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Hydrogen sorption in $LaNi_{4.98}Al_{0.02}$–H_2 at low temperatures

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Abstract

The $LaNi_{4.98}Al_{0.02}$–H_2 system has been investigated under atmospheres of hydrogen and inert gas (Ar) by differential scanning calorimetry (DSC). The effect was shown of hydrogen isothermal sorption temperature on the amount of hydrogen being sorbed and on sorption onset time. The dependence of partial molar enthalpy on hydrogen content in the intermetallic compound (IMC) was defined.

INTRODUCTION

This study is a continuation of that described in a previous paper by the same authors [1]. Thermodynamic characteristics of the hydrogen sorption processes have already been obtained for the $LaNi_5$–H_2 system by means of reaction calorimetry [2–7], but all these data were obtained for temperatures above 273 K or even near room temperature.

The aim of this work was to investigate sorption–desorption processes in the $LaNi_{4.98}Al_{0.02}$–H_2 system under elevated hydrogen pressures in the low temperature region by means of the differential scanning calorimeter (DSC) using a thermoconductometric apparatus for determination of the hydrogen evolved. This method allowed us to obtain the dependence of the partial molar enthalpy of hydrogen dissolution on its content in the hydride, and was used for the La-containing system for the first time.

EXPERIMENTAL

The samples of the intermetallic compound (IMC) were prepared by melting together stoichiometric quantities of the high-purity metals in a vacuum furnace with radiative heating. The homogeneity of the samples was confirmed by X-ray diffraction, and the stoichiometry of the samples was checked by chemical analysis.

Experiments on hydrogen sorption–desorption were conducted in the DSC 910 high-pressure cell of the TA 990 instrument (Du Pont, USA). The

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calibration of the DSC cell was based on the thermal conductivity of sapphire and the heats of melting of ultrapure metals (Ga, In and Sn), which allowed the calibration factor of the instrument to be obtained.

The relative quantities of hydrogen evolved from the hydride were determined by connection of the outlet from the DSC cell to the thermoconductometric detector of a Tsvet-110 chromatograph (USSR). Argon was used as carrier gas. This method has been described elsewhere [8] for Zr- and Hf-containing systems.

A previously used IMC was activated by heating under hydrogen at a pressure up to 1.6–2.0 MPa, followed by 2- to 3-fold cycling. The sample mass was ≈ 100 mg. Hydrogen isothermal adsorption was carried out at 1 MPa on a sample from which gas had first been desorbed under argon by heating to 450–550 K at a rate of 5 K min^{-1}, and then cooling to the prescribed temperature before admitting hydrogen into the cell. The hydrogen pressure was maintained with a precision of better than $\pm 1\%$. The hydrogen was purified by diffusion through membranes of a palladium alloy, thus ensuring a purity no worse than 99.99999%. Hydrogen desorption from the hydride IMC was conducted in an argon flow at a heating rate of 5 K min^{-1}.

RESULTS AND DISCUSSION

An IMC specimen pre-degassed by heating under argon (as described above) was cooled to a prescribed temperature and hydrogen was introduced under isothermal conditions (the temperature being maintaining constant to 0.1 K). After a certain time, the so-called sorption induction period, an intensive exo effect was observed, the value of which decreased with sorption temperature and was in the range of 130–300 J g^{-1} IMC (Fig. 1). The hydrogen sorption induction period is a linear function of isothermal sorption temperature, and increases with decreasing temperature from 3 min at 254 K to 4.2 min at 240 K. The total time required for sorption to proceed can be evaluated as 2–4 min, and is practically independent of sorption temperature. It should be noted that, at room temperature, interaction starts virtually at the instant hydrogen is introduced into the system. The amount of hydrogen sorbed (as from the data on desorption in an inert gas) decreases with increasing sorption temperature. Methodological limitations of the low-temperature experiment carried out here did not allow the sorption temperature to be decreased below 230 K, and it does not seem possible to draw any conclusions concerning the threshold temperature of interaction between $LaNi_{4.98}Al_{0.02}$ and H_2 as was done in refs. 9 and 10.

The alternative ΔH curve calculated according to equations from ref. 11 is shown in Fig. 2. It is evident that a satisfactory correspondence between calculated and experimental data exists.

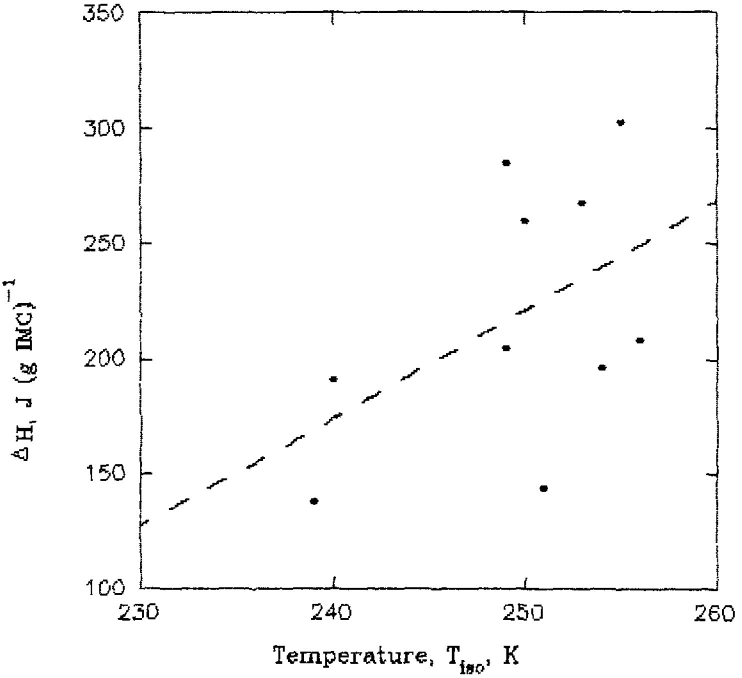

Fig. 1. Temperature dependence of ΔH (J g^{-1} IMC) of isothermal hydrogen sorption.

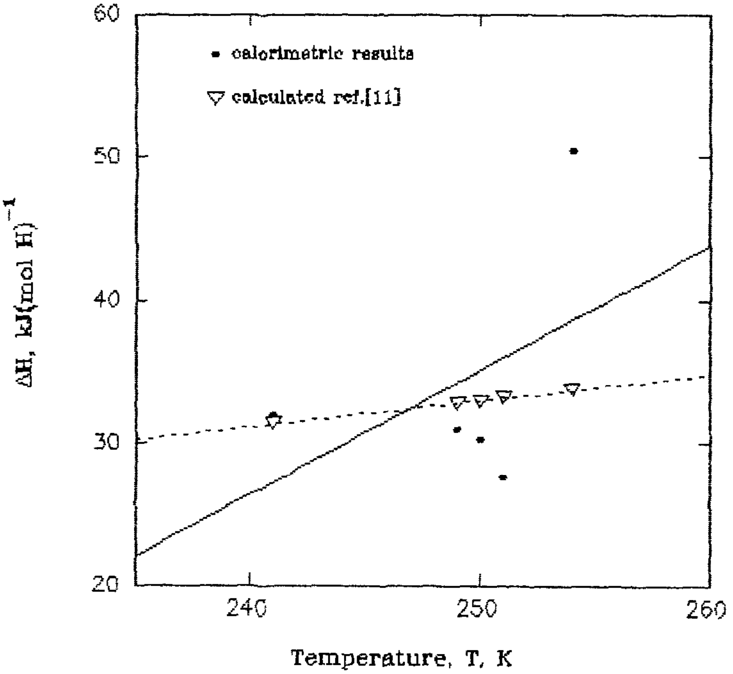

Fig. 2. Dependence of hydrogen desorbed from hydride IMC (n) in argon on temperature of isothermic hydrogen sorption.

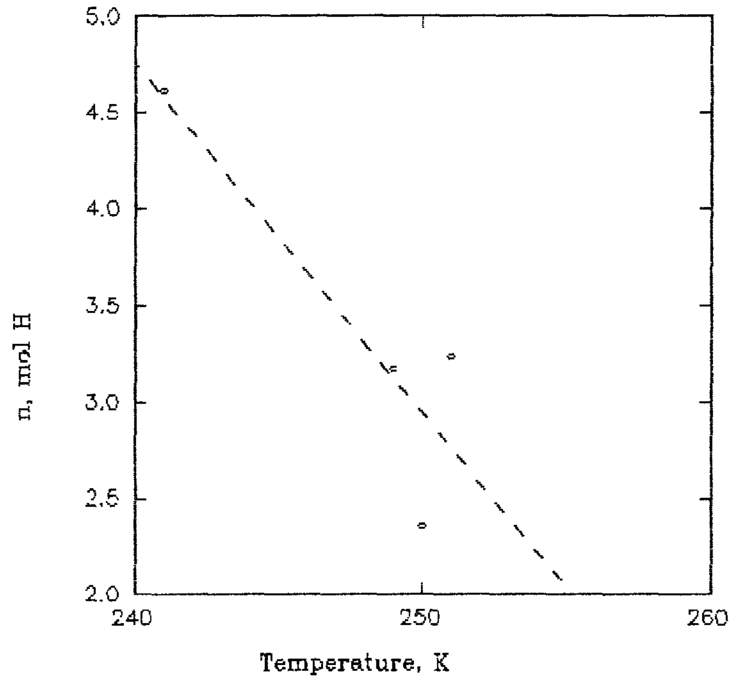

Fig. 3. Dependence of ΔH (kJ mol^{-1} H) of hydrogen desorption in argon on hydrogen content in $\mathrm{LaNi}_{4.98}\mathrm{Al}_{0.02}$.

As mentioned above, the amount of sorbed gas increases with decreasing hydrogen isothermal sorption temperature, this being attended by a decrease in integral enthalpy (Fig. 3).

In Fig. 4, the DSC and evolved gas analysis (EGA) curves are presented which were obtained in the desorption of hydrogen from IMC hydrides in an argon atmosphere. Hydrogen evolution from a hydride is accompanied by absorption of heat.

The dependencies of the partial molar enthalpy of hydrogen dissolution on its content in the IMC, calculated as presented in ref. 8, are shown in Fig. 5. The relationship is independent of hydrogen sorption temperature. In the α-solution region, a sharp decrease in the value of the partial molar enthalpy of hydrogen dissolution is observed, whereas the hydrogen content in the IMC increases, which corresponds well with the results of researches on this system [2–5]. The decrease $|\Delta \bar{H}_{\mathrm{H}}|$ in the α-solution region indicates that, in this region of hydrogen content, repulsive forces will appear between the hydrogen atoms and will cause an even distribution of atoms in the metallic matrix of the IMC. In the region of $0.2 < n < 0.4$ compositions (i.e. near the boundary of the α- and $\alpha + \beta$-regions), a discontinuity was found in the dependence of the partial molar enthalpy, which is connected with a phase transition.

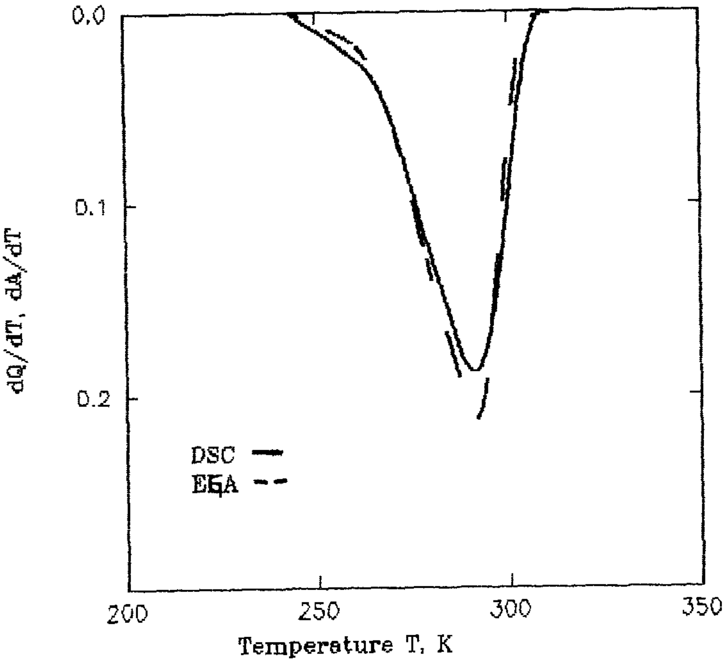

Fig. 4. Hydrogen desorption from $LaNi_{4.98}Al_{0.02}-H_2$ in argon (DSC, solid line; EGA, broken line). Temperature of isothermal sorption 241 K.

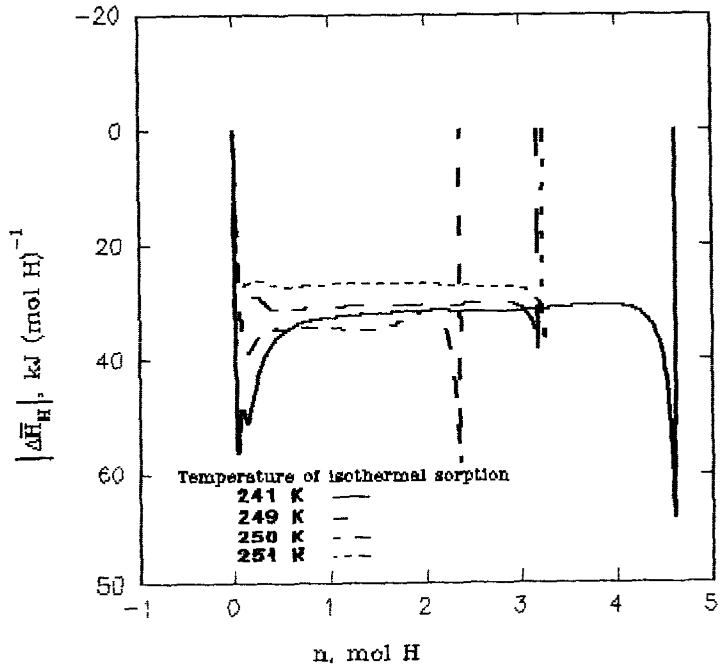

Fig. 5. Partial molar enthalpy of hydrogen desorption from $LaNi_{4.98}Al_{0.02}-H_2$.

After the formation of the α-solution, during further saturation with hydrogen, a certain constancy of $|\Delta \bar{H}_H|$ is observed [25–35 kJ mol^{-1} H, depending on the hydrogen sorption temperature]. In the region near the boundary of the $\alpha + \beta$- and β-hydrides, a discontinuity of the dependence of $|\Delta \bar{H}_H|$ vs. n is also observed. When the β-hydride phase is formed, $|\Delta \bar{H}_H|$ increases.

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