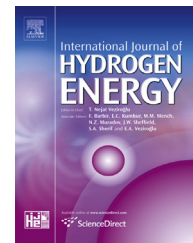




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Computer simulation of hydrogen thermal desorption by ODE-approximation

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ABSTRACT

One of the technological challenges for hydrogen materials science (including ITER project) is the currently active search for structural materials with various potential applications that will have predetermined limits of hydrogen permeability. One of the experimental methods is thermal desorption spectrometry (TDS). A hydrogen-saturated sample is degassed under vacuum and monotone heating. The desorption flux is measured by mass spectrometer to determine the character of interactions of hydrogen isotopes with the solid. We are interested in such transfer parameters as the coefficients of diffusion, dissolution, desorption. The paper presents a distributed boundary value problem of thermal desorption and a numerical method for TDS-spectrum simulation, where only integration of a non-linear system of low order (compared with, e.g., the method of lines) ordinary differential equations (ODE) is required. The results of computer simulation are presented.

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Introduction

Interest in the interactions of hydrogen with various materials is multifaceted [1–8]. It suffices to mention power engineering, protection of metals against hydrogen corrosion, chemical reactor design, rocket engineering. High safety motors can be designed using hydride hydrogen battery. Some problems of hydrogen materials science related to this paper were investigated in Refs. [9–16]. This work is a direct continuation of [17–20].

Practice has shown that the limitations are not only diffusion processes but also physical-chemical effects on the surface [1,2]. Transfer parameters depend on the process characteristics of producing the material batch, and one needs

effective algorithms for modeling instead of focusing on “tabular data”. We shall focus on the thermal desorption method (TDS) and take into account only the limiting factors and the information capacities of the TDS-experiment.

Let us elaborate on the paper [14] mobilizingly entitled “Towards a better understanding of measurements obtained by hydrogen thermal desorption spectroscopy ...” The paper summarizes the studies [11–13], presents a historical overview, compares the results of theoretical and experimental works. Authors of the paper use the finite element analysis software ComsolMultiphysics (associated with the computing environment MATLAB) to interpret the TDS peaks. Unfortunately, it is hardly possible in this standard software package to account for the boundary conditions caused by the dynamics of adsorption–desorption processes. Specialized

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software needs to be developed to deal with this problem. At the stage of TDS-degassing the authors of [14] accept zero boundary conditions for the concentrations of hydrogen (the authors specify it as shortcoming), and then focus on a detailed and reasoned analysis of the influence of traps with different binding energies.

In our present work the potential for interpretation of various TDS-peaks is not narrowed but (not without regret) expanded. Basic Fick's law is taken for the diffusion equation. The material is considered to be homogeneous. Capture by defects is negligible. Heating of the plate is relatively slow and uniform. The model does however take into account the dynamics of surface processes. Hydrogen atoms can be accumulated on the surface. Not all the atoms instantly combine into a desorbing molecule. The square-law characteristic of desorption conforms to the Sieverts' law (equilibrium concentration of dissolved hydrogen is proportional to the square root of the saturation pressure). For the considered range of high temperatures, we assumed that near-surface bulk hydrogen concentrations quickly (proportionally) “control” the surface concentrations (the condition of rapid dissolution in comparison with the typical diffusion time scale). These specifications define the range of the model's adequacy.

Even these simplifying assumptions are enough for a two peak structure of the TDS-spectrum to appear at some ratios of diffusion and desorption activation energies. Let us assume that desorption and diffusion processes are time-spaced. By way of clarity only, we go into detail on the experimental procedure. Surface processes are intensified faster than diffusion with a rise in temperature. Desorption “cleans” hydrogen off the surface and near-surface layers. This is how the first peak appears. As hydrogen in the subsurface volume is exhausted, the desorption flux begins to decline. The heating is however continued! The high concentration gradient near the surface is revealed and diffusion gets involved. Conforming to Fick's law, hydrogen is intensively translocated to the surface. Where desorption fails to control the increased influx from the bulk, the surface concentration increases and the second peak of desorption appears. Importantly, this interplay of desorption and diffusion is observed only for a certain ratio of the parameters. Desorption from a relatively extensive surface may overlook the increased influx from the small volume of a thin plate. In this case only a barely visible bend will appear on the TDS-spectrum curve.

Note that multiple peaks on a TDS-spectrum can be added if components corresponding to traps with different binding energies are added to the diffusion equation (see, e. g., [20]). The mathematical implementation is easy. But this kind of model would require the development of specialized software (in Ref. [20] difference schemes were used). For the simplified model in this paper, the authors offer an alternative numerical method for TDS spectrum simulation. With this method it suffices to integrate a system of low-order (compared, e. g., with the method of lines for the solution of distributed boundary-value problems) ordinary differential equations (ODE). Thereby experts in hydrogen materials science can use standard software packages (e. g., Scilab freeware). The suggested method is rather approximate, but mathematically there is no sense in striving for “visual coincidence” of model

and experimental curves where the experimental error is estimated at tens of percents.

Mathematical model of transfer

Dynamical boundary conditions

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. The adequacy range of the model is determined by the TDS-experiment conditions and assumptions fixed in the following. We assume that heating is slow, so that the diffusion flow can be considered proportional to the concentration gradient. The material is well high uniform to neglect the interplay of H with captures (the model with different types of capture was presented in Ref. [20]). Let us assume a standard model for diffusion in the bulk

$$c_t(t, x) = D(T)c_{xx}(t, x), \quad (t, x) \in Q_t, \quad (1)$$

where t —is time, $Q_t = (0, t_*) \times (0, \ell)$; $c(t, x)$ —diffusing H concentration; D —diffusion coefficient. D is a function of the temperature $T(t)$ given by the Arrhenius equation: $D(T) = D_0 \exp\{-E_D/[RT]\}$.

More detailed transfer models are known. In particular, we can take into account different channels of diffusion (trans-crystalline, intercrystalline, pipe) with exchange in between. If however the number of a priori unknown parameters is increased considerably then the parameters estimation problem becomes hardly foreseeable. The information content of TDS-experiment is limited, wherefore the coefficient D in Equation (1) is assumed to be an integral effective index.

The peculiarity of the accepted model is related to nonlinear dynamic boundary conditions. Let the plate be in contact with gaseous H_2 . The surface is a significant potential energy barrier (see Ref. [2], p.177–206; Gabis, Kompaniets, Kurdymov). Then (de)sorption processes are taken into account and the boundary conditions are modeled as follows:

$$c(0, x) = \bar{c}(x), \quad x \in [0, \ell], \quad t \in [0, t_*], \quad (2)$$

$$c_0(t) = g(T)q_0(t), \quad c_\ell(t) = g(T)q_\ell(t), \quad (3)$$

$$\dot{q}_0(t) = \mu(T)s(T)p_0(t) - b(T)q_0^2(t) + Dc_x(t, 0), \quad (4)$$

$$\begin{aligned} \dot{q}_\ell(t) &= \mu(T)s(T)p_\ell(t) - b(T)q_\ell^2(t) - Dc_x(t, \ell), \\ b(T) &= b_0 \exp\{-E_b/[RT]^{-1}\}, \quad s(T) = s_0 \exp\{-E_s/[RT]^{-1}\}. \end{aligned} \quad (5)$$

Here, $c_0(t) \equiv c(t, 0)$, $c_\ell(t) \equiv c(t, \ell)$ —boundary bulk H concentration (identity sign is used in terms of equality by definition); $q_0(t)$, $q_\ell(t)$ —concentrations on surfaces ($x = 0, \ell$); $g(T)$ —parameter of local equilibrium between concentrations on the surface and in subsurface bulk (coefficient of quick dissolution); μ —gas-kinetic coefficient; $p_0(t)$, $p_\ell(t)$ —gaseous (H_2) pressure; $b(T)$ —desorption 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 the transfer of molecular gas

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