Technical Physics, 2024, Vol. 69, No. 12

Hybrid model of hydrogen thermodesorption from structural materials

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Received May 3, 2024
Revised May 25, 2024
Accepted October 30, 2024

Thermodesorption spectrometry (TDS) is one of the effective methods for studying the interaction of structural materials with hydrogen isotopes. A thin plate made of a material with metallic properties is considered. The sample pre-saturated with dissolved hydrogen is slowly heated in a vacuum chamber. The degassing flux is recorded using a mass spectrometer. The TDS spectrum is the dependence of the desorption flux density on the current temperature is analysed. The paper presents a new hybrid model of thermodesorption, which operates with both volume-averaged concentrations and surface concentration. The dynamics of concentration is determined by nonlinear dynamic boundary conditions.

Keywords: hydrogen thermodesorption, numerical modelling.

DOI: 10.61011/TP.2024.12.60391.390-24

Introduction

In many application problems it would be enough to operate with the volume-averaged hydrogen concentrations. It is rather adequate for „porous“, powdered materials, when the geometric characteristics of the specimen are not significant. For the structural materials with the metal properties, the substantial effect of the surface adsorption, desorption, dissolution and atomic diffusion in the volume is specific. This causes the need for considering more detailed models, in particular, to describe the dynamics of the surface concentrations. The clarified model makes it possible after the parametric identification using the experimental data to forecast the material behavior in the hydrogen-containing medium (this is especially true for deuterium and tritium), including under the extreme conditions of material operation.

The purpose of this paper — is to present the hybrid model of thermal desorption, which combines a model in terms of the volume-averaged concentration and a more detailed model in the form of a diffusion equation with non-linear dynamic boundary conditions reflecting the processes on the surface. As a result, we come to the system of ordinary differential equations (ODE system of a relatively low order). Such model requires no specialized software. It is possible to numerically model various situations and conditions of material operation n any mathematical package (the authors used *Scilab*) without substantial expenditures of machine time.

In accordance with the purpose and nomination of „extended theses“ the concise treatment in the standard designations provides only the most necessary references.

1. Limitation by diffusion

Let us specify that ℓ — plate thickness, diffusion coefficient $D = D(T(t)) \equiv D[t]$, i.e. the heating is slow and even (T does not depend on x). Usually the linear heating is used: $T(t) = T_0 + \beta t$. When $T_{\max}$ is achieved, the heating stops.

For the volume-averaged concentration $X(t) \approx \frac{1}{\ell}\int_0^\ell c(t,x)dx\,\big(= \bar{c}(t)\big)$ they often use a linear model (see in more detail [1]): $\dot{X}(t) = -K(T)X(t)$, $X(0) = c_0$, $K(T) = \pi^2\ell^{-2}D(T)$, $T = T(t)(T_0 + \beta t)$. The value $X(t)$ has the meaning of the volume-averaged concentration of the dissolved hydrogen left in the specimen at $t > 0$. The model is operable, when the temperature is rather high, and we are interested in the integral flow of degassing. At the same time the kinetic coefficient $K(T)$ is proportionate to $D(T)$.

Note 1

It can be additionally normalized to the initial concentration: $\tilde{X} = \frac{X}{c_0}$, $\tilde{X}(0) = 1$. The equation will stay unchanged (linear and homogeneous), but a nondimensional variable $\tilde{X}(t)$ will already have the meaning of the remaining share of c_0. One can operate with the desorbed share $Y(t) = 1 - \tilde{X}(t)$ and then $\dot{Y}(t) = K(T)\big(1 - Y(t)\big)$, $Y(0) = 0$. Note that such simplest model, when only the diffusion limits strictly, will not respond to c_0, but will respond to the geometric parameter ℓ: $K(T) = K(T;\ell)$. In non-linear models we will not normalize to c_0 (in contrast to [1]).

2. Limitation by desorption

Under strict limitation by desorption the concentration in the volume is practically even: $c(t,x) \approx c(t) \Rightarrow X(t) \approx c(t)$. Then, based on the assumptions of the material balance, one may record $\ell\dot{X} = -2b(T)X^2$, $X(0) = c_0$, and consider $b(T)$ the effective recombination coefficient [2].

For unity the averaged degassing flow is to be counted in the hydrogen atoms: 1 H/(cm^{3}s).

Note 2

This is the second considered extreme case, when the diffusion is relatively quick, and only desorption limits strictly. Here the kinetic coefficient is $K(T) = \frac{2b(T)}{\ell}$. Instead of $D(T)$, $b(T)$ naturally appears, and dependence on ℓ remains. If we go to shares $\tilde{X} = \frac{X}{c_0}$, then $\frac{d\tilde{X}}{dt} = -\tilde{K}(T)\tilde{X}^2$, $\tilde{X}(0) = 1$, $\tilde{K}(T; \ell, c_0) = \frac{2b(T)c_0}{\ell}$. Additional dependence on the initial saturation appears. It should be taken into account for metals and alloys. Then one may record the response equation of the second order $\frac{d\tilde{X}}{dt} = -\tilde{b}(T)\tilde{X}^2$, interpreting $\tilde{b}(T)$ as the volume desorption coefficient. Therefore, let us leave the averaged concentration $X(t)$ as the variable, and leave c_0 in the source data: $X(0) = c_0$.

3. Averaging by diffusion and desorption processes

In the wide range of the experiment conditions the diffusion and desorption are substantially interdependent (dynamics of the processes on the surface dictates the boundary conditions for the diffusion equation). With account of $T = T(t) = T_0 + \beta t$, $dT = \beta dt$, $t \leftrightarrow T \in [T_0, T_*]$ instead of $X(t)$ one may record $X(T)\big(\approx \bar{c}(T)\big)$ and

$$\frac{dX}{dT} = -\beta^{-1}K(T)X^{\alpha}(T), \quad X(T_0) = c_0, \quad \alpha \in [1, 2],$$

$$K(T) = K_0 \exp\{-Q[RT]^{-1}\}.$$

Parameter $\alpha \in [1, 2]$ makes it possible to take into account the degree of participation of the limiting factors. We apply averaging both by concentration and the processes of diffusion and recombination. Coefficient $K(T)$ indirectly depends on α: at $\alpha \sim 1$ we focus on $\pi^2\ell^{-2}D(T)$, and at $\alpha \sim 2$ — on $2b(T)/\ell$. In [1] analytically analyzed this model (only it additionally considered the normalization of $X \to X/c_0 \in (0, 1)$, $t > 0$, and $K = K(T)$).

Note 3

Paper [3] presents the spectrum of models $\dot{X} = K(T)f(X)$, where $X(t)$ — the reacted fraction. Compared to the designations above in [3] $X = 1 - X/c_0$ is assumed, where on the right X — is the volume-averaged concentration. [4] studied the impact of the initial saturation. Paper [5] contains the detailed description of the proposed model and the wide list of references. Let us also note the substantial review [6].

4. Model with dynamic boundary conditions

Let us proceed to a more detailed model, clearly separating the volume and surface processes (following [7]). The boundary value problem of the degassing TDS will look as follows:

$$\partial_t c(t, x) = D(T)\partial_x^2 c(t, x), \quad t \in (0, t_*), \quad x \in (0, \ell),$$

$$c(0, x) = c_0, \quad x \in [0, \ell], \quad c_{0,\ell}(t) = g(T)q(t),$$

$$\frac{dq}{dt} \equiv \dot{q}(t) = -b(T)b(T)q^2(t) + D(T)\partial_x c(t, 0),$$

$$J(t) = b(T)q^2(t), \quad T(t) = T_0 + \beta t, \quad \beta > 0.$$

Here $c(t, x)$ — volume concentration (1H/cm^3); $q(t)$ — surface concentration (1H/cm^2); D, b, g — (Arrhenius by temperature) coefficients of diffusion, desorption, quick dissolution, size accordingly cm^2/s, cm^2/s, 1/cm; $J(t)$ — density of the desorption flow (atoms recombined into molecules), $[J] = 1/\mathrm{cm}^2\mathrm{s}$, 1 means one atom H. In virtue of $t \leftrightarrow T$, $J = J(T)$ may be expressed. Within such model, the curve is $\big(T, J(T)\big)$ and makes the TDS spectrum. Desorption is referred to the single (cm^2) part of the double-sided surface, $q_{0,\ell}(t) = q(t)$. To simplify recording $D(t) \equiv D\big(T(t)\big)$, $g(t) \equiv g\big(T(t)\big)$, $b(t) \equiv b\big(T(t)\big)$. Paper [8] implements the three-stage experiment of „breakthrough−overlow−thermal desorption“, which substantially improves its information value.

Let us complicate the diffusion equation with account of the reversible capture into the traps of various types (practically evenly distributed in the volume):

$$\partial_t c = D\partial_x^2 c - \Sigma_{\nu=1}^{m}[a_\nu^-[1 - Z_\nu]c(t, x) - a_\nu^+ z_\nu(t, x)],$$

$$\partial_t z_\nu = a_\nu^-(T)[1 - Z_\nu]c(t, x) - a_\nu^+(T)z_\nu(t, x),$$

where $z_\nu(t, x)$ — concentrations of H (1/cm^3), trapped by defects (microcracks, grain boundaries,...); $a_\nu^{\mp}$ — coefficients of absorption and release of H; $Z_\nu \equiv z_\nu(t, x)/\max z_\nu$.

5. Hybrid model of thermal desorption

Let us proceed to the main content of this paper. Let us set the objective of combining the two considered classes of models. Not to clutter the calculations, let us limit ourselves to one type of traps (for example, grain boundaries). Let us record the diffusion equation in the form of $\partial_t c + \partial_t z = D(T)\partial_x^2 c$, $T = T(t)$. A change in the total concentration $c + z$ is determined by the density of the diffusion flow $J_d = -D\partial_x c$. Continuity equation: $\partial_t(c + z) = -\partial_x J_d$. Let us integrate the equation by x:

$$\int_0^\ell \frac{\partial c}{\partial t}dx + \int_0^\ell \frac{\partial z}{\partial t}dx = \frac{d}{dt}\int_0^\ell c(t, x)dx$$

$$+ \frac{d}{dt}\int_0^\ell z(t, x)dx = D(T)\left[\frac{\partial c}{\partial x}\Big|_\ell - \frac{\partial c}{\partial x}\Big|_0\right].$$

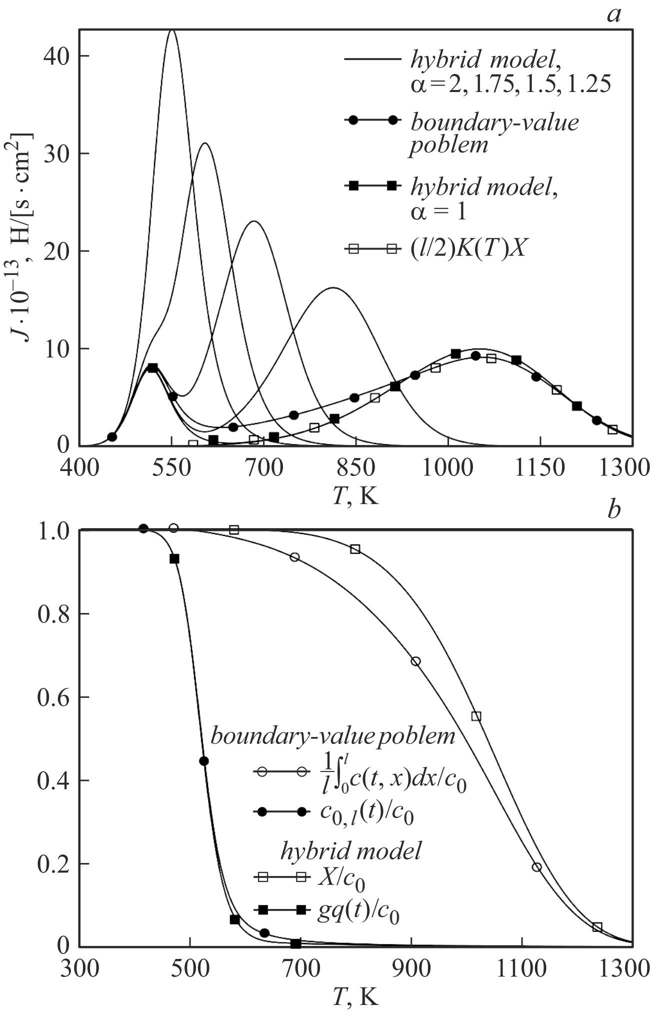

Figure 1. Comparison of models: boundary value problem and hybrid model; *a* — thermal desorption flows, *b* — comparison of relative concentrations.

Let us introduce the volume-averaged concentrations $X(t) = \frac{1}{\ell}\int_0^\ell c(t,x)dx$, $Y(t) = \frac{1}{\ell}\int_0^\ell z(t,x)dx$. In virtue of symmetry $\partial_x c(t,0) = -\partial_x c(t,\ell)$ we get $\dot X(t) + \dot Y(t) = -2D(T)\frac{\partial c}{\partial x}\Big|_0 \cdot \ell^{-1}$. Let us substitute the expression for $D\partial_x c|_0$ in the equation for the surface concentration:

$$\frac{dq}{dt} \equiv \dot q(t) = -b(T)q^2(t) - \frac{\ell}{2}[\dot X(t) + \dot Y(t)].$$

And for X, Y let us accept the averaged models. For X:

$$\dot X(t) = -K(T)X^\alpha(t), \quad X(0) = c_0,$$

$$K(T) \equiv K(T;\ell,\alpha) = K_0\ell^{\alpha-3}\exp\{-Q/[RT]\}.$$

Let us integrate using $x \in [0, \ell]$ the equation for z:

$$\partial_t z = a^-(T)c(t,x) - a^+(T)z(t,x), \quad z(0,x) = z_0$$

$$\Rightarrow \frac{d}{dt}Y(t) = a^-(T)X(t) - a^+(T)Y(t), \quad Y(0) = z_0.$$

Let us now record the model in compact form. Dynamics of concentrations:

$$\begin{cases} \frac{dq}{dt} = -b(T)q^2(t) + \frac{\ell}{2}[K(T)X^\alpha(t) - a^-X + a^+Y], \\ \frac{d}{dt}X(t) = -K(T)X^\alpha(t), \\ \frac{d}{dt}Y(t) = a^-(T)X(t) - a^+(T)Y(t). \end{cases}$$

Source data (at the even equilibrium initial saturation of the specimen):

$$q(0) = q_0, \quad X(0) = c_0, \quad c_0 = g(T_0)q_0,$$

$$Y(0) = z_0, \quad a^-(T_0)c_0 - a^+(T_0)z_0 = 0.$$

Note that the initial values c_0, q_0, z_0 are dependent. We are interested in the density of the desorption flow $J(t) = b\big(T(t)\big)q^2(t)$. In axes (T, J) we have the TDS spectrum (curve $J(T)$, $t \leftrightarrow T(t)$).

We have a system of three ODEs. But in fact it is numerically integrated in series. First we calculate $X(t)$ using the second equation. Substituting to the third one, we get the linear ODE for $Y(t)$. With the known $X(t)$, $Y(t)$ it is left to integrate numerially the first equation for $q(t)$.

6. Results of numerical modeling

Let us focus on the data on tungsten [9]. Parameter estimates depend substantially on the conditions of the experiment and specimens preparation, so let us perceive the values as the model ones (in numerical order). Accepted values of model parameters: $b_0 = 3.2 \cdot 10^{-7}\,\mathrm{cm^2/s}$, $[E] = \mathrm{kJ/mol}$, $E_b = 100$, $D_0 = 4.1 \cdot 10^{-3}\,\mathrm{cm^2/s}$, $E_D = 62$, $g_0 = 200\,\mathrm{cm^{-1}}$, $E_g = 0$, $c_0 = 6.567 \cdot 10^{17}\,\mathrm{cm^{-3}}$, $\ell = 0.05\,\mathrm{cm}$, $T_0 = 300\,\mathrm{K}$, $\dot T = \beta = 2\,\mathrm{K/s}$.

Fig. 1 presents the spectra and concentrations using the model in the form of the boundary value problem and the hybrid model. Two-peak curves are produced, and the peaks are comparatively isolated. With the growth of the reaction $\alpha = 2$ order the high temperature peak moves towards the low-temperature one. At $\alpha = 2$ we have the spectrum with one peak. Further see figures $\alpha = 1$. Fig. 2 illustrates the impact of parameters that the experimenter may vary. Fig. 3 presents numerical spectra with account of various defects. Curves with account of defects of „microcavity type“ ($a^- = 10^{-5}$, $E_{a^-} = 10$, $a^+ = 1.5$, $E_{a^+} = 35$, $z_{\max} = 10^{17}\,\mathrm{cm^{-3}}$). The initial concentration in the defects is determined on the basis of the equilibrium conditions. Here in fig. 3 the impact of defects of „hydride inclusion type“ is illustrated. The hydride decomposition starts at $T = 600\,\mathrm{K}$, $a^+ = 1.5$, $E_{a^+} = 25$, $z_0 = 10^{17}\,\mathrm{cm^{-3}}$.

The general conclusion on the results of numerical modeling consists in the following. The hybrid model demonstrated the consistency compliant with the physical representations both at the quality and quantity levels. One may assess the extent of impact of („derivatives“) at the

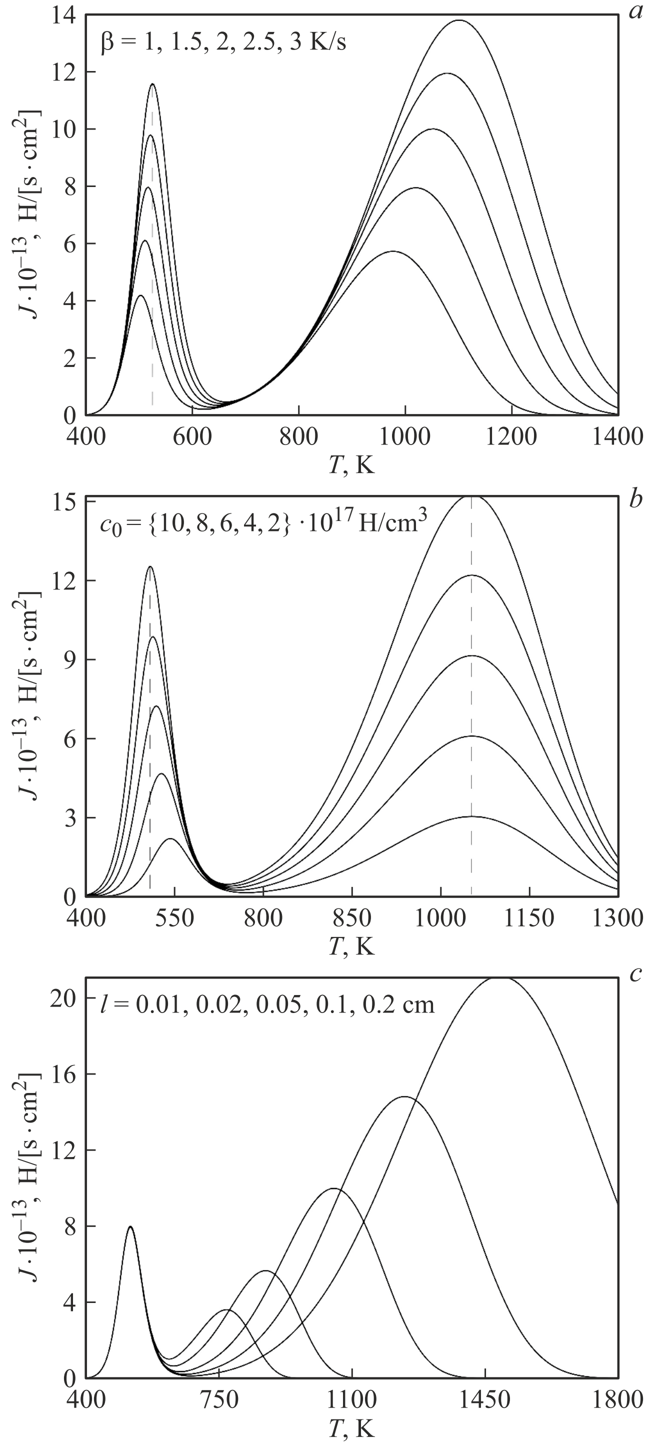

Figure 2. Hybrid model. Sensitivity of spectra to variation of parameters.

flow of degassing in variations of the model parameters and experiment conditions. If it is necessary to identify the qualitative differences at the level of „capture in the volume or dynamics with account of the surface", the experiments with the specimens of various thickness are most informative (fig. 2, *c*).

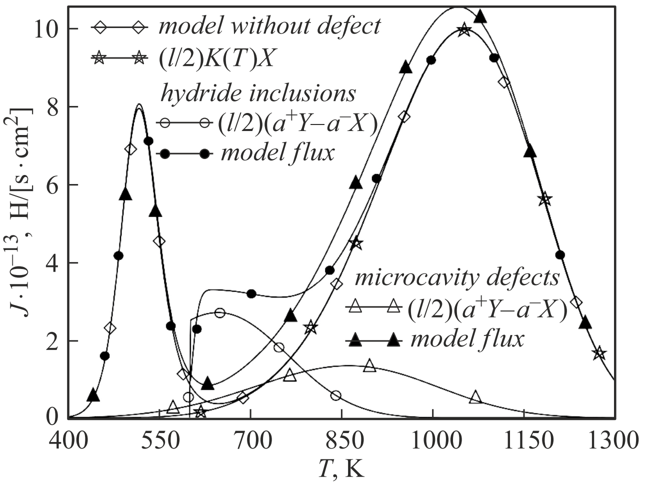

Figure 3. Hybrid model. Impact of defects.

Funding

The studies were financed from the federal budget for the implementation of the state assignment of the KarRC RAS (Institute of Applied Mathematical Research).

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by E.Ilinskaya