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Calorimetric Identification of a Eutectoid Phase Separation in the $LaNi_5$–H_2 System at $T \approx 350$ K

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The phase behavior of the $LaNi_5$–H_2 system for $305 < T < 430$ K and moderate hydrogen pressures has been studied by use of a heat-conduction calorimeter to measure the thermal desorption characteristics of hydrides which were prepared *in situ*. When the initial hydride composition is in the α–β coexistence range the data show that a eutectoidal phase transition initiates at $T \approx 350$ K. There is no evidence for hydride disproportionation during this process. The phase which is eutectoidally formed has the approximate composition $LaNi_5H_3$. © 1990 Academic Press, Inc.

Introduction

At elevated temperatures, the $LaNi_5$–H_2 system has been reported (*1–6*) to exhibit a phase in addition to the two already shown (*7*) to exist at ambient temperatures for $p_{H_2} < 2$ MPa. There is some variation in the experimental conditions reportedly required for its appearance, and so far it has not been isolated as a single-phase product. The third hydride phase, of approximate composition $LaNi_5H_3$, has been identified in powder diffraction spectra with X-ray (*1, 2*) and neutron (*4, 5*) radiation at $T > 360$ K and its existence supported by a combination of isothermal pressure–composition (p, x) techniques, with simultaneous calorimetry (*3*) at $T = 358$ K. The present study was undertaken to establish the temperature, T_E, of the eutectoidal tie line which is now implied in the phase diagram for $LaNi_5$–H_2. For this purpose, a heat-conduction calorimeter operating in temperature-scan mode has been used to follow the thermal desorption profiles of hydrides prepared *in situ*.

Experimental

The $LaNi_5$ (MPD Technology Corp.) was analyzed as $LaNi_{5.00\pm0.01}$ with better than 99.8 at.% metallic purity and with oxygen present at less than 2000 ppm atomic. The hydrogen (Matheson grade) had, nominally, less than 5 ppm atomic impurity.

The calorimeter (Setaram, France) was of the twin-cell, differential heat-conduction type. Inserted into the calorimeter were a pair of stainless-steel cells, one for containment of the $LaNi_5$ samples and the other to hold a nonreactive reference material, stainless-steel rods, which served to balance the thermal capacity of the two cells. In consequence, the close similarity in heat flow, via the thermopiles, between the calorimeter block and each cell during

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temperature scan, results in the favorable condition of there being only a small net thermopile signal from the calorimeter in the absence of events attributable to the sample. The cells were attached to a thermostated stainless-steel gas handling manifold to facilitate the preparation of hydrides by gas titration. Some other technical details of the apparatus have been previously reported (*8*).

Activation of $LaNi_5$ was achieved by H_2 absorption/desorption cycling, *in situ*, until two successive absorption cycles showed identical composition limits and uptake kinetics. This was accomplished in less than six cycles at ambient temperature and p_{H_2} = 1 MPa. From the activated material, hydrides with accurately known compositions within the β range ($x \approx 6.5$) were prepared at $T = 306$ K. The hydrogen content was then adjusted by stepwise desorption to give a known composition within the α–β coexistence region. After the preparation procedure, the system (i.e., reactors, hydride, and manifold) was closed and the hydrogen inventory remained unchanged through the remainder of the experiment. For temperature scanning, the calorimeter block temperature was increased at a selected rate between 3 and 5 K h^{-1}. Cooling rates were between -5 and -1 K h^{-1}. During the temperature changes, the resulting variation in hydride composition produces a change in pressure within the isolated system. The quantity of hydrogen in the gas phase, and hence that which remains in the hydride, can be calculated. Care must be exercised when assigning effective reactor volumes for this calculation. The thermal gradient of the system is changing continuously during the temperature scan, and the effective volumes have been measured in calibration experiments where the hydride is replaced by an inactive material of equal volume and the scan conditions duplicated.

In order to follow different (x, T) paths through the two-phase field, the system volume was altered by changing a standard volume which was attached to the isothermal manifold. Temperature scanning was then repeated. As an indication of the typical experimental conditions, for a sample mass of ≈6 g, the total system volumes were about 70 and 170 cm^3, and lower and upper temperature limits during scans were approximately 305 and 430 K. The hydrogen pressures at 430 K were approximately 1.4 and 2.7 MPa, for the larger and smaller system volumes, respectively.

Results and Discussion

Shown in Fig. 1 are two (q/t, T) curves obtained during temperature scanning of $LaNi_5H_x$ at 4 K h^{-1}. Each hydride was prepared from the same precursor $LaNi_5$ sam-

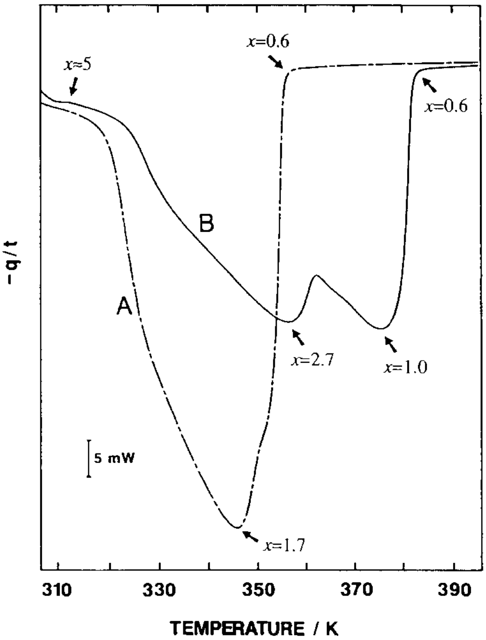

FIG. 1. Calorimetric response curves for the thermal desorption of $LaNi_5H_x$, shown as thermopile-power output (q/t) vs temperature. The scan rate was 4 K h^{-1} and curves A and B were obtained for large and small system volumes, respectively. The overall hydride composition at several stages during desorption is also shown.

ple and had an initial composition $x \approx 5$. Since the hydride is decomposing with increasing temperature, these curves do not represent constant pressure data. The curves shown are representative of all the measurements made with duplicate $LaNi_5$ samples, including data obtained with hydride repreparations from the same $LaNi_5$ sample after it had been dehydrided *in situ*. Measurements which were made at a given system volume were also reproducible after a sequence of temperature scan data was obtained at the alternate system volume. Thus, there is no calorimetric evidence which suggests that irreversible processes are occurring. Following the measurements, powder x-ray diffraction spectra of the product showed no reflections which would be indicative of disproportionation. In this regard it should be noted that during the scan, $LaNi_5H_x$ enters the α-phase at $T \approx 383$ K or $T \approx 355$ K for small and large volumes, respectively, so that the current experiment avoids any sample simultaneously experiencing high T and x, a combination of conditions which commonly have been found to favor disproportionation mechanisms of the hydride (*9, 10*).

The form of the curves (Fig. 1) is dictated by the quantity of heat (q) passing to or from the sample as the hydride undergoes a composition change, dx. In the case shown for increasing temperature, hydrogen desorption is occurring, this being an endothermic process. The existence of a minimum in the curves does not uniquely define a structurally significant composition or property. These features are the result of a number of factors which include, but are not limited to, ΔH for the reaction, $d(\Delta H)/dx$, dx/dT, and the accelerating kinetics, d^2x/dt^2, with increasing T. Which component predominates as a contributor to the measured q will vary with T and x. Note, however, that for the hydrides studied here: in two-phase regions $d(\Delta H)/dx$ is constant and large and dx/dT is large and, consequently, so is $|q|$; in single-phase regions $d(\Delta H)/dx$ is variable and smaller at the phase boundaries and dx/dT is small.

The data are interpreted in conjunction with the proposed phase diagram shown in Fig. 2, which also shows the approximate (x, T) paths followed by the samples in the two cases. The system volume for curve A was larger than that for curve B, so that (dx/dT) is also different for the two cases, and the α-phase for A is entered at a lower temperature. For A, the composition path which is followed remains within the α–β field throughout until the α-phase is entered. Consequently, curve A (Fig. 1) shows the continuously increasing endothermic effect (as dx/dT increases) of β to α conversion which reaches minimum $-q/t$ at $x \approx 1.7$ just prior to rapid entry to the α-region. The latter process is completed by $x = 0.6$ where dx/dT diminishes and, consequently $|q|$ is small. Curve B (Fig. 1) shows two principal features, with minima in $-q/T$ at $x \approx 2.7$ and $x \approx 1$, the latter just preceding rapid entry into the α-phase which again is complete by $x = 0.6$.

For case B the composition path passes through two two-phase fields, separated by the eutectoid tie line at T_E. The first of the

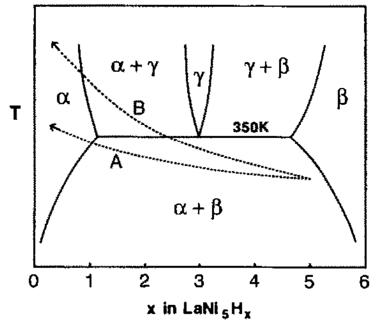

FIG. 2. Proposed phase diagram for the $LaNi_5$–H_2 system ($p_{H_2} < 3$ MPa) for T close to T_E. Phase boundary positions are approximate, but are also consistent with other data (*3*). Broken curves represent the composition paths followed by a desorbing hydride for the two system volumes used.

features observed is due to the continuing endothermic process of $\beta \Rightarrow \alpha$ conversion, and the second due to continuing $\gamma \Rightarrow \alpha$ conversion. The ΔH for each of these processes, which have been measured calorimetrically (*3*, *11*), are 31.8 and 30.7 kJ (mole H_2)$^{-1}$, respectively. At the eutectoid tie line, the overall reaction occurring is the three-phase process $\beta \Rightarrow \alpha + \gamma$. This process is exothermic, with $\Delta H = -1.1$ kJ (mole H_2)$^{-1}$, as calculated from the difference in enthalpies of the corresponding pairs of two-phase conversions listed above. The magnitude of the total q associated with the conversion is governed by the proportion of the sample remaining as β-phase immediately preceding the crossing of the eutectoid tie-line. The event thus appears in $(-q/t, T)$ as a reversal of the slope, and the separation of the two endothermic features is due to the continuing exothermic process of $\beta \Rightarrow \alpha + \gamma$.

The onset of the eutectoidal transition is not clearly delineated. At $T = 355$ K, the exothermic event has become dominant, and by $T = 362$ K the change in sign of $d(-q/t), dT$ indicates that the exothermic reaction is either complete or continuing only at a slow rate. The former temperature appears to define the upper bound value of T_E. However, evidence for the onset, at a significantly reduced conversion rate, is the deviation of $d(-q/t)/dT$ from linearity and with a less negative slope, prior to $T = 355$ K. This is selected at $T = 350$ K. The range in temperature over which the conversion persists, even with the slow scan rates used here, is a reflection of the sluggish kinetics found generally (*12*), for eutectoid systems where the rate-determining step is dependent upon a solid–solid diffusion mechanism. This value for T_E is consistent with the isothermal (p, x) data reported previously (*3*) for $T = 358$ K, a temperature at which both two-phase regions have been shown to exist.

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