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Mg₂Ni HYDRIDE: *IN SITU* HEAT CONDUCTION CALORIMETRY OF THE PHASE TRANSITION NEAR 510 K

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Summary

Precision twin-cell heat conduction (Tian-Calvet) calorimetry has been used to study the thermal effects associated with the solid state transition exhibited by Mg₂Ni hydride at approximately 510 K. Hydrides have been prepared *in situ*, at temperatures below and above that of the transition, and the products subjected to slow temperature scans through the transition, with hydrogen pressure being continuously monitored. The low temperature (LT) and high temperature (HT) hydrides have, within error, the same stoichiometry: Mg₂NiH_{3.91 ± 0.03}. Calorimetric data distinguishes three LT and two HT modifications, the predominating phase system depending on the thermal history of the hydride. Transition enthalpies for hydrides prepared in the LT and HT regions are significantly different with values of $\Delta H_{tr} = 3.99 \pm 0.05$ kJ (mol H₂)⁻¹ and 4.16 ± 0.04 kJ (mol H₂)⁻¹ respectively.

1. Introduction

When exposed to gaseous hydrogen at moderate temperatures and pressures, Mg₂Ni forms a hydride of composition Mg₂NiH_{~4} [1], with the actual hydrogen stoichiometry being reported within the range 3.8 to 4.0. At approximately 510 K, the hydride exhibits a solid state phase transition between high temperature (HT) and low temperature (LT) forms [2]. The structural modifications involved have been the subject of a number of studies based on X-ray, neutron or electron diffraction techniques [1 - 23]. A lack of agreement between the reported structures, particularly for the LT modification(s), had implied a complicated phase relationship, but a recent diffraction analysis [22] invoking the existence of planar stacking faults [24] and, subsequently, their apparent identification by electron microscopy [23], has helped to clear some of the conflict existing in the earlier work. However, there remain some anomalous phase phenomena, and Mg₂NiH_{~4} still represents a complex system, with LT and HT forms exhibiting disorder, the reported existence of a pressure stabilized LT phase

[5, 20] and the additional possibility of hydrogen deficiency [20, 25] for some of the structural modifications.

In the present work, precision calorimetric (Tian-Calvet) techniques have been applied to obtain the thermal characteristics associated with the phase transition. Hydrides have been prepared *in situ* and in the absence of air from high purity Mg_2Ni [26] at temperatures below and above the transition temperature. The hydrides were then subjected to slow temperature scans through the transition. In order to observe any composition changes, the hydrogen gas pressure above the hydride was continuously monitored. Evidence is presented which supports the existence of apparently stable structural modifications in addition to those previously identified by diffraction methods at ambient [1 - 23] and high pressures [5, 20, 25].

2. Experimental details

2.1. Calorimetry

The calorimeter, constructed by Setaram, Lyon, France, is of the twin-cell, differential heat conduction (Tian-Calvet) type, rated for operation at temperatures from 300 to 1250 K. The major construction material is alumina, the instrument size is 1 m (diameter) $\times$ 1.3 m and it weighs 150 kg. A stainless steel (type 316) reactor, designed to allow preparation of the hydride and containment of the powdered product (and an identical reactor containing a non-reactive reference material, stainless steel rods, of equal volume and approximate thermal capacity to that of the hydride) was inserted into the calorimeter detection zones and attached to an external thermostatted (305.00 ± 0.05 K) manifold to facilitate gas manipulations. To provide maximum accuracy in stoichiometry determination, the reactor free volume was minimized (approximately 15 cm^3), and the accessible sample volume was 8 cm^3 . The overall experimental arrangement is shown in Fig. 1. Some other technical features of this type of system have been described previously [27]. The principal instrument output is the net e.m.f. (P_1P_2) produced between the thermopiles, connected in electrical opposition, surrounding the calorimeter reaction and reference zones. For the treatment of the data, procedures described in detail by Calvet and Prat [28] and Gravelle [29] were followed. Briefly, the thermopile signal P_1P_2 is corrected for the existence of a "baseline" displacement, which in the present work is normally linear with temperature and can be selected following observation of the P_1P_2 character before and after the thermal event. Integration of P_1P_2 vs. time then yields an area which is proportional to the energy of the process occurring, the proportionality constant being the calorimeter sensitivity. Each thermopile consists of 450 Pt/Pt-10%Rh junctions which, for the present experimental configuration and within the temperature range employed (390 - 700 K), provides a calibrated sensitivity close to $3 \mu\text{V} (\text{mW})^{-1}$. Details of the calibration techniques will be described elsewhere [30]. Temperature control of the calorimeter and acquisition of

Fig. 1. Diagram of the twin-cell heat conduction calorimeter, reactors and gas handling manifold. *, stainless steel bellows seal valve (Nupro; 4BK); $\perp$, copper gasketed disconnect (Cajon; VCR).

data from the overall system was achieved with the use of a Hewlett-Packard 9825A computer and in-house written software [31]. The calorimeter was operated isothermally (within ± 0.02 K) during hydride preparations, and in a constant rate temperature scanning mode for phase transition investigations. Scan rates between ± 0.2 and ± 8 K h⁻¹ were used and scan linearity was better than 0.2% over the employed scan widths of 65 - 75 K. Scan reproducibility was excellent, this being a factor of particular importance in the present case, where inter-run comparison of data is necessary.

2.2. Mg_2Ni preparation

Material of composition Mg_2Ni was prepared as follows: (i) by direct combination of the high purity elements, at 740 - 860 K, in a vapour-exchange-diffusion reaction which was achieved inside a welded stainless

steel capsule, and is described in detail elsewhere [26]; (ii) by reaction of material with a composition $\text{Mg}_{2.42}\text{Ni}$ (HY-STOR 301; MPD Technology) with nickel powder in the required stoichiometric proportions to produce Mg_2Ni using the same technique. The products crushed easily to grey powders (less than $100\ \mu\text{m}$). Chemical and spectroscopic analyses of material from (i) yielded $\text{Mg}_{2.00\pm0.03}\text{Ni}$; less than 0.2 at.% total impurities and less than 1000 ppma oxygen. X-ray analysis using diffractometry ($\text{Mo K}\alpha$) and overexposed Guinier film ($\text{Cu K}\alpha$) techniques indicated that the samples were free from unreacted magnesium and nickel. There was no evidence, in the calorimetric data obtained during stepwise hydriding, of the anomalously high enthalpy values which would be associated with the formation of MgH_2 ($\Delta H_f(\text{MgH}_2) \approx -78\ \text{kJ}(\text{mol H}_2)^{-1}$ in comparison with $\Delta H_{\text{sol}}(\text{Mg}_2\text{NiH}_x) \approx -28$ to $-50\ \text{kJ}(\text{mol H}_2)^{-1}$ for $0 < x < 0.3$ [30, 32]) again indicating the absence of free magnesium.

2.3. Hydride preparation

Each Mg_2Ni sample (2 - 5 g) was activated, within the calorimeter, by fully hydriding-dehydriding several times at 573 K. The product was subjected to stepwise hydriding to confirm the form of the pressure *vs.* composition (*p-c*) isotherm. The calorimeter temperature was then set to that required for hydride preparation and the β phase, of composition close to $\text{Mg}_2\text{NiH}_{3.9}$, was prepared by addition of several large aliquots of hydrogen. For LT preparations, the rate of hydrogen addition was controlled to avoid a temperature excursion of the hydride into the HT region, owing to the exothermic absorption process. Preparation temperatures were 390, 420, 470 and 573 K, and in all cases the final hydrogen pressure p_{H_2} exceeded that of desorption p_{des} at the highest subsequent scan temperature (not more than 560 K), thus precluding hydrogen loss from the hydride resulting from thermal decomposition. Hydride stoichiometry was calculated using standard gas titration techniques, with gas pressures being recorded with a capacitance transducer (Setra, model 204; better than 0.05% reproducibility and hysteresis). Expansion factors (*i.e.* effective volumes) between manifold and reactors with sample and reference material in place were measured using helium at each of the preparation temperatures, and hydrogen loss from the system by permeation [33] through the portion of the stainless steel cells at temperature was measured in separate empty cell experiments. Overall stoichiometry accuracy is estimated at better than $\pm \frac{3}{4}\%$. The extent and/or completion of the hydriding reaction could be followed by pressure behaviour and P_1P_2 response, the latter being a particularly sensitive indicator of a slow continuation in hydrogen uptake even when p_{H_2} changes were insignificant. (For example, the enthalpy of formation of $\text{Mg}_2\text{NiH}_{\approx 3.9}$ from the hydrogen saturated α phase ($\text{Mg}_2\text{NiH}_{0.3}$) is, as calorimetrically measured [30, 32], $|\Delta H_f(\alpha \rightarrow \beta)| = 65.2\ \text{kJ}(\text{mol H}_2)^{-1}$. Thus an uptake of $10^{-5}\ \text{mol H}_2$, over a period of 1 h, would result in a continuous P_1P_2 signal of about $0.5\ \mu\text{V}$ from baseline, or approximately 16 times P_1P_2 noise levels. This quantity of gas represents 0.02% of the gas phase hydrogen within the

system at 1 MPa and, if it was absorbed by a hydride of typical mass 3 g, would produce a $\Delta x \approx 0.001$.) Following isothermal hydriding, all products were subjected to *in situ* temperature scanning through the solid state transition at approximately 510 K. A number of up and down scans were carried out, for each of the hydrides prepared, to check the reproducibility of the thermal events. Samples were subsequently dehydrided and the hydride then re-prepared from the same Mg_2Ni parent at a different temperature. Temperature scanning was continued, to observe any systematic changes in transition parameters associated with preparation temperature. This process was repeated several times to observe any longer term trends. Although the majority of the scans were carried out with $p_{\text{H}_2} \approx 0.6 - 0.8$ MPa above the hydride, in selected cases p_{H_2} was increased up to 6.6 MPa to ascertain any pressure dependence for the transition. The transition was also investigated, following a hydride heat treatment lasting several days, at 670 K and $p_{\text{H}_2} \approx 3.3$ MPa.

3. Results

The Mg_2Ni samples all activated readily at 573 K with overpressures of greater than 1 MPa. Within six hydriding-dehydriding cycles each was yielding a reproducible final composition. The p - c isotherms at 573 K exhibited plateaux with mid-composition absorption p_{abs} and desorption p_{des} hydrogen pressures of 0.40 and 0.34 MPa respectively. Details of the p - c features and thermochemistry, obtained by reaction calorimetry, will be reported elsewhere [30]. For hydrides prepared at 573 K, the typical period required to complete the hydrogen uptake was greater than 5 h, although 90% - 95% completion occurred within 30 min of a massive aliquot addition. Final compositions were $x = 3.92 \pm 0.02$, in Mg_2NiH_x , and no composition variation was measurable for $0.6 < p_{\text{H}_2} < 4$ MPa. Hydrides prepared at the lower temperatures exhibited considerably slower absorption kinetics and did not achieve the limiting composition even after several days at overpressures of 4 MPa. At 390 K and 420 K the intermediate composition attained was $x \approx 3.7$ and a slow absorption ($2 - 4 \times 10^{-6}$ (mol H_2) h^{-1}) persisted even after 70 h. At 470 K the intermediate composition $x \approx 3.85$ was attained, again with a slow (approximately 1×10^{-6} (mol H_2) h^{-1}) absorption persisting. Because of the significant overpressure required to drive the reaction at 390 and 420 K, meaningful plateau pressures were not obtained. However, at 470 K, $p_{\text{abs}} \leq 22.1$ kPa and $p_{\text{des}} \geq 15.0$ kPa. All of the Mg_2Ni samples which were hydrided at temperatures in the LT region absorbed additional hydrogen during the first temperature scan into the HT region, this process initiating either before (390 and 420 K preparations) or during (470 K preparation) the phase transition, with completion by 540 K. However, in all cases the final composition achieved was $x = 3.90 \pm 0.02$.

The P_1P_2 vs. temperature curves obtained during a typical sequence of scans of $\text{Mg}_2\text{NiH}_{\approx 3.9}$ undergoing its solid state transition are shown in Figs. 2

and 3, and detail from Fig. 3, at close to baseline levels, is shown in Fig. 4. The figures present data obtained with hydrides of the same parent Mg_2Ni sample, which were subjected to identical scan rates of 5.09 K h^{-1} (Fig. 2)

Fig. 2. $\text{Mg}_2\text{NiH}_{3.9}$, calorimeter response (thermopile output, P_1P_2 vs. temperature) in up-scan at $+5.09 \text{ K h}^{-1}$. Curves: A, hydride prepared at 573 K; B, hydride prepared at 470 K (initial up-scan); C, as for B (subsequent upscans). Inset, definitions of initiate, onset and peak temperatures T_I , T_O and T_P respectively.

Fig. 3. $\text{Mg}_2\text{NiH}_{3.9}$, calorimeter response in down-scan at -2.98 K h^{-1} . Curves : A, hydride prepared at 573 K; B, hydride prepared at 470 K and subsequently heat-treated at 670 K; C, hydride prepared at 470 K.

Fig. 4. Detail from Fig. 3; $\text{Mg}_2\text{NiH}_{3.9}$, calorimeter response in down-scan at -2.98 K h^{-1} . Curves as for Fig. 3 with P_1P_2 displacement to avoid overlap.

TABLE 1

$\text{Mg}_2\text{NiH}_{3.9}$ transition temperatures (T_I , T_O , T_P) (see Fig. 2) and enthalpies ΔH_{tr}

Curve	T_P (K)	T_O (K)	T_I (K)	ΔH_{tr} (kJ (mol H_2) $^{-1}$)
Fig. 2, A	515.2	512.6	498	4.16(4)
Fig. 2, B	522.0	516.2	497	3.9(1)
Fig. 2, C	514.6	511.9	495	3.98(4)
Fig. 3, A	507.8	509.7	511	4.15(4)
Fig. 3, B	505.0	506.8	508	4.10(4)
Fig. 3, C	502.7	504.6	506	3.99(5)

Temperatures are presented for the example curves (Figs. 2 - 4); ΔH_{tr} values are derived from all data; estimated standard deviations are given in parentheses.

and -2.98 K h^{-1} (Fig. 3). The preparation conditions for the individual hydrides are included with the figures. In Table 1 temperatures taken from the representative curves (Figs. 2 and 3) are presented; the corresponding temperatures for all hydride samples were within 1.5 K of those reported. The three parameters (T_I , T_O , T_P) associated with each event are the initiate, onset and peak temperatures respectively. They have been selected as shown in Fig. 2, with T_I being defined at the point of displacement of P_1P_2 , from baseline, of twice noise levels, or equivalent to a detected thermal power of approximately $20 \mu\text{W}$ (cf. the peak power levels produced, under the reported experimental conditions, of ± 10 to $\pm 200 \text{ mW}$). The selection of T_I is more subjective than either T_O or T_P , but nevertheless provides

a parameter to describe, within ± 2 K, the first significant thermal change exhibited by the hydride. As in other forms of thermal analysis, T_0 is taken as the defining temperature of the event, *i.e.* the transition temperature in this case. Also shown in Table 1 are the enthalpies for the transition ΔH_{tr} , these values being derived from data collected for 68 scans with 11 samples of hydrides prepared from Mg_2Ni from both preparation sources. The majority of the data was obtained for hydrides with $0.6 < p_{H_2} < 0.8$ MPa. However, for p_{H_2} up to 6.6 MPa no significant deviation in transition parameters was observed.

4. Discussion

The final composition of all the hydrides which were prepared as HT modifications, and those prepared in the LT region following the first up-scan through the transition, was $3.90 < x < 3.92$ with no significant composition differences between HT and LT hydrides within the total estimated error of $\pm \frac{3}{4}\%$. At 573 K, $Mg_2NiH_{\approx 3.9}$ exhibits immeasurably small hydrogen solubility for hydrogen pressures $0.6 < p_{H_2} < 4$ MPa, thus behaving as a line compound under these conditions with a stoichiometry approaching, but not attaining, an integral value of four. Because of the Mg_2Ni preparation techniques used, it is unlikely that the measured hydrogen content is low as a consequence of impurities in the starting materials (the presence of one or more impurity phases of magnesium, nickel, $MgNi_2$ and/or MgO have been reported in the Mg_2Ni samples used in most other studies). The presence of an unreacted portion of the Mg_2Ni samples is also unlikely once the HT region is entered, since there is no evidence, either calorimetrically or volumetrically, for a continuing slow hydrogen absorption and all Mg_2Ni samples, irrespective of the preparation history, behave consistently in terms of composition. In addition, in a separate study employing powder X-ray diffractometry techniques [34], fully activated and hydrided Mg_2Ni showed no reflections which could be indexed as either Mg_2Ni [26, 35] or its hydrogen saturated α phase $Mg_2NiH_{0.3}$ [10, 16]. However, fully activated and dehydrided Mg_2Ni exhibited X-ray spectra showing extensive residual structural distortion, this being reproducible and systematically anisotropic in character. Thus the metal atom geometry in virgin Mg_2Ni must distort considerably during the interstitial loading of the lattice, even to yield a composition of $x \approx 3.9$. For LT hydrides prior to the first up-scan through the transition, hydrogen absorption was never complete despite several days exposure to large hydrogen overpressures. Although reproducible behaviour was observed, and the lower temperature preparations consistently yielded lower x values, a slow hydrogen absorption always persisted, and these intermediate compositions are presumably limited by kinetics. However, in every instance, on initiating a temperature up-scan, the hydrogen absorption rate increased by a factor of $10 - 10^2$ and the final composition, $x = 3.90 \pm 0.02$, was achieved prior to the completion of the solid state transition into an HT modification. The calorimetric data

obtained before the initiation of the transition, and during the exothermic absorption of hydrogen, yielded an enthalpy for the absorption process of $-68 \pm 3 \text{ kJ (mol H}_2\text{)}^{-1}$, *i.e.* a value consistent with the measured [30, 32] enthalpy of formation of the β phase from the saturated α phase of $65.2 \text{ kJ (mol H}_2\text{)}^{-1}$ at 573 K.

In the course of previous structural investigations of $\text{Mg}_2\text{NiH}_{3.9}$, thermal analysis has been applied [2, 5, 8, 12, 14, 19, 20] to aid identification of the gross energetic processes associated with the phase transition. However, a calorimeter of Tian-Calvet design [28, 29], in which heat loss other than via the thermopiles is at an extremely low level, used in conjunction with the ancillary apparatus described earlier (Fig. 1), allows quantitative data to be derived. The use of larger samples and slow scanning techniques also ensures the acquisition of high resolution data. The features obtained calorimetrically during temperature scanning through the transition (Figs. 2 - 4) exhibit characteristics which are dependent on the preparation temperature of the hydride. The curves shown as examples were each obtained with hydrides prepared from the same Mg_2Ni parent sample, thus allowing direct comparison without introducing any significant uncertainties which could be attributable to particle size variations or thermal conductivity differences. For a hydride prepared in the HT region (*i.e.* $T > 530 \text{ K}$), thermal cycling through the transition yields curves with the character shown by curve A, Fig. 3 in down-scan and by curve A, Fig. 2 in up-scan. The features remain unchanged through many cycles and the process appears reversible, with a temperature hysteresis (approximately 5 K) occurring between up-scan and down-scan. A hydride, when prepared in the LT region (*i.e.* $T < 470 \text{ K}$), exhibits on the first up-scan through the transition, a broad low intensity peak (curve B, Fig. 2) the features of which are not reversible. Subsequent thermal cycling produces the curves shown by curve C, Fig. 3 in down-scan and by curve C, Fig. 2 in up-scan, which remain unchanged through many cycles and, as with the HT preparations, appear reversible with a similar temperature hysteresis. Thus over the temperature range employed and with the single exception of the initial LT up-scan, the transition features (Figs. 2 and 3; Table 1), distinguish two groups depending on whether the preparations were carried out within the HT or the LT regions. The transition parameters for HT preparations in comparison with LT preparations exhibit higher transition temperatures (ΔT_0 is approximately 0.5 K and 5 K for up-scan and down-scan respectively), with higher ΔH_{tr} , by approximately 4%, and with a curve profile which has a greater amplitude and smaller temperature width, the latter being more clearly apparent at less than half peak height (Fig. 2). There was no evidence, in either the volumetric or calorimetric data, for hydride stoichiometry changes through the transition sequences which occurred reversibly. During scanning, a measurable hydrogen absorption occurred only for LT preparations in the initial up-scan and prior to entry into the HT region.

The ΔH_{tr} and T_0 values which have been derived for the $\text{Mg}_2\text{NiH}_{3.9}$ preparations show reproducible and significant differences which imply the

existence of three LT and two HT structural modifications, with relationships as outlined in the following scheme.

LT(III) is the modification obtained by hydride preparation at temperatures $T < T_0$, and HT(II) is the modification obtained on hydride preparation at $T > T_0$ (the letters A, B and C refer to the associated thermal features in Figs. 2 and 3). Some comments can be made concerning the structural relationships. Firstly, for the conversion of $\text{LT(III)} \rightarrow \text{HT(I)}$, with a curve (B, Fig. 2) which has a low amplitude and broad temperature width (approximately 40 K), it is likely that, as prepared, LT(III) is inhomogeneous in terms of structural disorder and/or with localized composition variations. Secondly, the intermediate transition parameters of HT(I) following heat treatment at 670 K and $p_{\text{H}_2} \approx 3.3$ MPa, (curve B, Fig. 3), implies the existence of a continuous phase transition $\text{HT(I)} \rightarrow \text{HT(II)}$. A possible contributing factor at these elevated temperatures is a metal lattice anneal, the occurrence of which is supported by the observation [30] that dehydrided material from the heat treatment exhibits, on rehydriding, the slow absorption kinetics typical of unactivated (*i.e.* structurally undistorted) Mg_2Ni . If a minor hydrogen stoichiometry change is associated with $\text{HT(I)} \rightarrow \text{HT(II)}$, it would be masked by the large gas phase hydrogen losses from the system, which occur at these higher temperatures with significantly increased permeation rates.

One other feature of the transition, shown by the calorimetric data, is a small hump at approximately 491 K (Fig. 4). This feature is resolvable on a down-scan, and is presumably embedded in the extended approach ($495 < T < 510$ K; Fig. 2) into the main event in up-scan, thereby contributing to the modest increase in temperature width observed with LT preparations. The hump area (curve C, Fig. 4) corresponds, in energy, to approximately 1% that measured for $\text{LT(I)} \rightleftharpoons \text{HT(I)}$ and less than 0.1% (curve A, Fig. 4) that of $\text{LT(II)} \rightleftharpoons \text{HT(II)}$. However, the data does not differentiate as to whether this event is associated with the total sample mass (*i.e.* with low intrinsic enthalpy and the transition being sequential), or with a part of the sample (*i.e.* with high intrinsic enthalpy and an implied inhomogeneity). However, preparation of the hydride as LT(III) favours the appearance of the 491 K feature, suggesting a correlation with the structural inhomogeneity which is suspected for that modification.

5. Conclusions

A series of hydrides, prepared from high purity Mg_2Ni at temperatures below and above that of the phase transition at 510 K, have a stoichiometry

of $\text{Mg}_2\text{NiH}_{3.91}$ with no measurable compositional variation between LT and HT modifications within an estimated total error of $\pm \frac{3}{4}\%$. A total of three LT and two HT structural modifications have been identified for $390 < T < 600$ K and $0.6 < p_{\text{H}_2} < 4$ MPa. One modification, LT(III), has thermal characteristics attributable to gross structural and/or compositional inhomogeneity. The remaining four modifications exist in two reversible pairs, $\text{LT(I)} \rightleftharpoons \text{HT(I)}$ and $\text{LT(II)} \rightleftharpoons \text{HT(II)}$, the enthalpies of transition for which are $\Delta H_{\text{tr}} = 3.99 \pm 0.05$ kJ (mol H_2)⁻¹ and 4.16 ± 0.04 kJ (mol H_2)⁻¹ respectively. Despite the likelihood of type (I) and (II) pairs being structurally similar, their mutually exclusive existence implies a significant energetic or kinetic barrier to their structural interconversion.

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