Mathematical model of metal-hydride phase change
applied to Yttrium

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Abstract. We present a mathematical model for the kinetics of hydriding and dehydriding of metal powders. The single powder particle is considered. Its shape is approximated by one of the symmetric ones: sphere, long thin cylinder (wire), or flat thin plate. A few concurrent processes are considered. The model equations are derived from the mass conservation law. We consider the case of the "shrinking core" morphology, i.e., formation of the hydride skin on the surface of the particle with subsequent growth of this skin. We consider three successive stages of the phase change: skin development, skin growth, and final saturation or degassing. We apply the model to experimental data for Yttrium and show that the approximation of the experimental curves by the model ones is comparable for different cycles and different shapes for similar sets of the kinetic parameters. This also shows that shape of powder particles do not influence significantly on the kinetics of hydriding and dehydriding.

1. Introduction
Understanding the hydriding kinetics of powder particles is very important for energy storage applications [1, 2, 3]. According to the US Department of Energy objectives, loading of a hydrogen vehicle tank by 2015 must not exceed 2.5 min. This implies not only heat problems but also serious limitations on rate of hydrogen sorption by metal hydride powder. Existing articles give contradictory information about hydriding and dehydriding kinetics and its limiting factors. In [4, 5] we developed the model of hydriding of metal powders for close-to-equilibrium conditions. We considered a single powder particle. The model was verified on experimental data for uranium (prof. J. Bloch [6]) and magnesium. In [5] we studied the influence of particle’s shape on the kinetics of hydriding and found out that it is insignificant.

Here we develop this model for varying temperature and pressure and also for dehydriding. Models of dehydriding are constructed in e.g. [7, 8]. Hydriding and dehydriding possess certain
symmetry being both phase transition processes; thus it is important to describe them by a single model, so that only the parameters’ values distinguish the process.

Although detailed models of hydriding and dehydriding containing almost all possible elementary reactions exist (e.g. [9, 10, 11]) and are useful in general, they are hardly suitable for evaluating the kinetics parameters of the material, because it is difficult to estimate the role of each reaction by fitting experimental data.

On the other hand, considering a single limiting process, possibly different at different times, does not reflect the nature of the complex process, thus we deny it. Our model is based on the conservation laws and takes into account the most important elementary reactions.

The model is applied to experimental data of Yttrium. Yttrium hydride is known to change transparency depending on hydrogen concentration; this is used in switchable mirrors [12] and, currently, in solar cells [13]. These hydrides have been studied, yet by other methods, in e.g. [14, 15].

The powder particle’s shape is approximated by a symmetrical form; different forms provide similar quality of fitting of the experimental curves for similar sets of the kinetic parameters. This is another argument for low influence of the powder particle’s shape on the kinetics of hydriding and dehydriding.

We consider a single powder particle. Its form is approximated by sphere, long thin cylinder, or thin plate. In case of cylinders and plates we neglect the butts and the smaller sides. In all cases we consider the skin of the new phase (hydride for hydriding, metal with dissolved hydrogen for dehydriding) on a core of the old phase. This core has the same form as the particle. Note that length of cylinders and face area of plates are not important for the relative quantities such as fractions of the hydride phase or of the sorbed hydrogen. By "hydride" we mean hydride phase with some dissolved hydrogen (so concentration may be above stoichiometric). We describe the following stages of hydriding or dehydriding: formation of the skin of the new phase on the particle, propagation of the phase boundary, and final saturation (degassing) of the single-phase particle.

2. The mathematical model
Due to the higher activation energy of the diffusion through the hydride compared with the overall kinetics in bulk samples (for which the penetration is through the metal) [10], one can say the diffusion through the hydride is slower compared with that through the metal. So we consider only diffusion in the new phase: in case of hydriding diffusion in metal is fast, in case of dehydriding diffusion in hydride is neglected.

The hydrogen pressure $P(t)$ and the sample’s temperature $T(t)$ are considered to be known (i.e. measured in the experiment) and close to the equilibrium. The particle size is assumed to be constant during the cycle. However, it may decrease from one cycle to another since the powder grows finer during hydriding-dehydriding cycles. We assume spherical, cylindrical, or plane symmetry for the particles.

Let $D$ be the Fick’s diffusion coefficient in the new phase (i.e. metal in case of dehydriding and hydride in case of hydriding) and $c(t, r)$ and $c' = \text{const}$ be the distribution of the hydrogen concentration in the new phase and in the old phase. Here $r$ is the radius in spherical or cylindrical coordinate system or the Cartesian coordinate on the axis orthogonal to the plane of symmetry of a plate. Due to the symmetry the concentration is independent of the other spatial variables. Let $L$ be the size of the particle: radius in case of a sphere or cylinder and half-width in case of a plate. The size of the metal core under the hydride skin is denoted by $\rho(t), \rho(0) = \rho_0$. The shape of the particle is described by the constant $\sigma = 2, 1, 0$ for sphere,
cylinder, and plate respectively. In this case the Fick’s equation can be written as

\[
\frac{\partial c}{\partial t} = D(T) \left( \frac{\partial^2 c}{\partial r^2} + \frac{\sigma}{r} \cdot \frac{\partial c}{\partial r} \right) \quad r \in (\rho(t), L). \tag{1}
\]

At the phase boundary we have the constant concentration:

\[
c(t, \rho) = \bar{c} \tag{2}
\]

The physical meaning of \(\bar{c}\) is stoichiometric concentration in case of hydriding and equilibrium concentration in case of dehydriding. The local conservation law at this free boundary yields the Stefan-type equation

\[
(c' - c(t, \rho)) \frac{d\rho}{dt} = (1 - \nu)D(T) \frac{\partial c}{\partial r}(t, \rho). \tag{3}
\]

Here \(\nu\) is the fraction of the diffusion flux that goes through the phase boundary from the new phase to the old one. In case of dehydriding diffusion in the old phase is very slow and is neglected; therefore \(\nu = 0\). In case of hydriding we assume that \(\nu = 1\) (and thus \(\rho = \text{const}\)) if the old (metal) phase has gas-contacting surface; this means that all diffusion flux at the phase boundary goes to the metal phase with quick diffusion and is spent on the tangential growth of the nuclei and there is no radial growth. As soon as the skin is ready we have \(\nu = 0\) because redistribution is impossible due to symmetry. Models with any \(\nu \in [0, 1]\) were also considered.

One more boundary condition follows from the flux balance at the surface:

\[
\mu s(T)P - b(T)c^2(t, L) = D(T) \frac{\partial c}{\partial r}(t, L). \tag{4}
\]

In the left-hand side there are the adsorption and the desorption flux densities. All temperature-dependent parameters are assumed to obey the Arrhenius law, e.g.

\[
b(T) = b_0 \exp \left( -\frac{E_b}{RT} \right),
\]

where \(T\) is absolute spatially-constant temperature, \(R\) is the gas constant, \(b_0\) and \(E_b\) are constant parameters. The desorption flux density is linear with respect to pressure, \(\mu\) is the gas constant (we assumed that it is constant), \(s\) is for the adhesion coefficient (the ratio of the adsorbed hydrogen atoms to the falling ones during a unit time). Desorption flux density is proportional to the number of possible pairs of hydrogen atoms to be formed near the surface and thus \(c^2\).

Thus the domain \([0, \rho(t)]\) is occupied by the old phase, while \((\rho(t), L]\) is the new phase provided that the skin of the new phase is completed. We assume that the domain occupied by the new phase is always in the layer \(\rho < L\) and is symmetrical with respect to the chosen coordinates [4]. Then the equations written above hold both in complete or incomplete skin and it can be described by one additional variable: the fraction \(S(t)\) of area it covers at the surface of the particle. Initially \(S(0) = 0\). The equation for \(S\) follows from the global conservation law:

\[
W \dot{S}(t) = \nu D \frac{\partial c}{\partial r}(t, \rho) S + J'(1 - S(t)), \tag{5}
\]

where \(J' = \mu s'(T)P - b'(T)(c')^2\) is the sorption flux density for the old phase and

\[
W = \int_{\rho}^{L} \left( c(t, r) - c' \right) \frac{r^\sigma}{L^\sigma} dr \tag{6}
\]
is the amount of hydrogen in the skin (from $\rho$ to $L$) consisting of two phases. Equation (5) shows that $S$ hits 1 at finite time, i.e. the skin is ready at some time $t^*$, provided that $\nu > 0$. In case of dehydriding $\nu = 0$; then $S \rightarrow 1$ asymptotically. The skin is assumed to be ready when $1 - S$ becomes negligibly small. Indeed, differential equation (5) has a unique solution passing via any chosen point [16]; function $S \equiv 1$ is a solution in case $\nu = 0$, so no other solution can ever equal 1 (otherwise two different solution would pass via the same point). In other words, as $S$ tends to 1, its velocity becomes lower and lower, so $S$ never reaches the value 1. On the contrary, for $\nu > 0$ the velocity $\dot{S}$ is strictly positive, so $S$ reaches 1 after some finite time.

Equations (1)–(6) are solved simultaneously; in [17] a numerical method is described. In case of dehydriding the process is continuous, in case of hydriding at time $t^*$ the skin is ready and $\nu$ vanishes, so the process consists of two stages: skin formation and skin growth. One more stage of final saturation or degassing is described by the same equations except (2) with $\rho = 0$ and $j = 0$.

3. Results and discussion

We used this model for curves of hydriding and dehydriding of $Y$. The autoclave containing a sample with initial temperature and atomic ratio was in the chamber with the initial hydrogen pressure; the autoclave was quickly open and the pressure decrease or increase was written down. The autoclave’s volume ($\approx 10^{-6}$ m$^3$) was little compared to the chamber’s volume ($3.2 \cdot 10^{-4}$ m$^3$, $1.39 \cdot 10^{-3}$ m$^3$, $2.75 \cdot 10^{-2}$ m$^3$).

We had nine curves for dehydriding and four for hydriding of yttrium. The curves of the atomic ratio with respect to time were fitted by the least squares method. The fixed parameters were $\bar{c} = \hat{c} = 3 \cdot 10^{22}$ (this is the stoichiometric concentration of $YH_3$ calculated via yttrium’s density and atomic mass) and $c' = 0$ in case of hydriding, and $\bar{c} = 0.15\bar{c}$, $c' = \hat{c}$ for dehydriding. Here and below the length, time, and amount are measured in centimeters, seconds, and atoms respectively. Fitting for three shapes for different cycles of hydriding/dehydriding is in fig. 1–2 (an atomic ratio curve for hydriding and dehydriding is shown in each figure, the incut shows a magnified part so that all four lines are visible). The fitting is equally good.

**Figure 1.** Curves of hydriding and dehydriding; experimental (circles), model for spheres (solid), cylinders (dashed), and flat plates (dotted).

**Figure 2.** Curves of hydriding and dehydriding; experimental (circles), model for spheres (solid), cylinders (dashed), and flat plates (dotted).

Let us discuss the kinetic parameters. They are the same (except $L$ and $\rho_0$) for different shapes. For hydriding their values are shown in table 1. Parameter $b'$ is absent because $c' = 0$. For dehydriding the results are the same for diffusion coefficients higher than $10^{-11}$; this justifies using models with quick diffusion [7, 8]. Also the sorption flux for rather low pressures ($\approx 1$ bar compared to $\approx 5$ bar for hydriding) was much ($10^5$ times) lower compared to desorption flux.
Table 1. Evaluations of the kinetic parameters for hydriding

| $10^{12}D$ | $10^9s$ | $10^7s'$ | $10^{24}b$ |
|------------|----------|----------|------------|
| 5.88       | 1.58     | 3.25     | 4.00       |
| 5.71       | 1.85     | 3.11     | 4.00       |
| 7.00       | 0.89     | 1.29     | 2.00       |
| 7.00       | 0.89     | 1.29     | 1.66       |

and thus $s$ and $s'$ are not evaluated (the vacuum assumption holds). The parameter $b$ for all shapes is $10^{-31}$, the average value of $b'$ was $7.7 \cdot 10^{-31}$ and $3 \leq 10^{31}b' \leq 21$.

The difference between the desorption constant for $YH_3$ for hydriding (it is $b$) and dehydriding (it is $b'$) is explained by different temperature: for hydriding it was $\approx 400K$ and for dehydriding it was $\approx 500K$; this is enough to provide such difference because activation energy of desorption seems to be rather high.

Size of the particle $L$ and the initial size of the old phase core $\rho_0$ differ for different shapes and cycles.

Note that according to the Buckingham $\pi$-theorem the size $L$ can be changed in reasonable boundaries together with the parameters without influencing the results. The reason is that $L$ fixes the length unit (other units are concentration fixed by $\bar{c}$ and time fixed by the duration of the experiment). Changing $L$ is equivalent to changing meter to a new length unit. Thus it is impossible to evaluate $L$ and other parameters at the same time; only the quantities $\rho_0/L$, $DL^{-2}$, $b/L$, $s/L$, etc. can be evaluated, i.e. those that do not depend on the length unit. We used this invariance to make $b$ be the same for different cycles of dehydriding.

We see that the kinetic parameters are the same for different shapes and are similar for different experiments on hydriding and dehydriding; the approximation for different shapes is of reasonable quality. This shows that the powder particle’s shape does not influence noticeably on the kinetics of hydriding and dehydriding and thus adds arguments to the main conclusion of [5].

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