TDS-SPECTRA OF HYDRIDE POWDER DECOMPOSITION: MODELLING WITH SIZE REDUCTION EFFECT

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Introduction

Termodesorption spectrometry (TDS) method is widely used when studying metal-hydrogen systems. The sample is heated in a vacuum chamber, the desorption flux of hydrogen is registered and the kinetic parameters of the considered model are estimated. The flux dependence on temperature (the TDS-spectrum) may have few peaks which correspond to different sets of limiting factors. For references of the experimental see [1] and references therein. For high-temperature desorption peak and small powder particles diffusion can be considered quick. Distributed diffusion models are presented in [2,3]. We take into consideration the reversible capture of hydrogen atoms by material defects and reduction. The density increases while hydride decomposes (the volume decreases). This results in tensions: the powder becomes finer after hydrogenation/dehydrogenation cycles. We consider the stable size of the particles.

Mathematical models

The material is powder; thus let us consider a particle as a sphere of radius $L(t)$ with a hydride core of varying radius $\rho(t)$ inside (β phase). A spherical layer of width $L-\rho$ is metal with dissolved hydrogen (α phase). Two suppositions are commonly used for the desorption process: 1) hydrogen atoms come from the bulk to the surface and desorb forming molecules; 2) for "porous" materials hydrogen desorbs directly from the near-to-surface bulk. The heating is assumed to be monotonous (usually $T(t)=T_0+vt$), diffusion in the β phase – relatively slow. Critical concentration $c_\beta = Q$ has no time to change during the experiment. Dehydrogenation proceeds as hydride core shrinks and metal with dissolved hydrogen is degassed. All coefficients are considered Arrhenius with respect to temperature.

1. *The Simplest Model.* Atom flux with density $I(t)$ at the moving phase boundary initially has time to keep the equilibrium concentration in the α phase $c(t)=c_\alpha(t)=\bar{c}$. Here $\bar{c}=\eta Q$, $0<\eta<1$. In general case $Q=Q(T)$, $\bar{c}=\bar{c}(T)$, but for the erbium hydride we can suppose that Q, $\bar{c}$ are constant within the thin peak of TDS-spectra. The desorption flux density is square: $J(t)=b(t)\,\bar{c}^2, b(t)=b(T(t))$.

After hydride vanishes (i.e. $\rho(t_*)=0$) we have $\rho\equiv 0$ and $c(t)$ monotonically decreases. Let us consider these two stages. For traps concentration $z(t)$ we assume the equation $\dot{z}=a_1c-a_2z$. Here the coefficients of reversible capture are constant within the considered TDS-peak. For $t\ge t_s$ we have $\dot{z}=0, z=\bar{z}$, $a_2\bar{z}=a_1\bar{c}$, $\bar{c}+\bar{z}<Q$ and the balance is

$$QV(L_0)=QV(\rho)+(\bar{c}+\bar{z})[V(L)-V(\rho)]+$$
$$+\int_0^t S(L)\{b\bar{c}^2-\mu sp\}d\tau,\quad L_0=L(0).$$

Here $V(r)$ is for the volume of a sphere of radius r, $S(r)$ is for the area of its surface, μsp is for the density of the return flux of H due to the pressure $p(t)$ of H_2 in the chamber.

Let us denote the compression coefficient by γ. If in β phase sample's volume equals V then in α phase this volume is $\gamma V, \gamma<1$. Size reduction of the particle is proportional to that of the hydride core. Thus $(1-\gamma)[L_0^3-\rho^3]=L_0^3-L^3$, $L(t)=L(\rho(t))$.

After differentiating the balance equation on t we obtain the equation for $L(t)$ with the solution

$$L(t)=\frac{1-\gamma}{Q-\gamma(\bar{c}+\bar{z})}\int_0^t\{\mu sp-b\bar{c}^2\}d\tau+L_0.$$

Using $L(t)$ we determine $\rho(t)$ and $t_*:\rho(t_*)=0$. As volume $V(\rho)$ decreases proportionally to ρ^3, we can switch to degassing stage when $\rho<<1$ ($\rho<L_0/10$). The balance equation for it ($t\ge t_*, \rho\equiv 0$) is

$$\{[c(t+\Delta t)-c(t)]+[z(t+\Delta t)-z(t)]\}V(L_*)=$$
$$\{\mu s(t)p(t)-b(t)c^2(t)\}S(L_*)\Delta t+o(\Delta t),$$

where $L_* = L(t_*)$. Dividing this on Δt and considering a limit as Δt tends to zero we obtain:

$$\dot{c} = 3L_*^{-1}\{\mu sp - bc^2\} - a_1 c + a_2 z,\ c(t_*) = \bar{c},$$

$$\dot{z} = a_1 c - a_2 z,\ z(t_*) = \bar{z},\ a_1\bar{c} = a_2\bar{z},\ t \geq t_*.$$

Model peaks have spikes at moments when hydride ends. Size distribution results in significant smoothing and good approximation of experimental data.

More detailed description of the dehydrogenation process makes the models much more complex. Therefore we show only qualitative characteristics of the models below.

2. *A Switching Model.* We suppose that for the certain time desorption is low enough, so the equilibrium concentration is maintained in α phase. Hydride decomposes with the rate necessary to compensate the desorption outflow: $I = k(T)Q > b(T)\bar{c}^2$. When the desorption flux becomes high enough to overcome the maximum possible hydride decomposition flux, $c(t)$ will decrease. The switch condition follows from the fact that the fluxes must be equal ($c = \bar{c}$, $t \leq t_s$):

$$kQ\rho^2 = \{b\bar{c}^2 - \mu sp\}L^2,\ t = t_s.$$

To this moment the expression for $L(t)$ remains the same. Equations for $t \geq t_s$ are

$$-[Q - c(t) - z(t)]\dot{\rho}(t) = I(t),\ \rho(t_s) = \rho_s,$$

$$(L^3 - \rho^3)\,\dot{c} = 3[I\rho^2 + \{\mu\, sp - bc^2\}L^2 -$$

$$-(c + z)L^2\dot{L}] - \dot{z}(L^3 - \rho^3),\ c(t_s) = \bar{c}.$$

3. *Self-Control of Hydride Decomposition.* We suppose here that the balance of desorption flux and flux from hydride from the very beginning determine the dynamics of the dissolved hydrogen. At the same time $I(t) = k(T)Q\,(1 - c/\bar{c})$. Potential hydride decomposition rate is proportional to Q but the greater the concentration the slower the hydride decomposition.

4. *Models with Surface.* We assume that the surface and the bulk concentrations are connected by a condition of quick solution, $J(t) = b(T)q^2(t)$. Equations for the phase bound movement and the reversible capture are the same. Dynamics of the concentrations are obtained from the mass conservation law.

3. *A Model with Relatively Fast Diffusion*. We suppose that diffusion is rather quick, but not quick enough to make $c(t,r)$ constant with respect to r: $c = c(t,r)$, $r \in [\rho\,, L]$. From the diffusion equation in spherical coordinates

$$c_t(t,r) = D(T)\,[c_{rr}(t,r) + 2c_r(t,r)/r]$$

at high diffusion coefficient D and $c_t / D << 1$ by integrating $[...] = 0$ one obtains an expression $c(t,r) = A(t) + B(t)/r$. It is a slowly changing stationary distribution and is rode by low speed of phase bound compared to diffusion of hydrogen in the solution and desorption. Function parameters $A(t)$, $B(t)$ are defined from the mass conservation law. When the hydride core vanishes the hyperbola is reduced to the straight line $c(t,r) = c(t)$. After that, the degassing of metal with dissolved hydrogen takes place.

4. *The Distributed Models*. These models have the form of nonlinear diffusion boundary-value problems with moving bounds. Size reduction effect is taken into account. Desorption is either bulk or surface. Distribution of particle size is normal. The phase bound movement is described by the Stefan condition. Such problems require development of numerical methods: method of catching front in mesh point and method of domain transformation to stationary state. The function $\rho(t)$ becomes the functional parameter.

In the paper we present the results of numerical analysis of these models of TDS-method. In particular, the influence of the parameters is investigated. Model curves are compared with the experimental data.

References

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