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HIGH PRESSURE DIFFERENTIAL THERMAL ANALYSIS OF THE LANTHANUM NICKEL–HYDROGEN SYSTEM

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ABSTRACT

A high pressure differential thermal analysis apparatus is described which is capable of operation in the pressure range from 1–680 atm of hydrogen at temperatures from 20 to 900°C. This system has been used to investigate the $LaNi_5$–H_2 system from 1–200 atm.

INTRODUCTION

Several high pressure differential thermal analysis (DTA) systems designed for use with high pressure gases have recently been described in the literature[1–11]. The system described here was developed by one of the authors (R. P. W.) for studying gas–solid reactions at pressures up to 680 atm and sample temperatures from 20 to 900°C. Its operation was demonstrated by investigating the reaction of hydrogen with $LaNi_5$. In general, hydrogen reacts with a number of elements and alloys to form hydrides with relatively high heats of formation. The DTA system described here allows the hydride to be formed or decomposed by changing either pressure or temperature while keeping the other parameter constant. During the course of this investigation, it was found that sample passivation prevented direct measurement of thermodynamic variables such as enthalpy of reaction. C. J. N. determined an indirect method by which these variables could be determined.

Van Vucht et al.[12] observed that $LaNi_5$ can absorb large quantities of hydrogen, yet the dissociation pressure at room temperature is ~3.0 atm. Their measurements were made from 21 to 81°C at hydrogen pressures from 1 to 50 atm. Using pressure–temperature-composition (PTC) measurements they obtained a heat of formation of -20.9 kcal mol^{-1} and could determine the composition as a function of pressure and temperature. The present study extends the measurements on the $LaNi_5$ system to 250°C and 200 atm.

EXPERIMENTAL

Description of the apparatus

A schematic diagram of the DTA apparatus employed in these studies is shown in Fig. 1. It consists of a high pressure DTA cell, a pressure measuring system (not

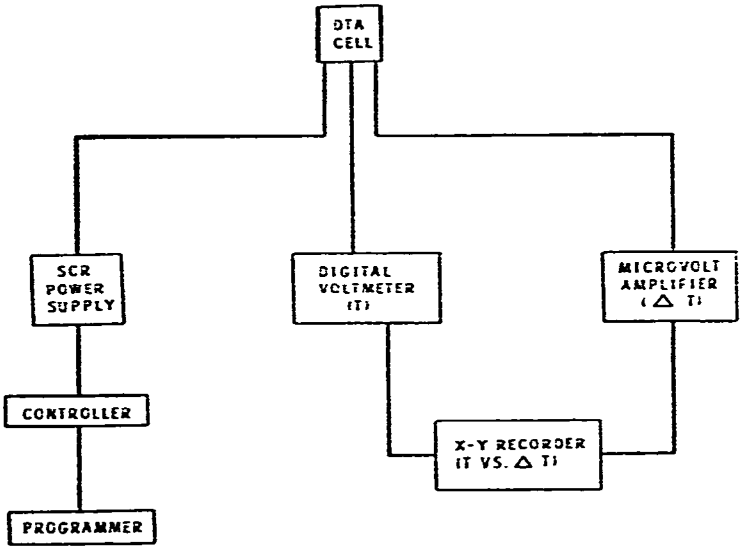

Fig. 1. Differential thermal analysis sytem layout.

shown in Fig. 1), a programmed furnace system, a module for measuring sample temperature, a differential amplifier and recording system. Details of the construction of the high pressure DTA cell are shown in Fig. 2. The pressure vessel is constructed of 316 stainless steel with high pressure electrical feedthroughs mounted in the base. The vessel is water-cooled by external coils and heated internally by a furnace constructed of iridium wire wound on an alumina form (Westgo Al 995). Inside the

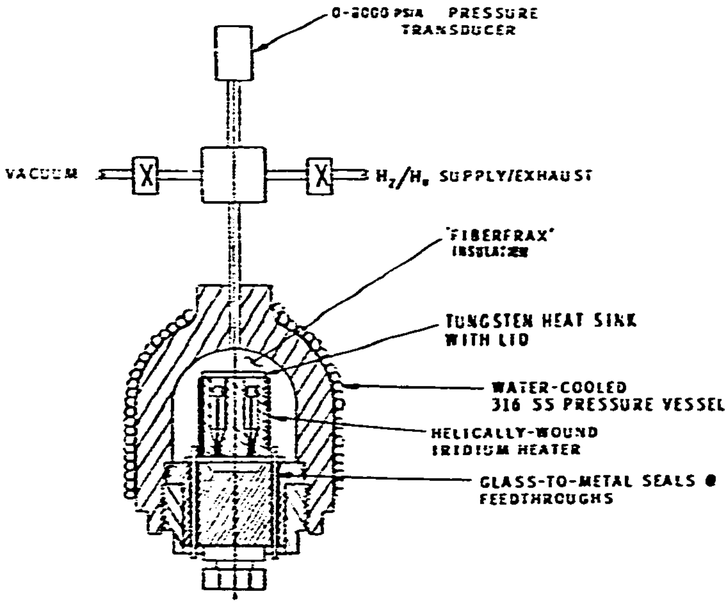

Fig. 2. Differential thermal analysis cell construction.

tubular furnace is a tungsten heat sink to provide uniform heating of the samples. The platinum reference and sample containers are 5 x 5 mm diameter cups welded to the thermojunctions of the chromel–chromel/alumel thermocouples. The cups can be protected with thin, matched liners made of an appropriate metal or ceramic if the material being investigated is highly reactive. Final closure of the vessel is made by torquing the mating parts and crimping a gold-plated copper O-ring.

The pressure is sensed by a Fairchild pressure transducer (Model TF150) and read on a digital voltmeter. The pressure transducer was found to be accurate to 0.5 atm. By minimizing the free gas volume in the hot zone of the DTA cell and using a pressure reservoir, the temperature can be cycled with less than a 5% change in the overall gas pressure.

A Data-Trak temperature programmer (Research Inc. FGE-5110) driving an Electromax III (Leeds & Northrup) current adjusting controller which in turn drives an SCR, provides temperature control for the system. The output of the SCR is ballasted with a variac which powers the sample furnace. The Data Trak gives a great deal of flexibility in selecting heating rates, ultimate temperatures and the cycling modes necessary to obtain reproducible sample response.

The sample temperature is measured with a chromel–alumel thermocouple and monitored with a digital readout (Numatron, Leeds & Northrup). The temperature response of the system was calibrated using standards (In, S) with known transition temperatures and enthalpies. The temperature difference (ΔT) between the reference and sample is amplified with a stabilized DC microvolt amplifier (Leeds & Northrup 9835B) and recorded with an X–Y recorder (Hewlett-Packard, 2 Fram).

The apparatus is pumped to pressures as high as 680 atm using a two-stage diaphragm pump (American Instruments Co., 46-14021 SP). All tubing and valves are commercially available, 316 stainless steel high-pressure equipment. Because of the potential explosive yield of the high pressure hydrogen, the DTA apparatus was located in a blast cell and experiments were conducted remotely.

Materials

The $LaNi_5$ samples used in these measurements were made by the Battelle Laboratories, Columbus, Ohio, under contract to the AEC. X-ray analysis showed the starting material to be single phase $LaNi_5$ within the limits of detectability. Bulk samples were weighed ($\sim$160 mg) and loaded for analysis. A corresponding amount of Al_2O_3 (based on the relative specific heats) was used for a reference material.

The hydrogen was obtained from Matheson Gas Products (Gold Seal, 99.999%). All lines and vessels were evacuated, flushed with pure helium, and evacuated again prior to admitting hydrogen.

Experimental procedure

In a typical run, the DTA cell was evacuated, pressure checked with purified helium and then evacuated again. The hydrogen was admitted and the pressure slowly raised until the sample reacted with the gas. This was easily detected by a sudden, large ΔT output on the X–Y recorder. It was found that both high pressure and temperature cycling were sometimes necessary to obtain an active sample that yielded repeatable results. The $LaNi_5$ bulk sample forms a very fine powder in situ after it has reacted with hydrogen. The fine powder minimizes problems with the kinetics of the reaction and provides a large active surface area. The initial hydriding of a sample of $LaNi_5$ typically occurs near 20 atm at room temperature. It is believed that this higher pressure is needed to break up the surface oxide film on the bulk material.

Typical thermograms obtained for $LaNi_5$ samples at different pressures and temperatures are shown in Fig. 3, each representing 15 separate tests. Heating rates from 5 to 10°C min^{-1} were normally used. The thermograms indicate that the onset of a peak shifts depending on whether the sample is being hydrided or dehydrided. This shift corresponds to the slight slope in the pressure-composition isotherms of the $LaNi_5$–H_2 system, as shown in Fig. 6, and to the slightly increased DTA cell pressure when the sample is in the cooling cycle. Two peaks are observed for the reaction at lower temperatures and pressures. These peaks are most probably an indication of two different surface conditions in the sample since the thermograms also give an indication of the kinetic processes of the reaction in addition to the temperature of the phase transition. The peaks are repeatable for a given pressure and temperature range

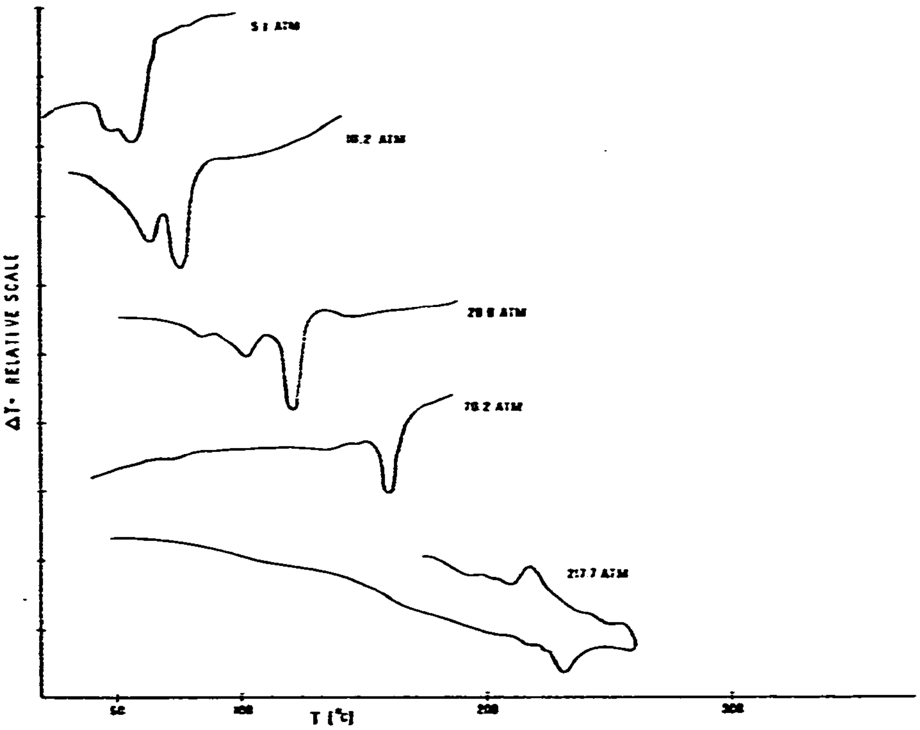

Fig. 3. Thermograms for $LaNi_5$ (162.7 mg of sample). Temperature is plotted vs. ΔT at several pressures for the case of dehydriding.

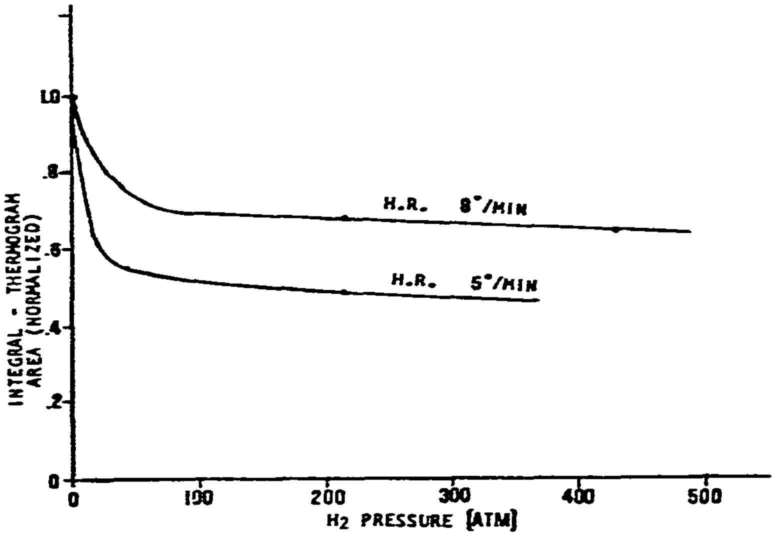

Fig. 4. Thermogram correction curves.

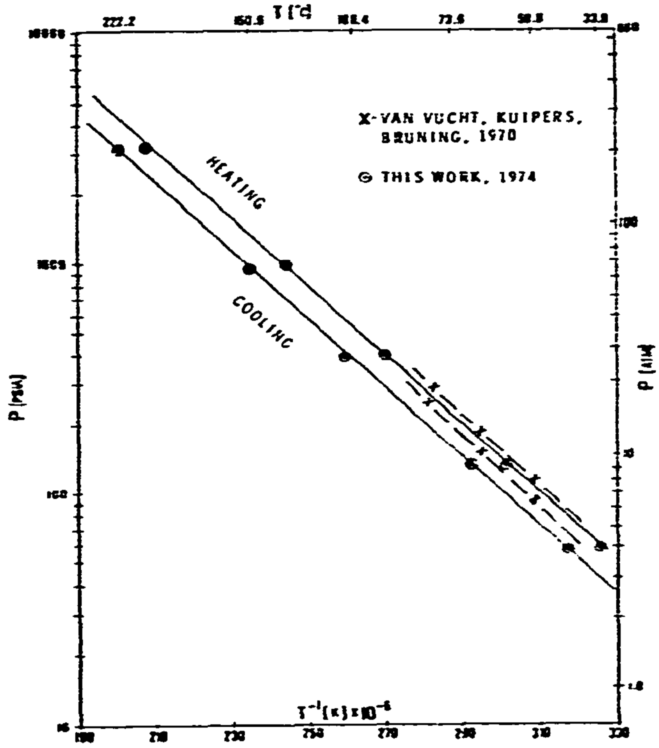

Fig. 5. Temperature for dehydriding and rehydriding as a function of pressure for LaNi$_5$.

but are reduced in area as the pressure and temperature are increased. Beyond 270 atm and 500 °C, the sample was irreparably changed so that it failed to respond to hydrogen at any pressure or temperature. The change in thermogram area with pressure was determined for indium and could be used to discriminate between equipment response and sample behavior (Fig. 4). It was found that the gradual reduction in the magnitude of the hydride peak corresponded to a decrease in the sample's ability to respond to hydrogen. It is postulated that the sample is increasingly oxidized from trace amounts of oxygen contained in the vessel as the temperature necessary to dissociate the hydride is increased (with increasing pressure).

If the temperatures for the onset of the phase transformation are plotted in a Van't Hoff plot (Fig. 5) they form straight lines and a least squares fit yields the following relations:

$$\text{Heating:}\quad \log P\,(\text{atm}) = \frac{-1480.0}{T\,(\text{K})} + 5.44 \tag{1}$$

$$\text{Cooling:}\quad \log P\,(\text{atm}) = \frac{-1477.0}{T\,(\text{K})} + 5.30 \tag{2}$$

The small differences between eqns (1) and (2) reflect the fact that the two-phase region of the phase diagram is following the Gibbs phase rule and the pressure is relatively constant across the two-phase plateau for a given isotherm. Small changes in plateau pressure such as these may be the result of temperature gradients in the sample and/or impurities in the sample.

Several pressure–composition isotherms are shown for a hypothetical hydride in Fig. 6. If this hydride is initially at room temperature and some pressure P, and is heated, the sample follows the dashed line from A to D. When the sample arrives at the temperature T_1 (point B), the rapid endothermic dissociation of the hydride occurs converting the sample to the metal phase. Because the kinetics of the reaction and thermal lags in the system may obscure the point at which the sample first arrives at the phase boundary between the metal and two-phase material (point C), this point may not be determined accurately until the cooling cycle. On cooling the sample to point C (corresponding to T_2), the rapid exothermic hydriding reaction is observed. Thus, using both the heating and cooling portions of the cycle, both phase boundaries can be determined. Note that in the two-phase region the pressure is almost constant for a given temperature over a wide range of stoichiometries. This is true until the critical temperature (T_c) is reached, above which no phase-change peaks are observed and the pressure changes rapidly with composition for a given temperature.

The integral form of Van't Hoff's equation (eqn (3)) may be derived for the pressure–temperature relation for a given composition.

$$\ln P\,(\text{atm}) = \frac{2}{(r''-r)R}\left(\frac{\Delta H}{T\,(\text{K})} - \Delta S\right) \tag{3}$$

Since the pressure is almost constant across the two-phase plateau (Fig. 6) this relation

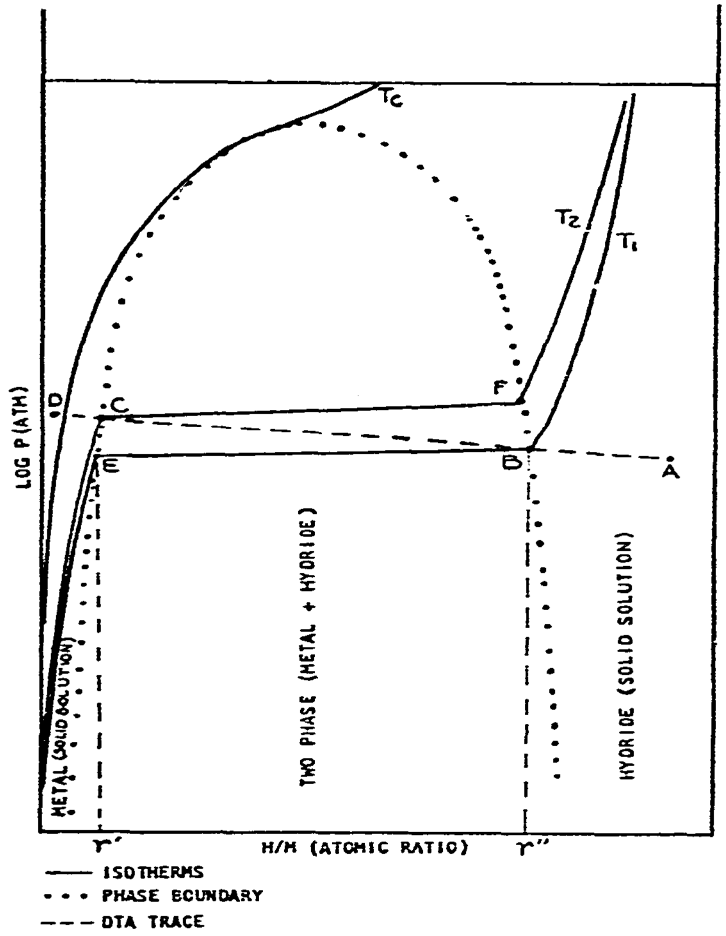

Fig. 6. Pressure–composition isotherms for a hypothetical hydride.

can be applied to the quasi-equilibrium conditions in the two-phase region at phase boundaries to determine the enthalpy (ΔH) and entropy (ΔS) of formation. Using Van Vucht's[12] measurements at 21 °C for the end-point composition ($r''-r'$) of the tie line (corresponding to atom ratios at the points B and E in Fig. 6), a least squares fit gives:

$$\text{Heating} \quad \begin{aligned} \Delta H &= -19.6 \pm 0.7 \text{ kcal mol}^{-1} \\ \Delta S &= -72.0 \pm 2.0 \text{ cal mol}^{-1}\text{ K}^{-1} \\ \Delta G_{298} &= 1.9 \pm 1.0 \text{ kcal mol}^{-1} \end{aligned}$$

$$\text{Cooling} \quad \begin{aligned} \Delta H &= -19.6 \pm 0.6 \text{ kcal mol}^{-1} \\ \Delta S &= 70.0 \pm 1.0 \text{ cal mol}^{-1}\text{ K}^{-1} \\ \Delta G_{298} &= 1.4 \pm 1.0 \text{ kcal mol}^{-1} \end{aligned}$$

These values compare favorably with Van Vucht's equilibrium, lower temperature, PCT measurements of

Right side of	$\Delta H = -20.0$ kcal mol^{-1}
two-phase plateau	$\Delta S = -73.0$ cal mol^{-1} K^{-1}
(heating)	$\Delta G_{298} = 1.9$ kcal mol^{-1}
Left side of	$\Delta H = -20.2$ kcal mol^{-1}
two-phase plateau	$\Delta S = -73.0$ cal mol^{-1} K^{-1}
(cooling)	$\Delta G_{298} = 1.5$ kcal mol^{-1}

Here the Gibbs free energy has been determined from standard thermodynamic relations.

When the area under the thermogram peaks was integrated and the heat of reaction determined by comparison with the indium heat of melting, it was found that only a fraction of the $LaNi_5$ sample (20%) was undergoing a reaction with hydrogen. Apparently even at lower temperatures much of the sample was not "activated" and had not reacted with the hydrogen. If the common technique of determining the integral of the peak of the hydriding reaction and comparing it to a standard had been used, the results for the heat of formation would have been erroneous. But by varying both pressure and temperature, Van't Hoff's equation can be employed to produce more reliable values for the thermodynamic potentials.

CONCLUSIONS

Differential thermal analysis can be a useful tool in determining qualitative properties of hydrides. Combining the DTA with high-pressure equipment increases its flexibility and permits investigations on the activation procedures necessary to make some materials respond to hydriding. In addition, basic thermodynamic data can be obtained when the DTA results are combined with limited PCT information.

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