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Kinetic investigations on the basis of isothermal DSC measurements of hydrogenation and dehydrogenation of magnesium hydride[1]

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Abstract

Results of kinetic investigations on the basis of isothermal DSC measurements by means of defined pressure changes are presented and interpreted for the Mg/MgH_2 system. From an evaluation of the experimentally obtained DSC-signals, the dependence of reaction rate on hydrogen pressure p_0, temperature and sample morphology could be described. Under certain conditions, it is possible to visualise individual rate-determining steps and, thus, to arrive at conclusions on the reaction mechanism. © 1998 Elsevier Science B.V.

Keywords: Activation energy; DSC; Kinetics; Magnesium hydride

1. Introduction

The hydrogenation and dehydrogenation of metals and metal alloys are simple heterogeneous reactions, the kinetics of which are of scientific as well as technological interest. Mg/MgH_2, as a typical representative of high-temperature hydrides, gains much attention in all respects, because it reaches the highest hydrogen content (7.65 wt%) among all the comparable metal hydrides. Due to its poor absorption kinetics, the high hydride stability and the low cycle stability, however, it has not yet found large-scale application in hydrogen or heat storage.

So far as thermodynamics and kinetics of the system is concerned, rather different results are found in literature. In order to establish a basis for further kinetic and thermodynamic interpretation of the results obtained from hydrides of intermetallic compounds of magnesium (e.g. La, Ce or Cu), it seems necessary to investigate the behaviour of MgH_2 much more in detail.

By means of isothermal DSC measurements an extensive kinetic characterisation of the system should be given, which implies formulation of statements on the dependence of reaction rate on hydrogen pressure p_0 and temperature. These results enable conclusions concerning the reaction mechanism.

2. Experimental

2.1. Sample material

Three different magnesium hydride samples were investigated.

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- Magnesium hydride from Th. Goldschmidt AG, Essen [1] – procedure of synthesis: autocatalytically produced MgH_2 with a mean particle size <53 μm
- Magnesium hydride from Max-Planck-Institut für Kohleforschung, Mühlheim (Dept. B. Bogdanovic) – procedure of synthesis: homogeneously catalytically produced MgH_2 with a mean particle size <60 μm
- Magnesium hydride, prepared by the authors – procedure of synthesis: synthesis from the elements (magnesium powder (<45 μm) has been exposed in an autoclave at 673 K and a hydrogen pressure of 35 bar (RT) for ca. 45 h)

2.2. Calorimetric measurements

A differential scanning calorimeter of the type DSC 111 from SETARAM has been applied. The isothermal DSC measurements (T=633, 653 and 663 K) with defined pressure changes were carried out in such a way that, in a gas storage tank of 1 l volume, a fixed hydrogen pressure was pre-set. By opening a valve connecting the gas reservoir vessel with the high-pressure crucible (sample, $V_{\mathrm{reservoir}} \gg V_{\mathrm{crucible}}$), the pressure in the measuring crucible had been changed within short, and thus the reaction had been started using time definition as a precondition for kinetic evaluation.

3. Results and discussion

The evaluation of DSC measuring curves has been accomplished by means of a curve fit on the basis of the TIAN equation and under the assumption of a first-order reaction [2].

While the absorption curve shows only one step of reaction and the evaluation by means of curve approximation is rather successful, the desorption curve shows distinctly a three-step sequence of reaction. In this case only a numerical evaluation is possible. Fig. 1 presents a typical resulting DSC curve of absorption and desorption of MgH_2.

In order to analyse systematic and statistical uncertainties, simulation measurements with electrically produced heat effect were carried out, and the reconstructed signal had been compared with the starting signal. The following results were obtained:

- The numerical evaluation is to be preferred to a balanced calculation on the basis of a model function.

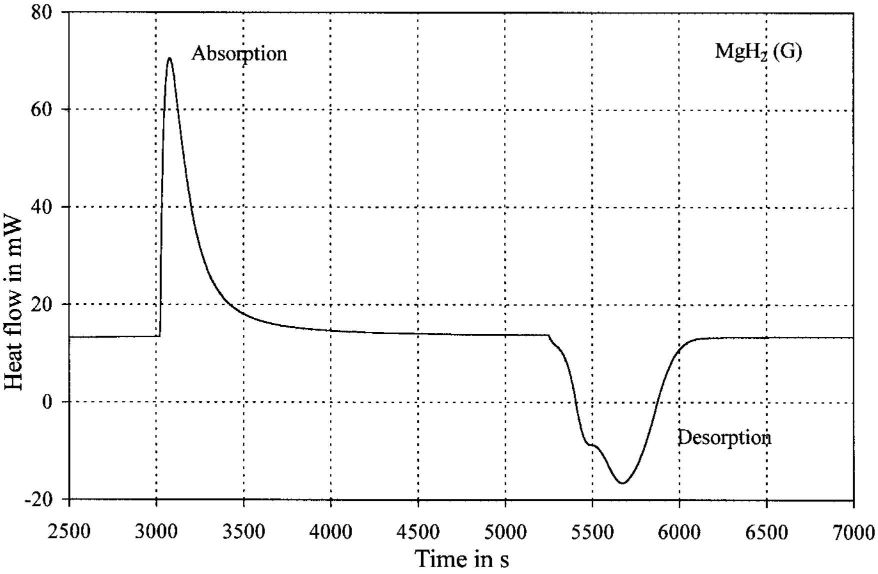

Fig. 1. DSC curve of hydrogenation and dehydrogenation of MgH_2 (G) at T=const.

- Half-life of heat production (reaction) should be lower, at least 10 times lower than constant of the measuring system.

3.1. Hydrogenation kinetics of magnesium

The given evaluation of absorption kinetics at constant temperature leads to first-order rate constants depending strictly linearly on pressure difference ($p_0 - p_{eq}$), where p_{eq} represents the thermodynamic equilibrium pressure (Fig. 2).

$$k = k_0(p_0 - p_{eq})$$

The temperature dependence on k_0 can be described by the Arrhenius equation. Apparently, the value of the activation energy does not depend on the sample and is on average E_A=100 kJ/mol (Fig. 3). In comparison, Stander [3,4] calculated an activation energy of 95.5 kJ/mol on the basis of isothermal gravimetric and volumetric measurements. The resulting different ordinate intersections are due to different sample surfaces.

The enthalpy change, $\Delta_R H_{sp}$ obtained under isothermal conditions are 1.47 kJ/g MgH_2 at a maximum independently of the sample. This value corresponds to a reacted fraction of 50% reference to MgH_2 and is in accordance with the reacted fractions obtained by Stander [3].

3.2. Kinetics of the dehydrogenation of magnesium hydride

At a given temperature the DSC curve of dehydrogenation has nearly the same shape and area. Due to the multistage reaction sequence a modelling evaluation is impossible, and a numerical evaluation has been undertaken, by which the desorption curve, first of all, has been numerically reconstructed. The values for the time constants were taken from electrical calibration. The integration of the resulting performance curve $\dot{q}(t)$ and the reference to q_{ges} leads to the reacted fraction-time curve $\alpha(t)$:

$$\alpha(t) = \frac{1}{q_{ges}} \int_0^t \dot{q}(t)\mathrm{d}t$$

The obtained reacted fraction–time curve are absolutely comparable to those curve behaviours known from literature [4], which were gained from pressure–time or volume–time measurements. The structure of the desorption curve is completely lost, when these integral method are used so that the importance of

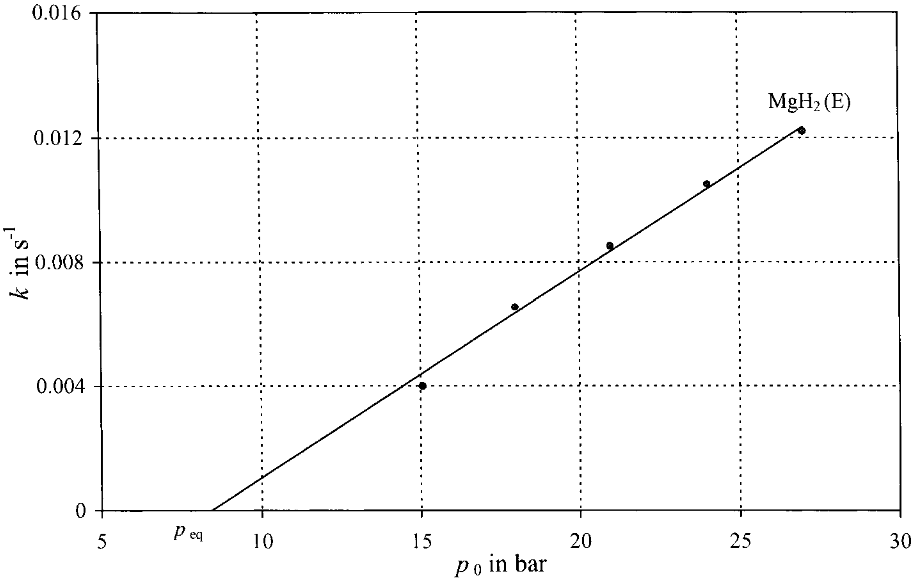

Fig. 2. Dependence of rate constants on pressure p_0 at constant temperature of MgH_2 (E).

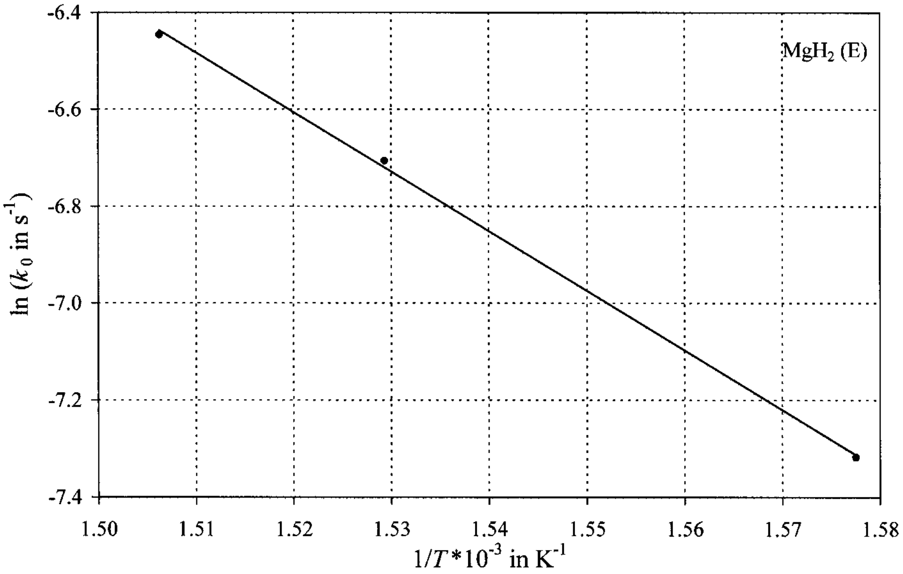

Fig. 3. Temperature dependence of k_0 for the absorption of MgH_2 (E).

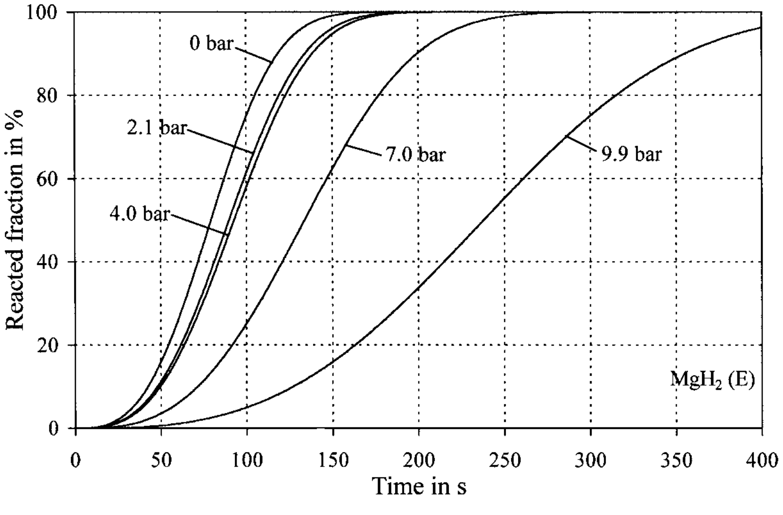

Fig. 4. Reacted fraction–time curves of MgH_2 (E) at different desorption pressures (T=663 K).

isothermal DSC measurements should be emphasised again.

The effect of pressure on the desorption rate of hydrogen can be taken from the reacted fraction–time curves of MgH_2 (E) in Fig. 4. The results show that the decomposition reaction of MgH_2 becomes slower with decreasing pressure difference (p_{eq}−p_0) at constant temperature. An influence on the reacted fraction cannot be observed.

4. Conclusions

On the basis of the presented results a detailed interpretation of the reaction mechanism is still impossible. Referring to the hitherto obtained results the following conclusions can be made.

The hydrogenation rate is primarily determined by the step of dissociative chemisorption of hydrogen. This is supported by the pressure-proportional velocity.

With the growth of magnesium hydride from the boundary into the grain, the diffusion possibilities of hydrogen are minimised. Thus, an apparent order of reaction results. The assumed first order has only a formal character.

Assuming that hydrogenation and dehydrogenation of magnesium and magnesium hydride, respectively, are based upon the mechanism of nucleation and growth, an influence of pressure difference (p_0-p_{eq}) on the number of nuclei developing cannot be derived as described by Vigeholm [5], because a dependence of reacted fraction on pressure p_0 could not be observed.

Obviously, the dehydrogenation of MgH_2 starts with a rapid formation of α-MgH_2 at the surface. The following incubation period is apparently characterised by the formation of Mg-nuclei. The more rapid crystal growth leads to the second maximum in the performance curve. The third maximum can be referred to the volume contraction, accompanying the formation of the magnesium phase, which leads to crack formation thus enabling additional options of diffusion. Furthermore, detailed studies on pressure dependence of desorption rate seem to be necessary in order to make a still more exact statements concerning the mechanism of reaction.

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