Kinetics of hydrogen desorption from the powders of metal hydrides

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Abstract

Desorption of hydrogen from the powders of metal hydrides (MH) is affected by several interplaying processes including hydrogen desorption from and recombination on the metal surface, diffusion within the bulk metal and different hydride phases, and decomposition of the hydride phase. In present work, possible mechanisms of hydrogen release from the MH are proposed and discussed. Analytical models are developed which cover common distributed and confluent cases. The models adequately fit the experimental data of the thermal desorption spectroscopy and barometric thermocycling studies. Rate constants of the reactions of hydrogen release from the MH are evaluated on the basis of the fitting of the experimental data by the proposed models. These data are of significant importance in the assessments of suitability of the MH in particular applications.
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1. Introduction

Kinetics of hydrogen desorption from the metal hydrides (MH) is a complex process which involves gaseous hydrogen and two (α-solid solution of hydrogen in the metal and a β-hydride) or more solid H-containing phases. Hydrogen desorption includes processes (elementary stages) proceeding in the bulk (phase transformations and bulk diffusion) and in the surface layer (recombination of hydrogen molecules). Since each stage contributes to the overall process, only in specific cases the rate-limiting process can be identified.

The most frequently applied model of the kinetics of phase transformations relevant to the process of H desorption was proposed by Avrami [1] and Johnson and Mehl [2]. The model is based on the approach describing this kinetics as nucleation and consequent growth of the nuclei of a new phase within the bulk of the matrix phase as the rate-limiting step.

Later, Rudman [3] has extended this approach to apply it to the metal–hydrogen systems considering hydrogen diffusion

as the rate-limiting process for the kinetics of dehydrogenation.

Mintz and Zeeri [4] further developed this approach. Their analysis extended a consideration of the conventional case of a shrinking core moving with a constant velocity of an interface to include two more complex situations:

(i) shrinking core moving with a decelerating with time velocity; the process is controlled by hydrogen diffusion through the growing layer of the product;
(ii) random multiple nucleation and growth of the new phase in the bulk material.

In addition, and for the first time, the factors causing deviation of the kinetic characteristics of the hydrogenated powders from a behaviour of a single hydride particle were taken into account. The influence of the: (i) particle size distribution; (ii) particle shape variations; (iii) time delay in the beginning of the desorption process in the specific particle compared to the average process in the powder were considered.

Recently, Castro and Meyer [5] have studied kinetics of hydrogen desorption by modelling of the spectra of hydrogen

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thermal desorption. Here, the dehydrogenation is described in a most general way. They related four alternative rate-limiting steps including

(i) bulk diffusion;
(ii) phase transformation;
(iii) bulk to surface transfer;
(iv) H–H recombination on the sample surface.

However, for practical purposes, it is very difficult to apply general models similar to those described in [4,5] to describe the experimental thermal desorption spectra for the specific metal–hydrogen systems. One reason for that is in ambiguity of the interpretation of the results in the case of the overlapping rate-limiting stages.

We believe that the simplified models allowing to quantitatively describe the experimental thermal desorption spectra, to determine the mechanisms of H desorption and to evaluate the rate constants, are of great importance.

The aim of the present paper, is to study kinetics of the elementary processes contributing to H desorption and to develop a method for the evaluation of the rate constants enabling the engineering calculations. The objects of this study are defined as the powders of the hydride-forming metals retaining their metallic properties on hydrogenation. The experimental results were obtained using thermal desorption spectrometry and the thermocycling (TC) method (a modified barometric method (BM)). Special attention was paid to the control of the temperature of samples, since hydrogen desorption from the hydrides is associated with absorption and transfer of the heat. Our approach in determining the most probable mechanisms of hydrogen absorption and desorption and evaluating the rate constants is based on analytical modelling. Adequacy of the suggested models is verified by their ability to describe the experimental results.

Since the approaches applied in literature, e.g. those from the paper [5] are too general, we were aimed to overcome this disadvantage. The following goals were defined for the present study. Since both TDS and the BM techniques provide rather simple experimental dependences we wished to functionally relate these dependences to the evaluated parameters. At the same time, we wish to develop the simplest possible model allowing to fit the family of the experimental curves measured at similar conditions with the same fitting parameters.

2. Experimentals details

The samples were heated in a stainless steel crucible. In the TDS experiments, the desorption flux of hydrogen was measured by a mass-spectrometer. In the TC experiments, the sample was heated and cooled in cycles under the pressure of hydrogen gas being in equilibrium with H_2 in a buffer cylinder with a known volume, V_b. Our setup allows to ensure a strictly linear with respect to time heating and cooling of the

samples. The presence of hydrogen allowed a fine temperature control over the hydride powder. While the temperature was lowered, hydrogen was absorbed by the sample. In turn, when the temperature was raised, hydrogen was released. The rates of gas desorption and absorption were determined by monitoring pressure changes in the buffer cylinder. Its volume was more than three orders higher compared the volume of the heated crucible. By modifying initial pressure, starting and final temperatures, one can scan the required areas of the phase diagrams of the studied metal–hydrogen system. A more detailed description of the TC method may be found in [6].

3. Results and discussion

3.1. Description of the models

The models used are based on the following assumptions:

1. The studied samples are fine powders. Their powdering from the initially mechanically crushed metal samples has been accomplished by the hydrogenation–dehydrogenation cycling. Spherical approximation is the most acceptable for the particles of such powders, as follows from the scanning electron microscopy studies. In the paper [7], we have presented experimental proofs that the shrinking core model more correctly describes the H absorption–desorption compared to the nucleation and growth model [8]. Thus, in the model we consider a spherical powder particle of radius L with a hydride core of radius $\rho \in [0, L]$.
2. Hydride phase and α-solid solution form an interface. It is generally accepted that local equilibrium of hydrogen concentrations in the lattices of the metal and hydrides takes place because of the high mobility of hydrogen atoms dissolved by the metals. We assume that the concentration, $c_\alpha(t, \rho) = c_\alpha^{\mathrm{crit}}$, in the solution corresponds to the left bound of the two-phase area of the phase diagram; the concentration $c_\beta(t, \rho) = c_\beta^{\mathrm{crit}}$ in the hydride corresponds to its right bound.

When two phases coexist, hydrogen desorption by a particle is described by a diffusion boundary-value problem of the Stefan type with a moving bound between the hydride and the solution. Diffusion in both phases obeys the Fick's law (the equations are in spherical coordinates):

$$
\begin{aligned}
\frac{\partial c_\alpha}{\partial t} &= D_\alpha \left(\frac{\partial^2 c_\alpha}{\partial r^2} + \frac{2}{r} \frac{\partial c_\alpha}{\partial r} \right), \quad r \in (\rho, L), \\
\frac{\partial c_\beta}{\partial t} &= D_\beta \left(\frac{\partial^2 c_\beta}{\partial r^2} + \frac{2}{r} \frac{\partial c_\beta}{\partial r} \right), \quad r \in (0, \rho).
\end{aligned}
\tag{1}
$$

Here, D_α and D_β are for the diffusion coefficients in the hydride and the solution phases.

On the surface boundary of the particle hydrogen concentration is determined by the balance of absorption, desorption

and diffusion fluxes:

$$bc_\alpha^2(t, L) = k_\alpha p - D_\alpha \frac{\partial c_\alpha}{\partial r}(t, L) \tag{2}$$

Here, b and k_α are the rate constants of hydrogen desorption and absorption. The Eq. (2) is based on the fact that the desorption proceeds from the layer of the α-solid solution where H content is low and Sieverts' law is applicable.

Due to the spherical symmetry there is no flux in the centre of the particle:

$$\frac{\partial c_\beta}{\partial r}(t, 0) = 0 \tag{3}$$

At the hydride-solution boundary the decomposing hydride maintains the critical concentration in the β-hydride; the concentration in the α-solution satisfies the conditions of local equilibrium:

$$c_\beta(t, \rho(t)) = c_\beta^{\text{crit}}, \quad c_\alpha(t, \rho(t)) = c_\alpha^{\text{crit}} \tag{4}$$

The velocity of hydride-solution boundary (the Stefan condition) is determined by the balance of diffusion fluxes and the flux of hydrogen that appears due to the decomposition of the hydride:

$$[c_\beta(t, \rho) - c_\alpha(t, \rho)]\frac{d\rho}{dt} = D_\alpha \frac{\partial c_\alpha}{\partial r}(t, \rho) - D_\beta \frac{\partial c_\beta}{\partial r}(t, \rho) \tag{5}$$

Please, note that the dependences (1)–(5) are derived from the conservation law (the total amount of hydrogen is constant) and are based on a description of the desorption process by known physical laws and equations. All parameters are assumed to be dependent from the Arrhenius temperature with certain individual pre-exponential factors and activation energies. For example, desorption coefficient is defined as $b = b_0 \exp(-E_b/RT)$.

At the beginning of desorption almost all hydride particles consist of the β phase and are covered by a thin layer of the α phase. Starting temperature is so low that the desorption rate is very small, while inside the particle H diffusion and phase transformations on the boundary cause the initial distribution of concentrations. From the mathematical point of view, the initial H distribution in the β phase is rather arbitrary: the only limiting condition is a spherical symmetry $\partial c_\beta/\partial r (0, 0) = 0$. It is expedient to consider $c_\alpha(0, r) = A + B/r$ as an initial distribution in the α phase. This distribution is stationary for the diffusion equation (1). The constants A and B are determined from the boundary condition (2) and condition of equilibrium in H content (4).

On heating, hydrogen desorption from a particle of metal hydride involves three consecutive stages:

1. *Initial degassing.* A flow of hydrogen diffuses from the β phase to the α phase. The phase boundary does not move, i.e. $\dot{\rho} = 0$; the hydride does not decompose. From the Stefan condition (5), we get the condition of a continuity of diffusion flux on the phase boundary. The described process lasts until the critical concentration c_β^{crit} is reached at the phase boundary.

2. *Decomposition of hydride.* The hydride core is shrinking. This process lasts either until the critical temperature is reached or until all the hydride is decomposed (i.e. until $\rho(t) = 0$).

3. *Final degassing.* Initial distribution is determined by the previous stage. The particle is diffusionally degassed:

$$\frac{\partial c_\alpha}{\partial t} = D_\alpha \left(\frac{\partial^2 c_\alpha}{\partial r^2} + \frac{2}{r}\frac{\partial c_\alpha}{\partial r} \right), \quad r \in (0, L) \tag{6}$$

$$bc_\alpha^2(t, L) = k_\alpha p - D_\alpha \frac{\partial c_\alpha}{\partial r}(t, L) \tag{7}$$

$$\frac{\partial c_\alpha}{\partial r}(t, 0) = 0 \tag{8}$$

The presented model involves significantly less parameters than the model proposed in [5]. However, the number of the parameters is still too large to solve the inverse problem. At present, we do not possess the experimental data that are the functions of such number of varying constants.

3.2. Confluent models and their comparison with the experiment

When the hydride powder particles are small enough, then even at moderate temperatures the diffusion is rather fast. Therefore, the gradients of concentration in the α-solution and in the hydride are close to zero. This is the confluence of the model. The limit $D_{\alpha,\beta} \to \infty$ leads to vanishing of the gradients, the models consist of the ordinary differential equations. In the ***confluent model***, the velocity of the hydride-solution boundary is determined by the total balance of hydrogen in the sample and the gas that has left the sample:

$$[c_\beta(t) - c_\alpha(t)]\,\rho^2(t)\dot{\rho}(t)$$
$$= -b(T(t))c_\alpha^2(t)L^2 - \dot{c}_\alpha(t)\frac{L^3 - \rho^3}{3} - \dot{c}_\beta(t)\frac{\rho^3}{3} \tag{9}$$

The flux of re-adsorption is here neglected. Here, $c_\beta(t)$ is for the critical concentration in β phase, $c_\alpha(t)$ is for the equilibrium concentration in α phase. The functions $c_\beta(t)$ and $c_\alpha(t)$ are obtained from the phase diagram. In particular, if $c_\alpha(t) = \text{constant}$, $c_\beta(t) = \text{constant}$, then Eq. (9) becomes simpler:

$$[c_\beta(t) - c_\alpha(t)]\,\rho^2(t)\dot{\rho}(t) = -b(T(t))c_\alpha^2(t)L^2 \tag{10}$$

An example of the TDS curve for this problem is given in Fig. 1a, curve 1. We suggest that the content of hydrogen in the sample corresponds to the two-phase area of the phase diagram. Then the temperature rise leads to the growth of the desorption flux; the desorption flux increases until the hydride is decomposed, i.e. until the hydride core shrinks to zero radius. The experimental curves obtained by us do not have such typical sharp form: as an example on
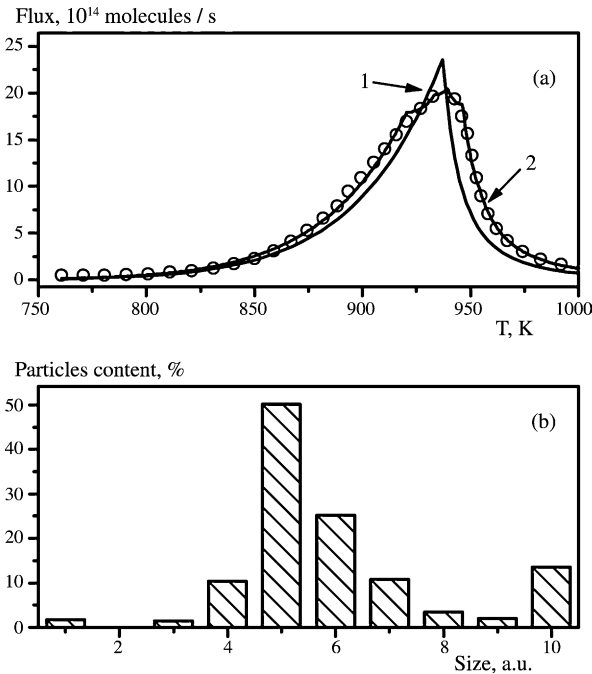
Fig. 1. (a) Experimental TDS curve of hydrogen desorption from erbium hydride powder (circles). Modelling results (solid lines): (1) confluent curve corresponding to Eq. (10), (2) an optimised fit by the model of desorption from a group of particles with a size distribution presented in plot (b).
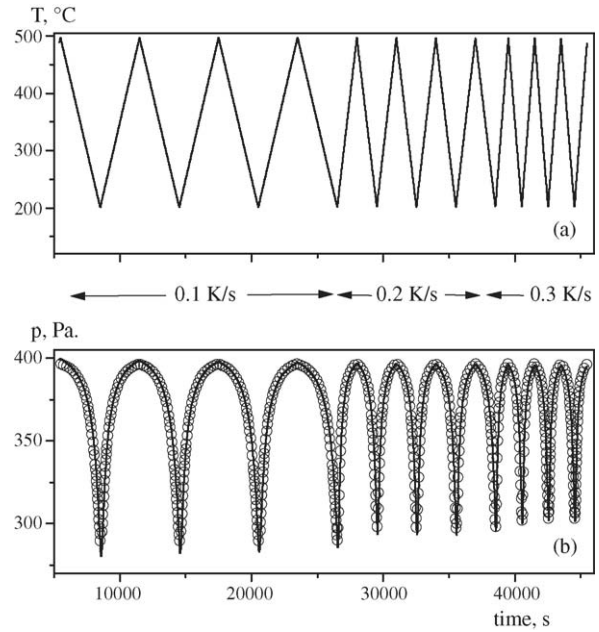

Fig. 2. Thermocycling of vanadium. (a) Temperature of the sample; (b) circles—experimental points of the measured pressure in the experimental setup, solid line—model fit.

the same figure there are presented experimental data of the rate of hydrogen desorption from the powder of erbium hydride at a heating rate 0.1 K/s. Smooth form of the experimental curve may be explained by size distribution of the powder particles. The dependence 2 in the Fig. 1a is the fitting curve. It is the result of desorption from a group of particles with a certain size distribution (presented at the Fig. 1b). Activation energy of hydrogen desorption from the erbium powder that provides the best fitting equals to $E_b = 160 \pm 20$ kJ/mol. Evaluation of the pre-exponent factor for the desorption yields $b_0 = 10^{-19}$ to 10^{-17} cm^6/(mg s) (10^{-25} to 10^{-23} m^6/(kg s)).

An alternative model that provides smooth curves even for a single particle takes into account a finite rate of decomposition from the hydride. It is described in our paper [4].

The TC method provides a possibility to evaluate the constants of desorption and absorption in case the temperatures and pressures correspond to the single-phase area. As example, we present the experimental results for vanadium (see Fig. 2), for the case when the temperatures are above the critical temperature. We again assume that the diffusion transport is quick.

Prior to the measurements the vanadium powder was sieved (40 μm sieve) in order to make it possible an application of a single-particle approximation for the interpretation of the data. Cycling was done in the temperature range 200–500 °C, the pressure range 200–400 Pa and heating/cooling rates 0.1, 0.2 and 0.3 K/s.

The total amount of hydrogen in the sample and in the buffer cylinder is described by the balance equation:

$$c(t)V_{\text{sample}} = 2V_b q(p_0 - p(t)) \tag{11}$$

Here, V_{sample} is the volume of the sample, q the number of hydrogen molecules in the unit volume at unit pressure, p_0 and $p(t)$ are initial and current pressure in the system. On the other hand, the change of hydrogen amount in the sample is determined by the rates of absorption and desorption:

$$\dot{c}(t)V_{\text{sample}} = k_\alpha p S_{\text{sample}} - S_{\text{sample}} b c^2(t) \tag{12}$$

Here, S_{sample} is the surface of the sample that is rather difficult to measure correctly for the powders. Let us transform the last equation taking into consideration a mass of the sample m_{sample}:

$$\dot{c}(t)m_{\text{sample}} = (k_a^* p - b^* c^2(t))m_{\text{sample}} \tag{13}$$

Eliminating the concentration $c(t)$ we obtain the following differential equation for the pressure. This equation was used for fitting of the experimental curves.

$$-\frac{2V_b q}{m_{\text{sample}}}\dot{p} = k_a^* p - 4b^* \left(qV_b \frac{p_0 - p(t)}{V_{\text{sample}}}\right)^2 \tag{14}$$

In the Fig. 2b, the solid line shows a fitting curve. The following parameters characterize hydrogen sorption and desorption by vanadium: $E_b = 96$ kJ/mol, $b_0 = 10^{-18}$ to 10^{-17} cm^6/(mg s) (10^{-24} to 10^{-23} m^6/(kg s)); $E_a = 22 \pm 4$ kJ/mol; $k_{a0} = (1-2) \times 10^{19}$ (Torr s mg)$^{-1}$ ((7–15) × 10^{23}(Pa s kg)$^{-1}$). We emphasize that this set provides a satisfactory fitting of the experimental data for the various heating

rates. Furthermore, we note a reasonably good agreement between our data and the value of the activation energy of H desorption from the vanadium hydride, 127 kJ/mol, reported in [9]. Some discrepancy in the data can be caused by the fact that the samples were studied in different forms, as powders (this work) or as thin films as in [9].

In conclusion, a general model describing hydrogen desorption from a hydride of metal powder's particle is developed in present work. This model has a reasonably low number of the parameters employed. Furthermore, confluent models for a "quick" diffusion were also considered. These models are valid even for moderate temperatures if the powder particles are small. Rather satisfactory fitting of the experimental results by these models shows that when the desorption rate is a limiting step, then a choice of the correct function of the particles distribution size allows to achieve a good agreement with the experimental data. Finally, the thermocycling method for a single particle of a sieved hydride powder in a single-phase area was considered. The model proposed allows to obtain a rather good fitting of the experimental curves and to evaluate the desorption and absorption rates.

Acknowledgement

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