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# Pressure DSC studies on the formation and reproducibility of double peaks in the sorption of $LaNi_5$-$H_2$ during thermal cycling

M.T. Hagström*, P.D. Lund

*Helsinki University of Technology, Department of Engineering Physics and Mathematics, Rakentajanaukio 2 C, 02150 ESPOO, Finland*

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## Abstract

Pressure Differential Scanning Calorimetry (PDSC) has been used to study the conditions of formation and disappearance of double peaks in the absorption and desorption of the $LaNi_5$-$H_2$ system during thermal cycling. Thermal absorption–desorption cycling reveals double-peak formation both in absorption and desorption phases. Splitting of a single peak into a double-one is induced below 60°C even in case of absorption. The double peak disappears, due to annealing at moderate temperatures in a hydrogen atmosphere, easier in absorption than in desorption. It reappears, however, easily when thermal cycling is continued. © 1997 Elsevier Science B.V.

*Keywords:* Annealing; Pressure DSC; Stability; Thermal cycling; Metal hydride

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## 1. Introduction

The existence of an intermediate hydride phase in the $LaNi_5$-$H_2$ system, $\beta$-$LaNi_5H_{3-4}$, between the $\alpha$-phase (solid solution) and the $\gamma$-phase ($LaNi_5H_6$) was discovered by Ono et al. [1,2]. They concluded on the basis of in situ XRD measurements that the $\beta$-phase formed above 70°C in desorption and above 94°C in absorption [3]. Shilov et al. [4] on the other hand, suggested apparently on the basis of desorption pressure-composition isotherms (PCIs) a temperature-composition (T-C) phase diagram in which the $\beta$-phase appears above −7°C. The stability of the new phase has thus been a source of confusion (e.g. [3–6]).

More recently, for example, Buckley et al. [7] have studied gravimetrically the stability of the PCIs in the $LaNi_5$-$H_2$ system. They concluded that the intermediate $\beta$-phase forms above 60°C in desorption and above 90°C in absorption, at least for not extensively cycled samples, and that the physical properties of the $LaNi_5$-$H_2$ system strongly depend on the thermal history. Pressure hysteresis as well as occurrence and stabilization of the $\beta$-phase were considered to be determined by constant competition between creation of lattice defects through hydrogen sorption and annihilation of those defects induced by high or modest temperatures when the alloy is in the dehydrogenated state.

In this work, we have studied the behaviour of the $LaNi_5$-$H_2$ system using PDSC which allows hydrides to be examined dynamically during thermal hydriding–dehydriding cycling at approximately constant pressure, in contrast to the commonly applied (nearly) isothermal methods where sorption reactions are induced by alternating pressure. In a PDSC curve,

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*Corresponding author. Fax: +358 9 451 3195; e-mail: markku.hagstrom@hut.fi.

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one (sharp) peak indicates that all of the hydrogen is equally bound to the host lattice, while two or more peaks indicate different binding energies. The corresponding phenomenon in isothermal conditions in the latter case is the splitting of the PCI-plateau. Nevertheless, information obtained from PDSC experiments cannot directly be related to structural data and that is why the terms $\alpha$-, $\beta$- and $\gamma$-phase used to describe the results of this study serve rather as analogous labels than proven equivalence between structural (e.g. in situ XRD) and energetic (PDSC) evidence of the dynamic behaviour of the studied system.

The purpose of this study is to show that PDSC can give valuable information about the dynamics of hydrogen sorption in metal-hydrogen systems and, in particular, to study the conditions of double peak ($\beta$-phase) formation and disappearance in the $LaNi_5$-$H_2$ system.

## 2. Experimental

### 2.1. *Materials*

The sample material was commercial $LaNi_5$ (Johnson Matthey) with a grain size of 100 to 1000 $\mu$m. A particle size analysis was carried out for samples that had gone through the initial activation plus 0, 2, 10, 50, 330 and $>$ 1000 (two samples) thermal cycles. The purity of the hydrogen gas used (AGA) was 99.9999 vol.%.

### 2.2. *Equipment*

TA Instruments PDSC together with Module 2910 and Thermal Analyst 2100 has been used in this study. The principle of operation of this equipment is quantitative DTA, that is, the measured quantity is the

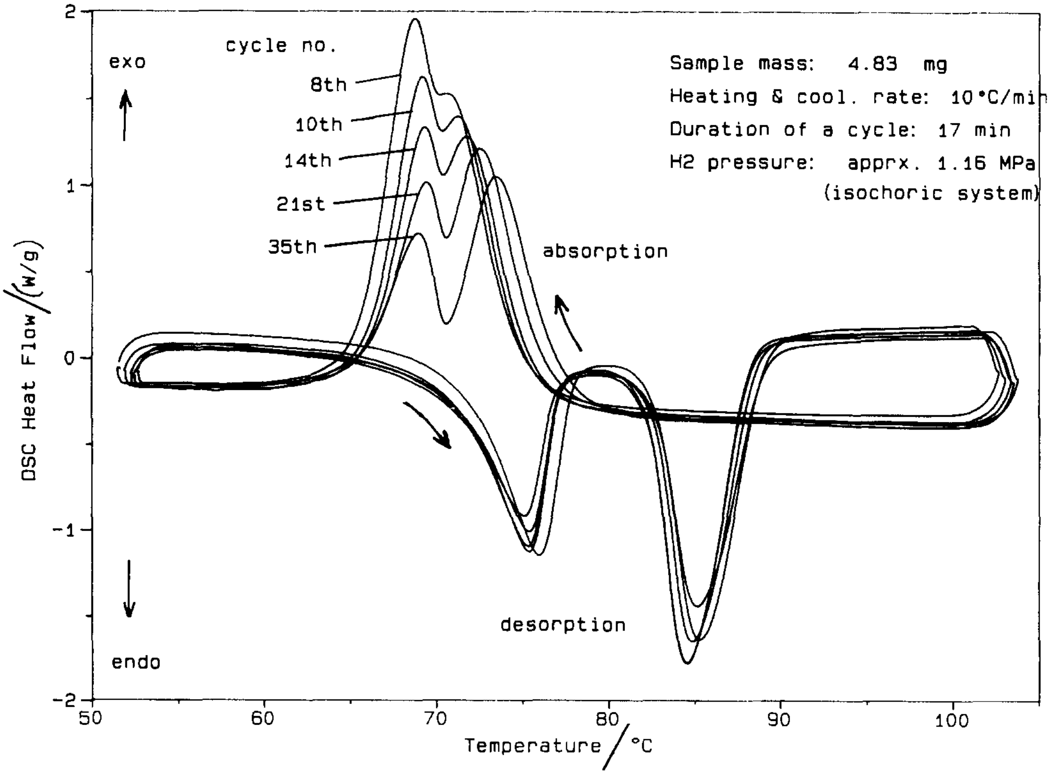

Fig. 1. Thermal cycling behaviour of a reactivated $LaNi_5$-$H_2$ system during the first 35 cycles after reactivation, preceding air-exposure time: 4 weeks. Earlier history of the sample: tens of thermal and pressure cycles at various conditions.

temperature difference between a sample and an inert reference (an empty crucible). Aluminium crucibles have been used. Temperature scale has been calibrated in a hydrogen atmosphere (0.8 MPa) with indium and bismuth. Hydrogen gas flow into the PDSC is controlled by a Bronkhorst Mass-Flow Controller (MFC, model: F 211C-FA) and the pressure in the overpressure range is measured by a Bronkhorst Electronic Pressure Controller (EPC, model: P-512C-FA-100A9). A vacuum pump (Leybold Trivac 1.6 B) has been connected to the pressure relief valve of the PDSC, in order to pump air out of the cell before hydrogen experiments. The same apparatus has been used previously, for example, to determine dynamic van't Hoff plots of candidate alloys for hydrogen storage [8].

### 2.3. *Procedures*

All samples (masses from 4 to 100 mg) were initially activated at room temperature by increasing the hydrogen pressure from vacuum until absorption (exothermal reaction) occurred. Immediately thereafter the samples were exposed to thermal hydriding–dehydriding cycles at various approximately constant pressures (from 0.44 to 4.5 MPa) applying various isothermal periods (from zero to a few days) at the end temperatures of the cycles (from 25 to 180°C). Only the sample used in the preliminary experiment (Fig. 1) had more complicated thermobaric history.

After the pressurization the apparatus was used in the isochoric mode which induces slight pressure changes during thermal cycling. However, since the total pressurized volume is large compared to the heated sample oven, pressure depends only weakly on temperature. Heating rates were varied from 3 to 20°C/min and cooling was usually allowed to happen spontaneously as there is no cooling accessory available to the TA PDSC. In the preliminary experiment (Fig. 1) a cooling rate of 10°C/min was used. Annealing was always performed under hydrogen overpressure to eliminate possible interference from the equipment. In addition to annealing, exposure to room air was used for various periods (from 1 to 42 days) to study the conditions of disappearance of the $\beta$-phase.

## 3. Results

### 3.1. *Particle size analysis*

The size of most of the nonuniform particles was effectively reduced to below 50 μm during the initial activation. The mean size was 17 to 24 μm (vol.%-base) irrespective of the number of thermal cycles completed before the analysis. This showed clearly that the absorption behaviour observed in the preliminary experiments (Fig. 1) could not be explained by further activation of the sample caused by reduced particle size during thermal cycling.

### 3.2. *Thermal cycling experiments*

Fig. 1 shows that in the case of a reactivated sample desorption occurs immediately in two temporal phases (two consecutive peaks) while absorption developes gradually from a single peak into a double-one. In the absorption curves, the peaks at a higher temperature are denoted as the $\alpha \rightarrow \beta$ conversion and the ones at a lower temperature as the $\beta \rightarrow \gamma$ conversion. The same applies to desorption except that the direction of the conversion is now the opposite. After about 35 cycles, the size of the corresponding peaks in absorption and desorption are equal, that is, sorption proceeds energetically in a symmetric way.

The behaviour of the $LaNi_5$-$H_2$ system during low pressure (0.44 MPa) and low temperature (25 to 58°C) cycling for the first 1000 cycles is shown in Fig. 2. The sample was held for 3 min at 58°C to make sure that desorption was not interrupted by the low end temperature of the dynamic thermal cycle. It can be observed that the double peak forms earlier in desorption than in absorption. Fig. 2 demonstrates that the $\beta$-phase forms below 60°C both in desorption and absorption during thermal cycling which seems to differ from the behaviour found in isothermal conditions.

After the $\beta$-phase had formed below 60°C, the sample was annealed at gradually higher temperatures to find out when the double peak would disappear. The main results are shown in Fig. 3. Curve 1 is the reference and Curve 2 shows that increasing the holding period up to 18 h at 67°C cannot erase the double peak. Holding the sample for 22 h at 86°C before cooling (Curve 3) is still not enough to trans-

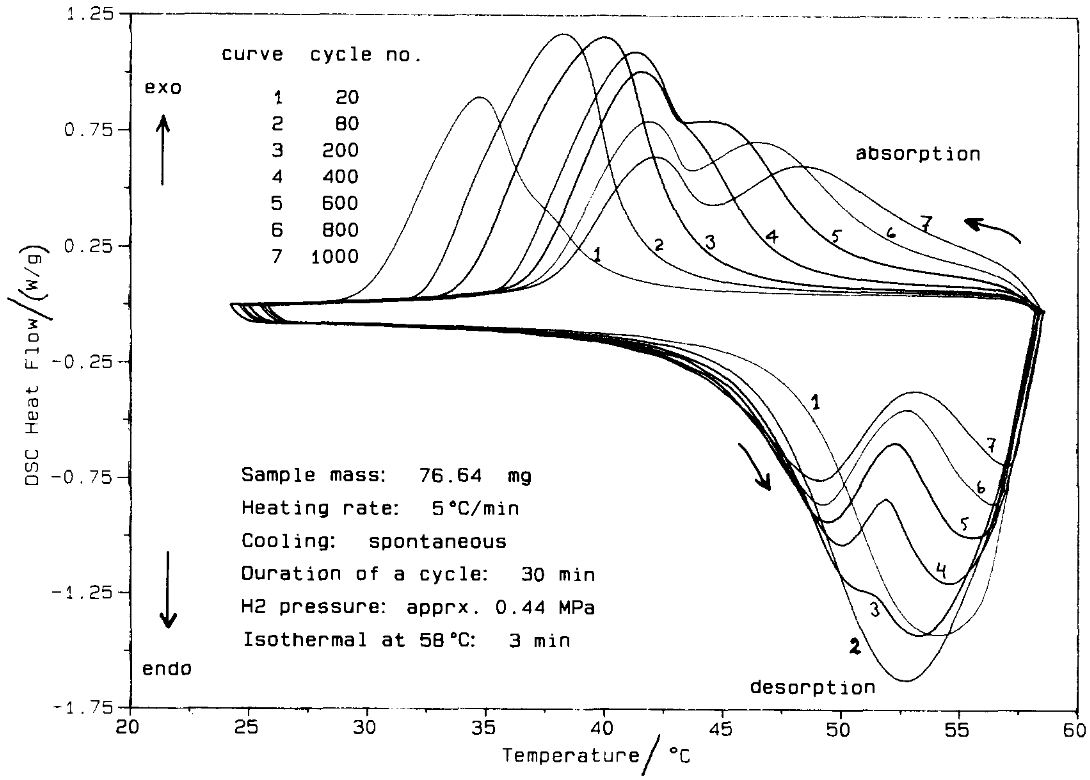

Fig. 2. Thermal cycling behaviour of a virgin $LaNi_5$-$H_2$ system during the first 1000 cycles, recorded immediately after the first stage activation. Isochoric system.

form the double peak into a single but the overall width of the absorption peaks is halved. This kind of change in the absorption behaviour may well look like a disappearance of the double plateau in PCI measurements as such a small difference in stability is easily overrun by too large aliquots of hydrogen or too insensitive equipment. Finally, the double peak was transformed into a single one when the annealing temperature was increased to 129°C (Curve 4). A preliminary conclusion is that a vacuum is not necessary to anneal lattice defects so that the $\beta$-phase no longer forms in the subsequent absorption. But, taking also into account the evidence of similar experiments at higher temperatures and pressures (not reported here), merely high annealing temperatures do not guarantee disappearance of the $\beta$-phase; rather, the difference between the absorption peak temperature and annealing temperature (at prevailing pressure) controls the effectiveness of annealing.

Having successfully erased the $\beta$-phase, the sample was cycled further. Fig. 4 shows gradual reappearance of the $\beta$-phase. This time the transformation from a single peak into a double peak occurred faster than for the fresh sample which indicates that the conditions for the $\beta$-phase formation were more favourable now. In later experiments with air exposed and reactivated samples it was found that the $\beta$-phase reappeared much faster. However, the initial formation of the $\beta$-phase happened always more slowly than in the preliminary experiment (Fig. 1). The reason for this is not quite clear but most presumably it is related to the complicated thermobaric history of that sample.

## 4. Discussion

Desorption occurred always as a double peak having initially formed. It was neither effected by holding

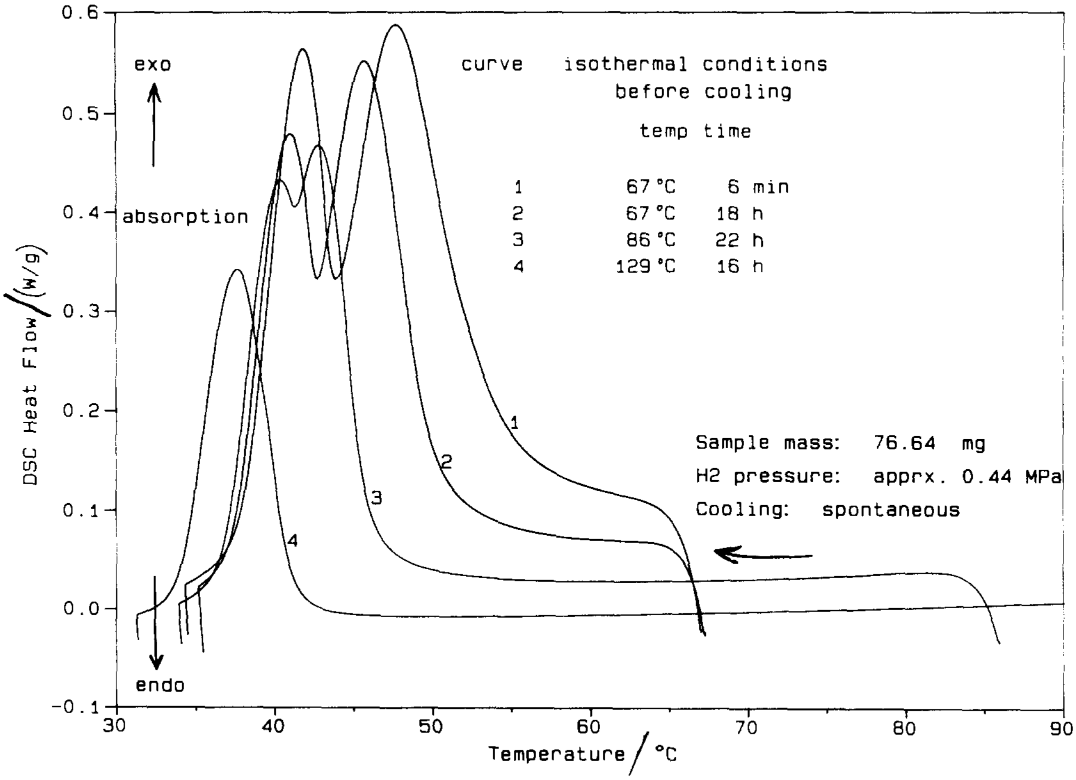

Fig. 3. The effect of low temperature annealing of the dehydrogenated $LaNi_5$ on the subsequent absorption behaviour, isochoric system. Annealing performed in an ascending temperature sequence after 1000 thermal cycles illustrated in Fig. 2 (the same sample as in Fig. 2).

periods at lower end temperature of thermal cycles nor these end temperatures (up to 100°C). Also preceding absorption behaviour had practically no effect upon subsequent desorption. So, it seems that the occurrence of the $\beta$-phase can be modified by annealing the $\alpha$- but not the $\gamma$-phase. It can also be concluded that desorption proceeds easier via the $\beta$-phase than absorption does. Possible explanation could be easier nucleation of the $\beta$-phase in the $\gamma$-phase than in the $\alpha$-phase [7]. Air exposure did not have any effect on the subsequent sorption behaviour, except for the reactivation.

In the light of earlier and present evidence, what actually determines the speed of the $\beta$-phase (re)formation is still unclear, but it could be suggested, supported by the findings of Buckley et al. [7], that the initial formation of the $\beta$-phase takes more time than reformation(s) because lattice defects (dislocations) have to be created and ordered to facilitate the appearance of the new phase. Moderate annealing conditions, on the other hand, are probably sufficient to disorder dislocations causing thus the disappearance of the $\beta$-phase; but most of the defects are still there making it easier for the $\beta$-phase to reappear as only reordering of dislocations will be needed.

Although a PDSC peak is easy to integrate in order to get a numerical value for the heat of a reaction (J/g sample material), it is of no absolute value in the case of metal-hydrogen reactions. This is due to the fact that, in the PDSC, the energy scale is calibrated using the known enthalpy of melting of a metal, for example, indium which means that there is no convective heat transport between the sample and the surrounding gas atmosphere. On the contrary, metal-hydrogen reactions are sorption processes in which the exchange of gas with the local atmosphere is an essential feature of the phenomenon. So, it is very difficult, if not impos-

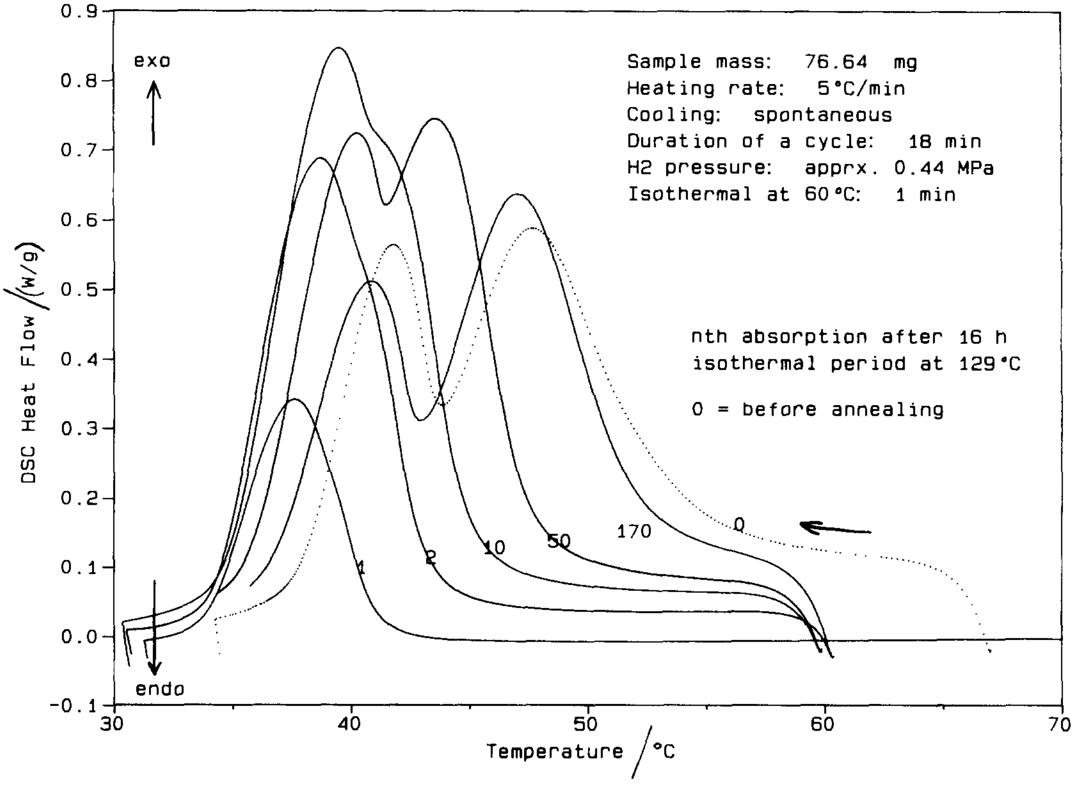

Fig. 4. The effect of further cycling of $LaNi_5$-$H_2$ system on the absorption behaviour after disappearance of the double peak due to annealing treatment, isochoric system (the same sample as in Fig. 2 and Fig. 3).

sible, to calibrate the equipment so that meaningful heats of hydrogenation reactions could be obtained by integrating the peaks.

## 5. Conclusions

Thermal absorption–desorption cycling of the $LaNi_5$-$H_2$ system promotes splitting of both absorption and desorption peaks into double peaks below 60°C. This two stage sorption process appears earlier and is more reproducible in desorption than in absorption. The occurrence of the double peak in absorption depends on the thermal history of the dehydrogenated alloy. Annealing at elevated temperatures erases the double peak from the subsequent absorption. Instead of vacuum, hydrogen atmosphere can be used during annealing. Temperature difference of less than 100°C between absorption peak temperature at prevailing pressure and annealing temperature is sufficient to make the double peak disappear in the following absorption. After disappearance of the double peak due to annealing, thermal cycling makes it reappear. This reformation happens faster than the initial formation.

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