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Isobaric and isothermal DSC measurements of metal–hydrogen systems[1]

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Abstract

The reversible formation reaction of hydrides from metals and hydrogen is used as a prototype of a gas–solid heterogeneous reaction in order to show that a sufficient thermodynamic and kinetic characterization of such reactions can be achieved by isothermal and isobaric DSC measurements. The isobaric measurements essentially provide thermodynamic data such as reaction enthalpy, yield and the pressure–temperature relation. On the other hand, the isothermal measurements can be used for kinetic evaluation due to the small number of parameters. Results are given for the Pd–H and La–Mg–H systems.

Keywords: DSC; Enthalpy; Kinetics; Hydride

1. Introduction

Within the scope of the plan of hydrogen and energy utilization, metal–hydrogen systems are of great importance to the reversible chemical bond of hydrogen in a condensed matrix [1]. In addition to the generation of high hydrogen densities by hydride formation, the energy exchange involved in the chemical reaction will allow coupling with heat storage, heat transfer and heat engines [2]. These different applications will require quite specific characteristics concerning the *P–T* relation, storage capacity, cycle stability, reaction enthalpy and reaction kinetics. These characteristics can be determined by isobaric

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and isothermal DSC measurements. Moreover, it is shown that the metal–hydrogen reaction

$$Me(s) + x/2H_2(g) \Leftrightarrow MeH_x \tag{1}$$

can be used as a prototype of a gas–solid heterogeneous reaction for interpretation of isobaric and isothermal DSC measurements.

Test results obtained for the Pd–H and La–Mg–H system are presented. The Pd–H system has been most thoroughly investigated [3], therefore it can be used as a model system. The miscibility gap between an α-phase poor in hydrogen and a β-hydride phase with an upper critical point is a characteristic feature of the Pd–H system [3]. In the La–Mg–H system the miscibility gap is apparently complete, i.e. there exist only the alloy (intermetallic compound) and the hydrides $MgH_2/LaH_2/LaH_3$ [4]. This different behaviour is reflected in the results of the DSC measurements. The kinetic evaluation will only refer to the isothermal measurements because in this case the number of adjustable parameters is considerably reduced compared with the evaluation of isobaric measurements.

2. Experimental

DSC measurements were performed by DSC 111 (SETARAM) up to hydrogen pressures of 30 bar and temperatures up to 470°C. The heating rate used for the isobaric measurements was 5 K min^{-1}. The isothermal measurements were performed in such a way that the pressure (absorption) and the vacuum (desorption), respectively were preset in a 1 l vessel. Subsequently, the connection with the measuring crucible was made within a very short period of time (<3 s). These defined initial conditions of the absorption and desorption reaction, respectively, were a requirement of the later successful kinetic evaluation. Measurement of the H_2 pressure was done using a MKS pressure sensor.

The palladium powder had a nominal purity of 99.9%. In the present work the intermetallic phases $LaMg_{12}$, La_2Mg_{17} and $LaMg_3$ were investigated as to their hydrogenation behaviour and synthesized from the elements. La and Mg powder were mixed, pressed and sintered and subsequently annealed in a steel crucible using an argon atmosphere just below the melting temperature. As shown by the X-ray diffraction pattern, the compounds were free from foreign phases.

3. Results and discussion

3.1. Palladium–hydrogen

Outside the miscibility gap there is a slight change of the hydrogen content dependent on the temperature. This means for isobaric DSC measurements that the heat flow involved will not be sufficient for detection. Only when achieving the miscibility gap, will the hydrogen content change rapidly ($x_\alpha \rightarrow x_\beta$) so that a DSC signal will result in accor-

Table 1

Absorption and desorption data for the system Pd–H at various pressures

P_{H_2} in 10^5 Pa	T_{des} in K	T_{abs} in K	$\Delta_R H_{des}$ in kJ mol^{-1} Pd	$\Delta_R H_{abs}$ in kJ mol^{-1} Pd	$\Delta x_{Hcalc.}$ in mol H	$\Delta x_{HDiagr.}$ in mol H
2.75	457.33	444.45	9.50	11.15	0.462	0.420
5.65	489.90	483.93	8.49	9.41	0.413	0.371
8.55	510.21	509.42	6.82	8.14	0.332	0.352
12.45	531.90	530.10	5.91	7.12	0.287	0.298

dance with the enthalpy change $\Delta_R H^{DSC}$. Because the miscibility gap decreases with rising pressure, the measured enthalpy change will decrease in this direction. The data summarized in Table 1 reflect this statement.

The onset temperature as a temperature of the isothermal lines of the miscibility gap has been obtained as secondary information from the isobaric DSC measurements (see Table 1). The P–T relation can be described by the van't Hoff equation

$$\ln P_{H_2} = -\frac{\Delta H^{Pl}}{RT} + \frac{\Delta S^{Pl}}{R} \tag{2}$$

where in accordance with $K_P = P_{H_2}$, ΔH^{Pl} and ΔS^{Pl} refer to 1 mol of absorbed and desorbed hydrogen, respectively. The resulting values are in good agreement with known values (see Table 2). The difference between the values of absorption and desorption can be explained by the known phenomenon of hysteresis [6].

According to the relation

$$\frac{\Delta_R H^{DSC}}{\Delta_R H^{Pl}} = x_\beta - x_\alpha = \Delta x_H \tag{3}$$

a statement of the miscibility gap width or, in the technical meaning, of the storage capacity can be achieved as a third piece of information. As can also be seen from Table 1, there is a positive comparison with known values [5] taking into account the considerable experimental uncertainties in the determination of the binodal curve. The measured enthalpy changes in isothermal conditions correspond to the integral enthalpies of mixing. Phenomena of hysteresis cannot be found because there is a correspondence of absorp-

Table 2

Comparison between $\Delta_R H^{Pl}$ and $\Delta_R S^{Pl}$ for the Pd–H system

	$\Delta_R H^{Pl}$abs in kJ mol^{-1} H_2	$\Delta_R H^{Pl}$abs in J/K mol^{-1} H_2	$\Delta_R H^{Pl}$des in kJ mol^{-1} H_2	$\Delta_R S^{Pl}$des in J/K mol^{-1} H_2
This work	−33.03	−82.69	41.12	98.35
Blaurock/Wicke	−32.11	−81.55	41.00	97.89

tion and desorption enthalpies with a mean deviation of ±0.8%. The $\Delta H(x_H)$ function can be derived on the basis of the known P–T–x_H relation. However, the potential kinetic evaluation seems to be of more interest. The small number of adjustable parameters compared with that of anisothermal evaluations and the very stable baseline of the isothermal DSC measurements have initiated this evaluation. The TIAN equation is used as a basis:

$$\dot{q} = \frac{\Delta T(t)}{R_{\mathrm{Th}}} + c_{\mathrm{PM}} \frac{\mathrm{d}\Delta T(t)}{\mathrm{d}t} \tag{4}$$

with

$$\tau = c_{\mathrm{PM}} R_{\mathrm{Th}} \quad \text{and} \quad \dot{q}_{\mathrm{mess}}(t) = \frac{\Delta T(t)}{R_{\mathrm{Th}}}$$

resulting in

$$\dot{q}(t) = \dot{q}_{\mathrm{mess}}(t) + \tau \frac{\mathrm{d}\dot{q}_{\mathrm{mess}}}{\mathrm{d}t} \tag{5}$$

In the simplest case, $\dot{q}(t)$ can be described assuming a first-order reaction with the equation

$$\dot{q}(t) = k q_{\mathrm{ges}} \exp(-kt) \tag{6}$$

where q_{ges} is the reaction enthalpy and k is the rate constant.

The insertion of Eq (6) in Eq (5) and subsequent integration results in

$$\dot{q}_{\mathrm{mess}}(t) = \frac{k q_{\mathrm{ges}}}{1 - \tau k} \left\{ \exp(-kt) - \exp\left(\frac{-t}{\tau} \right) \right\} \tag{7}$$

The isothermal DSC peaks can be well approximated to this equation by means of nonlinear regression. The physical reality was demonstrated by the fact that for the time constant τ a number of values result which, allowing for the heat capacity of the sample, correlate with values obtained from electrical calibrations.

The following results were obtained for the Pd–H system. The desorption rate is independent of the initial pressure. The temperature dependence of the rate constant can be described by the Arrhenius equation (see Fig. 1). The resulting activation energy of $E_A = 24.2$ kJ mol^{-1} shows good agreement with the activation energy of the diffusion such as determined from electrochemical measurements [7]. Accordingly, diffusion of hydrogen in palladium is the rate-determining step of the desorption.

The absorption rate is proportional to the pressure difference $(P - P_0)$, P_0 being the plateau pressure at the measuring temperature. Apparently, hydrogen dissociation on the palladium surface is the rate-determining step. Consequently, size, structure and impuri-

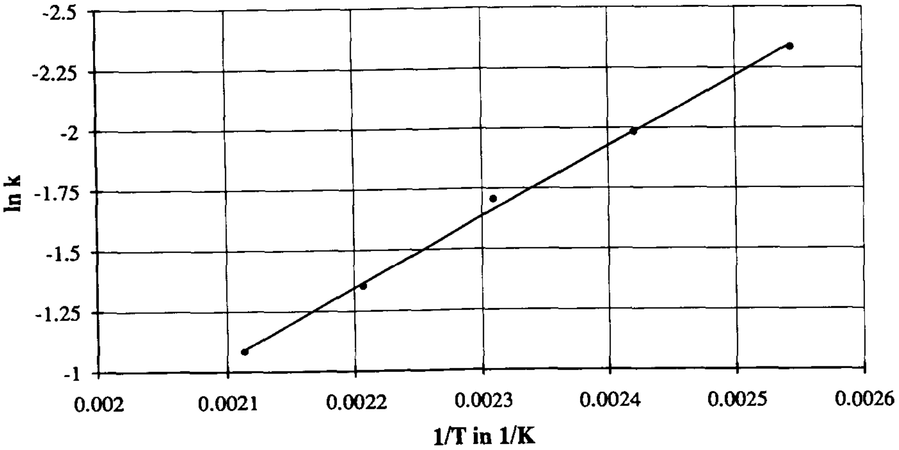

Fig. 1. Dependence of the desorption rate on the temperature for the system Pd–H.

ties of the palladium surface are parameters of the absorption rate. Further and more detailed investigations as a function of these parameters will be required for definite statements.

3.2. *Magnesium–lanthanum–hydrogen*

Magnesium hydride formation is characterized by a high activation energy [8] which can be considerably reduced by alloy formation. Ni, Cu, Fe and rare-earth elements are considered to be the second metal component. The intermetallic phases formed with magnesium show a different reaction behaviour in the presence of hydrogen. During the hydrogenation process the La–Mg compounds (La_2Mg_{17}, $LaMg_{12}$ and $LaMg_3$) are decomposed into the binary hydrides:

$$La_yMg_x + (y + x)H_2 \Leftrightarrow xMgH_2 + yLaH_2$$

The reaction is reversible when $P_{H_2} = 0$ during dehydrogenation.

The isobaric measurements show that the reaction enthalpy $\Delta_R H^{DSC}$ is independent of the pressure. As a result, substoichiometric hydrides can be excluded. The comparison of

Table 3

Results of the isobaric DSC measurements of La–Mg compounds

Compound	$\Delta_R H^{DSC}$ in kJ mol^{-1} Comp.	$\Delta_R H^{Pl}$ in kJ mol^{-1} H_2	$x_{Hexp.}$ in mol H	$x_{Htheor.}$ in mol H
$LaMg_{12}$	591.60	84.22	14.04	26
La_2Mg_{17}	829.19	81.19	20.43	38
$LaMg_3$	165.86	82.11	4.04	8

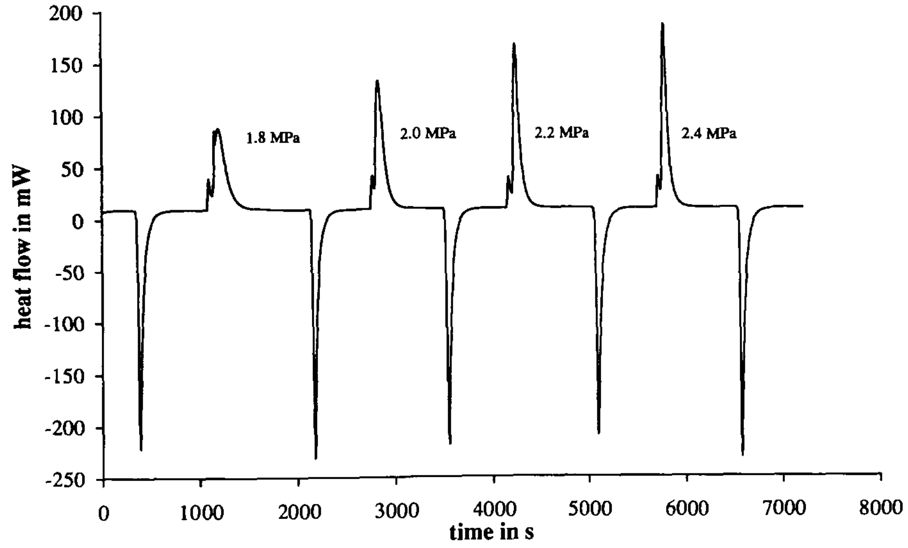

Fig. 2. Isothermic DSC curves of a La–Mg compound.

$\Delta_R H^{DSC}$ and $\Delta_R H^{Pl}$ according to Eq. (3) leads to the result that the theoretical yield will not be achieved (see Table 3) in correspondence with known results [9].

The results of the kinetic evaluation of the isothermal measurements are in analogy with the Pd–H system. As can be seen from the DSC curves in Fig. 2, the absorption rate increases with rising H_2 pressure. In each case, the relation

$$\frac{dc_H}{dt} = k(T)(P - P_0) \tag{8}$$

is satisfied for the hydrogenation reaction of the three intermetallic compounds investigated. Desorption will proceed in two superimposed reaction steps, a fact which does not allow a definite kinetic evaluation. Further investigations are planned.

In the case of hydrogenation and dehydrogenation reactions, respectively, it could be shown that gas–solid heterogeneous reactions can be extensively characterized by isobaric and isothermal DSC measurements. Use of a defined gas atmosphere appears to be most important and a necessity to the performance of such investigations. Efficient physical interpretation of dehydrogenation tests which were conducted in an inert atmosphere (Ar) could not be presented relating to the onset temperature and, even to a lower degree, to a kinetic evaluation.

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