

The activation of LaNi₅-H

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The hydrogen-absorbing intermetallic compound LaNi₅ was activated using manometric apparatus (an IMI-HTP manometric hydrogen storage analyser) at 333 K. Pressure-composition isotherms (PCIs) were measured through the first 8 hydrogenation cycles and show considerable change in the hydrogen absorption behaviour through the activation process. A series of isotherms at temperatures in the range 308 – 413 K were also measured. The higher temperature measurements show a clear indication of the formation of an intermediate γ phase between the solid solution α phase and β hydride phase. Van 't Hoff plots were determined from the measured isotherms and the average value for ΔH of 15.6 kJ/mol $\frac{1}{2}$ H₂ was found to be in good agreement with the literature.

Introduction

Hydrogen absorption by LaNi₅ was first studied by Neumann in the late 1960's [1], and its potential as a hydrogen storage material was subsequently recognized by van Vucht *et al.* [2]. Justi *et al.* [3] later suggested using the compound as a battery electrode material, although there are a number of practical drawbacks to the use of pure LaNi₅ for this application, including the poor long term cycling stability of the pure alloy and the relatively high absorption/desorption plateau pressure.

These problems were later largely solved by the partial substitution of the La and the Ni, and the resultant materials are now widely used in commercial Ni-MH batteries. There is therefore a large body of research on LaNi₅ and its derivatives, and the material is still of interest as a model hydrogen storage alloy. Recent developments include the partial substitution of the Ni by Sn to produce a material with excellent long term gas phase cycling stability [4].

LaNi₅ and hydrogen storage

LaNi₅ reacts readily with hydrogen gas at ambient temperature and above. The compound shows hydrogen absorption and desorption behaviour that is typical of many metal-hydrogen systems. At lower hydrogen pressures a relatively small amount of hydrogen is absorbed following a relatively large increase in hydrogen pressure. This is the α phase region, in which atomic hydrogen diffuses randomly between interstitial sites in the metal lattice. At a slightly higher pressure, at the onset of the so-called plateau region, an ordered hydride phase, known as the β phase, forms.

Over a relatively small pressure range, the hydrogen content increases dramatically as the β phase grows through the α phase matrix. Once the host lattice has been converted to the β phase, at the end of the plateau region, a relatively small amount of further hydrogen uptake occurs over a relatively large pressure range. It is this plateau region that is exploited in the compound's use as a hydrogen storage material and the practical reversible hydrogen storage capacity is defined approximately by the width of the plateau [5].

To assess a new material's suitability for use as a solid state hydrogen store it is essential to accurately determine its



Figure 1: The IMI-HTP Manometric Sorption Analyser.

hydrogen uptake behaviour, including both the reversible hydrogen storage capacity, and the pressure and temperature at which reversible hydrogenation occurs. In the case of LaNi₅, the hydrogen uptake described above follows an initial activation process in which the material is cycled in hydrogen. In this Application Note we demonstrate the use of the IMI-HTP manometric hydrogen storage analyser to characterize the hydrogen absorption and desorption behaviour of a commercial LaNi₅ sample both during and after the initial hydrogen activation process. Changes in the plateau pressures during activation are measured and, following full activation, the thermodynamic properties of the material are determined and compared to literature values.

Experimental details

Apparatus

The IMI-HTP manometric analyser (shown in Fig. 1) is a fully automated, high pressure, Sieverts apparatus that operates over a wide range of temperatures. The standard maximum operating pressure is 100 bars, with optional 200 bar capability, and the operating temperature range, depending on the choice of sample environment, is 77 – 773 K. The use of a turbomolecular pump, with an oil-free membrane backing unit, allows the high vacuum degassing of samples where necessary. The standard sample cell holds a maximum sample volume of 1 cm³, with the lower sample size dependent on the hydrogen sorption capacity of the studied material.

Activation

The LaNi₅ sample was supplied, in powder form (-100 mesh, 99.5% purity), by Alfa Aesar. The 765 mg sample was weighed on an external balance and then loaded into the IMI-HTP

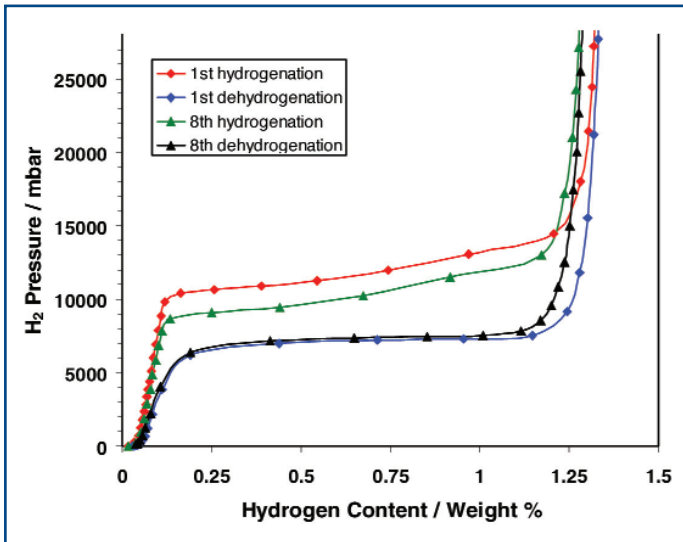


Figure 2: The pressure-composition isotherms (PCIs) at 333 K for the $\text{LaNi}_5\text{-H}$ system during the 1st and 8th hydrogenation cycles of the activation process.

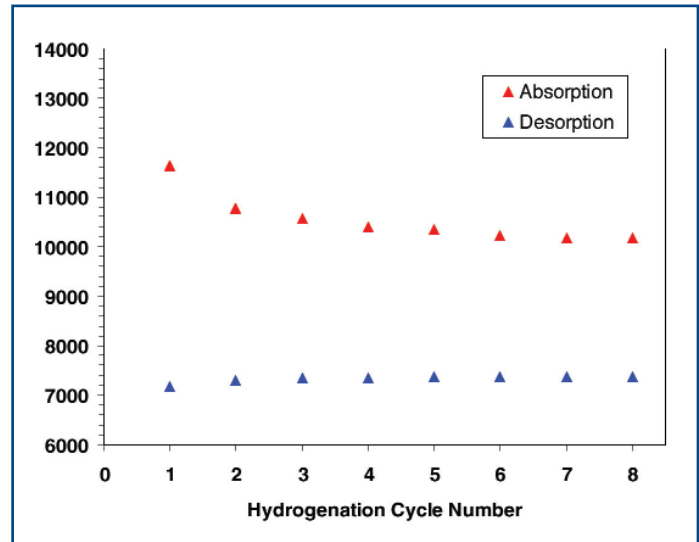


Figure 3: The plateau pressure against hydrogenation cycle number through the activation process at 333 K.

manometric hydrogen storage analyser. The sample was degassed for a period of 12 hours, at 573 K, with a base pressure at the turbomolecular pump inlet of $< 10^{-6}$ mbar. Following degassing, the sample was exposed to a hydrogen pressure of 80 bars, at a temperature of 333 K, for 30 minutes, to perform the initial hydrogen absorption. After subsequent evacuation,

a series of 8 isotherms were then determined at 333 K. The absorption/desorption kinetics were fitted in real-time by the IMLwin software, to determine a sufficient equilibration time. A minimum time of 2 minutes per equilibrium point and a maximum timeout of 15 minutes were set for each kinetic step in both the absorption and desorption isotherms in this work.

Thermodynamic properties

Following the activation process, a further series of isotherms were determined. Initially, 7 isotherms were measured in ascending order between 343 and 383 K. Then, a further 7 were measured in descending order down from 383 to 308 K. A second set of 4 isotherms were then measured at increasing temperatures between, 373 and 403 K, further extending the measured temperature range. A final series of isotherms were measured at various temperatures in ascending order from 353 to 413 K.

Results and discussion

Equilibrium properties during activation

Fig. 2 shows the absorption and desorption pressure-composition isotherms for the 1st and the 8th hydrogenation cycles during the hydrogen activation process. It can be seen that there is considerable change in the plateau pressure of the absorption isotherm between the 1st and the 8th cycles. In contrast, the change in the desorption plateau pressure is relatively small. The trapping of hydrogen in the material can also be seen, as an offset in the maximum measured hydrogen content, although the offset (physically) occurs at the low content end of the isotherm. The change in the plateau pressure during both absorption and desorption, during the first few

cycles, is shown in Fig. 3. The plateau pressure in each case was determined by calculating the equilibrium pressure at a hydrogen content of 0.65 wt.% (the approximate plateau mid-point) by linear interpolation between the two nearest data points. An error in each value may therefore be introduced due to this approximation.

However, a clear initial decrease in the absorption plateau pressure, followed by a gradual stabilization can be seen. The desorption plateau pressure, on the other hand, remains relatively constant, although a small initial increase is evident, and this contributes to the decrease in the overall observed hysteresis. The decrease in the absorption plateau pressure is consistent with the results of Kisi *et al.* [6], although their 1st cycle (303 K) isotherm data were measured on an unhydrogenated (virgin) sample, whereas the 1st cycle isotherm data shown here were measured after an initial high pressure hydrogenation performed in a single step, and so the data are not directly comparable. They also show data for three well-defined initial particle size ranges, whereas our data are for a more poorly defined -100 mesh ($< 149 \mu\text{m}$) powder.

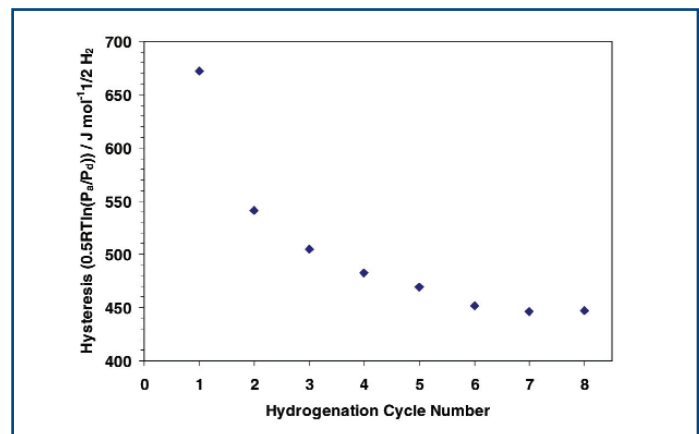


Figure 4: The hysteresis in the absorption/desorption plateau pressures, expressed as the uncompensated heat, as a function of hydrogen cycles through the activation process at 333 K.

The overall decrease in the hysteresis through the activation process is shown in Fig. 4, which plots the uncompensated heat [$\frac{1}{2}RT \ln(P_a/P_d)$] in units of J/mol $\frac{1}{2}H_2$ against cycle number. The values obtained, although higher, generally compare well with those from the literature. Luo *et al* [7] obtained values in the range 308 – 384 J/mol $\frac{1}{2}H_2$ for LaNi₅-H in the temperature range 228 – 323 K. In that case, the sample was thoroughly annealed and was confirmed to be homogeneous and single phase by metallography, powder X-ray diffraction (XRD) and electron microprobe analysis (EPMA). It had also been subjected to 25 hydrogenation/dehydrogenation cycles. The level of hysteresis observed may therefore be expected to be lower than for the non-annealed commercially-supplied sample used in the current work.

Thermodynamic properties

Fig. 5 shows the series of desorption isotherms determined in the first ascending temperature sequence, in the range 333 - 383 K, plotted on a logarithmic pressure scale. The formation of an intermediate γ phase [8] can clearly be seen at the higher temperatures. Formation occurs at an approximate hydrogen content of 0.8 wt.%, corresponding to H/M = 0.58, which is consistent with Buckley *et al*'s [8] observation of γ phase formation at H/M = 0.59.

The van 't Hoff plots taken from both the absorption and desorption isotherms measured at various temperatures are shown in Fig. 6. The plateau pressures were determined by calculating the equilibrium pressure at a hydrogen content of 0.6 wt.% by linear interpolation between the two nearest data points. A slightly lower value was chosen in the van 't Hoff plot determination to minimize the effects of the appearance of the γ phase in the higher temperature data.

An average value of $\Delta H = 15.6$ kJ/mol $\frac{1}{2}H_2$, determined from the fits to both of the data sets shown in the figure, agrees well with values from the literature [7]. For example, the value reported in the early study by van Vucht *et al* [2] was 7.2

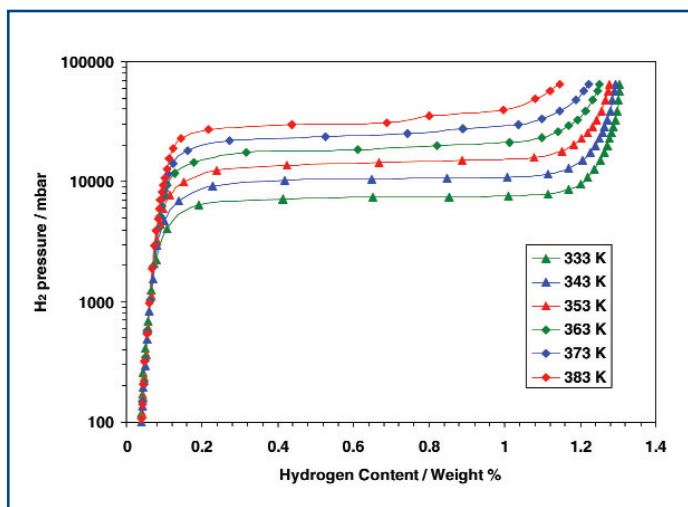


Figure 5: The desorption isotherms measured in ascending temperature order, directly following the hydrogen activation process. The 333 K isotherm is the 8th dehydrogenation from Fig. 1.

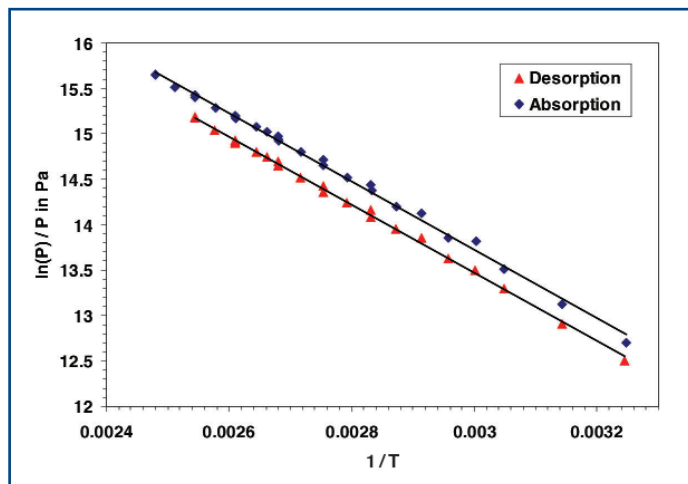


Figure 6: The van 't Hoff plots determined from the hydrogen absorption and desorption isotherms of the LaNi₅ sample.

kcal/mol $\frac{1}{2}H_2$ (~15.1 kJ/mol $\frac{1}{2}H_2$) while Luo *et al* [7] reported an average value of 15.4 kJ/mol $\frac{1}{2}H_2$. Calorimetric studies, meanwhile, report values in the range 14.8 – 16.0 kJ/mol $\frac{1}{2}H_2$ [7]. It is important to note that these values can be affected by a number of factors, including the sample's stoichiometry, the levels of impurities in the sample, the sample history, and issues relating to the activation and measurement protocol.

Conclusion

A LaNi₅ sample was activated using manometric apparatus (an IMI-HTP manometric hydrogen storage analyser) at 333 K. Pressure-composition isotherms (PCIs) were measured through the first 8 hydrogenation cycles and showed considerable change in the hydrogen absorption behaviour through the activation process. A series of isotherms at temperatures in the range 308 – 413 K were also measured. A clear indication of the formation of an intermediate γ phase between the solid solution α phase and β hydride phase was observed in the higher temperature measurements. Van 't Hoff plots were determined from the measured isotherms and the average value for ΔH of 15.6 kJ/mol $\frac{1}{2}H_2$ was found to be in good agreement with the literature.

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