Kinetics of formation and decomposition of metal hydrides

水素吸蔵材料の水素吸放出反応

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The formation and decomposition of metal hydrides can be described by reaction models with one rate determining partial step. The rate and time laws derived depend on the individual partial process which is considered to be rate determining. Relevant formulas are compiled in this paper and compared with experiments performed with $\text{LaNi}_{4.7}\text{Al}_{0.3}$ and $\text{Mg}(\text{Ni})$ powder samples.

Keywords: Kinetics, Absorption, Desorption, Metal hydrides

I. INTRODUCTION¹

Storage capacity and fast reaction rate are the most important properties for hydrogen storage alloys. Numerous experiments have therefore been performed to test the kinetics of various storage alloys.¹ Progress on the interpretation of the data is, however, in a poor state. The large part of the experimental results on real storage powder materials are compared with the laws of first order reaction kinetics^{2,3,4} or with a Johnson-Mehl type equation.⁵ First order reactions are typical for homogeneous reactions in a single phase where the reaction rate is proportional to the amount of the unreacted reactant, but they are not suited for the description of a heterogeneous gas/solid reaction. The Johnson-Mehl model is frequently used to explain a sigmoidal shape of the time law. The reason for this behavior, however, is not internal kinetics but successive activation of the sample surface poisoned by impurities. In this paper models will be presented, which are based on more realistic physical assumptions and yet simple enough to be solved analytically or with only a few programming steps on a personal computer. The results of the models are compared with measurements on $\text{LaNi}_{4.7}\text{Al}_{0.3}$ and $\text{Mg}(\text{Ni})$ ⁶ powders.^{7,8}

II. MODELS FOR HYDRIDE FORMATION

The particles of the storage alloy are assumed to be spheres with constant diameter. The hydride phase grows from the metal/gas interface to the center according to Fig. 1a, because hydrogen first forms a solid solution (α phase) with a concentration gradient

from the surface to the center and saturation of the α phase takes place first at the metal/gas interface. Also the lattice expansion associated with the β phase requires less energy at the solid/gas interface than in the bulk of the solid. The following reaction mechanism for the absorption of hydrogen by a storage alloy is composed of a set of five intermediate partial processes for the overall reaction (Fig. 1a):

- 1) physisorption of hydrogen molecules
- 2) dissociation of hydrogen molecules and chemisorption
- 3) surface penetration of hydrogen atoms
- 4) diffusion of hydrogen atoms through the hydride layer, either by an interstitial or by a vacancy mechanism
- 5) hydride formation at the metal/hydride interface

In order to obtain simple equations for the rate and time laws two further assumptions are employed: the assumption of only one rate determining step and the steady state condition. One of the steps one to five shall be much slower than all others and it is, therefore, rate determining. All other reaction steps are then in equilibrium. The steady state condition requires that the change of the concentrations of intermediate species, for example the concentration of physisorbed hydrogen molecules, are small when compared with the reaction rate of hydride formation. The activity of hydrogen at positions before and after the rate determining step can then be expressed by equilibrium relations which contain only the hydrogen pressure in the gas phase and the decomposition pressure of the hydride as parameters.

Experiments for the determination of the reaction kinetics are usually performed at constant hydrogen pressure where the hydrogen flux into the reaction chamber is measured or by determination of the pressure change in a closed system with constant

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Fig. 1. Reaction partial steps for the (a) absorption and (b) desorption of hydrogen by a spherical metal/hydride powder particle.

volume (Sieverts' method). The relation between the total amount of reacted hydride and the radius r_α of the α phase (see Fig. 1a) is given by

$$n(t) = n_{Me} Z \left(1 - r_\alpha(t)^3 / r_0^3 \right) \quad (1)$$

where $n(t)$ is the number of moles of reacted hydrogen atoms, r_0 and r_α are the radii of the particle and the α phase core according to Fig. 1a, n_{Me} is the number of moles of the metal hydride sample, and Z the stoichiometric factor of hydrogen in the hydride MeH_z . For measurements in a Sieverts' apparatus the relation between the hydrogen pressure and the total amount of reacted hydride is given by the equation of state for ideal gases

$$n(t) = \frac{2(p_0 - p(t)) V_{res}}{RT} \quad (2)$$

where V_{res} is the volume of the reservoir, RT the gas constant times the absolute temperature, p_0 the initial hydrogen pressure and $p(t)$ the pressure as a function of the reaction time t . The rate of hydrogen absorption $\dot{n}(t)$ is given by

$$\dot{n}(t) = - \frac{2\dot{p}(t) V_{res}}{RT} \quad (3)$$

The reaction rate is proportional to the current $I(t)$ of

H atoms in a single particle and given by the equation

$$\dot{n}(t) = NI(t); \quad N = n_{Me} \frac{3 V_m}{4\pi r_0^3} \quad (4)$$

where N is the number of hydride particles and V_m the molar volume of the hydride. From Eqs. (1) and (2) an expression for $r_\alpha(t)$ as a function of $p(t)$ can be derived:

$$r_\alpha(t) = r_0 \left(1 - \frac{2(p_0 - p(t)) V_{res}}{n_{Me} Z R T} \right)^{1/3} \quad (5)$$

With these relations between pressure and thickness of the hydride scale the rate laws for models with a single reaction step can be formulated.

A. Physisorption

The physisorption reaction is given by

where $\square$ denotes an empty physisorption site on the surface. Since physisorption of gas molecules on surfaces requires almost no activation energy and the impingement rate of the hydrogen molecules on the surface is very large at higher pressures, the gas phase is certainly in equilibrium with the physisorbed state and physisorption is not rate determining. The concentration θ_{ph} of physisorbed particles can then be expressed by the equilibrium relation

$$\frac{\theta_{ph}}{(1 - \theta_{ph}) p} = K_1(T); \quad (7)$$

$$K_1(T) = K_1^0 \exp(\Delta H_{ph}^0 / RT)$$

where $K_1(T)$ is the equilibrium constant and ΔH_{ph}^0 the physisorption enthalpy. Since the coverage with physisorbed hydrogen molecules is small at room temperature, θ_{ph} is proportional to the hydrogen pressure:

$$\theta_{ph} = K_1(T) p \quad (8)$$

B. Chemisorption

The next reaction partial step is dissociation of the H_2 molecules and chemisorption of hydrogen atoms on the surface of the hydride, given by the reaction

$$H_2(ph) + 2\Box(ch) \rightarrow 2H(ch) + \Box(ph) \quad (9)$$

The rate of a reaction is given by the reaction rate in forward direction minus the reaction rate in backward direction. The reaction rate in forward and backward direction is given as the product of the concentration of the reacting species multiplied by a rate constant k . The reaction rate per unit area for Eq. (9) is thus given by

$$\begin{aligned} v &= k_{2f}\theta_{ph} - k_{2b}\theta_{ch}^2; \\ k_{2f} &= k_{2f}^0 \exp(-A_{2f}/RT), \\ k_{2b} &= k_{2b}^0 \exp(-A_{2b}/RT) \end{aligned} \quad (10)$$

with k_{2f} and k_{2b} reaction constants in forward and backward direction respectively. A_{2f} and A_{2b} are the corresponding activation energies, and θ_{ch} the concentration of chemisorbed hydrogen. In Eq. (10) it is assumed, that enough vacant chemisorption and physisorption sites are available for the forward and backward reaction and factors $(1-\theta)$ are, therefore, set to one. If chemisorption is the rate determining step the concentration of the physisorbed hydrogen molecules can be given as a function of the hydrogen pressure by Eq. (8) and the concentration of chemisorbed hydrogen atoms can be expressed in terms of the decomposition or plateau pressure p_{pl} of the hydride phase. Since the net reaction rate is zero in the equilibrium state Eq. (10) becomes

$$v = k_2(p - p_{pl}); \quad k_2 = K_1 k_{2f} \quad (11)$$

The total reaction rate is proportional to the surface area NA_s of the hydride powder. A_s is the surface of one particle. The total flux of hydrogen is given by

$$\dot{n} = NA_s k_2 (p - p_{pl}) \quad (12)$$

For experiments at constant pressure this means, that the hydrogen flux is constant and proportional to $(p - p_{pl})$. For experiments in a Sieverts' apparatus this equation must be combined with Eq. (3) to yield the differential equation

$$\dot{p}(t) = -\tilde{K}(p(t) - p_{pl}); \quad \tilde{K} = \frac{NA_s k_2 RT}{2V_{res}} \quad (13)$$

with the solution

$$p(t) = (p_0 - p_{pl}) \exp(-\tilde{K}t) + p_{pl} \quad (14)$$

If the chemisorption is not the rate determining reaction step, the chemisorbed hydrogen atoms are in equilibrium with the gas phase ($H_2 + 2\Box(ch) = 2H(ch)$) and the concentration is given by

$$\frac{\theta_{ch}^2}{p(1-\theta_{ch})^2} = K_2(T) \quad (15)$$

or for small coverages

$$\theta_{ch} = \sqrt{K_2} \sqrt{p} \quad (16)$$

C. Surface penetration

The transfer of chemisorbed hydrogen on the surface to the first subsurface layer in the hydride can be considered as a single diffusion jump, but with an activation energy different from diffusion in the bulk of the hydride. Therefore, it can be necessary to formulate this step separately. Diffusion of hydrogen is assumed here to take place by a vacancy mechanism of hydrogen in the hydride lattice. The assumption of an interstitial mechanism would lead to similar results. The surface penetration process is described by

where $\Box_\beta(r_0)$ denotes a vacancy in the lattice of the β phase just below the surface. The reaction rate per unit area is thus given by

$$v = k_{3f}\theta_{ch}c_{\Box_\beta}(r_0) - k_{3b}(1-\theta_{ch}) \quad (18)$$

where $c_{\Box_\beta}(r_0)$ is the vacancy concentration in the subsurface layer. It must be noted, that $c_{\Box_\beta}(r_0)$ is in equilibrium with the α/β interface and is, therefore, constant. With the procedure following Eqs. (10) to (12) and again omitting factors $(1-\theta)$ this yields

$$\dot{n} = NA_s k_3 \left(\frac{\sqrt{p}}{\sqrt{p_{pl}}} - 1 \right); \quad (19)$$

$$k_3 = k_{3f} \sqrt{K_2} \sqrt{p_{pl}} c_{\Box_\beta}(r_0)$$

Thus, for experiments at constant pressure the hydrogen flux is constant again, but the reaction rate is now proportional to $(\sqrt{p} - \sqrt{p_{pl}})$. For

experiments in a Sieverts' apparatus the differential equation

$$\dot{P}(t) = -\tilde{K} \left(\sqrt{P(t)/\sqrt{P_{pl}}} - 1 \right); \quad (20)$$

$$\tilde{K} = NA_s k_3 RT/2 V_{res}$$

is obtained. This equation has no analytical solution and can only be solved numerically.

In subsequent sections the equilibrium concentration of the hydrogen vacancies with the gas phase is needed. It is given by

$$c_{\square\beta}(r_0) = \sqrt{K_3(T)/\sqrt{P}} \quad (21)$$

which is the equilibrium condition for the reaction $H_2 + 2\square_{\beta}(r_0) = 0$.

D. Diffusion

The next reaction partial step is the diffusion of hydrogen atoms from the subsurface through the hydride layer to the α/β interface. The diffusion current density for a system with radial symmetry is given by

$$j = -bc \frac{\partial \mu}{\partial r} \quad (22)$$

where b is the mobility, c the concentration and μ the chemical potential of the diffusing species. With the activity $a = \gamma c$ and $\mu = \mu_0 + RT \ln a$ Eq. (22) can be written as

$$j = \frac{ba}{\gamma} \frac{\partial}{\partial r} (\mu_0 + RT \ln a) = \frac{b}{\gamma} RT \frac{\partial a}{\partial r} \quad (23)$$

where the minus sign has been omitted since we are only interested in the absolute value of j . Assuming a steady state the total current $I = 4\pi r^2 j$ is constant in the range $r_0 \geq r \geq r_{\alpha}$. Eq. (23) can then be rewritten as

$$\frac{I}{r^2} = \frac{4\pi}{\gamma} bRT \frac{\partial a}{\partial r} \quad (24)$$

and finally integrated over r from r_{α} to r_0 to yield

$$I \left(\frac{1}{r_{\alpha}} - \frac{1}{r_0} \right) = 4\pi D (c_{\square\beta}(r_0) - c_{\square\beta}(r_{\alpha})) \quad (25)$$

where D is the diffusion constant, the Einstein relation $D = b kT$ was used and a vacancy mechanism for the diffusion of hydrogen in the hydride is assumed. The vacancy concentrations $c_{\square\beta}(r_0)$ and

$c_{\square\beta}(r_{\alpha})$ can again be expressed by the activities of hydrogen in the gas phase (Eq. (21)), $1/\sqrt{P}$, and at the metal/hydride interface, $1/\sqrt{P_{pl}}$:

$$I \left(\frac{1}{r_{\alpha}} - \frac{1}{r_0} \right) = 4\pi D \sqrt{K_3} \left(\frac{1}{\sqrt{P}} - \frac{1}{\sqrt{P_{pl}}} \right) \quad (26)$$

For experiments at constant pressure Eq. (26) must be combined with Eqs. (1) and (4) to yield the differential equation

$$\dot{P}(t) = 4\pi N D r_0 \sqrt{K_3} \frac{(1/\sqrt{P} - 1/\sqrt{P_{pl}})}{\left(\left(1 - \frac{P(t)}{n_{Me} Z} \right)^{-1/3} - 1 \right)} \quad (27)$$

For experiments in a Sieverts' apparatus Eq. (26) must be likewise combined with Eq. (3), (4) and (5) to yield

$$\dot{P}(t) = - \frac{3 D V_m \sqrt{K_3}}{\tilde{K} r_0^2} \times \frac{(1/\sqrt{P_{pl}} - 1/\sqrt{P(t)})}{\left(\left(1 - \frac{\tilde{K}}{Z} (P_0 - P(t)) \right)^{-1/3} - 1 \right)}; \quad (28)$$

$$\tilde{K} = \frac{2 V_{res}}{n_{Me} RT}$$

which, again, must be solved numerically.

E. Hydride formation

The final reaction step is the formation of new hydride at the metal/hydride interface. For the vacancy mechanism considered here the reaction is given by

For this reaction the forward reaction rate per unit area is constant and decreases with the surface area of the metal core (see Fig. 1a):

$$I = 4\pi r_{\alpha}^2 (k_{5f} - k_{5b} c_{\square\beta}(r_{\alpha})) \quad (30)$$

With the same treatment as used above the differential equations

$$\dot{P}(t) = 4\pi N k_5 r_0^2 \left(1 - \frac{P(t)}{n_{Me} Z} \right)^{2/3} \left(\frac{1}{\sqrt{P_{pl}}} - \frac{1}{\sqrt{P}} \right) \quad (31)$$

are obtained for experiments at constant pressure and

$$\dot{p}(t) = -\frac{4\pi NRTk_5 r_0^2}{2V_{res}} \left(1 - \frac{\tilde{K}}{Z}(p_0 - p(t))\right)^{2/3} \times \left(\frac{1}{\sqrt{p_{pl}}} - \frac{1}{\sqrt{p(t)}}\right); \quad \tilde{K} = \frac{2V_{res}}{n_{Me}RT} \quad (32)$$

for experiments in a Sieverts' apparatus.

III. MODELS FOR HYDRIDE DECOMPOSITION

With the equations of the preceding section the hydrogen desorption process can be reviewed quickly. The α phase is formed first at the metal/gas interface of the spherical particles according to Fig. 1b. Again five reaction partial steps are required for the overall reaction:

- 1) hydride decomposition at the hydride/metal interface
- 2) diffusion of hydrogen atoms through the α phase
- 3) surface penetration of hydrogen atoms
- 4) recombination of chemisorbed hydrogen atoms and physisorption
- 5) desorption to the gas phase

The geometrical relations Eqs. (1) to (5) hold with minor changes also for the desorption reaction. In Eq. (1) r_α must be replaced by r_β , Eqs. (3) and (4) must be equipped with an overall minus sign and in Eq. (5) p_0 and p must be exchanged. The individual reaction steps then have the following form:

A. Hydride phase decomposition

The first reaction partial step for the desorption process is the decomposition of the hydride at the metal/hydride interface and formation of α phase. In the α phase the hydrogen atoms are dissolved as interstitials. The reaction is thus given by

where $\square_\alpha(r_\beta)$ represents an empty interstitial site in the α phase at the α/β interface. Since the activities of MeH and Me are unity the reaction rate per unit area is given by

$$v = k_{1a}(1 - c_\alpha(r_\beta)) - k_{1b}c_\alpha(r_\beta) \quad (34)$$

where $c_\alpha(r_\beta)$ denotes the concentration of hydrogen in the α phase at the α/β interface. The concentration $c_\alpha(r_\beta)$ is in equilibrium with the gas phase and can be expressed by the hydrogen pressure

with the help of Sieverts law. The total reaction rate of an individual particle is proportional to the surface of the reaction front. Thus, with $(1 - c_\alpha) \approx 1$, Eq. (34) becomes

$$I = 4\pi r_\beta^2 k_1 (\sqrt{p_{pl}} - \sqrt{p}) \quad (35)$$

For experiments at constant pressure this yields the differential equation

$$\dot{p}(t) = 4\pi N k_1 r_0^2 \left(1 - \frac{p(t)}{n_{Me}Z}\right)^{2/3} (\sqrt{p_{pl}} - \sqrt{p}) \quad (36)$$

and for experiments in a Sieverts' apparatus

$$\dot{p}(t) = \frac{4\pi NRTk_1 r_0^2}{2V_{res}} \left(1 - \frac{\tilde{K}}{Z}(p(t) - p_0)\right)^{2/3} \times \left(\sqrt{p_{pl}} - \sqrt{p(t)}\right); \quad \tilde{K} = \frac{2V_{res}}{n_{Me}RT} \quad (37)$$

B. Diffusion

The diffusion can be formulated in a similar way as in section 2.1.4. The diffusion mechanism here is diffusion of interstitials and not of vacancies. The differential equation becomes

$$\dot{p}(t) = 4\pi ND r_0 \sqrt{K_3} \frac{(\sqrt{p_{pl}} - \sqrt{p})}{\left(\left(1 - \frac{p(t)}{n_{Me}Z}\right)^{-1/3} - 1\right)} \quad (38)$$

for experiments at constant pressure and

$$\dot{p}(t) = \frac{3DV_m \sqrt{K_3}}{\tilde{K}_0^2} \frac{(\sqrt{p_{pl}} - \sqrt{p})}{\left(\left(1 - \frac{\tilde{K}}{Z}(p(t) - p_0)\right)^{-1/3} - 1\right)} \quad (39)$$

$$\tilde{K} = \frac{2V_{res}}{n_{Me}RT}$$

for experiments in a Sieverts' apparatus.

C. Surface penetration

The step from the last interstitial site inside the α phase to the surface is given by

where $\square_{ch}$ denotes empty chemisorption sites and

$\square_\alpha(x_0)$ subsurface vacancies. The total reaction rate is given by

$$\dot{n} = \tilde{K}(\sqrt{p_{pl}} - \sqrt{p}); \quad \tilde{K} = NA_s k_3 \quad (41)$$

It is constant for experiments at constant pressures. For experiments in a Sieverts' apparatus the differential equation

$$\dot{p}(t) = \tilde{K}(\sqrt{p_{pl}} - \sqrt{p}); \quad \tilde{K} = \frac{NA_s k_3 RT}{2r_0 V_{res}} \quad (42)$$

is obtained. The reaction rate is proportional to $(\sqrt{p_{pl}} - \sqrt{p})$ and constant for pressures small compared to the plateau pressure.

D. Recombination and desorption to the gas phase

The next reaction partial step is the recombination of chemisorbed hydrogen atoms and formation of physisorbed hydrogen molecules on the surface

The total reaction rate is given by

$$\dot{n}(t) = \tilde{K}(p_{pl} - p); \quad \tilde{K} = NA_s k_2 \quad (44)$$

Again, the reaction rate is constant for experiments at constant pressure. For experiments in a Sieverts' apparatus the differential equation

$$\dot{p}(t) = \tilde{K}(p_{pl} - p); \quad \tilde{K} = \frac{NA_s k_2 RT}{2r_0 V_{res}} \quad (45)$$

holds which is again constant for pressures small compared to the plateau pressure. The solution of Eq. (45) is given by:

$$p(t) = (p_0 - p_{pl})\exp(-\tilde{K}t) + p_{pl} \quad (46)$$

The final reaction partial step, the desorption of physisorbed molecules to the gas phase, is not considered as a rate determining step because of the low activation energies involved.

IV. EXPERIMENTAL

Many measurements of reaction kinetics are performed under not well defined experimental conditions. Two important requirements are frequently violated: deviations from isothermal conditions caused by the reaction heat and poisoning of the sample surface by impurities^{9,10}. In the present investigations volumetric Sieverts' techniques are employed: The hydrogen pressure change due to the hydrogen absorption and desorption is measured

in a closed system with constant volume. Special attention was given to the problems of surface contamination and heat transfer.

Surface contamination. In order to avoid surface impurities our apparatus was equipped with a diffusion pump and had a base pressure of 10^{-6} mbar. For the experiments hydrogen with 99.9999% purity was used. After activation by several loading cycles the experiments were subsequently performed without time delay between loading and degassing in order to minimize surface contamination in the course of the experiments.

Heat transfer. Since the experiments should be performed under isothermal conditions, the heat of reaction has to be removed from the sample. For the $\text{LaNi}_{4.7}\text{Al}_{0.3}$ we used an Al heat buffer of 92 weight% Al powder as a heat sink^{11,12}. Since there will always be some temperature rise in the course of an experiment, only the beginning of the experimental pressure drop should be used for comparison with model calculations. There the temperature changes are small and the system is still far from the equilibrium state. Since the reaction rate for $\text{Mg}(\text{Ni})$ is small the heat production is less detrimental and the $\text{Mg}(\text{Ni})$ measurements can be performed without heat buffer.

Fig. 2. Results of model calculations for the absorption of hydrogen. Simulation of a volumetric measurement in a plot of pressure change vs. reaction time for different rate determining reaction steps.

V. RESULTS AND DISCUSSION

A. Hydride formation

Results of model calculations. Fig. 2 shows the results of model calculations for different rate determining reaction partial steps. A simulation of experiments in a Sieverts' apparatus is chosen. The pressure change in the reactor is plotted as a function of reaction time. The reaction constants chosen for the different model types give similar initial reaction rates except for the diffusion model. The models with chemisorption, surface penetration and hydride formation yield quite similar curves. However, a completely different behavior is obtained for the

Fig. 3. Results of volumetric measurements for the hydrogen absorption of $\text{LaNi}_{4.7}\text{Al}_{0.3}$ at 343 K for various initial pressures and model calculations for (a) chemisorption and (b) diffusion as rate controlling steps.

model with diffusion as rate determining step. Here the initial reaction rate is much higher for the same total reaction time.

Limitations of the models. The models are derived for spherical particles with uniform radius. However, the models with chemisorption and surface penetration control are not sensitive to size or shape effects. Only the total surface area of the powder sample, denoted by NA_s in Eqs. (12) and (19), is important for both models. For rate control by diffusion and hydride formation the shape and size enters the equations. The size of the powder particles appears in the final equations only as a constant overall factor and, therefore, does not affect the shape of the time law. For a more complex diffusion model it has been demonstrated by M. H. Mintz and Y. Zeiri¹³ that the effect of shape and size distributions of powder particles on the shape of the calculated curves is relatively small.

The existence of a two phase region from the beginning with a shrinking α phase core is another restricting assumption which neglects the initial process of hydrogen solution in the α phase. Furthermore, the validity of the equations ends after completion of the β phase and disregards concentration changes in the β phase.

The limitation to only one rate determining step throughout the entire absorption reaction must be

kept in mind, if the surface models are applied: if at the beginning of the reaction a surface process is rate determining, it is possible that towards the end, when the system approaches equilibrium and the concentration gradient in the hydride is small, diffusion becomes rate determining. Therefore, the models should be checked in regions far from equilibrium.

Experimental results and comparison with model calculations. Fig. 3 shows the hydrogen absorption curves of activated $\text{LaNi}_{4.7}\text{Al}_{0.3}$ powder for three different hydrogen pressures together with results of model calculations. The temperature of the sample was 343 K. For the initial hydrogen pressures chosen in a Sieverts' apparatus equilibrium is reached before the sample is completely hydrided. In the first five seconds of the experiment the hydrogen uptake is very fast. After that a slower pressure change is measured and the equilibrium pressure is reached after about 100 s. In this late phase of the reaction the deviation from isothermal conditions causes larger errors due to the increase of the decomposition pressure of the hydride. It must be noted that no sigmoidal shaped reaction curve occurs. This indicates that the commonly observed behavior may be caused mainly by surface contaminations of the sample.

Comparison of the experimental curves with simulated curves for diffusion control (Fig. 3b) demonstrates that the curvature of the experimental curves cannot be represented by the diffusion model. The chemisorption model (Fig. 3a), however, agrees quite well with the first part of the hydriding curves. The reason for the deviation of the calculated from the experimental curves after five seconds can be a transition from chemisorption to diffusion control or, more likely, departure from isothermal conditions in the course of the experiment and therefore reduction of the reaction rate due to the higher plateau pressure p_{pl} (see Eq. (13)). As shown in Fig. 2 the models for surface penetration or hydride formation yield results which are very similar to those of the chemisorption model and can therefore be fitted as well. Two additional arguments demonstrate that chemisorption is the rate determining step. If the initial reaction rate is plotted versus $p - p_{pl}$ a linear relation is obtained which is described best by Eq. (12). Another strong argument for a surface reaction are experiments with nickel instead of aluminum as a heat buffer. The initial reaction rate is increased by about a factor of two.⁷ Since nickel is known to catalyze the dissociation of hydrogen^{14,15,16} this indicates again that dissociation and chemisorption of the hydrogen molecules is the rate determining step for this reaction.

In Fig. 4 typical experimental results for $\text{Mg}(\text{Ni})$

Fig. 4. Results of volumetric measurements for the hydrogen absorption of Mg(Ni) [6] at 593 K for various initial pressures.

Fig. 5. Results of model calculations for the desorption of hydrogen. The pressure increase in an evacuated receiver is plotted as a function of the reaction time for different rate determining steps.

Fig. 6. Result of a volumetric experiment on hydrogen desorption of $\text{LaNi}_{4.7}\text{Al}_{0.3}$ at 298 K and model calculations for various rate determining steps.

powder samples starting from different initial pressures are shown. Mg(Ni) is a magnesium powder with a 2 wt% Ni coating.⁶ The surface coating serves as a catalyst for the hydrogen desorption from magnesium hydride.¹⁷ Up to pressures of about 8 bar the reaction rate increases with increasing pressure. Above 9 bar the initial reaction rate is still enhanced, but after the powder is loaded to about 50% the reaction rate decreases to a value smaller than found at lower pressures. Although each of the individual experiments could be represented by a diffusion model, this complex behavior cannot be explained by a single model because all of them

Fig. 7. Results of desorption measurements for $\text{LaNi}_{4.7}\text{Al}_{0.3}$ at various temperatures and model calculations for diffusion as rate determining step.

Fig. 8. Result of a volumetric experiment on hydrogen desorption of Mg(Ni) at 565 K and model calculations for various rate determining steps.

Fig. 9. Results of desorption measurements for Mg(Ni) at various temperatures and model calculations for surface penetration as rate determining step.

show increased reaction rates with increasing pressure. Therefore, for the absorption of hydrogen by Mg(Ni) a more complex mechanism must be employed, based on a combination of a nucleation of hydride islands on the surface and the shrinking core model as suggested by B. Vegholm and coworkers.¹⁸

B. Desorption

Results of model calculations. In Fig. 5 the results of model calculations for the various desorption types are shown. The parameters V_{res} and n_{Me} are chosen in such a way that the sample is not completely dehydrided and the reaction ends at the

equilibrium (plateau) pressure of a two phase sample. Again, the initial reaction rates are similar for the models with a rate determining step on an inner or outer surface. Only the diffusion model shows a much larger curvature.

Experimental results and comparison with model calculations. Fig. 6 shows the result of a desorption experiment with $\text{LaNi}_{4.7}\text{Al}_{0.3}$ powder at 298 K together with calculated curves. The experiments are performed in a closed system by measurement of the pressure change. The volume of the receiver is chosen large enough to achieve a final pressure well below the plateau pressure. In contrast to the absorption reaction of the same material the experimental curve cannot be fitted by the two models with a rate determining step at the outer particle surface. The best fit of the experiment is obtained by the diffusion model and an acceptable agreement by the model with hydride decomposition control. As discussed for the absorption process the deviations of the calculated from the measured curves can be attributed to a change of the rate determining step in the course of the experiment or, more likely, to deviation from the isothermal conditions and/or to size and shape variations of the particles. The models with a rate determining step at the outer surface end with a sharp bend at the end of the reaction. This behavior is due to the neglect of hydrogen desorption from the α phase. This process can in principle be incorporated in a more complex model but it would not improve much the understanding of the phenomena. In contrast to the absorption process the driving force for the desorption reaction, i.e. the decomposition or plateau pressure, cannot be chosen independently of the temperature. It is nevertheless interesting to fit experiments performed with $\text{LaNi}_{4.7}\text{Al}_{0.3}$ at different temperatures to the diffusion model (Fig. 7) The agreement with the diffusion model is quite good at all temperatures. An activation energy of 28 kJ was chosen for the diffusion constant D in Eq. (39), which is within the range of results of other measurements.¹⁹

Fig. 8 shows the result of a desorption experiment for $\text{Mg}(\text{Ni})$ at 565 K together with results of model calculations. The reaction shows a linear behavior until about 70% of the hydrogen is desorbed. Therefore, in contrast to $\text{LaNi}_{4.7}\text{Al}_{0.3}$, the diffusion model cannot represent the experimental curve. Good agreement is obtained for the surface models. In Fig. 9 results of three desorption measurements for $\text{Mg}(\text{Ni})$ at different temperatures are shown. Again, the surface penetration model fits all curves well and the activation energy determined has with 120 kJ a reasonable value higher than the heat of the α/β transformation (52 kJ/mol H_2)²⁰

VI. CONCLUSIONS

The models presented are based on simple, but physically reasonable mechanisms with only one rate determining step for spherical powder particles. The results of measurements for $\text{LaNi}_{4.7}\text{Al}_{0.3}$ and $\text{Mg}(\text{Ni})$ powder samples demonstrate that they are able to explain basic features of the reaction mechanism.

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