Modeling high-temperature TDS-spectra peaks of metal–hydrogen systems

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Abstract

In the paper we present several mathematical models of dehydrogenation kinetics of metals for the TDS (thermal desorption spectrometry) method. Diffusion is assumed to be fast. This allows considering only ordinary differential equations.
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1. Introduction

In this paper we discuss some models applied to the widely used experimental method of thermal desorption spectrometry (TDS) [1–6] applied to dehydrogenation of metals. A sample of studied material (e.g. hydride) is placed into an evacuated vessel and heated. The desorption flux of hydrogen from the sample is measured. We are interested in kinetics of dehydrogenation of metals. We assume that temperature is rather high so that diffusion is relatively fast. Then it is possible to make models using ordinary differential equations.

The material is a powder. We consider a single particle and model it as a sphere of radius L. Real particles of hydride powders are not spherical; yet the sphere is a good approximation for small particles when diffusion is fast. Inside the particle there is a hydride core (β phase) of radius ρ. A spherical layer of width $L - \rho$ is metal with dissolved hydrogen (α phase). Usually the heating is linear: $T(t) = \upsilon t + T_0$.

Let $c_\alpha(t, r)$, $c_\beta(t, r)$ be the concentrations of hydrogen dissolved in α and β phases at time t, r is for radius. Since diffusion is fast, we can assume that $c_\alpha(t, r) = c_\alpha(t)$, $c_\beta(t, r) = c_\beta(t)$. For some materials one can also assume that $c_\beta(t) = c_\beta^{\text{crit}} = \text{const}$. Otherwise $c_\beta(t) \geq c_\beta^{\text{crit}}$. Here c_β^{crit} is the critical concentration in hydride. We model the desorption flux density with a square dependence on the concentration: $J(t) = b(T)c_\alpha^2(t, L)$ (bulk desorption). The boundary-value problems of dehydrogenation of metals with surface desorption are considered in [7,8]. We assume also that all parameters are Arrhenius temperature dependent, in particular $b(t) = b(T(t)) = b_0 \exp\{-E_b/[RT(t)]\}$.

2. Constant concentration in hydride

Here we consider the case when $c_\beta(t) = c_\beta^{\text{crit}}$. The concentration dynamics is driven by two fluxes: the desorption flux and the flux of hydrogen decomposition. To avoid singularity in the obtained differential equations at $t = 0$ we should consider a thin "initial cover": a layer of metal with dissolved hydrogen around the hydride core. Let $V(r)$ and $S(r)$ be the volume and area of a sphere of radius r. The balance equation for decomposing hydride is

$$c_\beta V(\rho(t)) + c_\alpha(t)(V(L) - V(\rho(t))) + S(L) \int_0^t b(\tau)c_\alpha^2(\tau)\, d\tau$$

$$= \text{const.} \tag{1}$$

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Differentiating on t we obtain

$$(c_\beta^{\text{crit}} - c_\alpha(t))\rho^2 \dot\rho + \dot c_\alpha(t)\frac{L^3 - \rho^3}{3} + L^2 b(t)c_\alpha^2(t) = 0 \quad (2)$$

Now let us consider the hydrogen balance near the phase bound. Denote the density of hydrogen flux from the hydride phase by $I(t, c_\alpha(t))$. During the time $\mathrm{d}t$ the hydride core was decreasing. Denote the decrement of its radius by $\mathrm{d}\rho < 0$. At time t the thin spherical layer of width $|\mathrm{d}\rho|$ (denote its volume by $\mathrm{d}V > 0$) consisted of hydride and contained hydrogen with concentration c_β^{crit}. At time $t + \mathrm{d}t$ this layer contained dissolved hydrogen with concentration $c_\alpha(t)$. The amount $(c_\beta^{\text{crit}} - c_\alpha(t))\,\mathrm{d}V$ is gone towards the surface by the flux I because there are no other sinks. Since $\mathrm{d}V = 4\pi\rho^2|\mathrm{d}\rho| = -4\pi\rho^2\,\mathrm{d}\rho$, it follows that

$$-4\pi\rho^2(c_\beta^{\text{crit}} - c_\alpha(t))\dot\rho = 4\pi\rho^2 I(t, c_\alpha(t))$$

$$\Rightarrow (c_\beta^{\text{crit}} - c_\alpha(t))\dot\rho = -I(t, c_\alpha(t)) \quad (3)$$

The last equation is a Stefan condition at the moving bound. The initial data is $\rho(0) = \rho_0 < L$. Substituting (3) in (2), we get:

$$\dot c_\alpha(t)(L^3 - \rho^3(t)) = 3I(t, c_\alpha(t))\rho^2(t) - 3L^2 b(t)c_\alpha^2(t),$$

$$c_\alpha(0) = \bar c \quad (4)$$

Here $\bar c$ is some initial value for the concentration. It is reasonable to assume that $\bar c$ is the equilibrium concentration. Eqs. (3) and (4) is a system of ODE for the unknown functions $c_\alpha(t), \rho(t)$. Note that both equations are derived from the conservation law.

Now let us consider certain expressions for the density of the flux $I(t, c_\alpha(t))$.

The first expression is $I(t) = k(t)c_\beta^{\text{crit}}[1 - c_\alpha(t)/\bar c]$. The factor in brackets describes the influence of c_α on the flux: if $c_\alpha \ll \bar c$ then $I(t) \approx k(t)c_\beta^{\text{crit}}$, but if $c_\alpha \approx \bar c$ then $I(t) \approx 0$. In Fig. 1 there are the model and the experimental curve (erbium, $\upsilon = \dot T = 0.05$ K/s, $T_0 = 694$ K). Parameters: $L = 10^{-3}$ cm, $b_0 = 6 \times 10^{-18}$ cm^4/s, $E_b = 1.6 \times 10^5$ J, $k_0 = 4.2 \times 10^{-5}$ cm/s, $E_k = 1.1 \times 10^4$ J, $c_\beta^{\text{crit}} = 8 \times 10^{21}$ cm^{-3}, $\bar c = 0.15c_\beta^{\text{crit}}$ (equilibrium concentrations in β and α phases). If it is clear that $c_\alpha(t) \ll \bar c$, one can simplify the expression: $I(t) = k(t)c_\beta^{\text{crit}}$.

The second expression for $I(t, c_\alpha(t))$ is $k(t)[c_\beta^{\text{crit}} - c_\alpha(t)][1 - c_\alpha(t)/\bar c]$, i.e. proportional to the difference of concentrations. The last factor is discussed a few lines above. Again, the simplification is possible: $I(t) = k(t)[c_\beta^{\text{crit}} - c_\alpha(t)]$. This is interesting: substituting it to (3) we get $\dot\rho = -k(t) = -k(T(t))$: hydride decomposition depends only on temperature.

The third possible way to describe hydride decomposition is to suppose that hydride decomposition is fast enough to maintain the equilibrium concentration in the solution. Desorption outflow is compensated by hydride decomposition.
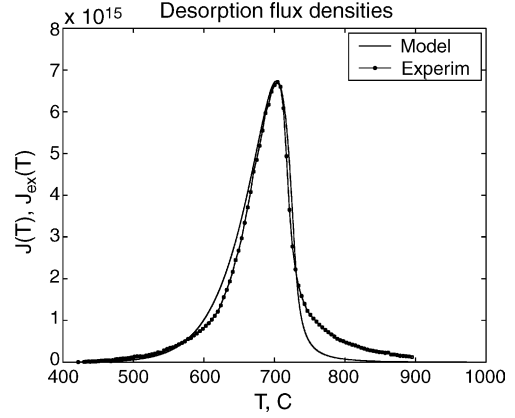

Fig. 1. Model and experimental curves.

Then $\dot c_\alpha = 0 \Rightarrow c_\alpha \equiv \bar c$ until hydride ends. From (4) it follows that $I = bc_\alpha^2 L^2 \rho^{-2}$. When the hydride core disappears, the left hydrogen desorbs, thus $c_\alpha(t)$ decreases. Eqs. (3) and (4) may under these assumptions be solved explicitly:

$$\rho^3 = L^3 - \frac{3\bar c^2 L^2}{c_\beta^{\text{crit}} - \bar c}\int_0^t b(\tau)\,\mathrm{d}\tau,$$

$$c_\alpha(t) \equiv \bar c, \ t < t_s, \ \rho(t_s) = 0, \ \rho(0) = L \quad (5)$$

$$c_\alpha(t) = \bar c\left(1 + \frac{3\bar c}{L}\int_{t_s}^t b(\tau)\,\mathrm{d}\tau\right)^{-1}, \quad c_\alpha(t_s) = \bar c, \ t \geq t_s \quad (6)$$

In spite of simplicity of this model (only two parameters: b_0 and E_b), it gives rather good results with particle size distribution taken into consideration. In Fig. 2 there are the model curve and the experimental one the same as in Fig. 1 with traps (see Section 4) taken into account. Size distribution is normal, mean radius $\bar L = 5 \times 10^{-3}$ cm, $\sigma = 10^{-3}$ cm. Parameters: $b_0 = 5 \times 10^{-18}$ cm^4/s, $E_b = 1.6 \times 10^5$ J, $c_\beta^{\text{crit}} = 5.8 \times 10^{21}$ cm^{-3}, $\bar c = 0.15c_\beta^{\text{crit}}$, the traps coefficients are constant: $a_1 = a_2 = 10^{-3}$ s^{-1}.

Particles in the powder are of different sizes. Some models provide good fitting of experimental curves even for a single particle. Otherwise size distribution should be taken into account. Let the density of particle radii distribution be $N(L)$. The mean flux density then is calculated as $\bar J(t) = \int_0^\infty J(t, L)S(L)N(L)\,\mathrm{d}L(\int_0^\infty S(L)N(L)\,\mathrm{d}L)^{-1}$. Here $J(t, L)$ is for the desorption flux density from a particle of radius L. Numerically it is sufficient to consider 20–50 radii to obtain rather smooth mean curve.

3. Varying concentration in hydride

Now let us assume that the concentration $c_\beta(t)$ may change in time. One more connection between concentrations or fluxes is necessary.

One possibility is the local equilibrium $c_\beta(t) = \gamma(t)c_\alpha(t)$. The Stefan condition is derived similarly to (3): $(\gamma(t) - 1)c_\alpha(t)\dot{\rho} = -I(t, c_\alpha(t), c_\beta(t))$. Here $I(t, c_\alpha, c_\beta)$ is the hydride decomposition flux density. From balance equation (1) with $c_\beta = c_\beta(t)$ we obtain

$$\dot{c}_\alpha(t)(\gamma(t)\rho^3 + L^3 - \rho^3)$$
$$= 3\rho^2 I(t, c_\alpha(t), c_\beta(t)) - 3L^2 b(t)c_\alpha^2(t) - \dot{\gamma}(t)c_\alpha(t)\rho^3 \quad (7)$$

Another possibility is the expression for the flux density $I_d(t, c_\alpha(t), c_\beta(t))$ on the phase bound: $I_d(t, c_\alpha(t), c_\beta(t)) = \gamma_1(t)c_\beta(t) - \gamma_2(t)c_\alpha(t)$. This flux can remove some hydrogen from hydride even if it does not decompose if $c_\beta(t)$ is high enough. "Superfluous" hydrogen atoms come to the solution and are immediately distributed there evenly. Density of the hydride decomposition flux I may be modeled by formulae from Section 2. The Stefan condition is $(c_\beta(t) - c_\alpha(t))\dot{\rho} = -I(t, c_\alpha(t), c_\beta(t))$. Considering the balance in hydride we derive the equation $\dot{c}_\beta(t)\rho = -3I_d(t, c_\alpha(t), c_\beta(t))$. The equation for $c_\alpha(t)$ is $(1/3)\dot{c}_\alpha(t)(L^3 - \rho^3(t)) = I(t, c_\alpha(t), c_\beta(t))\rho^2(t) + I_d(t, c_\alpha(t), c_\beta(t))\rho^2(t) - L^2 b(t)c_\alpha^2(t)$, $c_\alpha(0) = \bar{c}$.

4. Influence of traps

Numerical experiments (e.g. Fig. 1) show that model curves lie almost always below experimental ones at high temperatures (i.e. in the end of the experiment). This means that after hydride has decomposed and most hydrogen has desorbed, the left hydrogen desorbs less quickly than models predict. One of the possible explanations of this fact is interaction with the traps. The traps are defects of metal, cavities, admixtures, etc. that can capture hydrogen atoms when their concentration is high and release them when the it becomes lower. Denote the concentration of hydrogen captured by the traps by $z(t)$ (the traps are distributed evenly). Assume that probability for an atom to be captured is proportional to $c_\alpha(t)$
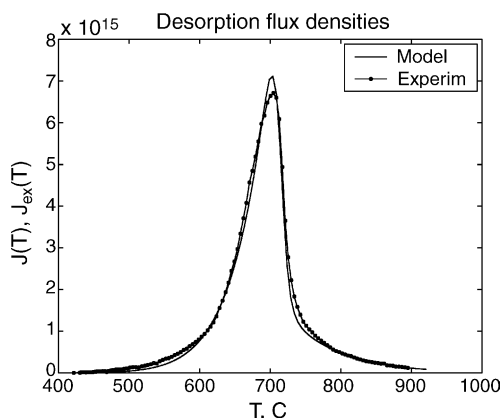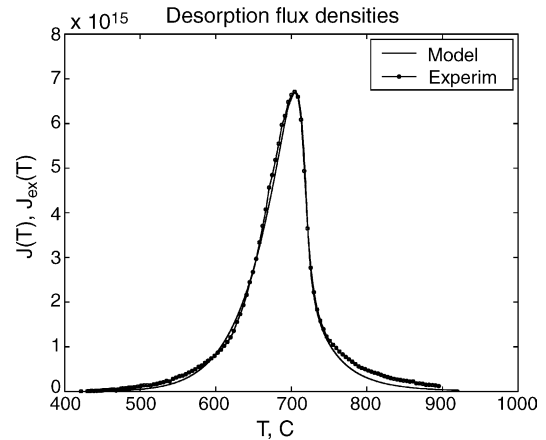

Fig. 3. Traps taken into account.

and probability for a captured atom to be released is proportional to $z(t)$. The proportionality factors a_1, a_2 may depend on temperature (in the Arrhenius way). Thus we obtain the linear equation: $\dot{z} = a_1(t)c_\alpha(t) - a_2(t)z(t)$. Let us show how the Eqs. (3) and (4) change. Other models are modified similarly. The Stefan condition (3) with traps taken into account has the form $(c_\beta^{crit} - c_\alpha(t) - z(t))\dot{\rho} = -I(t, c_\alpha(t))$. Eq. (4) will change to:

$$\dot{c}_\alpha(t) = 3\frac{I(t, c_\alpha(t))\rho^2(t) - L^2 b(t)c_\alpha^2(t)}{L^3 - \rho^3(t)} - a_1(t)c_\alpha(t)$$
$$+ a_2(t)z(t) \quad (8)$$

In Fig. 3 there is the experimental curve (the same as in Fig. 1) and the model curve. Parameters: $L = 10^{-3}$ cm, $b_0 = 4 \times 10^{-18}$ cm^4/s, $E_b = 1.6 \times 10^5$ J, $k_0 = 9.2 \times 10^{-5}$ cm/s, $E_k = 1.2 \times 10^4$ J, $c_\beta^{crit} = 7.5 \times 10^{21}$ cm^{-3}, $\bar{c} = 0.15c_\beta^{crit}$, $a_1 = 3.3 \times 10^{-3}$ s^{-1}, $E_1 = 4.7 \times 10^3$ J, $a_2 = 2.7 \times 10^{-3}$ s^{-1}, $E_2 = 0$ J.

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Fig. 2. Traps and size distribution taken into account.