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Complete List of Authors:	Drozdov, Igor; University Koblenz, Natural Sciences Vassen, Robert; Forschungszentrum Juelich, IEF-1 Stoever, Detlev; Forschungszentrum Juelich, IEF-1

Modelling and Evaluation of Hydrogen Desorption Kinetics Controlled by Surface Reaction and Bulk Diffusion for Magnesium Hydride

I. V. Drozdov*, R. Vaßen and D. Stöver

Institute of Energy Research IEF-1, Forschungszentrum Jülich
Leo-Brandt-Strasse, D-52425, Jülich, Germany

Abstract

The 'shrinking core' model has been applied for the evaluation of hydrogen desorption kinetics during decomposition of magnesium hydride. According to our estimation, the full desorption time is expected to have a quadratic dependence on the size of powder particles, if the bulk diffusion of hydrogen atoms in magnesium is a rate controlling step. However, for the actual diffusion rate for hydrogen in magnesium bulk the diffusion cannot significantly influence the overall desorption kinetics for micro- and nano- powders.

Keywords: Hydrides, hydrogen storage, magnesium, desorption, diffusion.

1 Introduction

1.1 Preliminary remarks

Magnesium hydride is considered to be a potentially useful hydrogen storage material [1] due to its relatively high hydrogen content (up to 7.66 wt.%).

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*Corresponding author, e-mail: drosdow@uni-koblenz.de

At the same time, major drawback of its application is the insufficiently fast desorption kinetics, especially the desorption at moderate temperatures below 300^oC. [3, 4]

Hydrogen accumulates within the magnesium body in the form of stoichiometrical magnesium hydride MgH_2 [5, 6]. The *absorption* process occurs in several steps, generally defined as follows (e.g. [7, 8]):
1) adsorption of hydrogen molecules on the surface of a magnesium particle, followed by their dissociation into hydrogen atoms $H_2 \to 2H$;
2) diffusion of dissolved hydrogen atoms into the Mg - bulk (α-phase);
3) formation of the magnesium hydride MgH_2 (β-phase) at the $\alpha-\beta$ interface $Mg + 2H \to MgH_2$.

The desorption process occurs in the reverse order, namely [9, 10]:
1) magnesium hydride decomposes at the $\alpha-\beta$ interface and hydrogen atoms dissolve in the metallic bulk $MgH_2 \to Mg + 2H$;
2) the dissolved hydrogen atoms move to the surface of particle by diffusion transport;
3) the chain of several surface reactions (association of hydrogen atoms on the surface followed by release of gaseous molecular hydrogen from the surface of powder particle $2H \to H_2$) provides the surface degassing.

The overall hydrogen absorption/desorption rate is therefore a function of the rate of above steps. In turn, the steps of of the entire processes are dependent on each other [7], since the rate of each process is strongly related to the rate of the previous one. Therefore, the resulting kinetics are determined by the slowest process of the entire chain and is called the ‘rate controlling step’. Identification of the rate controlling process is a crucial problem for understanding the mechanisms governing the kinetics of sorption and desorption This knowledge is necessary for systematic improvements of kinetic properties of sorption materials of materials, especially the magnesium hydride.

One of the commonly used ways to improve the sorption/desorption kinetics for powder is the modification of its specific surface area. This could be achieved by:
1) refinement through the mechanical milling [11, 12, 13]
2) changing of the particle surface morphology [14, 15, 16, 17].

The goal for the different analytical and phenomenological models is particularly to identify, which one of the above steps of [1),2),3)] is affected by these treatments and to what degree.

There is a certain relation between sorption kinetics and the specific surface. In turn, the specific surface area of the powder corresponds to the characteristic size of particles. It has been proven experimentally that the desorption rate increases with the decrease of the particle size [18, 19, 20] (it applies equally to sorption as well). The reasons which are mentioned in the literature are:

a) the increase in specific surface area;

b) the reduction in diffusion paths for hydrogen atoms [20].

If we take into consideration the three desorption steps as outlined above, the first statement relates to the surface reaction $H_2 \rightleftharpoons 2H$ whereas the second one relates to the diffusion of H-atoms in the bulk.

The *surface reaction* can never be neglected [21], since the exchange between the surrounding gas and the metal surface follows the Sievert's law [23, 24, 25, 26]. As a result, the threshold pressure for both absorption and desorption, which is the so called *plateau pressure* for hydride formation/decomposition, corresponds to the concentration of hydrogen atoms on the surface. On the other hand, this concentration is related to the concentration of hydrogen atoms dissolved in the magnesium bulk (α-phase) [27, 28, 29]. This concentration further depends on the thermodynamic properties of the interface reaction $MgH_2 \rightleftharpoons Mg + 2H$. On the $\alpha - \beta$ interface, this concentration cannot overcome a maximal (critical) value.

The relatively high negative enthalpy of formation of magnesium hydride (about $-85kJ/molH_2$) [30] can be a key factor for a slow absorption and fast desorption kinetics respectively. However, it should be kept in mind that the reaction $Mg + H_2 \rightleftharpoons MgH_2$ comprises at least two substeps $2H + Mg \rightleftharpoons H_2 + Mg$ (surface dissociation/recombination) and $MgH_2 \rightleftharpoons Mg + 2H$ (interface hydride formation/decomposition). The overall enthalpy represents mainly the latter reaction. Thus another factor, which possibly affects the *desorption* kinetics is the former one (surface reaction). This process, although characterized by a relatively low enthalpy and activation energy [31], has nevetheless a low overall cross-section for low concentration because of a strong concentration-dependence of recombination rate.

1.2 Main results and conclusions

If the overall desorption rate is controlled by the *surface reaction*, the desorption time τ (1/rate) can be expected to show a linear dependence on the particle size L at isobaric desorption.This conclusion was claimed in our recent investigation [21], based on simlpe considerations of dimensionality and has been confirmed by the exact solution of the simplified model for *surface controlled desorption.*

The results of this previous modelling [21] shows furthermore, that the surface reaction provides the crucial impact on the desorption kinetics. This suggestion is especially confirmed by the strong dependence on the external gas pressure. It leads finally to the evidence that the experimentally observable "sigmoidal" shape of kinetic curves is in fact an artificial effect of the volumetric measurement and is strongly dependent on the volumetric setup.

However in case of the *diffusion*-controlled kinetics, the total desorption time increases quadratically in the L, as it will be shown in the present paper below and is in an accordance with the general dimensional analysis readily performed [22]. The estimation with the real values for metal hydrides leads to the conclusion that the bulk diffusion *cannot be considered* as a rate controlling step for desorption. The same argumentation can be also applied for absorption process as well. The factors responsible for a slow sorption or desorption kinetics should be found therefore in surface or interface reaction. This is the most important claim resulting from the work presented here.

This result suggests the tendency for future development of materials aimed to modify the surface morphology (like the wet-ball-milled powders [17]) and to impact the parameters of chemical processes on the surface and interface respectively. The most interesting topic for theoretical reserach is the investigation of the interface reaction. It can be performed in framework of the solution of generalized Stefan problem. To this end, the consistent analytical formulation of moving boundary in terms of reaction rates is needed. (A word forward, this formulation is readily performed and sholud be preprinted shortly)

Generally, it can be supposed that the sorption/desorption kinetics controlled by each of three different steps should have also a related characteristic exponent γ in $\tau \sim L^{\gamma}$. Hence, the influence of several rate controlling factors on the overall sorption rate can be recognized by using powders with different particle sizes. Especially the influence of the bulk diffusion and its characteristic exponent can be estimated with a simple analytical model.

1.3 Theoretical assumptions of the model

The theoretical formulation for any model of the sorption/desorption kinetics leads to the boundary problem with a moving boundary (*Stefan problem*). The local formulation of the Stefan problem aims to describe the local evolution of the moving boundary surfaces in each point of them. The resulting solutions could be sufficiently sensitive to certain boundary and initial conditions. But in fact, with an interpretation of the experimental data we have mostly the situation when only the overall rate, the absorbed or desorbed amount as a function of time, is available. Moreover, for practical applications it merely required to predict only the full sorption/desrption time as a function of material properties.

In this regard, we restrict our discussion to the situation, that the morphology of powder particles does not vary significantly from the spherical one and morphology variations do not influence the overall sorption kinetics significantly. Further, the great difference between concentrations of hydrogen atoms in α and β phases (over 10^3 times) justifies the approach, where the variation of the concentration profile of dissolved hydrogen is caused only by the boundary movement.

As supposed, the association $2H \to H_2$ comes about due to the $H - H$ lateral interaction. Typically, the pairwise lateral interactions strongly depend on the nearest and next-nearest neighbor interaction between dissolved H-atoms. Because of a relatively low concentration on the metallic bulk (stoichiometric index γ of H in MgH_γ is about 0.01) we can assumme that the long-range lateral interaction of hydrogen atoms to each other does not influence significantly the concentration, which in turn obeys the diffusion equation. On the other hand, the low surface concentration provides a low cross-section of the surface reaction.

These simplifying assumptions allow to obtain analytical solutions for overall desorption kinetics, which can be directly compared with available experimental data. Thus the influence of factors, such as the diffusion rate, should be clearly visible in the predicted results, as it will be performed in the next sections.

2 Theoretical background of the model

2.1 Local description

A number of models [32, 33, 4] based on pure phenomenological interpretation, describe the desorption/absorption kinetics as the time-dependent mass fraction of the absorbed/desorbed gas. This dependence is usually investigated and presented in the experimental results.

On the other hand it is clear, that each chemical/physical process which occurs at the particle surface, $\alpha - \beta$ interface or in the bulk, is a strictly *local* process. It means that the rate of any process - diffusion, decomposition, recombination in a certain space point (x, y, z) (or infinitesimally small volume) can only depend on the quantities (temperature, concentration, gradients) taken in the same space point.

Without loss of generality we restrict the discussion to the *desorption* process. The rate of MgH_2-dissociation ($\beta \rightarrow \alpha$-transition) at a point of the interface (and the resulting movement of the interface) can only be dependent on temperature, concentration of α-dissolved hydrogen, gradient of the concentration, diffusion flux, eventually also higher derivatives of concentration, geometrical properties of the interface (curvature, lattice orientation etc.) defined in this point.

The integral representation of the local behavior leads to the resulting dependence on *global* measured parameters, such as the amount of the desorbed hydrogen or the ratio hydrogen/metal in a single particle or in the whole sample.

In this sense, we suppose that μ is the molar rate of the dissociated magnesium hydride at the interface - *surface decomposition rate* - that means the molar amount of magnesium hydride that is decomposed during the time dt per surface area element $d\sigma$:

$$\mu := \frac{dm_{MgH_2}}{dt\ d\sigma} = \mu(T, c_\alpha, \nabla c_\alpha, ...), \ \left[\frac{mol}{m^2 \cdot s}\right]. \tag{1}$$

The variable concentration of hydrogen atoms is only the concentration of the dissolved hydrogen c_α in the magnesium bulk (α-phase) between the interface from inside and the surface from outside. Mathematically it is considered as a dynamic scalar field $c_\alpha = c_\alpha(x, t)$ i.e. the function of time t and space point x in any coordinate system.

The local interface movement rate should be therefore

$$\frac{\partial}{\partial t}(\mathbf{x} \cdot \mathbf{d}\sigma)_I = (c_\beta - c_\alpha|_I)\mu, \ [m/s], \tag{2}$$

here x_I denotes the position of the local point of the moving interface between solid MgH_2 and a region with $Mg + H$ in the chosen coordinate system $\vec{x}$,
$c_\alpha|_I = c_\alpha(x_I, t)$ is the concentration of dissolved H-atoms $[mol/m^3]$ at the interface I,
c_β is the concentration of H-atoms $[mol/m^3]$ in the stoichiometric hydride,

which is always constant. Geometrically, this process is described like the problem of moving solid-liquid interface in a solidification problem.

The model can be further simplified by the following assumptions:

- There is the critical concentration $\bar{c}_\alpha$ of the dissolved hydrogen atoms. This requirement is based on the characteristics of $\alpha - \beta$ phase transition. The transformation of $\beta \rightarrow \alpha$ (decomposition of hydride) stops if the critical concentration at the interface is reached;
- The diffusion of dissolved hydrogen atoms obeys the Fick's diffusion law
  $$\mathbf{j} = -D\nabla c_\alpha \tag{3}$$
  where the diffusion efflux $\mathbf{j} = \mathbf{j}(\mathbf{x})$ in the point x is the molar rate of dissolved hydrogen transported away from the interface through the diffusion. The coefficient D (rate of diffusion) in every point is supposed to be generally independent from the concentration and its local derivatives, because correlations between dissolved hydrogen atoms in the α-phase are sufficiently weak due to the very low concentration (stoichiometric index ε in α phase of MgH_ε is typicallly about 0.01) and do not contribute to the bulk diffusion rate. The temperature dependence $D(T)$ is also disregarded, since only isothermal processes are considered.

As suggested above, the molar concentration c_α of dissolved hydrogen atoms can never overcome its critical value $\bar{c}_\alpha$. Furthermore we assume that the rate μ is a function only of the concentration c_α.

Once the critical concentration $\bar{c}_\alpha$ (for the given temperature T) is reached, the further process runs at the constant $c_\alpha|_\mathbf{I} = \bar{c}_\alpha$ at the interface, where the balance equation reads:

$$\mu(\bar{c}_\alpha) = -D(\nabla \mathbf{c}_\alpha \cdot \mathbf{d}\sigma)|_I. \tag{4}$$

In this simplified case, the evolution of the interface is governed only by the diffusion flux. The kinetic equation (2) for the interface is then simplified to:

$$(c_\beta - c_\alpha|_I)(\mathbf{d}\sigma \cdot \dot{\mathbf{x}}_\mathbf{I}) = -D(\nabla \mathbf{c}_\alpha \cdot \mathbf{d}\sigma)|_I. \tag{5}$$

Additionally, since the diffusion rate D remains constant between $\alpha - \beta$ interface and magnesium surface, the concentration c_α obeys the second order

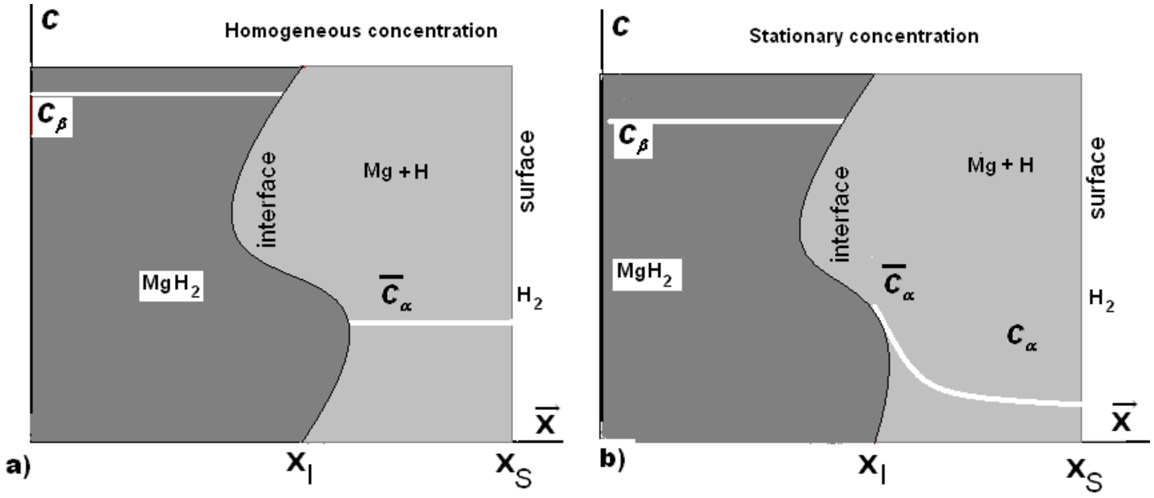

Figure 1: **Concentration of Dissolved Hydrogen: Homogeneous versus Stationary**

diffusion equation (‘heat equation’)

$$\frac{\partial c_\alpha}{\partial t} = D\nabla^2 c_\alpha \tag{6}$$

within this domain.

The difference between the *homogeneous* and *quasi-stationary* models is illustrated in the Fig.1

The **Case a)** corresponds to a fast diffusion. The concentration profile remains thus always homogeneous. In a strictly mathematical sense, this *homogeneous* concentration as considered in [21] can only be valid for an infinite high diffusion rate D. For a finite D a homogeneous profile does not provide, strictly speaking, any diffusion flow and cannot actually produce any desorption. Instead, we assume that the concentration profile obeys the stationary diffusion equation (6) with $\dot{c_\alpha} = 0$ (Laplace equation) in each point of α-domain at any time. The effective time-dependence of $c_\alpha(x,t)$ results from the time-dependent boundary condition (5). In Mathematics a condition of this type is called ‘Stefan condition’.

If the finite diffusion rate is taken into account (Fig.1 **Case b)**), the diffusion flux induces the concentration profile $c_\alpha(x)$. Here the dissociating hydride (interface) is the *source* and the particle surface, which is releasing molecular hydrogen, is the *sink* of the flux. For each current position of

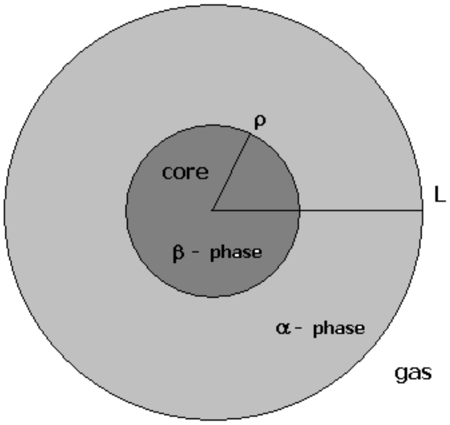

Figure 2: **spherically symmetric particle**

the interface, the profile is assumed to be stationary, obeying the condition $\dot{c}(x,t) = 0$ in each point. It varies slowly with the time because of the moving source boundary, in this case, the interface.

2.2 The spherically symmetric model for desorption with a quasi-stationary concentration profile

Following the 'shrinking core' scenario [9, 10, 21], we consider a magnesium particle with decomposing hydride core inside. Further simplification is established through the radial symmetry of the model, as illustrated in Fig. 2. We relate the center of spherical coordinate system to the central point of radial symmetric particle of a constant radius L with the radial symmetric β-core of a variable radius ρ, like it has been made in a number of similar models [9, 10]. The core shrinks through the hydride decomposition $MgH_2 \rightarrow Mg + 2H$. Between the core interface and particle surface we assume the *quasi-stationary* concentration profile for dissolved H-atoms.

This profile $c_\alpha(r)$ is dependent only on the radial distance r. The only possible nontrivial solution for the radial Laplace equation

$$\frac{\partial^2}{\partial r^2}c + \frac{2}{r}\frac{\partial}{\partial r}c = 0 \tag{7}$$

in the domain $\rho \leq r \leq L$ is the ansatz

$$c(r) = \frac{A}{r} + B \tag{8}$$

with some constants A, B whereas the case $A > 0$ corresponds to the desorption, and $A < 0$ to the absorption process. To proceed with this *quasi-stationary inhomogeneous* model, the ansatz (8) should be fixed at surface and interface by the boundary conditions, as follows.

i) on the $\alpha - \beta$- interface it holds:

$$c_\alpha(r)|_{r=\rho} = \bar{c}_\alpha, \tag{9}$$

which reads for (8) in radial coordinates

$$c_\alpha(\rho) = A/\rho + B = \bar{c}_\alpha, \tag{10}$$

and the core radius ρ obeys the kinetic equation (5) for interface, which has now the form

$$(c_\beta - \bar{c}_\alpha)\dot{\rho} = -DA/\rho^2 \tag{11}$$

This is the equation (5) written in radial coordinates, where the interface movement velocity $\dot{r_I}$ reads now $\dot{\rho}$;

ii) on the surface of the particle we have:

$$-D_\alpha \nabla c|_{r=L} = DA/L^2 = bc_\alpha(L)^2 - kp, \tag{12}$$

i.e. the Sievert's law, split between the surface desorption and re-adsorption factors b, k, as introduced by [10, 9] and explained in detail in [21]. The kinetic constant b can be interpreted as a rate of the surface process $2H_{\text{(dissolved)}} \rightarrow H_{2\text{(gas)}}$ (actually the surface desorption), whereas the constant k corresponds to the reverse process (surface re-adsorption). Here the constants b, k as well as the critical concentration $\bar{c}_\alpha$ and the resulting *plateau pressure* $\bar{p} = b\bar{c}_\alpha^2/k$ are the material properties and do not depend on the particle size or specific surface [34].

For the radial coordinate r it reads

$$\left[bc_\alpha(r)^2 = D_\alpha c'_\alpha(r) - kp\ \right]|_{r=L} \tag{13}$$

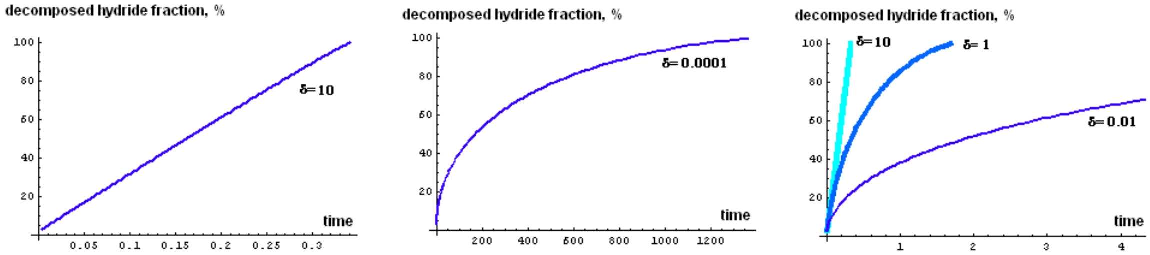

Figure 3: **effect of relative diffusion rate: fast** $\delta = 10$**, slow** $\delta = 0.0001$**, comparison** $\delta = 10, 1, 0.01$

The conditions i)-ii) provide the 'constants' A, B of the ansatz (8). The procedure of solution is described in detail in (18-20). The result of the exact integration of (11-13) for the core evolution $\rho(t)$, performed in terms of the dimensionless relative core radius $\bar{r} = \rho/L$ and the dimensionless parameters $\delta = \frac{D}{2b\bar{c}_\alpha L}$ $\eta = 1 - \frac{k\ p}{\bar{c}_\alpha^2 b}$ reads (see appendix):

$$t(\rho) = L\frac{c_\beta - \bar{c}_\alpha}{6\delta k\bar{p}\eta}\left[2\delta + 1\ \ - 3\bar{r}^2 - 2(\delta - 1)\bar{r}^3\right] \tag{14}$$

and for the total desorption time

$$\tau = \frac{c_\beta - \bar{c}_\alpha}{3k(\bar{p} - p)}\left[L + \frac{k\bar{p}}{\bar{c}_\alpha D}L^2\right] \tag{15}$$

A comparison of desorption kinetics for different values of δ (corresponding to different diffusion rates), resulting from (14), is given in Fig.3. The mass fraction of the decomposed hydride is proportional to the volume of the hydride core $v \sim \rho^(1/3)$.

The effect of refinement resulting from (15 is illustrated schematically in Fig.4

The simplified accounting of diffusion in the desorption kinetics performed above provides a transparent physical interpretation. The first term, linear in particle size L, corresponds to desorption controlled by surface processes only $(\bar{p}, k)$ as it follows from the dimensional suggestions, and it does not depend on the diffusion rate D. The second term contributing additionally to the desorption time, is quadratic on L, and grows if the diffusion rate decreases. One is interested in a range of parameters, where the contribution of the second term becomes sufficiently comparable to the first one. To this end we estimate the dimensionless expression $k\bar{p}L/\bar{c}_\alpha D$ compared to unity. From

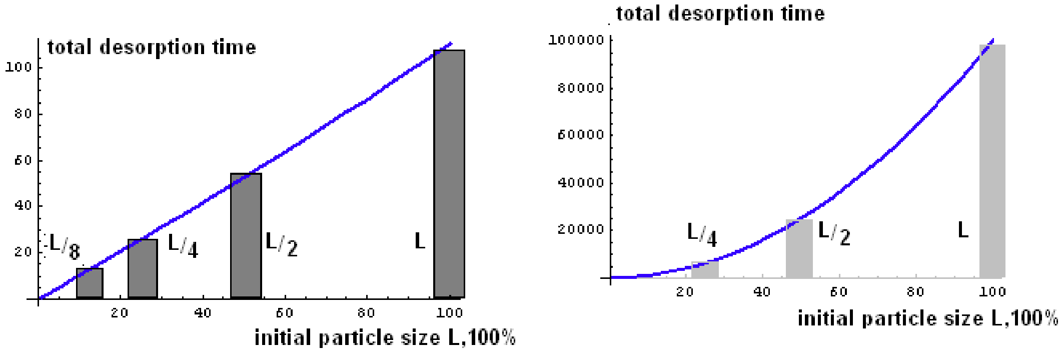

Figure 4: **relative effect of refinement: a) at fast diffusion, b) at diffusion 10^4 times slower**

the results of the previous modeling [21] we took values of the typical order of magnitude. We obtain then, even for very coarse particles of $L \sim 10^{-6}m$, a very fast surface re-adsorption rate $k \sim 10^{-12}$, a very slow diffusion $D \sim 10^{-8}$, a typical critical α-concentration $\bar{c}_\alpha = 600$ and a typical threshold pressure $\bar{p} \sim 1\ MPa$ we obtain the desired value $k\bar{p}L/\bar{c}_\alpha D \sim 1.67 \cdot 10^{-7}$. For real values of diffusion $D \sim 10^{-3}$ and nano-powders with $L \sim 10^{-9}m$ it decreases to the order of 10^{-15}.

3 Results and discussion

3.1 Improvement of the previous formulation

The scenario of 'shrinking core' has been applied again for hydrogen desorption from magnesium hydride, as an extension of the previous model with *homogeneous* concentration of dissolved hydrogen atoms in the α-phase, recently considered in [21], where a *very fast diffusion* was assumed. When comparing the characteristic time of α-diffusion with the kinetics of desorption, we have concluded that diffusion through the α-phase was too fast to be a rate controlling step.

In opposition to the recent investigation [21], the finite diffusion rate D has been taken into account as the quasi-stationary inhomogeneous concentration profile of the hydrogen in α-phase. The desorption was assumed to take place at the constant external hydrogen pressure p. Additionally, the $\alpha - \beta$-interface reaction rate **1)** has been excluded as a possible rate controlling step, i.e., this reaction is assumed to be significantly faster than **2)** and **3)** (defined in the introduction, Sec.1).

3.2 Results

The resulting solution for kinetics of desorption is obtained analytically. In the result for the total desorption time the contribution dependent on diffusion rate is separated from the main contribution arising from the pure α-surface-controlled desorption. It is quadratically dependent on the particle size L. The same conclusion follows from the simple dimensional suggestions and is confirmed by the detailled dimensional analysis, [21], [22]. It is apparently similar to the case of surface diffusion through the porous shell, but it has generally different issues, since the surface diffusion relates to the surface (dimension *length* ^{2}*)* , while the bulk diffusion has the dimension *length* ^{3} . The relatively simple dimensional analysis does not provide, however, the exact formula, obtained above. This relation contains the effect both rate controlling steps - surface reaction and diffusion, since the former one can be never neglected for sorption or desorption in metals.

The relative order of magnitude of the diffusion-controlled retardation for conventional conditions appears to be negligibly small compared to the leading surface-controlled part linear in L.

3.3 Numerical estimations

We assume for example, that the diffusion rate is in the range of $D \sim 1.54 \cdot 10^{-6} e^{\frac{-40\ 000}{RT}}$ ... $1.54 \cdot 10^{-6} e^{\frac{-24\ 100}{RT}}$, $[m^2/s]$ [35, 36]. At a temperature of $T = 350^o C$ it corresponds to $D \sim 6.8 \cdot 10^{-10} ... 1.5 \cdot 10^{-8}\ m^2/s$. If we take m=100 mg powder with particle radius of about $L \sim 1\mu m$, the total surface area of this sample will be about $\sigma = 3m/(\rho L) = 0.207m^2$, where $\rho = 1450kg/m^3$ is the density of the hydride. The minimal gradient of concentration c_α for dissolved hydrogen atoms can be roughly estimated to be $\nabla c_\alpha \sim \bar{c}_\alpha / L$. Therefore, the expected release rate of molecular hydrogen $\dot{\nu}_{H_2}, [mol/s]$, provided by the diffusion, should be of order

$$\dot{\nu}_{H_2} \sim \frac{3}{2} \frac{m \bar{c}_\alpha / LD}{\rho L^2}. \tag{16}$$

For the actually measured 100mg sample with $L = 1.6nm$ the above equation provides a total transport rate in range of $(3.023 ... 66.68) \cdot 10^2 mol/s$.

The release rate, actually observed for this sample in a volumetric equipment, can be estimated according to

$$\dot{\nu}_{H_2} \sim \frac{\{V/T\}}{R}\frac{\Delta p}{\Delta t} \qquad (17)$$

with $\{V/T\}$-volumetric factor, R-gas constant, $\Delta p/\Delta t$- pressure increase in time Δt

Thus for a temperature T=350^oC, the pressure increase $\Delta p = 54743Pa$ in $\Delta t = 3542s$ and the corresponding release rate $\dot{\nu}_{H_2}$ can be calculated to be about $1.87 \cdot 10^{-7}\ mol/s$ for the given volumetric setup ([17, 21]).

Even for a hydrogen bulk diffusion in the β-phase, which is three orders of magnitude slower (at this temperature $D \sim 2.5 \cdot 10^{-13}\ m^2/s$)[37], the estimated release rate for the total diffusion transport of hydrogen still remains four orders of magnitude higher than the corresponding measured value. Hence the overall desorption kinetics are not restricted by a finite diffusion rate.

This result gives rise to the conclusion, that the *bulk diffusion cannot be a rate-controlling step* for the resulting kinetics, concerning both desorption and absorption processes.

For conventional particle sizes and known material properties this process is always sufficiently fast, much faster than two other stages, namely the α-surface desorption and the $\alpha - \beta$-interface decomposition controlled thereby. Thus an accounting of bulk diffusion appears to be irrelevant for purpose of practical applications to hydrogen storage. Nevertheless, the finite diffusion rate could play a significant role at very low temperatures and low external pressures, (e.g.during hydrogen formation in the interstellar dust [38]).

The increase of the *desorption* kinetic rate which is observed upon the decrease of particle size should be rather referred to increasing specific surface, according to suggestions of [21]. In this case, the *rate-controlling step* is the surface reaction. This conclusion was also supported by e.g. *density-functional (DFT)* calculations [31]. An interplay between reaction kinetics on surface and interface and local surface effects becomes significant for smaller particle sizes. It can be also responsible for qualitative and quantitative changes in the sorption behavior observed upon further refinement of powders. A consideration about shorter diffusion paths seems to be unfounded in this context.

3.4 Application and validity for absorption kinetics

A similar suggestion could be applied also for the absorption. Likely, the *absorption* kinetics appears to be locked after the starting phase (especially at high external pressure) through the formation of β-grains on particle surface [4, 39]. Conjoined together, they form a β-shell, which prevents further uptake of hydrogen. According to the explanation provided in the literature [7, 40], the diffusion of the hydrogen in the β-bulk is remarkably (three orders) slower as in the α-bulk. The result of the present investigation questions this hypothesis. It has been shown that even for a diffusion rate of ten-eleven orders a slower diffusion has no considerable effect on the sorption kinetics for nano-particles. The results of [40] cannot be directly applied to the formula (15), since the evaluated value $D \sim 10^{-20}\ m^2/s$ (for 305K) deals with the 'overall diffusion' rate, including *surface-to-bulk* and *bulk-to-interface* transitions. On the other hand, the increase of the diffusion rate from this value to the D at 623K [37] mentioned above corresponds to the activation energy of 78.7 $kJ/mol\ H$ or 0.81 eV per H-atom, and should be related rather to the evaluated value 1.78 eV/H_2 for gas-MgH_2 surface transition [31].

3.5 Outlooks

An issue for the slow absorption could be found in the properties of the MgH_2-surface obverse to the surrounding gas (e.g. another kinetic constants b, k), as well as in the properties of $Mg + 2H \rightarrow MgH_2$ - formation reaction β-sides.

An another and very possible reason for the slow sorption/desorption kinetics could be the **step 1)**- the $\alpha - \beta$ interface reaction, described by the function μ in 1. The first estimations on this aspect with different forms of this function are readily performed [41].

Anyway, for a correct establishment of reasons we require a further series of especially arranged experiments to distinguish contributions of each stage separately,

Especially the thermodynamic and kinetic characteristics of the surface and interface reactions should be possible to distinguish from each other.

4 Conclusion

An analytical modelling provides the exact formula for desorption kinetics for metal (magnesium) hydride. The surface reaction and bulk diffusion were considered as a possible rate controlling steps for desorption kinetics. The contribution of the surface reaction is linearly dependent on the particle size, while the one of the diffusion is quadratic.

It allows to identify the effect of each reaction at the refinement of hydride powders.

It has been shown, that the bulk diffusion cannot be a rate controlling step, the remaining possible reasons responsible for slow desorption are thereofore the surface and eventually interface reaction.

For the ultimate conclusion on the effective kinetics rate controlling, further experiments especially arranged to distinguish contributions of each stage separately are required.

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A Mathematical Appendix

A.1 Solution of the kinetic equation

For the sake of convenience, we introduced relative dimensionless core radius $\bar{r} = \rho/L$ according to the usual procedure. The algebraic solution of the boundary conditions system (13) and (10) provides the constants A, B as functions of $\bar{r}$:

$$B(\rho) = \bar{c}_\alpha - \frac{A}{\rho},$$
$$A(\rho) = \bar{c}_\alpha L \frac{w-1}{P}(w - \sqrt{w^2 - \eta}),$$

where the dimensionless variables η, w are introduced as

$$\eta(p) = 1 - \frac{k\ p}{\bar{c}_\alpha^2 b}$$
$$w := 1 + P\frac{\bar{r}}{1-\bar{r}}; \quad \text{with } P := \frac{D}{2b\bar{c}_\alpha L}.$$

The resulting kinetic equation for the evolution of the β-core (11) becomes in these terms:

$$\frac{(1-w)dw}{(w-\sqrt{w^2-\eta})(w+P-1)^4} = \frac{4b^2\bar{c}_\alpha^3}{D(c_\beta - \bar{c}_\alpha)}dt \tag{18}$$

For example, with a starting setup at a low pressure $p = 1\ kPa$, $\eta \approx 1$, and other values
$D = 1.54 \cdot 10^{-3}$; $L = 15 \cdot 10^{-9}$; $k = 4.6 \cdot 10^{-13}$; $b = 0.55\ k$; $\bar{c}_\alpha = 300$;
we obtain for the dimensionless integration variable $w(\bar{r} = 0.99999) = 6.76 \cdot 10^{19}$ at the start and $w(\bar{r} = 0.00001) = 6.76 \cdot 10^9$ at the end of desorption.

Even for a very slow diffusion (e.g. five orders of magnitude slower, about $D \sim 10^{-8}$) w remains still between $w(\bar{r} = 0.99999) \sim 10^{14}$ and $w(\bar{r} = 0.00001) \sim 10^4$, compared to unity.

It means that an approximation $\eta \to 0$ compared to w remains valid practically without restrictions. Using this observation, the expression $w - \sqrt{w^2-\eta}$ in (18) is replaced by $\eta/(2w)$. The resulting equation is then integrated immediately for a constant pressure p, providing

$$\frac{\alpha(\alpha+1)}{3}(\alpha+w)^{-3} - (\alpha+\frac{1}{2})(\alpha+w)^{-2} + (\alpha+w)^{-1} = \frac{2\eta b^2\bar{c}_\alpha^3}{D(c_\beta-\bar{c}_\alpha)}t \tag{19}$$

with $\alpha := \delta - 1 = \frac{D}{2b\bar{c}_\alpha L} - 1$.

Since the boundary values of w are $w(\bar{r} \to 1) = \infty$, $w(\bar{r} \to 0) = 1$ (the start and end of desorption respectively), the solution (19) obeys the initial condition at $t = 0$ and gives the full desorption time

$$\tau = \frac{D(c_\beta - \bar{c}_\alpha)}{12\eta b^2\bar{c}_\alpha^3}\frac{2\alpha^2+5\alpha+3}{(\alpha+1)^3} = \frac{c_\beta - \bar{c}_\alpha}{3k(\bar{p}-p)}\left[L + \frac{k\bar{p}}{\bar{c}_\alpha D}L^2\right] \tag{20}$$

as a final result. Here, $\bar{p} = b\bar{c}_\alpha^2/k$ is denoted as the *threshold (or plateau) pressure* [21], the outer pressure $p < \bar{p}$ is assumed to be constant *(isobaric desorption).*

Further, in terms of $\delta := \alpha + 1 = \frac{D}{2b\bar{c}_\alpha L}$, we can represent the result in a more compact form.

$$t = L\frac{c_\beta - \bar{c}_\alpha}{6\delta k\bar{p}\eta}\left[2\delta + 1 \ - 3\bar{r}^2 - 2(\delta - 1)\bar{r}^3\right] \tag{21}$$

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