Determination of effective recombination coefficient by thermodesorption method

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Yu.V. Zaika*, E.K. Kostikova

Institute of Applied Mathematical Research, Karelian Research Centre, Russian Academy of Sciences, Pushkinskaya st. 11, Petrozavodsk 185910, Russia

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ABSTRACT

The degassing by thermodesorption method (TDS) of structural material sample previously hydrogen saturated is considered. The mathematical model of TDS-experiment and parametric identification method are presented. The data for nickel and tungsten in numerical simulations are used. The two-peak problem and effect ("derivatives") of diffusion and desorption parameters on the TDS-spectrum are illustrated. Diffusion coefficient is known but the recombination parameters on surface remain to be estimate. The estimation algorithm needs no special mathematical software and allows to scan a material in wide temperature range. Integral smoothing processing of measurements is applied in the algorithm to secure its noise resistance.

Introduction

Interest in the interactions of hydrogen with various materials is multifaceted [1–16]. It suffices to mention power engineering, protection of metals against hydrogen corrosion, chemical reactor design, rocket engineering. For instance, while a radioactive isotope of hydrogen, tritium, will presumably (in the long term) be applied in thermonuclear reactors, the problem of tritium diffusion leakage and its accumulation in structural materials may arise. Hydrides help to retain substantial amounts of hydrogen. Hence the high expectations attached to the relatively safe hydrogen batteries and motors: no high pressures or low temperatures involved. Reversible metal alloyage by hydrogen is the basis for plasticization and thermal hydrogen processing of titanium alloys.

Enthusiasts speak not only of hydrogen energy but even of hydrogen economy [5].

Mathematical models of hydrogen isotopes' interaction with structural materials and methods for their parametric identification are needed to enhance the performance of experimental research, solve applied problems and draw general conclusions. Practice has shown that the limitations are not only diffusion processes inside the metal, but also physical–chemical effects on the surface [2,3]. Transfer parameters depend on the process characteristics of producing the material batch, and one needs effective algorithms for processing measured curve instead of focusing on "tabular data". Adsorption, dissolution, diffusion, … per se are subjects for theoretical and experimental studies. Each additional coefficient however leads to a leap to a new difficulty level of the inverse problem of parametric identification. We shall focus on the thermodesorption method and take

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* Corresponding author.
E-mail addresses: zaika@krc.karelia.ru (Yu.V. Zaika), fedorova@krc.karelia.ru (E.K. Kostikova).

into account only the limiting factors and the information capacities of the TDS experiment explicated below.

Mathematical model

Boundary value problem

We consider hydrogen transfer through a test metal sample (plate thickness ℓ). For brevity we speak of a metal plate, although it may be a multialloy or an intermetallic compound. We assume that heating is relatively slow, well nigh uniform, so that the diffusion flow can be considered proportional to the concentration gradient. Let us assume a standard model for diffusion in the bulk [17]:

$$\partial_t c(t,x) = D(T)\partial_x^2 c(t,x), \ (t,x) \in Q_{t_*}, \\ c(0,x) = \varphi(x), \ x \in [0,\ell], \tag{1}$$

where t — time, $Q_{t_*} = (0,t_*) \times (0,\ell)$; $c(t,x)$ — diffusing hydrogen (monoatomic) concentration; D — diffusion coefficient. For definiteness we assume that D is a function of the temperature $T(t)$ given by the Arrhenius equation with the pre-exponential factor D_0 and the activation energy E_D (R is the universal gas constant): $D = D_0\exp\{-E_D/[RT(t)]\}$. Such $f(T)$ relationships are plotted by S-shaped saturation curves. More disaggregate transfer models are known. Among other factors, we can take into account various diffusion channels (transcrystalline, grain boundary, along defects) and the interchange between them. In the inverse problem (the difficulties involved being commonly known) we focus only on the limiting factors and the feasibility of parametric identification by TDS-method. Some problems of the parametric identification of hydrogen permeability models with constant temperature throughout the experiment are considered, for instance, in Refs. [18,19].

The boundary conditions are set by the following equations

$$\mu s(T)p_{0,\ell}(t) - b(T)c_{0,\ell}^2(t) = \mp D(T)\partial_x c\big|_{0,\ell}, \tag{2}$$

$c_{0,\ell} \equiv c(t,x)\big|_{x=0,\ell}$. Here, μ is the kinetic coefficient; $s(T)$ — coefficient indicating that only a minor part of the "bombarding" molecular hydrogen is trapped as atoms on the surface (denote by s the adhesion coefficient, remembering however that this coefficient sums up the overall process balance of physisorption–dissociation–chemosorption of molecular gas into monoatomic form on the surface); $p_0(t)$, $p_\ell(t)$ — gaseous (H$_2$) pressure on the relevant membrane side. Given the multistage process "average", the coefficient of *desorption in the bulk b* is the *effective coefficient of recombination* [7,11]. The absorption flux density of H atoms can be simulated by $\mu sp(1 - \theta)^2$, where θ is the degree of surface packing. In the low concentrations range $\theta \ll 1$, which is in agreement with quadratic desorption, diffusion equation linearity and $D \neq D(c)$. The kinetic constant dependence on temperature ($\mu \propto 1/\sqrt{T}$) is usually ignored compared to the exponent in $s(T)$. Formally, keeping in mind the inverse problem and the measurement limitations, the 'entire dependence' on T can be integrated into $s(T)$ (similarly to $b(T)$), perhaps not regarding $s(T)$ as an Arrhenius parameter.

Hydrogen occurs in the model (1), (2) both as molecules and in monoatomic form. For consistency, the count is based on atoms: $[c] = 1/\text{cm}^3$, $[Dc_x] = [J] = 1/\text{cm}^2 \text{ s}$ ($J \equiv bc^2$). E exponents are named activation energies, although they may represent linear combinations of activation energies and heat energies of lower-level process stages, and have different signs. We shall not elaborate on the limits of the model's applicability as it occupies a specific niche in the wide research spectrum. In the case of equilibrium (all derivatives equal zero) we get $\bar{c} \propto \sqrt{\bar{p}}$, which agrees with the Sievert's law validity range.

The model is targeted at the problems where processes on the surface are essential: coatings or even walls, where reducing the number of zeros in boundary conditions on extensive time intervals is desirable. The effect of a slow accumulation can be quite significant. Be warned that in reading experimental results one should take care to state the actual procedure for computing the reliably "measured" coefficient.

Let us describe the TDS experiment in more detail.

Thermal desorption spectrometry (TDS)

Gaseous hydrogen under a reasonably high constant pressure of $\bar{p}$ is fed into a chamber with a strip (thin plate) of the metal or alloy studied. The strip is heated by electric current to a temperature $\bar{T} = \text{const}$ to increase the sorption rate. After the sample had absorbed a sufficient amount of hydrogen (to the equilibrium saturated state), it is quenched (the heating current is turned off). The physical–chemical processes slow down sharply, and significant amounts of hydrogen stay inside the sample. The chamber is then vacuumized, and the sample is simultaneously reheated ($t_0 = 0$, $t \geq 0$). The heating rule can vary widely. Let us limit ourselves to the heating rates such that in practice $T(t,x) = T(t)$, $D = D(T)$. Molecular hydrogen pressure in the chamber is measured by mass spectrometer. The desorption flux from the surface controls the pressure (the desorption flux density is $J(t) \equiv b(t)c_{0,\ell}^2(t)$):

$$p(t) = \theta_1 \int_0^t J(\tau)\exp\{(\tau - t)\theta_0^{-1}\}\mathrm{d}\tau. \tag{3}$$

We shall hereinafter use contracted notation for simplicity (identity sign is interpreted as equality by definition): $b(t) \equiv b(T(t))$, $D(t) \equiv D(T(t))$, $s(t) \equiv s(T(t))$. The TDS method fulfills the symmetry conditions:

$$p(t) = p_0(t) = p_\ell(t), \ \varphi(x) = \varphi(\ell - x), \\ c_0(t) = c_\ell(t), \ D(t)\partial_x c\big|_0 = -D(t)\partial_x c\big|_\ell.$$

The constant θ_1 depends on the strip surface area S ($\theta_1 = S\theta_2$), θ_0 and θ_2 are determined by the actual parameters of the experimental unit, such as the chamber volume V and the vacuum system evacuating capacity v ($\theta_0 = V/v$). The measurement model (3) was chosen relying on practical experience: injection of a hydrogen dose into the chamber (δ-pulse) causes a surge in pressure with subsequent exponential decline. Equation (3) is classic in the measurement theory ($\theta_1\exp\{...\}$ is an instrument function, see, for example, Ref. [1]). Specific features of the problem are reflected by function $J(t)$. In the differential notation after differentiation of (3) $J(t) = (p(t)/\theta_0 + \dot{p}(t))/\theta_1$. When the heating rate is slow the pressure derivative $\dot{p}(t)$ is usually ignored: $J(t) = \eta p(t) = p(t)/(\theta_0\theta_1)$. Coefficient $\eta = 1/(\theta_0\theta_1)$ is determined from calibration