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Studying hydrogen permeability by method of concentration pulses

V.V. Popov[a,*], I.E. Gabis[b], N.I. Sidorov[c], Yu.V. Zaika[a]

[a] *Institute of Applied Mathematical Research of Karelian Research Centre of Russian Academy of Sciences, 185910, Pushkinskaya str. 11, Petrozavodsk, Russia*

[b] *V.A. Fock Institute of Physics, St. Petersburg State University, 198504, St. Petersburg, Russia*

[c] *Institute of Metallurgy, Ural Division of Russian Academy of Sciences, 620016, Ekaterinburg, Russia*

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Abstract

The experimental method of concentration pulses applied for studying hydrogen permeability of construction materials is considered. An algorithm of parametric identification is constructed. Parameter estimations for hydrogen transport in amorphous and recrystallized ferrum alloys are presented.

Keywords: Metals; Surfaces and interfaces; Gas–solid reactions

1. Experiment and mathematical model

The method of concentration pulses (MCP) is an effective method for studying hydrogen permeability [1,2]. A membrane made of the studied material divides an evacuated vessel into two parts. The temperature of the sample is constant. At one side (input side) a constant pressure is provided. At the other side (output side) gas is pumped out by a vacuum system. Hydrogen is ad(ab)sorbed at the input side, diffuses, and desorbs from the output side into the vacuum. Hydrogen pressure at the output side is measured with a mass-spectrometer. The desorption flux density $J = J(t)$ is calculated by using the measured pressure. A splitter (a piece of glowing tungsten or a glow discharge device) is situated in the vessel with molecular hydrogen in order to produce atomic hydrogen. Turning the splitter on and off with a certain period provides almost rectangular concentration pulses of dissolved hydrogen in the sample near the surface. The period should be large enough, so that stationary values of J are obtained.

Let us consider a model of hydrogen transport that takes into consideration diffusion, reversible capture of hydrogen by traps, and bulk desorption:

$$\frac{\partial c}{\partial t}(t,x) = D\frac{\partial^2 c}{\partial x^2}(t,x) - a_1 c(t,x) + a_2 z(t,x), \tag{1}$$

$$\frac{\partial z}{\partial t}(t,x) = a_1 c(t,x) - a_2 z(t,x), \quad (t,x) \in (0,t^*)\times(0,\lambda), \tag{2}$$

$$c(0,x) = \varphi(x), z(0,x) = \psi(x), \quad x \in [0,\lambda], \tag{3}$$

$$\mu s p_0(t) - b c_0^2(t) = -D\frac{\partial c}{\partial x}(t,0), \quad c_0(t) = c(t,0), \tag{4}$$

$$\mu s p_\lambda(t) - b c_\lambda^2(t) = D\frac{\partial c}{\partial x}(t,\lambda), \quad c_\lambda(t) = c(t,\lambda). \tag{5}$$

Here $c(t,x)$ is for the concentration of dissolved atomic hydrogen, $z(t,x)$ the concentration of hydrogen captured by traps, D the diffusion coefficient of dissolved hydrogen, μ a kinetic constant, s the sticking probability of hydrogen molecules to the surface, b for the desorption, a_1, a_2 are the coefficients of hydrogen capture and release by traps, and $p_0(t)$, $p_\lambda(t)$ are for pressures of molecular hydrogen at input and output sides of the membrane. The pressure p_0 is low enough so that the concentrations c, z are relatively low: the model parameters depend only on temperature, their dependence on concentrations may be neglected in the condi-

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* Corresponding author. Tel.: +7 8142 766312; fax: +7 8142 766313.
E-mail address: popov@krc.karelia.ru (V.V. Popov).

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tions of the MCP. If the vacuum pump is powerful enough we may neglect hydrogen return at the output side: $\mu s p_{\lambda \approx 0}$. Output desorption flux density $J(t) = bc_\lambda^2(t)$ is determined as a solution to the integral equation using the pressure $p_\lambda(t)$. The boundary conditions (4), (5) describe the balance of absorption, desorption, and diffusion fluxes on the surfaces. If hydrogen can be accumulated on the surface of the sample (the surface desorption), Eqs. (4) and (5) may be replaced by dynamical boundary conditions [3,4]: differential equations for the surface concentrations. We assume that the pressure at the input side is constant: $p_0(t) = \bar{p}_0$. Model coefficients are Arrhenius with respect to temperature, e.g. $D = D(t) = D_0 \exp\{-E_D/RT\}$. The MCP experiments are held at constant temperature; thus temperature dependence is not important in the discussion and is not mentioned in the following. The stop time t^* is chosen so that the oscillations of the output flux reach a steady state. Let us specify the general model (1)–(5) for the MCP. We assume that the transition processes at the input side are quick both when the splitter is on and off:

$$c(t, 0) = Q_0 + (-1)^k Q_1, \quad t \in \left(\frac{k\pi}{w}, \frac{(k+1)\pi}{w}\right), \tag{6}$$

$$\bar{c}_0 = Q_0 - Q_1, \qquad \bar{c}_0^h = Q_0 + Q_1, \quad Q_0 > Q_1 > 0,$$
$$\bar{c}_0 = \sqrt{(\mu s \bar{p}_0 - \bar{J})/b}. \tag{7}$$

In the model of stepped near-to-surface concentration (6) (it replaces boundary condition (4)) the numbers Q_0, Q_1 describe the splitter efficiency, w for the oscillation frequency, $\bar{c}_0$, $\bar{c}_0^h$ for the concentrations of dissolved hydrogen near the surface of the input side while the splitter is on and off, $\bar{J}$, $\bar{J}^h$ for the appropriate stationary values of the output desorption flux density. The chosen frequency w should be small enough in order for the flux to reach these levels. The values Q_i are not given, we know only how the concentration changes in time. Eq. (7) is obtained from (4) and (5) if the splitter is off, so that $J(t)$ reaches its lower stationary value and the concentrations in the bulk become linear with respect to $x (Dc_x(t, 0) = Dc_x(t, \lambda) = -\bar{J},\ \mu s p_\lambda(t) = 0,\ \bar{J} = bc_\lambda^2)$.

2. Algorithm of parametric identification

Firstly we shift the time origin: the segment $[0, 2\pi/w]$ corresponds to the period of stationary oscillations. If the output flux is stationary, the concentration distributions in the bulk are linear (in Eqs. (1)–(5) all time derivatives are zero, $t_k = k\pi/w$):

$$c(t_k, x) = \frac{\bar{J}(t_k)(\lambda - x)}{D} + \sqrt{\frac{\bar{J}(t_k)}{b}}, \tag{8}$$

$$\bar{c}_0 = Q_0 - Q_1 = \sqrt{\frac{\bar{J}}{b}} + \frac{\bar{J}\lambda}{D}, \tag{9}$$

$$\bar{c}_0^h = Q_0 + Q_1 = \sqrt{\frac{\bar{J}^h}{b}} + \frac{\bar{J}^h \lambda}{D}. \tag{10}$$

Eqs. (9) and (10) correspond to turned off/on splitter respectively.

Stationary oscillations do not depend on the initial distributions (3). Let us expand the concentrations on the period of stationary oscillations to the Fourier series:

$$c(t, x) = \sum_{-\infty}^{+\infty} c_n(x) \exp\{inwt\},$$
$$z(t, x) = \sum_{-\infty}^{+\infty} z_n(x) \exp\{inwt\}. \tag{11}$$

Substituting these expansions to Eqs. (1) and (2) we obtain:

$$inwc_n(x) = Dc_n''(x) - \frac{a_1 inw}{inw + a_2} c_n(x),$$
$$z_n(x) = \frac{a_1}{inw + a_2} c_n(x). \tag{12}$$

The general solution has the form (the choice of a root λ is not important)

$$c_n(x) = A_n \exp\{\lambda x\} + B_n \exp\{-\lambda x\},$$
$$\lambda^2 = \frac{(a_1 + a_2)inw - (nw)^2}{D(inw + a_2)}, \quad A_n, B_n = \text{const.} \tag{13}$$

Denote by $J_{\langle n\rangle}$, $L_{\langle n\rangle}$ the Fourier coefficients of the functions $J(t)$, $L(t) = \sqrt{J(t)}$:

$$J_{\langle n\rangle} = \frac{w}{2\pi} \int_{t_0}^{t_2} J(\tau) \exp\{-inw\tau\}\, d\tau,$$
$$L_{\langle n\rangle} = \frac{w}{2\pi} \int_{t_0}^{t_2} L(\tau) \exp\{-inw\tau\}\, d\tau.$$

Using the expressions for $c_n(\lambda)$, $c_n'(\lambda)$ from $J(t) = bc_\lambda^2(t)$ and (5) $(\mu s p_\lambda(t) = 0)$ we obtain:

$$\begin{cases} A_n + B_n = c_n(0), \\ A_n \exp\{\lambda\lambda\} + B_n \exp\{-\lambda\lambda\} = \dfrac{L_{\langle n\rangle}}{\sqrt{b}}, \\ A_n \exp\{\lambda\lambda\} - B_n \exp\{-\lambda\lambda\} = \dfrac{-J_{\langle n\rangle}}{D\lambda}. \end{cases} \tag{14}$$

Rewrite the stepped dependence (6) of the input concentration on t in the form

$$c(t, 0) = Q_0 - iQ_1 \sum_{n=\pm 1, \pm 3, \ldots} 2(n\pi)^{-1} \exp\{inwt\}. \tag{15}$$

We obtain $c_n(0)$ from (15) using (8)–(10) (below $\bar{L} = \sqrt{J}$, $\bar{L}^h = \sqrt{J^h}$, $X = D/\sqrt{b}$):

$$c_n(0) = Q_0 = \frac{[X(\bar{L}^h+\bar{L})+\lambda(\bar{J}^h+\bar{J})]}{2D}, n = 0;$$
$$c_n(0) = 0, n = 2m;$$
$$c_n(0) = \frac{-2iQ_1}{n\pi} = -i\frac{\left[X(\bar{L}^h-\bar{L})+\lambda(\bar{J}^h-\bar{J})\right]}{Dn\pi}, \quad n = 2m-1.$$

Substituting $c_n(0)$ to (14) and eliminating A_n, B_n we obtain after transformations:

$$\frac{-2J_{\langle n\rangle}\ \sinh(\lambda\lambda) + \lambda\lambda(\bar{J}^h + \bar{J})}{\lambda[2L_{\langle n\rangle}\ \cosh(\lambda\lambda) - (\bar{L} + \bar{L}^h)]} = X, \quad n = 0, \tag{16}$$

$$\frac{-J_{\langle n\rangle}\ \sinh(\lambda\lambda)}{\lambda L_{\langle n\rangle}\ \cosh(\lambda\lambda)} = X, \quad X = \frac{D}{\sqrt{b}}, \quad n = 2m, \tag{17}$$

$$\frac{n\pi J_{\langle n\rangle}\ \sinh(\lambda\lambda) + i\lambda\lambda(\bar{J}^h - \bar{J})}{\lambda[i(\bar{L} - \bar{L}^h) - n\pi L_{\langle n\rangle}\ \cosh(\lambda\lambda)]} = X, \quad n = 2m-1. \tag{18}$$

Let us denote the left-hand side by a fraction $F_1[n, \lambda(n, D, a_1, a_2)]/F_2[n, \lambda(n, D, a_1, a_2)]$. The difference of these fractions must be zero due to (16)–(18). This allows to use the following object functions for determining D, a_1, a_2 $(X = \mathrm{Re}F_1/\mathrm{Re}F_2 = \mathrm{Im}F_1/\mathrm{Im}F_2)$:

$$G_1(n_1, n_2, D, a_1, a_2) = \left|\frac{F_1[n_1, \lambda(n_1, D, a_1, a_2)]}{F_2[n_1, \lambda(n_1, D, a_1, a_2)]} - \frac{F_1[n_2, \lambda(n_2, D, a_1, a_2)]}{F_2[n_2, \lambda(n_2, D, a_1, a_2)]}\right|, \tag{19}$$

$$G_2(n_1, n_2, D, a_1, a_2) = \left[\frac{1}{2}\left(\frac{\mathrm{Re}F_1(n_1)}{\mathrm{Re}F_2(n_1)} + \frac{\mathrm{Im}F_1(n_1)}{\mathrm{Im}F_2(n_1)}\right) - \frac{1}{2}\left(\frac{\mathrm{Re}F_1(n_2)}{\mathrm{Re}F_2(n_2)} + \frac{\mathrm{Im}F_1(n_2)}{\mathrm{Im}F_2(n_2)}\right)\right]^2. \tag{20}$$

If there are no noises, the minimal values of these functions are zero. The first object function is used for rough search in the wide range of parameters. The second is used for further improvement. Provided D, a_1, a_2 are given, the complex of parameters $X = D/\sqrt{b}$ is better determined for the harmonics with even n from the expression $X = (\mathrm{Re}F_1(n)/\mathrm{Re}F_2(n) + \mathrm{Im}F_1(n)/\mathrm{Im}F_2(n))/2$. Then b may be obtained from X and D. The parameter s is calculated using the formula

$$s\mu\bar{p}_0 = (\bar{J}\lambda X^{-1} + \bar{L})^2 + \bar{J}. \tag{21}$$

This follows from (9) and the stationary boundary condition (4): $\mu s\bar{p}_0 - b\bar{c}_0^2 = \bar{J}$.

The parameters D, a_1, a_2 in the left-hand sides of Eqs. (16)–(18) define only the values of $\lambda(n, D, a_1, a_2)$. Therefore, different sets of parameters D, a_1, a_2 exist such that the appropriate values of λ are the same and provide a minimum of the chosen object function. Choosing D and solving the optimization problems $G \to$ minwith respect to a_1, a_2 we obtain the values of $a_1(D)$, $a_2(D)$. The object functions (with respect to a_1, a_2 while D is fixed) are behave like a ravine and may have several minima. Numerical research showed that it is expedient to use the sum of the object functions for a pair of an even and an odd harmonics, for example, $G(1, 3, D, a_1, a_2) + G(3, 4, D, a_1, a_2)$ (Figs. 1 and 2). The reason is that the ravine's direction depends on evenness of the harmonics.

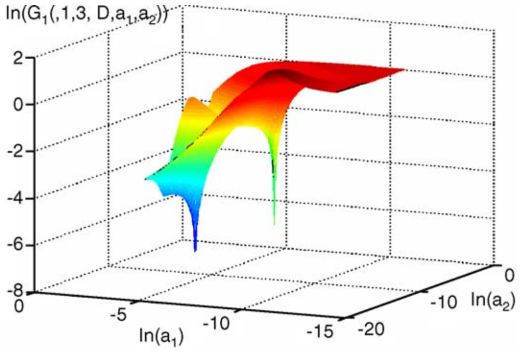

Fig. 1. A false minimum of the object function (19), model data.

Here is the computational algorithm of parameter identification.

(i) Consider the model with no traps: $a_1 = a_2 = 0$ in Eq. (1). Estimate D by solving a one-dimension optimization problem $G(n_1, n_2, D, a_1, a_2) \to \min$ $(\lambda = \sqrt{inw/D})$. One should choose the harmonics of different evenness, e.g. $n_1 = 3$, $n_2 = 4$. Obtained estimate of D is lower than the real D.

(ii) Consider the model with traps: $a_i \neq 0$. Increase D from obtained estimate with small enough increment. For each value of D determine the parameters a_1, a_2 by minimizing function (19). Improvement is possible using (20). Optimal values of a_i at the previous step serve as the initial data.

(iii) Calculate the value of X. Determine b using X. Obtain s using formula (21).

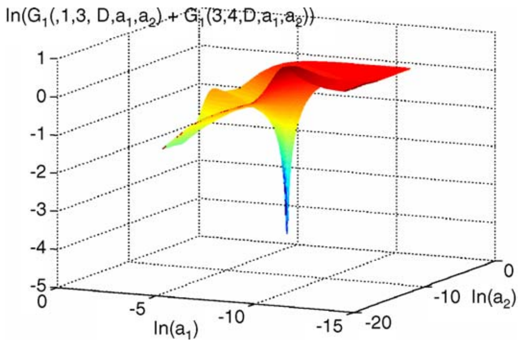

Fig. 2. No false minima for the sum of the object function (19), model data.

Table 1
Identified parameter values for the experimental data

No.	T (°C)	D (cm^2 s^{-1})	a_1 (s^{-1})	a_2 (s^{-1})	$\overline{c}_0^h$ (cm^{-3})
Amorphous ferrum alloy					
1	225	4.0×10^{-8}	6.01×10^{-2}	4.16×10^{-2}	1.41×10^{18}
2	250	7.0×10^{-8}	6.02×10^{-2}	9.50×10^{-2}	3.39×10^{17}
3	275	8.5×10^{-8}	4.51×10^{-2}	6.14×10^{-2}	1.57×10^{17}
Recrystallized ferrum alloy					
4	175	2.5×10^{-8}	1.54×10^{-2}	1.82×10^{-2}	6.22×10^{17}
5	200	2.8×10^{-8}	5.13×10^{-3}	2.60×10^{-2}	2.42×10^{18}
6	225	3.5×10^{-8}	6.53×10^{-3}	9.55×10^{-3}	1.79×10^{18}

(iv) The set that provides the best proximity of the experimental flux and the model flux calculated for the current set of the parameters in the sense of the least squares is treated as a solution.

Note, if the general method of discrepancy minimizing is used, it will be necessary to integrate numerically the model equations at each iteration. The presented algorithm significantly saves computational resources.

We have studied the dependence of the ratio error of parameter identification on various conditions; the following recommendations may be given.

(i) The period of turning the splitter on must be chosen so that the transition processes in the flux $J(t)$ took ≈ 60–90% of the period length. The transition process should not be lost on a background of the stationary processes.
(ii) It is expedient to choose the splitter's efficiency to provide approximately 5–10 times difference between the stationary flux densities that are reached on the semiperiods.
(iii) Low-number harmonics should be used in algorithm, because high-number ones are smoothened by the membrane and are usually noisy.
(iv) It is expedient to hold the experiments for two different pressures $\overline{p}_{02} > \overline{p}_{01}$. Then the values of b, s are determined precisely.

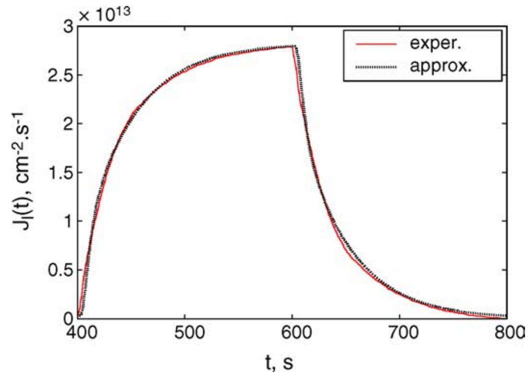

Fig. 3. Amorphous alloy, $T = 225\,°$C.

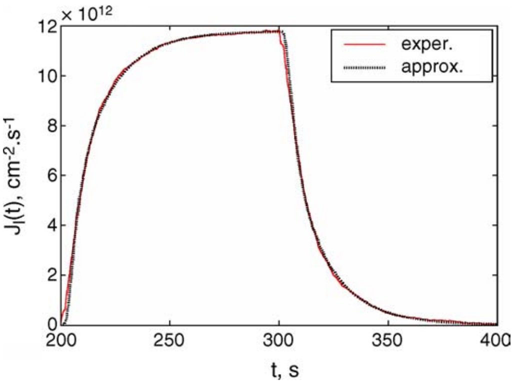

Fig. 4. Amorphous alloy, $T = 250\,°$C.

3. Identification results

We used the presented algorithm to estimate the parameters of the model (1)–(6) for the experimental data of amorphous and recrystallized ferrum alloy $\mathrm{Fe_{77.3}Ni_{1.1}Si_{7.7}B_{13.6}C_{0.2}P_{0.009}}$ [5]. The glow discharge served as a splitter, $\lambda = 2 \times 10^{-3}$ cm, $\overline{p}_0 = 2$ Torr. Parameter estimations are presented in Table 1. Figs. 3–6 show the experimental fluxes and the model fluxes constructed using the identified parameters. The experimental data are noisy and the recommendations above (necessary for the minimal ratio error) do not completely fit. Thus, we succeeded only in determining the order of $b \approx 10^{-17}$ to 10^{-18} cm^4 s^{-1}, $s \approx 10^{-9}$ to 10^{-10}. The inverse problems of mathematical physics have well-known difficulties: usually the solution is highly sen-

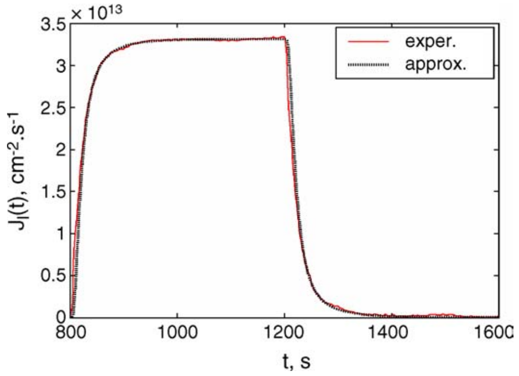

Fig. 5. Recrystallized alloy, $T = 200\,°$C.

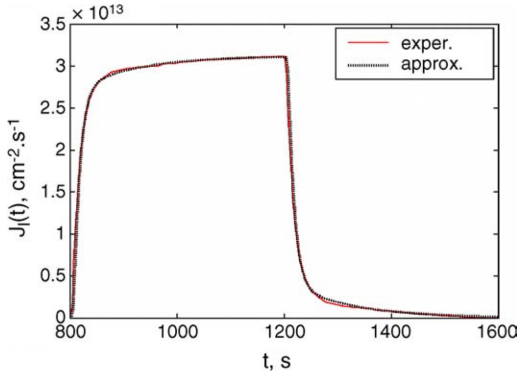

Fig. 6. Recrystallized alloy, $T = 225\,^{\circ}\mathrm{C}$.

sible to experimental and computational errors. The MCP allows stable determination of the bulk parameters D, a_1, a_2. The surface parameters b, s affect the output flux significantly less and thus are determined more roughly. The reason is, if one significantly increases s, the return flux $bc_0^2(t)$ will also grow and compensate the additional afflux. Thus, the penetrating flux will not change essentially.

The algorithms of numerical modelling and parametric identification for the class of models with bulk and surface desorption are implemented as a software package. It was used for parameter estimation of hydrogen permeation through membranes.

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