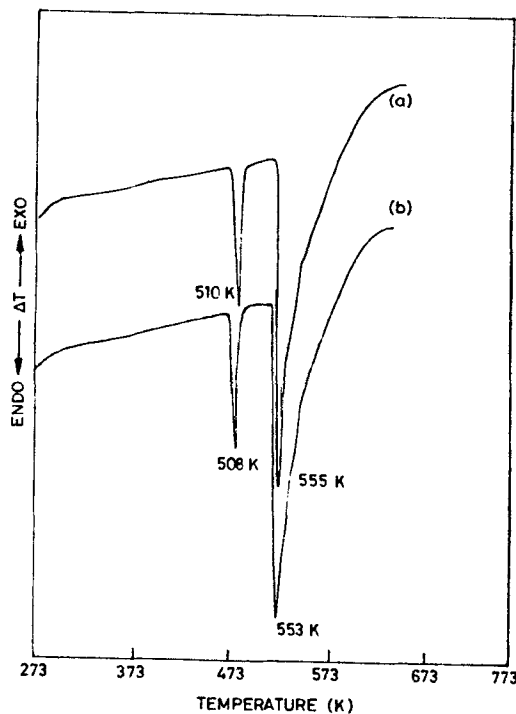


Figure 1. DTA curves for the dehydrating behaviour of Mg_2NiH_4 under hydrogen atmosphere: (a) Synthesized. (b) Hystor-301.

510 K could be attributed to the structural transition from LT-hydride form to HT-form (Gavra *et al* 1979; Hirata 1984; Noreus and Werner 1984) and is associated with a small change in the composition as observed from TGA studies. This allotropic transition appeared reversibly during repeated heating-cooling cycles. The heat change involved in the transition was calculated as $3.3 \text{ KJ mol}^{-1} \text{ H}_2$ by Gavra *et al* (1979) employing a differential scanning calorimetry (DSC) technique. However, only one broad endotherm is observed during the decomposition of Mg_2NiH_4 in argon atmosphere. The endotherm starts at the phase transition temperature. Therefore, it is assumed that the broad endotherm is due to both the phase transition and decomposition of the hydrides. The endotherm is not separated even at a lower heating rate of 5 K per min.

TGA studies suggest that the desorbed hydrogen in Mg, Mg_2Ni and Mg_2Cu hydrides corresponds to the stoichiometry of the hydride formed. In addition, a small weight loss is observed in the case of Mg_2NiH_4 in the phase transition region suggesting a different composition of the polymorphic varieties, i.e. the LT-monoclinic phase being the stoichiometric phase (Mg_2NiH_4) and the HT-cubic phase being the sub-stoichiometric phase ($\text{Mg}_2\text{NiH}_{4-x}$).

Based on the method of Shilov *et al* (1983), the enthalpies and entropies of formation of the magnesium and its intermetallic hydrides were calculated from the DTA data. The calculated thermodynamic quantities along with the desorption temperatures are given in table 2. The results are comparable with the data deduced from p-c-T relationships and calorimetric measurements. However, the values cal-

culated from DSC measurements by Gavra *et al* (1979), Ono *et al* (1982b) and Hirata (1984) are 47.3, 59.0 and 58.9 KJ mol⁻¹ H₂ respectively. They are somewhat lower than the values calculated from the DTA studies or from the conventional p-c-T relationships and calorimetric measurements.

Acknowledgement

Thanks are due to the Department of Non-Conventional Energy Sources (DNES), Ministry of Energy, Government of India, New Delhi for the award of a research grant.

References

- Akiba E, Nomura K, Ono S and Suda S 1982 *Int. J. Hydrogen Energy* **7** 787
- Alefeld G and Volkl J 1978 *Hydrogen in metals II—Topics in applied physics* (Berlin: Springer-Verlag) vol. 29
- Andresen A F, Andersen E and Pattersen K 1981 *Acta Crystallogr. Suppl. C* **A37** 152
- Andresen A F and Maeland A J 1978 *Hydrides for energy storage—Proc. Int. Symp.* (Oxford: Pergamon Press)
- Bambakidis G 1981 *Metal hydrides—NATO advanced study Institutes Series B: Physics* (New York: Plenum Press) vol. 76
- Bouten P C P and Miedema A R 1980 *J. Less-Common Metals* **71** 147
- Bowerman B S, Wulff C A, Biehl G E and Flanagan T B 1980 *J. Less-Common Metals* **73** 1
- Bowerman B S, Wulff C A and Flanagan T B 1979 *Z. Phys. Chem. N.F.* **116** 197
- Buchner H 1978 *Int. J. Hydrogen Energy* **3** 385
- Buchner H, Bernauer O and Streub W 1978 in *Proc. Second World Hydrogen Energy Conf. on Hydrogen Energy Systems* (eds) T N Veziroglu and W Seifritz (New York: Pergamon Press) vol. 3, p. 1677
- Carter G C and Carter F L 1984 in *Metal hydrogen systems* (ed) T N Veziroglu (New York: Pergamon Press)
- Darnaudery J P, Pezat M, Darriet B and Hagenmuller P 1981 *Mater. Res. Bull.* **16** 1237
- Darnaudery J P, Pezat M and Darriet B 1983a *J. Less-Common Metals* **92** 199
- Darnaudery J P, Darriet B and Pezat M 1983b *Int. J. Hydrogen Energy* **8** 705
- Fischer P, Halg W, Schlapbach L, Stucki F and Andresen A F 1978 *Mater. Res. Bull.* **13** 931
- Flanagan T B and Oates W A 1972 *Ber. Bunsenges. Phys. Chem.* **76** 706
- Gavra Z, Kimmel G, Gefen Y and Mintz M H 1985 *J. Appl. Phys.* **57** 4548
- Gavra Z, Mintz M H, Kimmel G and Hadari Z 1979 *Inorg. Chem.* **18** 3595
- Gelatt C D, Ehrenreich M and Weise J A 1978 *Phys. Rev.* **B17** 1970
- Genossar J and Rudman P S 1981 *J. Phys. Chem. Solids* **42** 199
- Hayakawa H, Ishido Y, Nomura K, Uruno H and Ono S 1984 *J. Less-Common Metals* **103** 277
- Hirata T 1984 *Int. J. Hydrogen Energy* **9** 255
- Hirata T, Matsumoto T, Amano M and Sasaki Y 1981 *J. Phys.* **F11** 521
- Ishido Y, Kawamura M and Ono S 1982 *Int. J. Hydrogen Energy* **7** 173
- Lebsanft E 1979 *J. Phys.* **E12** 699
- Lundin C E, Lynch F E and Magee C B 1977 *J. Less-Common Metals* **56** 19
- Lutz H M and De Pous 1977 in *Proc. Second Int. Cong. on Hydrogen in Metals* (Paris: Pergamon Press) vol. 1, p. 1F5
- Mintz M H, Gavra Z, Kimmel G and Hadari Z 1980 *J. Less-Common Metals* **74** 263
- Mueller W M, Blackledge J P and Libowitz G G 1968 *Metal hydrides* (New York: Academic Press)
- Murray J J, Post M L and Taylor J B 1981 *J. Less-Common Metals* **80** 201
- Murray J J, Post M L and Taylor J B 1983 *J. Less-Common Metals* **90** 65
- Noreus D and Olsson L G 1983 *J. Chem. Phys.* **78** 2419
- Noreus D and Werner P E 1981 *Mater. Res. Bull.* **16** 199
- Noreus D and Werner P E 1984 *J. Less-Common Metals* **97** 215
- Ono S, Hayakawa M, Suzuki A, Nomura K, Nishimiya N and Tabata T 1982b *J. Less-Common Metals* **88**

- Ono S, Ishido Y, Imanari T, Tabata T, Cho Y K, Yamamoto R and Doyama M 1982a *J. Less-Common Metals* **88** 57
- Ono S, Ishido Y, Akiba E, Jindo K, Saweda Y, Kitagawa I and Kakutani T 1984 in *Hydrogen energy progress V—Proc. 5th world Hydrogen energy conf.* (ed) T N Veziroglu (Toronto: Pergamon Press) p. 1291
- Pasturel A, Colinet C C, Guegan A P and Achard J L 1982 *J. Less-Common Metals* **84** 73
- Pedersen A S, Kjoller B, Larsen B and Vigeholm B 1983 *Int. J. Hydrogen Energy* **8** 205
- Post M L, Murray J J and Taylor J B 1984 *Int. J. Hydrogen Energy* **9** 137
- Reilly J J and Wiswall R H 1967 *Inorg. Chem.* **6** 2220
- Reilly J J and Wiswall R H 1968 *Inorg. Chem.* **7** 2254
- Reilly J J and Wiswall R H 1974 *Inorg. Chem.* **13** 218
- Sandrock G D and Huston E L 1981 *Chem. Tech.* **11** 754
- Schefer J, Fischer P, Halg W, Stucki F, Schlapbach L, Didisheim J J, Yvon K and Andresen A F 1980 *J. Less-Common Metals* **74** 65
- Schefer J, Fischer P, Stucki F, Schlapbach L, Baerelocher Ch, Yvon K, Didisheim J J, Jorgensen J D and Andresen A F 1981 in *Prog. Rep. AF-SSP-118* (Zurich: Institut fur Reaktortechnik Eidgenossische Technische Hochschule) p. 52
- Seiler A, Schlapbach L, von Waldkirch Th, Shaltiel D and Stucki F 1980 *J. Less-Common Metals* **73** 193
- Shilov A L, Padurets L N and Kost M E 1983 *Russ. J. Inorg. Chem.* **57** 338
- Soubeyroux J L, Fruchart D, Mikou A, Pezat M, Darriet B and Hagenmuller P 1984a *Mater. Res. Bull.* **19** 969
- Soubeyroux J L, Fruchart D, Mikou A, Pezat M and Darriet B 1984b *Mater. Res. Bull.* **19** 1119
- Stampfer J F, Holley C E and Suttle J F 1960 *J. Am. Chem. Soc.* **82** 3504
- Stucki F 1983 *Int. J. Hydrogen Energy* **8** 49
- Switendick A C 1972 *Solid State Commun.* **8** 1463
- Tanguy B, Soubeyroux J L, Pezat M, Portier J and Hagenmuller P 1976 *Mater. Res. Bull.* **11** 1441
- Van Mal H H, Buschow K H J and Miedema A R 1974 *J. Less-Common Metals* **35** 65
- Wenzl H and Lebsanft E 1983 *J. Phys.* **F10** 2147
- Yvon K, Schefer J and Stucki F 1981 *Inorg. Chem.* **20** 2776
- Zolliker P, Yvon K and Beerlocher Ch 1986 *J. Less-Common Metals* **115** 65