

LaNi₅ hydride formation. The effect of the thermal conductivity of the holder on the kinetics

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Abstract

Samples of LaNi₅H₆ were synthesized in a high-pressure thermobalance; several sample containers were used, differing in shape, lateral surface and thermal conductivity. Comparative studies were made using thermal analysis. Experimental results show that a large lateral surface of the sample holder improves the heat transfer. In the case of the other holders, the temperature variations are important and experiments cannot be carried under isothermal conditions.

INTRODUCTION

Intermetallic compounds, and LaNi₅ in particular, absorb large amounts of hydrogen under moderate conditions of temperature and pressure. The exothermic formation of LaNi₅ is accompanied by an important energy production. As shown previously [1], during the reaction, the effective sample temperature is different from the imposed temperature of the furnace. This difference is about 20 K when 300 mg of LaNi₅ are hydrided and is always less than 2 K in the case of a sample mass smaller than 30 mg. Earlier, Suda et al. [2], and Goodell and Rudman [3] reported the experimental procedures used to enhance heat transmission through metal hydride beds. According to these authors, kinetic results can be obtained from experiments carried out using about 5 mg samples under isothermal conditions ($\Delta\theta < 10$ K). This paper reports some experimental results in order to clarify the effects of sample temperature changes on the hydriding

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TABLE 1
Thermal conductivities

Material	Thermal conductivity/ ($\text{J m}^{-1} \text{s}^{-1} \text{K}^{-1}$)	Material	Thermal conductivity/ ($\text{J m}^{-1} \text{s}^{-1} \text{K}^{-1}$)
Plexiglass ^a	0.21	Hydrogen gas	0.18
Stainless steel	30	LaNi ₅	0.48 [5]
Copper	358		

^a Plexiglass: methyl polymethacrylate (PMMA).

kinetics. First, the studies were carried out using sample holders characterized by very different thermal conductivities, see Table 1. Then, in order to modify the heat quantity produced, experiments were carried out with increasing sample masses from 70 to 300 mg. In conclusion, the influence of these heat transfer modifications on the hydriding kinetics and, in particular, on the shape of the experimental curves, is analysed.

APPARATUS AND SAMPLES

Mass measurements are carried out in a high-pressure (0–1 MPa) microbalance with a limiting accuracy of $1 \mu\text{g}$. The device was constructed from a Setarm MTB 10-8 symmetrical beam-zero balance. For the thermogravimetric experiments, the temperature was recorded on a chromel–alumel thermocouple located just beneath the sample holder. In order to determine the sample temperature changes throughout the experiment, two thermocouples were used: one in the LaNi₅ bed and the other in an inert powder. A temperature gradient indicated the temperature difference between the two samples. The sample holder is a cylindrical flat-bottomed cup, 0.5 mm thick and 5 mm deep with a diameter of 10 mm. Other holders have the cross-section shown in Fig. 1b; the large lateral surface ensures a maximum heat exchange with the surrounding gas phase. These holders were machined from materials such as stainless steel, copper or plexiglass.

The LaNi₅ compounds were prepared by induction melting of the pure

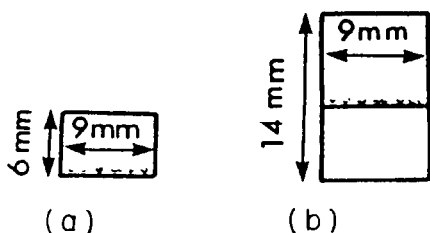


Fig. 1. Holder schemes: (a) small holder; (b) holder with large lateral surface.

components in a vacuum. Pellets of about 200 mg were scattered in the holder; then they were covered with silica wool so that sample particles could not be ejected from the holder during the explosive fragmentation of LaNi_5 . The LaNi_5 samples were activated by performing about twenty absorption–desorption cycles ($T = 313 \text{ K}$, $P_{\text{H}_2} = 1.5 \text{ MPa}$) in order to pulverize the LaNi_5 samples to a homogeneous grain size ranging from 10 to $20 \mu\text{m}$.

EXPERIMENTAL RESULTS

The effect of the holder (material and shape)

Hydride formations were carried out at 294 K with an activated sample of LaNi_5 under different hydrogen pressures. Figure 2 shows the sample temperature changes with respect to time. The curves all show a maximum which varies with the holder material: curve a, copper with a large surface area; curve b, copper; curve c, stainless steel; curve d, plexiglass. The

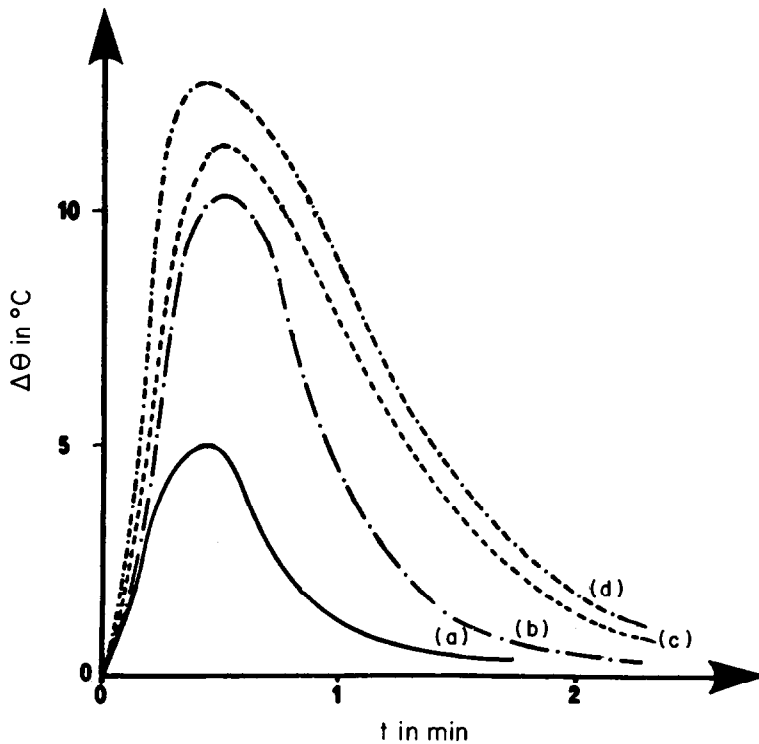


Fig. 2. Temperature change versus time: curve a, copper holder with large lateral surface; curve b, copper holder; curve c, stainless steel holder; curve d, plexiglass holder. ($T_i = 294 \text{ K}$; $P_i = 0.5 \text{ MPa}$.)

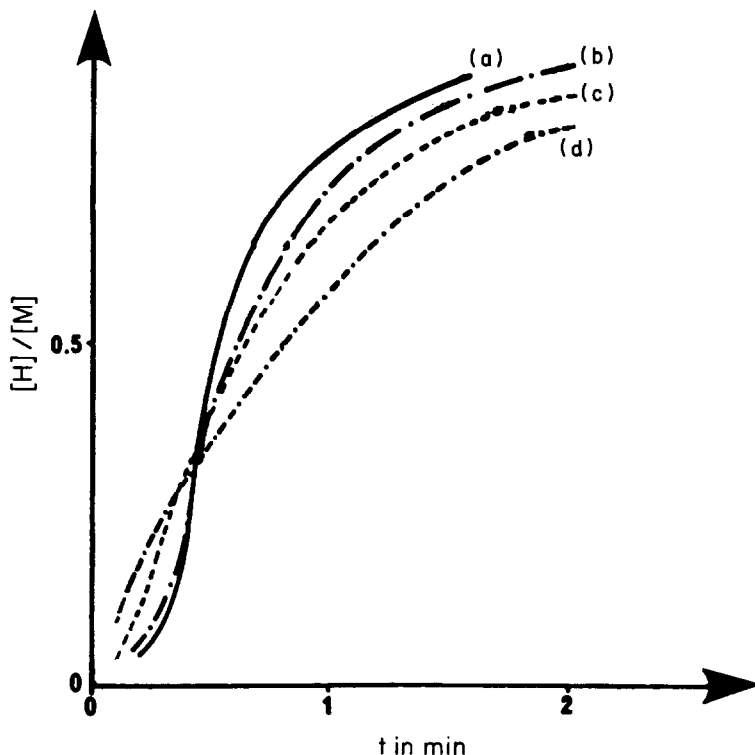


Fig. 3. LaNi_5 hydrogen concentration versus time: curve a, copper holder with large lateral surface; curve b, copper holder; curve c, stainless steel holder; curve d, plexiglass holder. ($T_i = 294 \text{ K}$; $P_i = 0.9 \text{ MPa}$.)

temperature increase is large with the classical sample holders, irrespective of the thermal conductivity of the holder. In the case of the copper holder with a large lateral surface area (curve a), the temperature change is reduced by a factor of 2.

Figure 3 shows the LaNi_5 hydrogen concentration versus time. In the first stages of hydridation, the curves show that the greater the thermal transfer (copper holder), the smaller the instantaneous rate (curve a). At half-reaction time, the instantaneous rate is maximum in the case of the large surface copper holder (curve a); this point coincides with the maximum temperature increase (compare Fig. 2, curve a). These results have already been noted by Gerard et al. [1].

Modification of the heat quantity produced by increasing mass

Copper holder

Hydride formation was achieved with LaNi_5 samples of different masses (30, 70 and 200 mg) under the same experimental conditions ($T = 294 \text{ K}$ and $0.5 \text{ MPa} < P_{\text{H}_2} < 1.5 \text{ MPa}$). When the mass was less than 70 mg, the

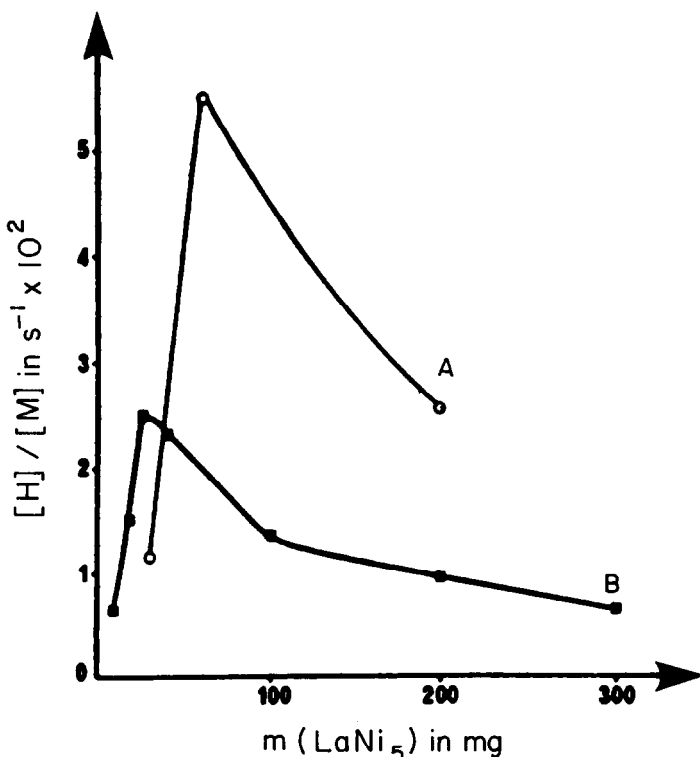


Fig. 4. Reaction rate as a function of mass: curve A, copper holder with large lateral surface; curve B, stainless steel holder. ($T_i = 294$ K; $P_i = 0.6$ MPa.)

maximum temperature changes were about 1–2 K and so are considered negligible to a first approximation. For a mass of 200 mg, the LaNi₅ powder temperature changes with the hydridation (Fig. 2, curve (a)). However, independently of the mass, the representative curve (hydrogen concentration versus time) is sigmoidal and the instantaneous rate can be accurately determined at half the reaction time.

Figure 4, curve A shows the rate data in relation to the sample mass for experiments carried out under a hydrogen pressure of 0.6 MPa. The hydriding rate increases with mass to a maximum at 70 mg, and then decreases as the mass increases from 70 to 200 mg.

Stainless steel holder

Figure 4, curve B shows the curve obtained previously by Bayane and Gerard [6] in the case of a steel holder. The hydriding rate reported as a function of the sample mass shows a maximum for a sample of 30 mg ($P_{H_2} = 0.6$ MPa). For a greater mass such as 70 mg, the instantaneous rate is always smaller in the case of a steel holder.

DISCUSSION

Experimental results reported previously show that reaction rates are not measured in isothermal conditions. The augmentation of a temperature determined while the sample is hydriding can be important in relation to the sample surroundings.

The analysis of these results is based on the original work of Rudman [7], i.e. on the determination of the heat flow effects. The hydriding reaction generates heat in proportion to the reaction rate $d\alpha/dt$. This reaction rate is given by the equation

$$\frac{d\alpha}{dt} = \frac{d([H]/[M])}{dt} = A(P - P_e) \exp(-E_a/RT) \quad (1)$$

where $0 < \alpha < 1$ and α is the fraction of LaNi_5 transformed, E_a is the activation energy, P the imposed hydrogen pressure, P_e the equilibrium hydrogen pressure (a function of temperature) and A a constant that depends on sample activation.

The heat generated by the reaction is then transferred from the sample to the holder and to the surrounding gas phase. The whole system is shown schematically in Fig. 5.

The temperature of the system can be determined using the heat flow equation [7, 8]

$$\frac{d\alpha}{dt} n_{\text{LaNi}_5} \frac{\Delta H}{2} + \delta h(T_a - T_i) + \sum m_i C_{pi} \frac{dT}{dt} = 0 \quad (2)$$

where T_a is the actual temperature, T_i is the imposed tube temperature, $\sum m_i C_{pi}$ is the heat capacity of the system (sample and holder) and δ , where $0 < \delta < 1$, is a coefficient corresponding to the effective heat transfer between the sample and the holder; h is the thermal transfer factor which depends on hydrogen conductivity, the sample and holder materials, the interface area between the holder and the surrounding gas and the thickness of the gas layer; h can be expressed by the general equation

$$h = \frac{\lambda S}{e}$$

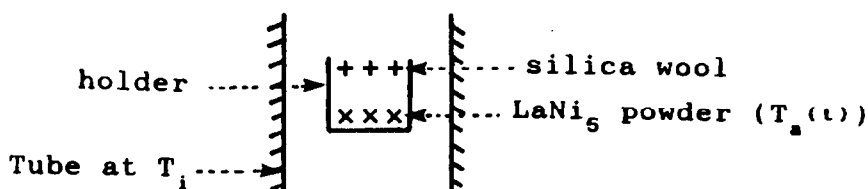


Fig. 5. Position of the holder in the thermobalance tube. $T_a(t)$ is the actual sample temperature and depends on time, and T_i is the imposed laboratory tube temperature.

where λ is the material conductivity, S the transfer interface and e the material thickness.

The inflexion point of the curve $[H]/[M] = f(t)$ corresponds to the highest temperature of the sample T_m . At this plot [7] $dT_m/dt = 0$ and eqn. (2) can now be written as

$$(d\alpha/dt)_{\max} n_{\text{LaNi}_5} \Delta H/2 + h(T_m - T_i) = 0 \quad (3)$$

or

$$\frac{T_m - T_i}{(d\alpha/dt)_{\max}} = -\frac{1}{h} n_{\text{LaNi}_5} \Delta H/2 \quad (4)$$

From this equation, it follows that h must be constant for experiments carried out under different pressures if the sample is placed in the same holder, because the thermal conductivity of hydrogen is nearly constant between 0.5 and 1.5 MPa and is independent of temperature.

Determination of h from experimental results

Stainless steel holder

The h values are then determined from experiments carried out at 294 K with LaNi_5 masses of 100, 200 and 300 mg. The ΔH value was extrapolated from bibliographic data [9–11], i.e. about 31.5 kJ. As shown in Table 2, the average h is about $9 \times 10^{-3} \text{ J s}^{-1} \text{ K}^{-1}$. By increasing the temperature from 294 to 312 K, the h value becomes close to those values reported in Table 2, i.e. $8.8 \times 10^{-3} \text{ J s}^{-1} \text{ K}^{-1}$ for the 100 mg sample and $9 \times 10^{-3} \text{ J s}^{-1} \text{ K}^{-1}$ with 200 mg.

TABLE 2

The thermal transfer factor for the stainless steel holder

T/K	m/mg	P/MPa	$h/(\text{J s}^{-1} \text{ K}^{-1})$
294	100	0.6	8.8×10^{-3}
294	100	0.7	8.5×10^{-3}
294	100	1.1	9.0×10^{-3}
294	200	0.52	9.2×10^{-3}
294	200	0.74	9.2×10^{-3}
294	200	0.95	9.0×10^{-3}
294	300	0.6	8.8×10^{-3}
294	300	0.8	9.5×10^{-3}
294	300	1.1	8.6×10^{-3}

TABLE 3

The thermal transfer factor for the plexiglass holder

T/K	m/mg	$h/(J s^{-1} K^{-1})$
294	200	5.3×10^{-3}
304	200	5.08×10^{-3}

Plexiglass holder

The h values deduced from the experiments carried out with a 200 mg sample are not very different from those obtained with the stainless steel holder; they are lower by a factor 2, as shown in Table 3.

Copper holder

Table 4 shows the h values obtained from experiments carried out with the copper holder characterized by a large lateral surface (Fig. 1(b)). As previously indicated, the thermal transfer factor is independent of the temperature.

A comparison of the h values relative to the different holder materials shows that this thermal factor depends on the conductivity of the material and also on the dimensions of the holder. However, the large differences in the thermal conductivities of plexiglas ($0.21 J m^{-1} s^{-1} K^{-1}$), stainless steel ($30 J m^{-1} s^{-1} K^{-1}$) and copper ($358 J m^{-1} s^{-1} K^{-1}$) induces a relatively small decrease in the sample self-heating (12, 10 and 8 K, respectively) while the temperature change halves when the lateral surface of the holder doubles (see Fig. 2, curves a and b).

From these observations, the theoretical h value can be approached as closely as possible by considering, to a first approximation, the sample container and the adjacent gas-phase surroundings. The thermal transfer factor can be expressed as a function of the thermal resistivity

$$h = \frac{\lambda S}{e} = \frac{1}{R_{th}} \quad (5)$$

TABLE 4

The thermal transfer factor for the large lateral-surface copper holder

T/K	m/mg	$h/(J s^{-1} K^{-1})$
294	200	5.5×10^{-2}
304	200	5.3×10^{-2}
312	200	5.8×10^{-2}
322	200	4.8×10^{-2}

TABLE 5

Different thermal resistivities

	$R_{\text{holder}}/$ ($\text{J}^{-1} \text{ s K}$)	$R_{\text{gas}}/$ ($\text{J}^{-1} \text{ s K}$)	$1/h'_{\text{exp}}/$ ($\text{J}^{-1} \text{ s K}$)	$h'/$ ($\text{J s}^{-1} \text{ K}^{-1}$)
Plexiglass	63	55	186	5.4×10^{-3}
Stainless steel	0.3	55	104	9.2×10^{-3}
Copper (large surface)	0.001	13	19	5.2×10^{-2}

with

$$R_{\text{th}} = R_{\text{holder}} + R_{\text{gas}} + R'_{\text{gas}} + R_{\text{quartz wool}} + \dots \quad (6)$$

R_{gas} is defined as the resistance of the gaseous layer located between the sample holder and the inner laboratory tube. The R'_{gas} determination requires an estimate of the gas layer in which thermal transfer actually occurs. This evaluation is difficult because the layer thickness depends on the importance of the temperature gradient. The thickness and area of the silica wool are not functions of the container; therefore, the wool thermal resistance is constant. The h' thermal resistivity values can be determined from data relative to thermal conductivity and the shape of the holder (R_{holder}) and by considering the gas layer located between the holder and the laboratory tube (R_{gas}) (Table 5).

CONCLUSIONS

With a plexiglass holder, the thermal resistances of plexiglass and hydrogen gas are comparable and relatively important. Under these conditions, the heat produced during the reaction cannot be easily evacuated. As a consequence, an important self-heating is produced from the beginning of the reaction which can reach 20 K.

With a copper or stainless steel holder, thermal resistance is small compared to that of the pulverized sample or hydrogen gas. Also, the heat produced by the reaction is first located in the sample, after which it is rapidly transferred through the holder to the hydrogen gas. The sample temperature then increases more slowly than previously and the temperature gradient does not exceed 5 or 6 K.

From a kinetic point of view, the first seconds of the hydriding reaction correspond to nuclei germination. A temperature increase corresponds to an increase in the number of activated germination sites, and the instantaneous reaction rate increases until the temperature increase induces a decrease in the thermodynamic driving force ($P - P_e(T)$) in the rate equation, eqn. (1). Then the $e^{-E_a/RT}$ factor can become less influential than the ($P - P_e(T)$) term and, finally, the instantaneous rate begins to slow down. These changes in the sample temperature are more or less important

according to the holder material and shape. They can explain the shift in the inflexion point in the curve $[H]/[M] = f(t)$. With a copper holder, the curve is nearly sigmoidal, while in the case of plexiglass the instantaneous rate seems to decrease continuously. In summary, as shown theoretically by Rudman [7] and more recently by Dantzer and Orgaz [8], thermal transfer modifies the shape of the $[H]/[M] = f(t)$ curve. Therefore, a kinetic study provides a knowledge of the experimental conditions at any moment and, in particular, of the temperature changes in the sample. Indeed, this parameter influences two factors of the rate equation: the thermodynamic force, and the term containing the activation energy.

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