THERMAL STUDIES ON Mg_2NiH_4: EXISTENCE OF ADDITIONAL HYDRIDE PHASE IN THE Mg_2Ni–HYDROGEN SYSTEM

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ABSTRACT

(TG–DTA) thermal analyses of the Mg_2NiH_4 system revealed the presence of another hydride phase with composition Mg_2NiH. The kinetic parameters for the phase transition as well as for the decomposition of the two hydride phases have been evaluated from DTA data using temperature programmed 'Arrhenius plots'. The thermodynamic quantities, namely the enthalphy and entropy changes for the two phases, have been evaluated and compared with the data reported in the literature.

INTRODUCTION

Magnesium and its alloy hydrides are found to be promising energy (hydrogen) storage materials for both stationary and mobile applications [1]. Among the magnesium alloys, the intermetallic compound Mg_2Ni forms a ternary hydride Mg_2NiH_4 with favourable hydrogen content, moderate stability and rapid kinetics [2]. Mg_2NiH_4 has been shown to exist in two crystallographic forms [3]. The low temperature (LT) phase crystallizes in a monoclinic structure and the high temperature (HT) phase in a cubic structure. This transition around 510 K is due to a small composition change between the LT- and HT-forms as revealed by X-ray diffraction (XRD), differential thermal analysis (DTA) and thermogravimetry (TG) studies reported earlier [4]. During these thermal analysis studies, a two-stage decomposition step is observed for the Mg_2NiH_4 sample. Simultaneous TG–DTA studies have been carried out on these samples under different experimental conditions. The results indicate that the decomposition of Mg_2NiH_4 follows a multi-step process, suggesting the existence of a new phase in the Mg_2Ni–hydrogen system.

EXPERIMENTAL

The sample preparation and the experimental technique employed have been described in detail elsewhere [4]. The samples used in the present

investigation are either fresh Mg_2NiH_4 or partially and/or completely decomposed Mg_2NiH_4 phase. These samples were subjected to simultaneous TG–DTA studies under a hydrogen pressure of 1 atm. from room temperature to 625 K with different heating rates ranging from 2.5 to 20 K min^{-1}.

RESULTS AND DISCUSSION

Figure 1 shows DTA curves for the decomposition reaction of Mg_2NiH_4 during the heating of samples of different batches at various heating rates between 2.5 and 20 K min^{-1} under a hydrogen pressure of 1 atm. Curve (a) in Fig. 1 is correctly positioned on the temperature scale while the others are
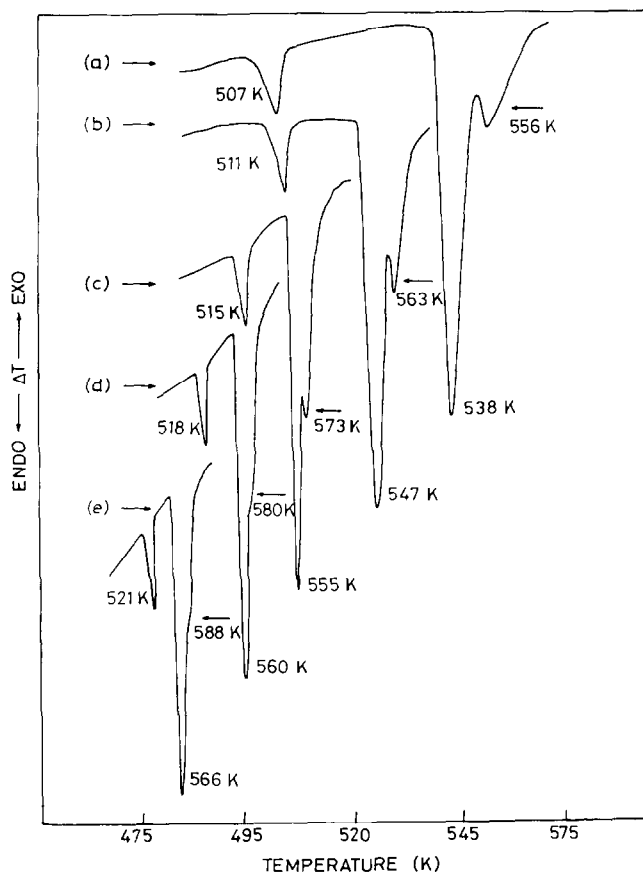

Fig. 1. DTA patterns of Mg_2NiH_4 as a function of heating rates under 1 atm. hydrogen pressure: (a) 2.5; (b) 5; (c) 10; (d) 15; (e) 20 K min^{-1}. Curve (a) is correctly positioned on the temperature scale while the others are shifted to avoid peak overlap.

shifted to avoid peak overlap. The exact peak maximum temperature values (for both phase transition and decomposition) and the corresponding heating rates are indicated in Fig. 1 itself.

At higher heating rates (15 and 20 K min^{-1}) two endothermic peaks are noticed corresponding to a reversible phase transition at lower temperatures around 510 K and due to decomposition at higher temperatures around 550 K. However, on the high temperature side of the endothermic peak at 550 K, a shoulder or small peak (a diffuse peak at higher heating rates, say 15 and 20 K min^{-1}, and a clear peak at lower heating rates such as 2.5, 5 and 10 K min^{-1}) is seen. The appearance of the additional peak on the high temperature side may be due to the decomposition of another phase and is well separated at lower heating rates, namely 2.5 K min^{-1} as shown in Fig. 1.

The above observation is supported by the TG results which show a step-wise weight change corresponding to the peak maximum temperature in the DTA pattern. Figure 2 gives the differential thermogravimetric (DTG) plots of Mg_2NiH_4 samples under various experimental conditions. The weight loss regions shown in Fig. 2(c) correspond to the endothermic processes taking place during the decomposition of Mg_2NiH_4 (see Fig. 1). The small peak observed in the phase transition region (around 510 K)
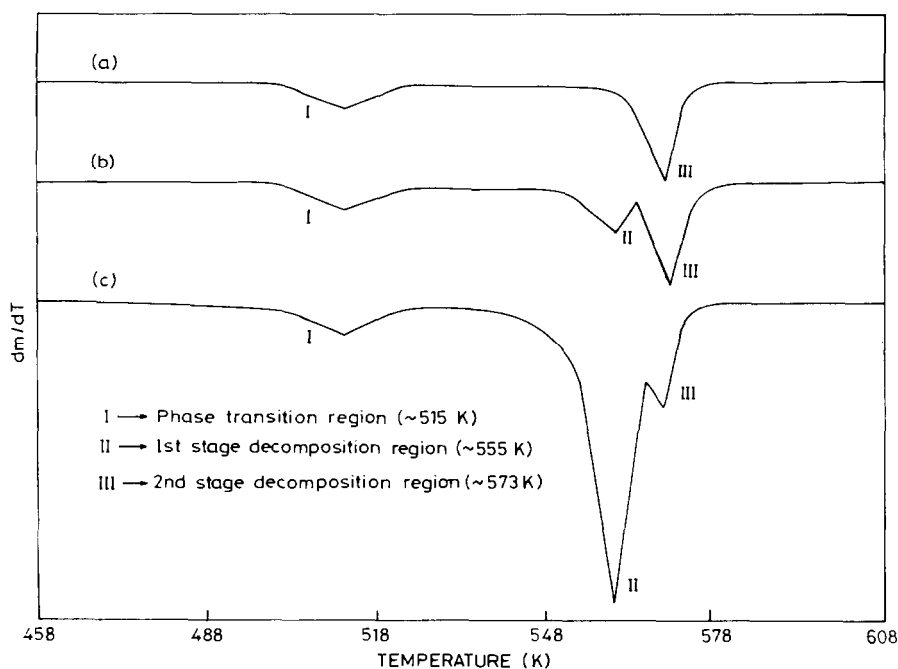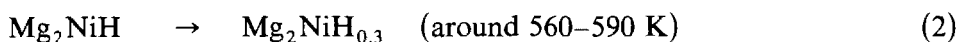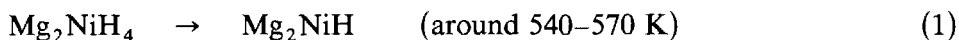

Fig. 2. DTG plots of Mg_2Ni hydride at a constant heating rate of 10 K min^{-1} under 1 atm hydrogen pressure: (a) Mg_2NiH phase; (b) mixture of Mg_2NiH_4 and Mg_2NiH phases; and (c) fresh Mg_2NiH_4.

suggests a different composition for the polymorphic varieties of Mg_2NiH_4. That is, the LT-monoclinic phase changes to HT-cubic phase with a small loss in hydrogen content as reported earlier [4]. The weight loss in this region is approximately 5%. The subsequent weight changes at higher temperatures can be attributed to the decomposition reactions. Thus, the weight loss corresponding to the step-wise decomposition is found to be 65–70% and 20–25% around 555 K and 570 K respectively for the first and second stages of decomposition.

Hence, it is concluded from the DTA patterns and TG measurements observed in the present study that a two-step decomposition process is actually taking place according to the following scheme:

$$Mg_2NiH_4 \quad \rightarrow \quad Mg_2NiH \quad \text{(around 540–570 K)} \tag{1}$$

$$Mg_2NiH \quad \rightarrow \quad Mg_2NiH_{0.3} \quad \text{(around 560–590 K)} \tag{2}$$

Thus suggesting an additional phase Mg_2NiH in the Mg_2Ni-H_2 system.

In order to substantiate this, partial and/or complete decomposition of the Mg_2NiH_4 phase was carried out to produce the Mg_2NiH phase [reaction (1)] under conditions identical with those employed for the thermal studies. The reddish-brown colour of Mg_2NiH_4 changes to brownish-black on decomposition at 550 K corresponding to the Mg_2NiH phase. On further heating at 570 K the sample changes to the α-phase (black), namely $Mg_2NiH_{0.3}$. The partially and fully decomposed samples were subjected to TG–DTA analyses and compared with the fresh Mg_2NiH_4 sample. The DTA patterns obtained for these samples are given in Fig. 3.

It is clear from Fig. 3 that the completely decomposed (Mg_2NiH_4 phase alone) sample shows only one endotherm (curve a) at higher temperatures (570 K) corresponding to the decomposition of Mg_2NiH phase as shown for the fresh Mg_2NiH_4 sample in curve (c). However, partially decomposed Mg_2NiH_4 which is a mixture of Mg_2NiH_4 and Mg_2NiH phases shows a small endotherm on the low temperature side (555 K) which corresponds to the decomposition of the Mg_2NiH_4 phase in addition to the endotherm on the high temperature side (575 K) due to the Mg_2NiH phase (curve b). Similar results are also observed from TG studies (Fig. 2).

Lupu and coworkers [5,6] reported a multi-pressure plateau region for the desorption isotherms for the hydrides of Be- and Fe-substituted Mg_2Ni alloys. The thermodynamic parameters reported for these phases are given in Table 1 together with the values for the unsubstituted alloy (Mg_2Ni) calculated from DTA data by the method of Shilov et al. [7]. It is reported [5,6] that the plateau regions in the substituted alloys are well separated. This suggests the existence of different phases and has been explained on the basis of hydrogen atom site location in the metal lattice. That is, hydrogen occupies different types of interstices which are constituted by different metal atoms. Hence, the stabilities of the phases are different, accounting for different decomposition temperatures.
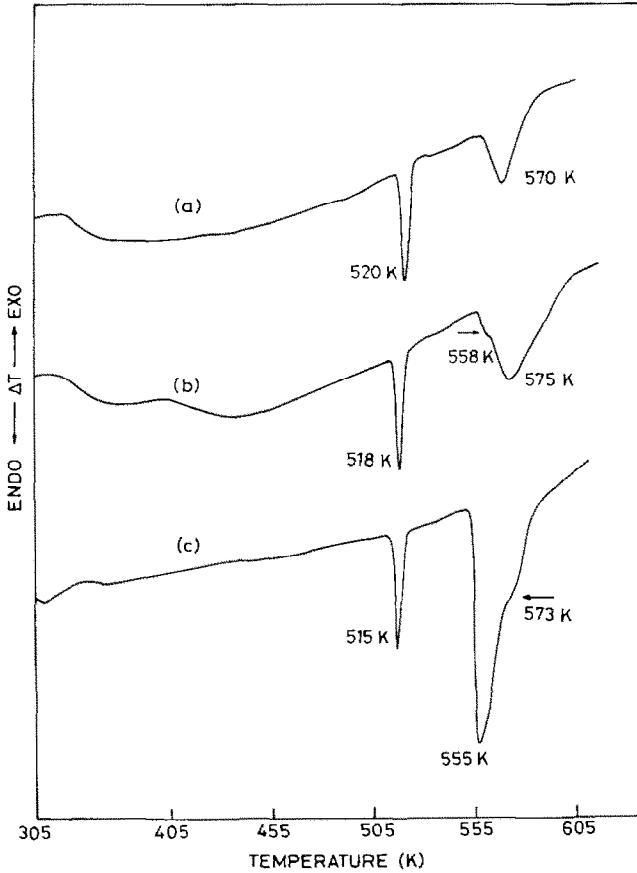
Fig. 3. DTA patterns of Mg_2Ni-hydride under similar conditions for the samples shown in Fig. 2.

In a similar way, one can expect that Mg_2NiH_4 may also exhibit a multi-plateau region as indicated from the results of the thermal studies. However, two-plateau regions have not been seen in the desorption isotherms reported earlier [2]. This could be due to the fact that the plateau regions overlap and show only a single plateau region under the higher temperature and pressure conditions normally employed for this system. The existence of multi-phases in the Mg_2NiH_4 system could be explained on the basis that the Mg_2Ni alloy also possesses different types of interstices, similar to those of Be- and Fe-substituted alloys, thereby allowing the hydrogen atoms to occupy different sites.

The occupation of various sites by hydrogen atoms has been reported by Zolliker et al. [8] from their structural studies on Mg_2NiD_4. Accordingly, 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 nearest Mg

TABLE 1

Thermodynamic parameters for the hydrides of Mg_2Ni (from DTA results) and substituted Mg_2Ni alloys (from $p-c-T$ relationships)

Alloys [a]	ΔH $[kJ\ (mol\ H_2)^{-1}]$	ΔS $[J\ K^{-1}\ (mol\ H_2)^{-1}]$
Mg_2Ni		
Phase I	−65.8	−118.6
Phase II	−68.4	−119.4
$Mg_2Ni_{0.85}Be_{0.15}$ [b]		
Phase I	−70.7	−131.0
Phase II	−91.3	−159.1
$Mg_2Ni_{0.75}Fe_{0.25}$ [c]		
Phase I	−82.9	−148.6
Phase II	−85.8	−152.0

[a] Phases I and II correspond to the first and second stages, respectively, of decomposition regions of the hydrides.
[b] Data from ref. 5.
[c] Data from ref. 6.

atom neighbours. Hence, it is clear that different types of sites are available for hydrogen atom occupation in the Mg_2Ni system. The pressure differential scanning calorimetry (DSC) study on the hydrogenation of Mg_2Ni alloys by Hirata [9] showed two exothermic transitions suggesting that hydrogenation occurs in two separate temperature ranges. The appearance of two exotherms could be due to the formation of different phases as proposed from the thermal studies on this system.

Kissinger [10] has developed a method to calculate the activation energy for the decomposition reactions from DTA measurements by variation of the heating rate regardless of reaction order according to the equation

$$d[\ln(\phi/T_m^2)]/d[1/T_m] = -E_d/R \qquad (3)$$

where ϕ is heating rate, T_m is peak maximum temperature, and E_d is the activation energy for the decomposition reaction. The plots obtained for the phase transition and decomposition stages of the Mg_2NiH_4 sample from DTA data are given in Fig. 4. Typical values of activation energy, shape index and reaction orders for the decomposition of Mg_2NiH_4 calculated according to the procedure given in ref. 10 are given in Table 2.

If the temperature rises (during the reaction) at a constant rate ϕ, then the maximum rate of the decomposition reaction occurs at a temperature T_m defined by [10]

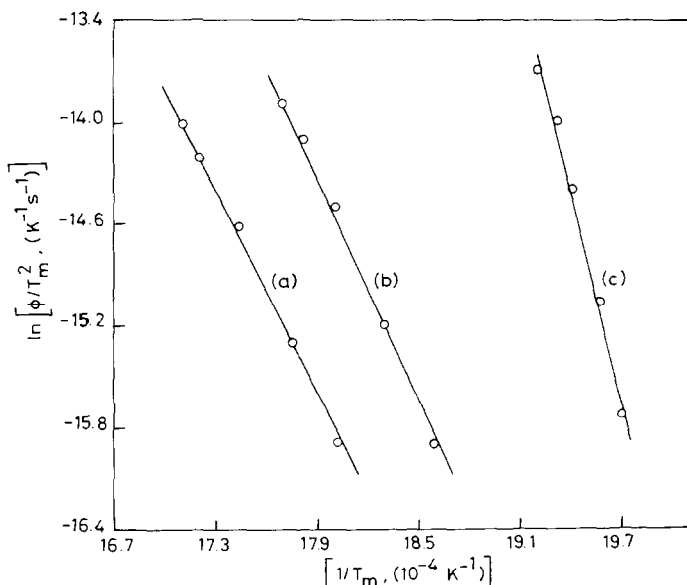$$\frac{E_d\phi}{RT_m^2} = An(1-x)_m^{n-1}\,e^{-E_d/RT_m} \qquad (4)$$

Fig. 4. Temperature programmed 'Arrhenius plots' for the decomposition of the Mg_2NiH_4 sample: (a) second stage of decomposition; (b) first stage of decomposition; and (c) phase transition region.

TABLE 2

Kinetic data from DTA results for the decomposition of Mg_2NiH_4

DTA peak positions	Peak max. temp., T_m (K)	Activation energy, E_d (kJ mol^{-1})	Shape index, [a] s	Reaction order, n
Phase transition region	505–520	328.4	0.24	0.6
First stage decomposition region	540–570	182.9	2.0	1.8
Second stage decomposition region	560–590	166.3	2.1	1.8

[a] s is a measure of asymmetry in the DTA peak [10].

or

$$k_T = E_d\phi/RT_m^2 \tag{5}$$

where k_T is the rate constant at temperature T. The values of rate constant are calculated using the values of E_d. The calculated values for the Mg_2NiH_4 decomposition reaction is of the same order of magnitude as reported from conventional methods [11].

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