

Calorimetric investigations on kinetics of the dehydrogenation process in the system lanthanum–magnesium–hydrogen

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Abstract

A kinetic study of the dehydrogenation of several magnesium-based alloys/compounds with lanthanum is presented and the results are referred to the kinetics of the dehydrogenation process of pure magnesium hydride. Measurements were performed in a differential scanning calorimeter (DSC) by applying various pressure steps to the samples at isothermal conditions. Different thermokinetic models were fitted to the experimentally obtained DSC curves as well as the power curves, calculated from the DSC curves, to evaluate the kinetic parameters. The derived dehydrogenation rate is discussed in terms of its dependence on hydrogen pressure and temperature. Under certain conditions, it is possible to visualise individual rate-determining steps. Considering these results first mechanistic considerations on the dehydrogenation reaction of the magnesium-based alloys/compounds can be drawn. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Kinetics; Magnesium alloys; Hydride; DSC

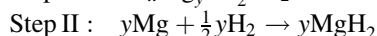
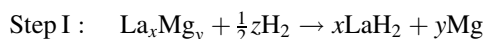
1. Introduction

In the last years, numerous studies on the effect of metal additives [1–3] on the reaction of magnesium with hydrogen were performed, in order to find an optimal alloy or intermetallic compound for hydrogen storage.

Magnesium-rich alloys or compounds exhibit a hydrogen storage capacity close to pure magnesium and made them interesting for potential storage systems. But, the Mg–H system shows also very poor hydrogenation–dehydrogenation kinetics. To overcome this disadvantage, an optimisation of hydrogenation–dehydrogenation kinetics by alloying pure

magnesium with certain amounts of lanthanum should be achieved.

During the first hydrogenation or activation of La–Mg alloys with hydrogen these compounds decompose under formation of the binary hydrides of magnesium and lanthanum. Based on results of an earlier study [4], the following set of equations were derived:



Evidently, lanthanum hydride has a catalytic effect on all subsequent hydrogenation–dehydrogenation cycles.

The present study is focussed on a kinetic description of the dehydrogenation of La–Mg–H alloys. As shown in former studies [5], calorimetric techniques (differential scanning calorimeter, DSC) are exceptionally useful to follow hydrogenation reactions and

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hydrogenation cycles as well as to obtain kinetic parameters by the same runs. Power curves, calculated from the DSC curves show a two-stage reaction, whereby the main reaction effect is attributed to the decomposition of the MgH_2 . Rate constants were obtained by fitting the parameters of various thermokinetic rate models to the main reaction effect. The data represent the influence of absorption and desorption pressure on the following hydrogenation–dehydrogenation process and the pressure and temperature dependence of the dehydrogenation rate. Based on these results, a model of the rate-limiting step and the mechanism of the dehydrogenation process were proposed.

2. Experimental

2.1. Sample material

The studied magnesium-rich alloys or intermetallic compounds with lanthanum (Mg powder, >99.8% purity, <45 μm , Fluka; La powder, 99.9% purity, –40 mesh, Aldrich) were prepared by melting the elements under argon flow at a temperature of 1000 K.

These initial alloys or intermetallic compounds have been hydrogenated in an autoclave (according to the reaction sequence mentioned above) at 673 K and a hydrogen pressure of 50 bar.

All synthesized samples and their hydrogenated products were submitted to *X-ray diffraction (XRD) analysis*.

2.2. Calorimetric measurements

The dehydrogenation kinetics of the intermetallic La–Mg–H compounds was investigated by means of pressure-cyclic DSC measurements at constant temperatures. A differential scanning calorimeter of the type DSC 111 (Setaram) was used. The isothermal measurements were carried out in such a way that a defined hydrogen pressure was preset in a gas storage tank of 1 l volume connected to a high-pressure crucible of 150 μl volume. By opening the valve, which connects the gas reservoir vessel with the measuring crucible, the pressure in the crucible was changed within shortest time. In the case of the desorption, the valve was only then opened if in the

gas storage tank the ultimate pressure of the vacuum pump ($p = 10^{-3}$ mbar) was achieved. These defined initial conditions of the desorption reaction are strongly required for a later successful and reliable kinetic evaluation. Measurement of the hydrogen pressure (hydrogenation) or vacuum (dehydrogenation) was done using a MKS pressure sensor. In the following, the specification of the desorption pressure, $p_D = 0$, always corresponds to the ultimate pressure of vacuum pump.

3. Results and discussion

3.1. Model calculation

The kinetic evaluation was done by fitting a modified kinetic equation on the basis of the Tian-equation [6] to the experimental data:

$$\dot{q}(t) = \frac{kq}{1 - \tau k} (e^{-kt} - e^{-t/\tau}) \quad (1)$$

where $\dot{q}(t)$ is the DSC signal, q the reaction enthalpy, τ the time constant and k is the rate constant. The equation can be well-approximated to the isothermal DSC peaks by means of non-linear regression.

Additionally, a numerical evaluation was carried out by calculating power curves from the measured DSC curves. Using the resulting power curves, the kinetic evaluation was done by curve fits on the basis of different kinetic rate models, whereby the models were applied to the whole power curves or to sections of them. The integrated and differentiated form of these kinetic models is shown in Table 1. In each case, the error of the curve fit is below 5%.

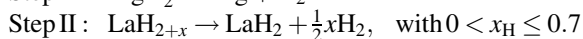
3.2. Results of the model evaluation

In a first step, the desorption experiments were done in such a way that a fast pressure change starting from the absorption pressure p_A of the previous hydrogenation cycle to a desorption pressure $p_D = 0$ was applied. As shown in Fig. 1, the heat flow curve of dehydrogenation of these alloys/compounds always shows only one reaction step at a desorption pressure $p_D = 0$. By numerical deconvolution of the heat flow curves, a two-stage reaction becomes obvious in the resulting heat power curves consisting of a main

Table 1
Integrated and differentiated form of different thermokinetic rate models

Number	Kinetic rate model		Description
	Integrated form	Differentiated form	
1	$\alpha = kt^2C$	$(d\alpha/dt) = \dot{q}(t) = 2kt/A$	Parabolic law
2	$-\ln(1 - \alpha) = kt$	$(d\alpha/dt) = \dot{q}(t) = qkt e^{-kt}$	DELMON constant nucleation rate
3	$-\ln(1 - \alpha)^{1/2} = kt$	$(d\alpha/dt) = \dot{q}(t) = 2qk^2t e^{-(kt)^2}$	AVRAMI-EROFEEV nucleation and two-dimensional growth
4	$-\ln(1 - \alpha)^{1/3} = kt$	$(d\alpha/dt) = \dot{q}(t) = 3qk^3t^2 e^{-(kt)^3}$	AVRAMI-EROFEEV nucleation and three-dimensional growth

reaction effect and a small subsequent effect (see Fig. 2). Taken into account previous results concerning the hydrogenation in this system [4], the dehydrogenation is to be considered as the reverse of the hydrogenation reaction under the given experimental conditions.



In contradiction to the presented results, under isobaric temperature-cyclic DSC measurements of these activated magnesium-rich alloys/compounds only the decomposition of MgH_2 was found. We conclude that the second reaction step proceeds only under isothermal conditions and a desorption pressure $p_{\text{D}} = 0$.

Due to the overlapping of both the reaction steps in the DSC curves as well as in the calculated power

curves, a reliable peak separation is not justified. Therefore, a kinetic description of the second reaction step is not reasonable. The following discussion is referred to the main reaction step.

A tendency regarding the influence of the lanthanum content of the different alloys/compounds on the dehydrogenation rate cannot be derived from the calculated rate constants. Due to the low scatter of the derived rate constants of <10% at a given temperature, these values were averaged and the following temperature function of the rate constant k was derived:

$$\ln k = -\frac{11508}{T} + 14.3 \quad (2)$$

Assuming a linear dependence of the rate constant k , the following expression at $p_{\text{D}} = 0$ is obtained:

$$k = k_0 p_{\text{eq}} \quad (3)$$

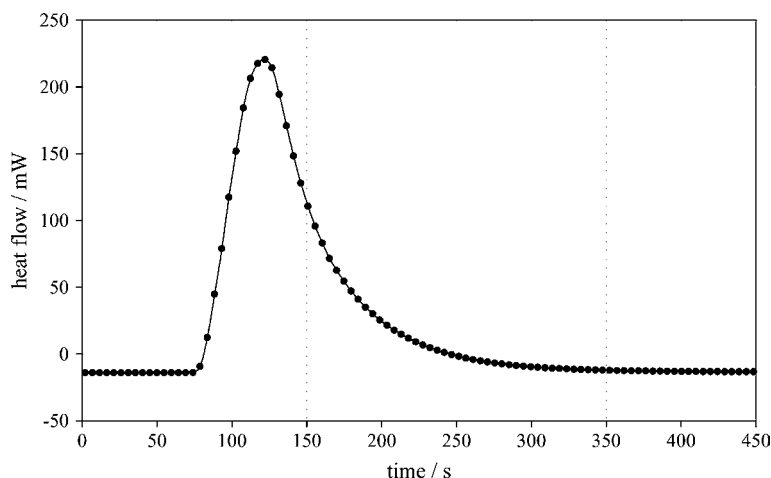


Fig. 1. Example of a measured DSC curve of dehydrogenation of activated $\text{La}_2\text{Mg}_{17}$ at $T = 375^\circ\text{C}$ and $p_{\text{D}} = 0$.

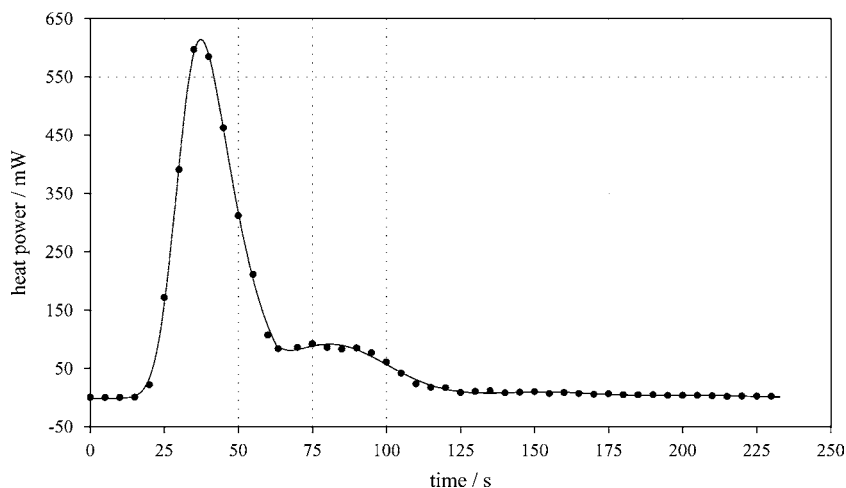


Fig. 2. Example of calculated power curve of dehydrogenation of activated $\text{La}_2\text{Mg}_{17}$ at $T = 375^\circ\text{C}$ and $p_D = 0$.

$$\ln k = \ln k_0 + \ln p_{\text{eq}} \quad (4)$$

In a previous study [4] for the intermetallic compound $\text{La}_2\text{Mg}_{17}$, a temperature function of the equilibrium pressure p_{eq} was determined:

$$\ln p_{\text{eq}} = -\frac{10497}{T} + 18.4 \quad (5)$$

From Eqs. (2), (4) and (5), the following expression for temperature dependence of the rate constant k_0 results:

$$\ln k_0 = -\frac{1011.9}{T} - 4.06 \quad (6)$$

$$k_0 = 1.73 \times 10^{-2} e^{-1011.9/T} \quad (7)$$

The resulting activation energy E_A of the dehydrogenation reaction of the intermetallic compound $\text{La}_2\text{Mg}_{17}$ amounts to only 8.4 ± 0.6 kJ/mol and is substantially smaller compared with the value for pure MgH_2 of $E_A = 47.8$ kJ/mol [5].

Furthermore, in an extended experimental program the pressure dependence of dehydrogenation rate of the intermetallic compound $\text{La}_2\text{Mg}_{17}$ was investigated at a temperature of 375°C . In this case, desorption experiments were performed in such a way that a fast pressure change was applied starting from an absorption pressure, $p_A = 24$ bar, to a defined desorption pressure p_D .

The dehydrogenation rate constants resulting from the model calculation are plotted as a function of

pressure. Best correlations were obtained for the quadratic and linear pressure dependence. However, a quadratic pressure dependence of the rate constants k must be excluded, because the resulting equilibrium pressures p_{eq} from that model have no physical background with respect to the pressure difference ($p_{\text{eq}} - p_D$) as driving force of reaction. In Fig. 3, it is represented the linear pressure dependence of rate constants calculated by the models 2 and 4 and the Tian-equation. The equilibrium pressure p_{eq} is given by the intersection of the line fit with the x -axis. The obtained values of p_{eq} correspond well with the absorption pressure p_A at 375°C quantified by isobaric temperature-cyclic DSC measurements. In these previous experimental investigations were shown that in the system La-Mg-H , the absorption pressure p_A represents the equilibrium pressure [4]. The consistency of the experimentally determined equilibrium pressure with the calculated equilibrium pressure points out that the real processes of the dehydrogenation in the system La-Mg-H are well described by the selected kinetic model and the linear pressure dependence.

The rate constants k_0 calculated from the slopes of the lines as well as the corresponding equilibrium pressures p_{eq} are summarized in Table 2. The form of the rate expression support the assumption that the dehydrogenation reaction in this system bases on the mechanism of nucleation and growth. When the nuclei form a closed metal layer, the M/MH_x interface keeps

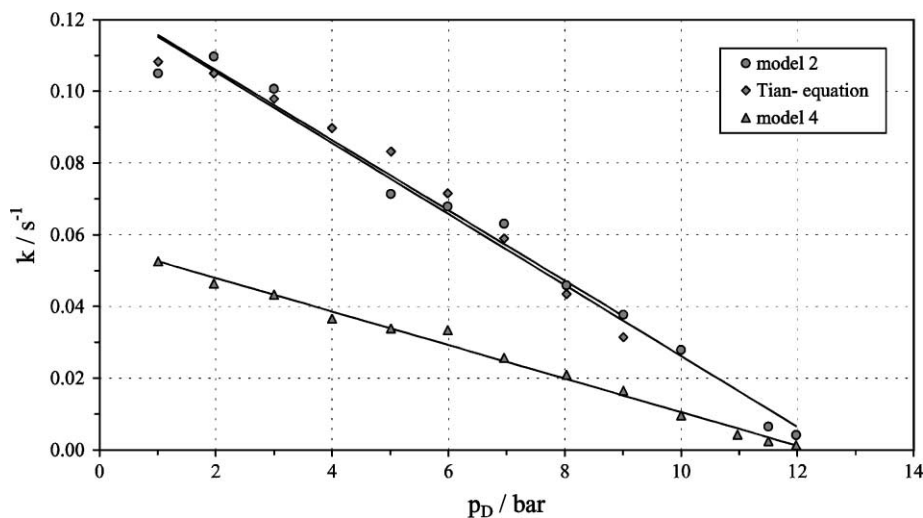


Fig. 3. Dependence of rate constants calculated by different kinetic rate models on desorption pressure for the dehydrogenation process of activated $\text{La}_2\text{Mg}_{17}$ at $T = 375$ °C.

Table 2

Calculated values of the equilibrium pressure p_{eq} and rate constants k_0 of dehydrogenation of $\text{La}_2\text{Mg}_{17}$ at a temperature of 375 °C

Model calculation	k_0 (s^{-1})	p_{eq} (bar)
Tian-equation	0.0098	12.82
Model 1	0.0105	12.42
Model 2	0.0046	12.37

no longer contact to the particle surface and presumably the diffusion of the H-atoms through this metal layer becomes rate controlling. The influence of diffusion on the reaction is confirmed through the linear pressure dependence of the rate constants. In comparison to the dehydrogenation process of the pure MgH_2 ($k_0 = 5.18 \times 10^{-4} s^{-1}$), the dehydrogenation reaction in the system La–Mg–H proceeds 10–20 times faster.

In addition to the presented results, investigations on the influence of the desorption pressure p_D on the subsequent hydrogenation of the intermetallic

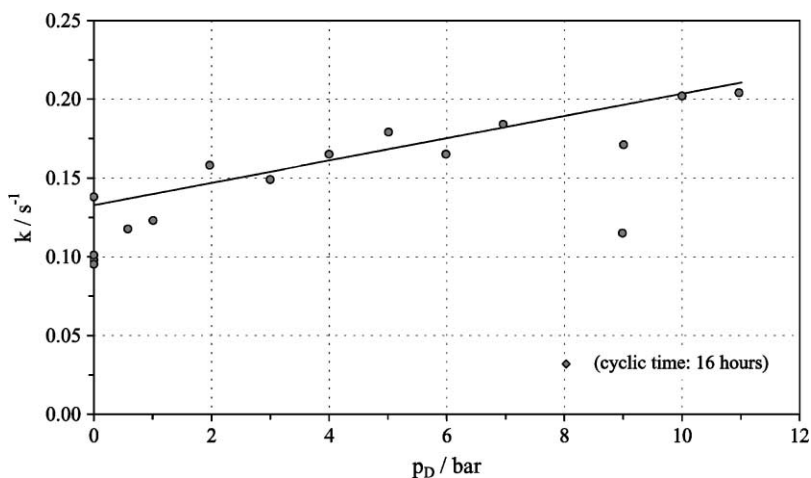


Fig. 4. Influence of desorption pressure p_D on the rate of the subsequent hydrogenation of activated $\text{La}_2\text{Mg}_{17}$ at $T = 375$ °C.

compounds were done. The isothermal DSC measurements has been carried out by a fast change of the pressure starting from the present desorption pressure p_D to a certain absorption pressure p_A at a temperature of 375 °C. The rate constants k of the hydrogenation as function of the previous applied desorption pressure p_D is plotted in Fig. 4 for the compound $\text{La}_2\text{Mg}_{17}$. A clear linear dependence was also observed in these experiments, but in far less extent as indicated by the plot. Of special interest is the observed effect, derived from Fig. 4, that an extension of the cyclic interval between absorption and desorption from 1 to 16 h leads to a significant decrease of the hydrogenation rate, which then becomes similar to the values of pure magnesium. Only after three sequential cycles with a cycle time of one hour the original rate was restored. Of course, this observation must be supported by further experiments.

4. Conclusions

On the basis of the presented results of the isothermal pressure-cyclic DSC measurements the following conclusions for the dehydrogenation process in the system La–Mg–H can be drawn.

1. The kinetics of the dehydrogenation of an activated La–Mg alloy or compound was investigated by pressure change experiments. A thermokinetic model, which describes a three-dimensional spherical nucleation and growth, was applied to obtain rate constants for these processes. These calculated rate constants depend linearly on the pressure.
2. The independence of the dehydrogenation rate on the previous hydrogenation pressure indicates the formation of a closed hydride layer on the particle surface during the hydrogenation, as already discussed by Khrussanova and Peshev [7]. Consequently, the M/MH_x interface keeps no longer contact to the particle surface and finally, the rate of dehydrogenation is independent on the area of particle interface M/MH_x. This statement does not confirm the proposed model of Khrussanova and Peshev [7].

3. Under the selected isothermal conditions, the dehydrogenation reaction of these intermetallic compounds/alloys takes place near at the thermodynamic equilibrium. This argument is supported by the obtained equilibrium pressures p_{eq} resulting from the linear dependence of the rate constants k from desorption pressure p_D .
4. The dehydrogenation rate depends not on the lanthanum content. This result is in agreement with the assumption that lanthanum dissolved in magnesium, enhances the rate of hydrogenation–dehydrogenation of magnesium.

Finally, a catalytic influence of lanthanum on the dehydrogenation rate has been proven by the present study and by comparing the results of the systems La–Mg–H and Mg–H. Just like in case of the hydrogenation of these compounds/alloys, a dependence of the dehydrogenation rate on lanthanum content was not found. The conclusion can be drawn that lanthanum, dissolved in magnesium enhances the rate of the hydrogenation–dehydrogenation process. The results open new chances for a technical application of the system La–Mg–H as hydrogen storage material. For this reason, further and more detailed investigations will be required for definite statements.

Acknowledgements

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