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Modelling and proper evaluation of volumetric kinetics of hydrogen desorption by metal hydrides

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ABSTRACT

A simple model of the hydrogen desorption kinetics of metal hydrides is formulated and solved analytically. The particle surface reaction is assumed to be a rate-controlling-step. Then a volumetric measurement of hydrogen desorption process is evaluated on an example of wet ball milled magnesium hydride, and can be applied generally for any metal hydride.

The solution reproduces the shape of experimental curves for desorption process. In the case of surface-controlled kinetics, a volumetric measurement requires a special evaluation of results, predicted by the solution of the model. An improved evaluation of the volumetric measurement of hydrogen desorption from magnesium hydride powders using the model has been demonstrated.

Introduction

Metal hydrides are considered as a potential hydrogen storage material because they have a high storage capacity by weight. Especially the magnesium hydride reaches the theoretical maximal value of 7.66 wt%. The main drawbacks of this material are still its high desorption temperature (over 300 °C), low desorption pressure and generally sluggish sorption kinetics, commonly typical for hydrides (of light metals in the first instance) [1–3].

We restrict the following discussion on this material only, retaining that the modelling outlined below is non-specific and applicable for other metal hydrides. In recent years, significant progress has been made using nanocrystalline metal hydride powders produced by high-energy milling and adding suitable catalysts in order to improve the sorption kinetics.

To explain the sorption behaviour of this material a number of theoretical and empirical models has been proposed [4–6]. The models and applications to *absorption* kinetics refer usually to the classical Johnson-Mehl-Avrami's 'nucleation-and-growth' scenario [7–11], whereas the *desorption* allows some simplified schemes [6,5]. In the present paper, the confluent 'shrinking core' model [6] (also known as 'contracting envelope', as applied for absorption [9]) was taken as a basis. It has reduced number of parameters compared to that mentioned in Ref. [5], thereby restricting ambiguity in measurement interpretations.

Sorption experiments are generally performed on powders. A *particle size* and the resulting *specific surface* of the powder is

recognized to have a strong influence on desorption kinetics [8], as well as general performance for hydrogen storage applications [12]. Our recent measurements approved, that the kinetics increases with decreasing of the particle size (i.e. increasing of the specific surface). For powder preparation *wet-ball-milling procedure (WBM)* was used. The powder produced using this technique, possesses increased specific surface, compared to a conventional dry-ball-milled (DBM) one. Correspondingly, the WBM powder shows better sorption kinetics [13, 14, 15].

It suggests that the specific surface plays a significant role of in ab-/desorption processes and gives rise for the key assumption of the present modelling — the resulting *kinetics is determined* mainly *by the surface reaction*. The outcomes, as it will be shown below, are in particular:

  - 'sigmoigal shape' of kinetic curves are a pure artifact of volumetric measurement and is determined by a surface kinetic constant;
  - thermodynamics of the interface reaction is only responsible for critical concentration of the dissolved hydrogen.

These key values allow for a proper evaluation of measurement results and for conclusions about crucial factors, affecting the improvement of kinetic properties of hydrogen storage materials.

General remarks

Suggestions for geometrical and dimensional relations
The transport of hydrogen into or out of a metal particle with a characteristic size d occurs through its surface. In the current model it is assumed that the desorption rate of the hydrogen is controlled mainly by the *surface reaction* and is therefore linearly proportional to the surface of the particle $S \sim d^2$. The total hydrogen reservoir is linearly proportional to its volume $V \sim d^3$. Thus, the characteristic sorption time τ is linearly dependent on characteristic particle size, $\tau \sim d$. This linear dependence should hold in the leading order if we compare powders with the different particle sizes. Therefore, assuming two particles 1 and 2 with characteristic sizes d_1, d_2 the corresponding characteristic sorption times τ are related to each other as $\tau_1/\tau_2 \sim d_1/d_2$.

Influence of the diffusion rate
Apart from the geometrical suggestion, it was frequently reported that the finite diffusion rate of hydrogen has an effect on desorption kinetics [4]. For the current model this factor was neglected because of the very fast diffusion rate [16,17]. This assumption is also justified by theoretical modelling [36,39]. A detailed quantitative comparison is given in the discussion (Discussion).

Influence of pressure
According to the Sievert's law ($c^2 \sim p$, where c-volume concentration of atoms in metal at the surface, p-outer gas pressure), all surface reactions are highly sensible to the pressure change. Hence this parameter is expected to be one of the most responsible for the overall reaction rate.

Summary of notations
In the present model, the desorption kinetics measured volumetrically, is determined by:

- p_0 — initial gas pressure
- $\overline{p}^{des} = b(c_\alpha^{des})^2/k$ — threshold (equilibrium) pressure (at a given temperature T), when the process is stopped, where:
  * c_α — critical (saturation) concentration of dissolved hydrogen atoms in the α-phase.
  * b and k — surface desorption and re-adsorption kinetic constants respectively, so that b/k is the Sievert's constant. c_α, b, k are temperature-dependent.
- c_β — concentration of the hydrogen atoms in stoichiometric hydride (β-phase); assumed to be always constant.
- $\varepsilon = \frac{3}{2}\frac{R\mathscr{P}m}{L\varrho_{MgH_2}\{V/T\}}$ — the parameter of the experimental setup, where:
  * L-effective particle size, m-specimen mass $\mathscr{P}$-purity
  * $\{V/T\}$- volumetric effective ratio, characterizes the volumetric setup with the given total volume V and sample temperature T
- p_{max} is the gas pressure, maximal reachable by complete desorption

The model describes the desorption at constant volume V and temperature T (volumetric). A linear approximation correspondses to the case of constant pressure (Solution) (gravimetric). The solution immediately reproduces experimental results. The modelled curves fit the experimental data. The modelling and measured results are compared and discussed (Practical validation of the model).

Experimental details

Material properties

The sorption measurements were performed on both conventional and ball milled powders. During high-energy milling the particle size decreases significantly. Without catalysts the desorption temperature of the high-energy-milled Mg hydride is still higher than 573 K. Also the *wet ball milling* method was used to produce nanocrystalline Mg hydride, which is different to the conventional high-energy ball milling, as it was reported in our recent research [15].

Three kinds of specimens were involved in the sorption experiments:

1. *as-received* powder with the particle size 20—100 μm and different shapes, used as a reference.
2. *dry-ball milled* (DBM) — the powder after conventional procedure. The particle size was 0.5 ~ 4 μm, with mainly *spherical* morphology of surface.
3. The *wet-ball-milled* (WBM) powder. In contrast to the DBM, particles are much finer in order of 30—500 nm and possess a multi-porous surface with large clusters of porosities due to reaction with organic solvent (THF). It provides a significant increase of specific surface of the WBM powder.

The main phase of the dry and wet-ball-milled MgH_2 nanocrystals is similar to that of the as-received compound,