

Modelling of discrete TDS-spectrum of hydrogen desorption

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Abstract. High concentration of hydrogen in metal leads to hydrogen embrittlement. One of the methods to evaluate the hydrogen content is the method of thermal desorption spectroscopy (TDS). As the sample is heated under vacuumization, atomic hydrogen diffuses inside the bulk and is desorbed from the surface in the molecular form. The extraction curve (measured by a mass-spectrometric analyzer) is recorded. In experiments with monotonous external heating it is observed that background hydrogen fluxes from the extractor walls and fluxes from the sample cannot be reliably distinguished. Thus, the extraction curve is doubtful. Therefore, in this case experimenters use discrete TDS-spectrum: the sample is removed from the analytical part of the device for the specified time interval, and external temperature is then increased stepwise. The paper is devoted to the mathematical modelling and simulation of experimental studies. In the corresponding boundary-value problem with nonlinear dynamic boundary conditions physical-chemical processes in the bulk and on the surface are taken into account: heating of the sample, diffusion in the bulk, hydrogen capture by defects, penetration from the bulk to the surface and desorption. The model aimed to analyze the dynamics of hydrogen concentrations without preliminary artificial sample saturation. Numerical modelling allows to choose the point on the extraction curve that corresponds to the initial quantity of the surface hydrogen, to estimate the values of the activation energies of diffusion, desorption, parameters of reversible capture and hydride phase decomposition.

1. Introduction

The interest in the interaction of hydrogen and its isotopes with metals, alloys and intermetallic compounds is multifarious [1–6]. It is sufficient to mention problems in power production, protection of metals from hydrogen corrosion, chemical reactor design, rocket production.

High concentration of hydrogen in metal leads to hydrogen embrittlement. Common metallurgical concentrations of dissolved hydrogen range from 0.1 to 100 ppm. The authors of [7] have developed the hydrogen analyzer AV-1. The device allows to measure the hydrogen concentration in a solid sample using industrial laboratory facilities. A cylindrical sample is placed into the quartz vacuum extractor. The extractor is exposed to a given external temperature in the furnace. The contact between the sample and the extractor walls is point-like, the thermal conductivity of quartz is negligible, wherefore the heat transfer is determined by thermal radiation. As the sample is heated, atomic hydrogen diffuses inside the bulk and is desorbed from the surface in the molecular form. The extraction curve is measured by a mass-spectrometric hydrogen analyzer and recorded. The dependence of the desorption flux on the sample temperature at uniform heating called the TDS-spectrum usually has several



clear-cut peaks. In addition to the diffusion, the surface processes and the capture of hydrogen atoms by different types of defects are limiting factors. Experiments with monotonous external heating show that background hydrogen fluxes from the extractor walls and fluxes from the sample cannot be reliably distinguished. Thus, the extraction curve is not reliable. In this case discrete TDS-spectrum is used. The sample is removed from the analytical part of the device for the specified time interval, and external temperature is then increased stepwise. The problem is formulated in the following way. It is necessary to have the adequate mathematical model of mass spectrometric analyzer measurements and the computational algorithm for plotting of model dependence of hydrogen desorption flux with respect to the time and to the temperature (of the sample surface). Then it is possible to estimate a hydrogen permeability parameters and to determine which physical-chemical processes are dominant within the different TDS-peaks at the spectrum. This can help specialists to understand how a structural material will behave in a hydrogen environment under specific conditions of long-term exploitation. If these conditions are extreme, the possibilities of experimental researches are limited and the role of mathematical modelling is very important. For numerical simulation, we use heat parameters which are suitable for aluminium and some of its alloys when modelling the desorption flux.

2. Mathematical model

Heating equation. The sample has the form of a cylinder with dimensions: radius of the base is $L = 4 \cdot 10^{-3}$ m, height is $H = 2 \cdot 10^{-2}$ m. If heating of the sample is uniform (sufficiently slow, $T = T(t)$, $[T] = \text{K}$), the temperature dynamics can be described by the differential equation

$$\dot{T}(t) = \sigma \varepsilon S (\tilde{c} \rho V)^{-1} [T_e^4 - T^4(t)], \quad T_0 = T(0) = 293 \text{ K}. \quad (1)$$

Here, $T_e = \text{const} \in [300, 900]$ is temperature of the extractor wall, $S = 2\pi LH$, $V = \pi L^2 H$ are the surface area and the cylinder capacity, $\sigma = 5.67 \cdot 10^{-8} \text{ J} \cdot \text{s}^{-1} \text{ m}^{-2} \text{ K}^{-4}$ is the Stefan-Boltzmann constant. For aluminium: $\rho = 2.71 \cdot 10^3 \text{ kg} \cdot \text{m}^{-3}$ is the bulk density, $\tilde{c} = 1.15 \cdot 10^3 \text{ J} \cdot \text{kg}^{-1} \text{ K}^{-1}$ is the specific heat capacity, $\varepsilon = 7 \cdot 10^{-5} (T + 64.3)$ is the heat absorption coefficient.

Since the assumption about uniform heating does not have adequate accuracy for all values of T_e , we consider an alternative distributed model. Since the geometry of the extractor is tubular heating of the sample mainly proceeds through the lateral surface. Thus, we speak of a lower estimate of the heating of symmetry center of the sample. The considered equation (1) is majorized from above. The radiosymmetrical model is:

$$\frac{\partial T}{\partial t} = \varkappa \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \cdot \frac{\partial T}{\partial r} \right), \quad \frac{\partial T}{\partial r} \Big|_{r=0} = 0, \quad \lambda \frac{\partial T}{\partial r} \Big|_{r=L} = \alpha [T_e^4 - T^4(t, L)],$$

$T(0, r) = T_0 < T_e$, $r \in [0, L]$. Here, λ is the heat conduction coefficient (for aluminium in the range of $T \in [T_0, T_e]$ $\lambda \approx 236 \text{ J} \cdot \text{s}^{-1} \text{ m}^{-1} \text{ K}^{-1}$), $\varkappa = \lambda (\tilde{c} \rho)^{-1}$ is the thermal diffusivity, $\alpha = \sigma \varepsilon$. The finishing time t^* of computing is determined by the stationary distribution $T(t, 0) \approx T_e$, $t > t^*$. The auxiliary problem of numerical modelling of heating is the following: to estimate quickly how much the distribution $T(t, r)$ differs from the uniform heating $T(t)$ under given T_e , L , H , and thermal and physical characteristics of the material. For instance, when we use $T_0 = 293 \text{ K}$, $T_e = 773 \text{ K}$ and the L , H stated above the assumption about uniform heating of aluminium sample is true: the difference $T(t) - T(t, 0)$ is within a hundredth of a degree. We obtain this result in the distributed model where heat absorption by butt ends is disregarded. Peak temperature is reached in 2.2 hours, heating being practically linear within an hour. Hereinafter, suppose that heating of the sample is uniform.

Diffusion model with defects. Consider the boundary-value problem of thermodesorption for the cylinder taking into consideration diffusion in the bulk, hydrogen capture by defects of two

types, penetration from the bulk to the surface and desorption (surface desorption model):

$$\frac{\partial c}{\partial t} = D(T) \left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \cdot \frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial z^2} \right) - a_1[1 - W]c + a_2w + a_3\gamma, \quad r \in (0, L), \quad z \in (0, H), \quad (2)$$

$$\frac{\partial w}{\partial t} = a_1(T)[1 - W]c(t, r, z) - a_2(T)w(t, r, z), \quad W \equiv \frac{w}{w_{\max}}, \quad t \in (0, t_*), \quad (3)$$

$$\dot{\gamma}(t) = -a_3\gamma(t), \quad \gamma(t_{\text{crit}}) = \bar{\gamma} \Rightarrow \gamma(t) = \bar{\gamma} \exp\{[t_{\text{crit}} - t]a_3\}, \quad a_3 = 0, \quad t < t_{\text{crit}},$$

$$c(0, r, z) = \bar{c} = \text{const}, \quad w(0, r, z) = \bar{w} = \frac{a_1\bar{c}}{a_2 + a_1\bar{c}w_{\max}^{-1}}, \quad r \in [0, L], \quad z \in [0, H],$$

$$\partial_r c|_{r=+0} = 0, \quad \partial_z c|_{H/2} = 0, \quad D(t) \equiv D(T(t)), \quad b(t) \equiv b(T(t)), \quad g(t) \equiv g(T(t)),$$

$$\frac{\partial q_1}{\partial t}(t, z) = -b(t)q_1^2(t, z) - D(t)\frac{\partial c}{\partial r}\Big|_{r=L}, \quad c(t, L, z) = g(t)q_1(t, z), \quad (4)$$

$$\frac{\partial q_2}{\partial t}(t, r) = -b(t)q_2^2(t, r) - D(t)\frac{\partial c}{\partial z}\Big|_{z=H}, \quad c(t, r, H) = g(t)q_2(t, r), \quad (5)$$

$$\frac{\partial q_3}{\partial t}(t, r) = -b(t)q_3^2(t, r) + D(t)\frac{\partial c}{\partial z}\Big|_{z=0}, \quad c(t, r, 0) = g(t)q_3(t, r),$$

$$\dot{T}(t) = \sigma \varepsilon S (\tilde{c} \rho V)^{-1} [T_e^4 - T^4(t)], \quad \varepsilon = 7 \cdot 10^{-5} (T(t) + 64.3), \quad T(0) = T_0.$$

Here, $c(t, r, z)$ is the concentration of dissolved (diffusion movable) hydrogen atoms in the metal; $w(t, r, z)$ is H concentration in the defects with reversible capture (for instance, microcavities); w_{\max} is the peak concentration of reversible capture; $\gamma(t)$ is H concentration in traps; they begin to release hydrogen only when some critical temperature T_{crit} is reached (it is typical for the inclusion of hydride phases); a_i are the traps dynamic coefficients ($a_3 > 0$ only at $T \geq T_{\text{crit}}$); $q_1(t, z)$, $q_{2,3}(t, r)$ are the surface concentrations (on the lateral surface of the cylinder and on the butt ends); g is the fit coefficient for concentrations of hydrogen atoms in the bulk and on the surface (quick dissolution parameter); D , b are the diffusion and the desorption coefficients.

Initial concentration $c(0, r, z) = \bar{c}$ is constant (it forms during the material production). When necessary, it is possible to take account of the decrease in H concentration in the near-surface layer (for instance, as the result of mechanical and thermal pre-treatment) without essential changes in the numerical algorithm. Similar correction takes place for hydrogen traps of the hydride phase type: $\gamma(0, r, z) = \tilde{\gamma}(r, z)$, $\partial_t \gamma = -a_3(T)\gamma(t, r, z)$. Suppose that $a_i > 0$ are constant within the considered temperature range ($T \in [T_0, T_e]$). Changes in the time-dependent case of $a_i(t) \equiv a_i(T(t))$ are insignificant.

For practical purposes we consider capture in a simple integrated form. Detailed description of geometry of defects and their distribution in the sample essentially complicates the model. It is difficult to obtain these parameters experimentally as an input model data. Since the sample sizes are macro the defects may be considered as uniformly distributed. To simplify the model description we consider one generalized trap with reversible capture and one with hydride-like decomposition. It is possible to consider several traps with their individual $a_i^{(j)}$ and $T_{\text{crit}}^{(k)}$.

We assume that diffusion and desorption coefficients depend on the temperature in an Arrhenius way: $D(T) = D_0 \exp\{-E_D/[RT]\}$, $b(T) = b_0 \exp\{-E_b/[RT]\}$. Here $E_{D,b}$ are activation energies. We use a shorthand notation $D(t) = D(T(t))$, $b(t) = b(T(t))$. The time interval $[0, t_*]$ is determined by relative degassing of the sample: $J(t) \approx 0$, $t \geq t_*$ ($J(t) \ll J_{\max}$). The conditions $\partial_r c(t, +0, z) = 0$, $\partial_z c(t, r, H/2) = 0$ are consequences of symmetry.

A more precise model of dissolution on the surface (considering the lateral surface for clarity):

$$k^+(T)c(t, L, z)[1 - q_1(t, z)q_{\max}^{-1}] - k^-(T)q_1(t, z)[1 - c(t, L, z)c_{\max}^{-1}] = -D(T)\partial_r c(t, L, z).$$

Under saturation ($q_1 \rightarrow q_{\max}$, $c \rightarrow c_{\max}$) the output flux to the surface and dissolution into the bulk become less. However, when diffusion is considerably slower than dissolution and concentrations are low, we obtain the condition of quick dissolution $c \approx gq$, where $g = k^-/k^+$. If the surface is isotropic (in the sense $E_{k-} \approx E_{k+}$), then the parameter g weakly depends on T .

For traps which begin to release hydrogen only when critical temperature is reached (traps of the hydride phase type) we took only the trap capacity and decomposition rate into account. Modelling of the dehydriding process is a separate complicated problem, which results in nonlinear boundary-value problems with moving free phase boundaries and with conditions of the Stefan type (see, for example, [8]).

Since the initial data are symmetrical we have $q_3 = q_2$, so we construct the difference approximation only for a half of the cylinder ($z \in [H/2, H]$) with corresponding boundary conditions ($\partial_z c|_{H/2} = 0$, $\dot{q}_2 = \dots$). For the defect with reversible capture the constant \bar{w} is determined according to $\partial_t = 0$: $a_1(T_0)[1 - \bar{w}/w_{\max}]\bar{c} - a_2(T_0)\bar{w} = 0$. For the trap of the decomposition type the values of $\bar{\gamma} = \text{const}$, T_{crit} , a_3 are set using information about the hydride.

The presence of derivatives \dot{q}_i (accumulation on the surface [9]) corresponds to the possibility of H migration along the surface until atoms form H_2 molecules which are desorbed from the surface. In the case of bulk desorption (for “porous” material atoms combine in H_2 molecules in the near-surface layer and leave the sample) instead of dynamic boundary conditions we use nonlinear conditions: $D(t)\partial_r c(t, L, z) = -\tilde{b}(t)c^2(t, L, z)$, $D(t)\partial_z c|_{z=0, H} = \pm\tilde{b}(t)c^2|_{z=0, H}$. To estimate the influence of surface accumulation we consider the bulk and surface desorption coefficients satisfying the condition $\tilde{b} = b/g^2$ ($\dot{q} \approx 0$).

Thus, the aim of the model is to analyze the dynamics of hydrogen concentrations without preliminary sample saturation. The problem has a practical context, so we apply minimal math-based environment to describe basic processes. Further detailed elaboration leads to an increase of the set of parameters. The inverse problem of their estimation becomes complicated [10].

Specification of the problem statement. The aim of the research is to develop the difference scheme and computational algorithm for modelling of desorption flux from the cylindrical sample:

$$J(t) = 4\pi b(t) \left[L \int_{H/2}^H q_1^2 dz + \int_0^L q_2^2 r dr \right], \quad \tilde{J}(t) = 4\pi \tilde{b}(t) \left[L \int_{H/2}^H c^2(t, L, z) dz + \int_0^L c^2(t, r, H) r dr \right].$$

Hydrogen molecules is desorbed, but we compute the desorption flux in atoms ($[J] = 1/\text{s}$). The criterion of computation correctness is the material balance (the total amount of hydrogen including the desorbed hydrogen is constant).

Under uniform monotonous heating it is convenient to consider the TDS-spectrum (the curve $J = J(T)$) together with the flux dependence on t . It is believed that first TDS-spectrum peak corresponds to initial surface hydrogen, another one corresponds to bulk hydrogen. However, while the surface hydrogen is desorbed, hydrogen atoms penetrate from the bulk to the surface. The problem of estimating the corresponding correction is important. Let t_s be the time when the initial amount of surface hydrogen is exhausted. At the numerical modelling stage the time t_s is determined from the equation

$$\int_0^{t_s} J(\tau) d\tau = 4\pi \left[L \int_{H/2}^H q_1(0, z) dz + \int_0^L q_2(0, r) r dr \right].$$

Numerical modelling allows to choose the point on the extraction curve that corresponds to the initial quantity of the surface hydrogen, to estimate the values of the activation energies of diffusion, desorption, parameters of reversible capture and hydride phase decomposition. Such problem is the inverse ill-posed problem of model parametric identification. Presented article is only devoted to the model description and direct problem of numerical simulation.

3. Results of numerical modelling

The iterative algorithm is developed on the basis of implicit difference schemes and the Thomas algorithm. Input data are $L, H, D_0, E_D, b_0, E_b, g_0, E_g, \bar{c}, w_{\max}, \bar{\gamma}, T_0, T_e, T_{\text{crit}}, a_1, a_2, a_3, \sigma, \rho, \tilde{c}$. Desorption flux curves are represented in the figures. Varied coefficient values correspond to the curves in the following way: the first value is for the curve with the highest maximum, the last one is for that with the lowest maximum. The small circle shows the time when the initial surface hydrogen is exhausted. The developed software (algorithm for numerical thermodesorption modelling) is applicable in a wide range of parameters. In our figures for demonstrative purpose we confine ourselves to values of the parameters presented below. We define $\bar{\gamma} = 10^{22} \text{ m}^{-3}$, $w_{\max} = 10^{22} \text{ m}^{-3}$. The default common parameters are the following: $b_0 = 2 \cdot 10^{-7}$, $E_b = 12 \cdot 10^4$, $D_0 = 2 \cdot 10^{-3}$, $E_D = 6 \cdot 10^4$, $g_0 = 10^3$, $E_g = 0$, $T_0 = 293$, $T_{\text{crit}} = 700$, $T_e = 773$, $a_1 = 0.3$, $a_2 = 0.1$, $a_3 = 10^{-4}$, $L = 4 \cdot 10^{-3}$, $H = 2 \cdot 10^{-2}$, $\bar{c} = 10^{22}$.

The algorithm of discrete TDS-spectrum construction in accordance with the experiment is the following. Each stage of the numerical experiment is carried out at a given external temperature $T = T_e$ (initial sample temperature is $T_0 < T_e$), maximum stage duration is 3 hours. The total amount of desorbed hydrogen Q is calculated (as integral of $J(t)$) at given external temperature T_e up to the time when the desorption flux becomes comparable with the background flux in the scale of maximum value J_{\max} (but the interval no more than specified 3 hours). A point on the plane (T, Q) is obtained. Then T_e increases stepwise and we reiterate the calculations starting at temperature T_0 with initial concentration distributions from the previous stage. Dependence J with respect to current temperature T ($T(t) \leftrightarrow t$) is shown in Fig. 1. The impact of different kinetic parameters for the surface desorption can be seen in the next six figures. Fig. 2 illustrates the influence of the preexponential factor b_0 on the desorption flux curve. Changes are: $b_0 = 5 \cdot 10^{-9}$; $5 \cdot 10^{-8}$; $2 \cdot 10^{-7} \text{ m}^2 \text{ s}^{-1}$. The influence of the activation energy E_b can be seen in Fig. 3, changes in order of decrease of the maximum are: $E_b \cdot 10^{-4} = 10$; 11; 12 $\text{J} \cdot \text{mol}^{-1}$. Changes for Fig. 4 are: $D_0 = 2 \cdot 10^{-3}$; $5 \cdot 10^{-4}$; $10^{-4} \text{ m}^2 \text{ s}^{-1}$. For the next four figures the solid line is for the surface desorption model, the dashed line is for the bulk desorption model. Fig. 5 shows discrete TDS-spectra with temperature step size h_{T_e} equal to 50 K. Discrete TDS-spectra modelling with $h_{T_e} = 75 \text{ K}$ is presented in Fig. 6. The small cross shows the time when the initial surface hydrogen is exhausted.

Thus, parameter variations agree with physical ideas, and the model may be used for kinetic parameter identification of degassing of real materials.

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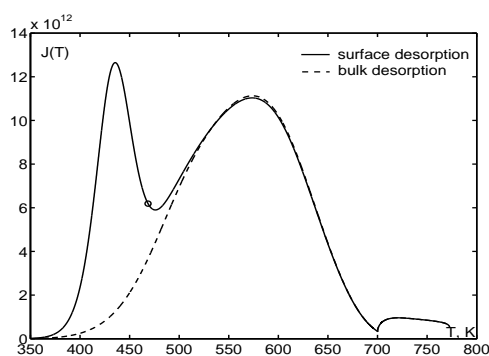


Figure 1. TDS-spectrum $J(T)$.

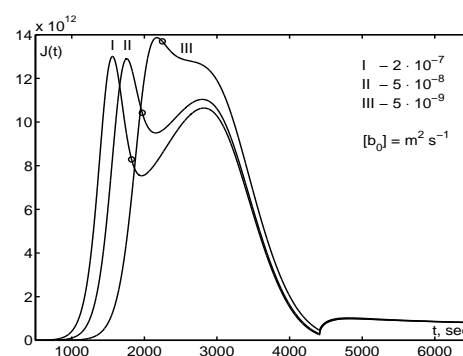
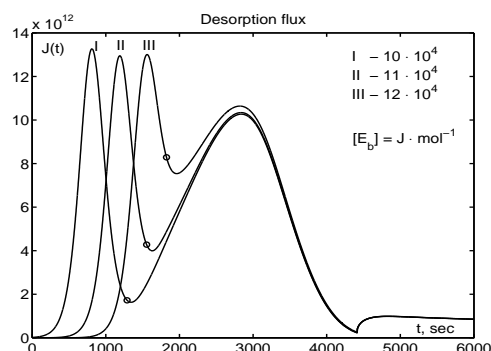
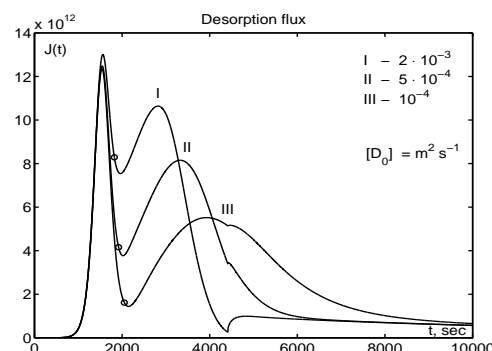
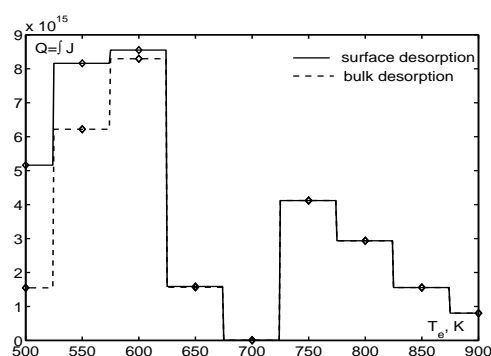
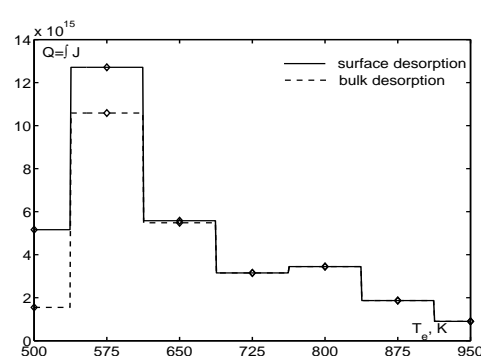


Figure 2. The impact of the parameter b_0 .

**Figure 3.** The impact of the parameter E_b .**Figure 4.** The impact of the parameter D_0 .**Figure 5.** Discrete TDS-spectra, $h_{T_e} = 50$ K.**Figure 6.** Discrete TDS-spectra, $h_{T_e} = 75$ K.

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