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Qualitative and parametric identification of two-peak hydrogen thermal desorption spectra

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Two variants of modeling the thermal desorption of hydrogen isotopes from structural materials are considered. The first is in the form of superposition of first- and second-order reactions for volume-averaged concentrations. The second is a distributed model in the form of a nonlinear boundary value problem with dynamic boundary conditions reflecting processes in the volume and on the surface of the material. It is shown that when identifying the spectra, it is necessary first to identify the physicochemical causes of various thermal desorption peaks (this is the interaction with inhomogeneities of the material with different binding energies or the dynamics of the surface−volume interaction), and only after that to estimate the kinetic parameters of a physically based model.

Keywords: hydrogen thermodesorption, numerical modeling.

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The interest towards interaction of hydrogen isotopes with structural materials is caused, in particular, by the problems of protection against hydrogen corrosion and the prospects of hydrogen energy [1–4]. One of the effective experimental methods is thermal desorption spectrometry. The sample (for certainty — a thin plate of the metal or alloy to be tested) is pre-saturated with dissolved hydrogen at a temperature and pressure high enough to intensify absorption. It is then slowly (in practice — usually linearly) heated in a vacuum chamber. With the help of a mass spectrometer, the degassing flow is determined. The dependence of the flux density on the current temperature gives the spectrum of thermal desorption. Based on this information, certain characteristics of the structural material interacting with hydrogen are judged. A spectrum often consists of several isolated peaks. Their interpretation is the task of spectrum analysis.

The following scheme is usually used. The spectrum is decomposed into the sum of Gaussians or other symmetrical curves (the peak of thermal desorption is, strictly speaking, not symmetrical). Each of them is interpreted as first- or second-order reactions, operating with an averaged concentration of hydrogen by volume and binding energies in various kinds of traps (micro-cavities, grain boundaries, other material heterogeneities). Then, using the Kissinger method, pre-exponents (frequency factors) and coupling energies are estimated.

Let us consider the average model under conditions of uniform heating at a relatively low rate β, [K/s]:

$$\frac{dX}{dT} = -\frac{K(T)}{\beta} X^{\alpha}(T), \quad X(T_0) = X_0, \quad \alpha \in [1, 2], \tag{1}$$

$$K(T) = K_0 \exp\left\{-\frac{Q}{[RT]}\right\}, \qquad T \in [T_0, T_*],$$

$$T(t) = T_0 + \beta t, \qquad dT = \beta dt.$$

Here, T_0 — is the initial (usually room) temperature when hydrogen desorption is virtually non-existent. Temperature T_* — end of the experiment when desorption is small on the scale of the maximum flow. Variable $X(T)$ — the current volume-averaged hydrogen concentration of the sample (can be normalized to X_0). The multiplier $K(T)$ — is the kinetic Arrhenius temperature coefficient, K_0 — frequency multiplier, Q — the activation energy, $[K] = 1/s$. At $\alpha = 1$ we obtain a model for the averaged concentration when the degassing is limited by diffusion [5, p. 27]. With $\alpha = 2$ we obtain a model of thermal desorption of a dissociatively chemosorbed diatomic gas (a special case of Polyany's equation−), $K(T)$ can be considered as the effective recombination coefficient [3]. The fractional order $\alpha \in [1, 2]$ takes into consideration the contribution of the limiting (in interaction) processes of diffusion and recombination. Concentration-averaged models well approximate the main (most informative) part of the isolated burst on the thermal desorption spectrum (c increase in temperature, the kinetic coefficient $K(T)$ increases, and the average concentration decreases, which forms the peak density of the degassing flux $w = -dX/dT$).

Let us move on to another model — a nonlinear diffusion boundary value problem with dynamic boundary conditions for surface concentration. Numerical simulations show that the following scenario is possible. First, as it heats up, desorption occurs from the surface and from the near-surface volume (the first peak). The temperature rises, and a large concentration gradient is formed near the surface. There is a significant activation of diffusion from the volume to the surface and a repeated burst of degassing is observed.

Following the paper [6, p. 177–206], clearly separating the bulk and surface processes, consider a more detailed model of the degassing of a thin metal plate with a thickness of l under conditions of slow uniform heating:

$$\partial_t c(t,x) = D(T)\partial_{xx}c, \quad t \in (0,t_*), \quad x \in (0,l), \qquad (2)$$

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

$$\dot{q}_0(t) = dq_0/dt = -b(T)q^2(t) + D(T)\partial_x c(t,0),$$

$$\dot{q}_l(t) = dq_l/dt - b(T)q^2(t) - D(T)\partial_x c(t,l),$$

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

Here $c(t,x)$ — is the concentration of dissolved atomic hydrogen; $q(t) = q_{0,l}(t)$ — surface concentration; D, b, g — Arrhenius coefficients of diffusion, desorption, rapid dissolution (quasi-equilibrium of surface and near-surface volume concentrations); $J(T)$ — is the desorption density of atoms recombined on the surface into molecules.

Prior to proceeding to parametric identification, it is necessary to physically substantiate the degassing scenario itself (based on the available experimental data). From a mathematical point of view, a problem arises: how to understand from the spectrum which of the variants of the presented models should be preferred? The multi-peak spectrum is very difficult to interpret unambiguously, inasmuch as in reality there is an overlap of many variants, not just these two.

For the purpose of certainty, in this paper we will focus on the experimental data on stainless steel X20CrNiMnVN18-5-10 [7,6]. The indicated figure (see also Fig. 1 of this paper) shows the two-peak spectrum of thermal desorption of hydrogen from steel. The authors of the paper [7], using the tools of the Origin package, approximate the spectrum by the sum of five symmetrical curves, lorencecians. The first, low-temperature, peak is explained by diffusion processes, the second — binds to various traps and is approximated by four lorencens. Approximation of the spectrum by symmetrical curves can lead to the emergence of additional terms (physicochemical processes, the reality of which must be substantiated).

In the computational experiments presented below, we use both models to approximate the experimental two-peak spectrum, avoiding consideration of additional terms explained by traps of different types. A computational algorithm for solving boundary value problems of thermal desorption based on implicit difference schemes, including accounting for the capture of a diffusant by various kinds of traps, is described in detail in [8].

Fig. 1 shows an approximation of the experimental two-peak spectrum of thermal desorption of hydrogen from steel by the sum of two reactions (1) of fractional order for volume-averaged hydrogen concentrations. For each peak, the initial conditions X_0, activation energies (similar values for both peaks were obtained), the values of kinetic frequency coefficients, and the order of reactions were determined. For the low-temperature peak, the main contribution is made by surface processes, $\alpha = 1.87$. For the high-temperature peak ($\alpha = 1.15$), diffusion processes in the sample volume play a major limiting role. The resulting spectrum is the sum of the two peaks.

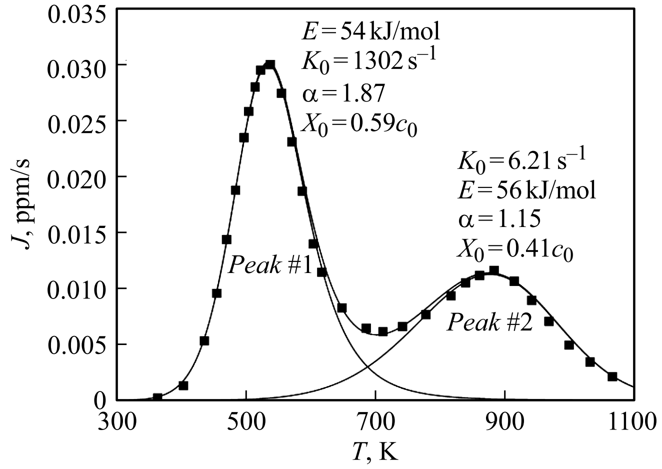

Figure 1. Experimental spectrum. Decomposition by the sum of reactions.

The same experimental spectrum is approximated by the model curve obtained by solving the boundary value problem [2]. The processes are not simply summed up (as in the desorption dynamics model for averaged concentrations). The interaction of surface processes and diffusion in the sample volume is recorded as nonlinear dynamic boundary conditions. The authors used the following parameter values: $l = 0.1$ cm, $[E] =$ kJ/mol, $b_0 = 1.95 \cdot 10^{-13}$ cm^2/s, $E_b = 44$, $D_0 = 0.9$ cm^2/s, $E_D = 80$, $g_0 = 255$ cm^{-1}, $E_g = 8.5$, $T_0 = 300$ K, $\beta = 1/3$ K/s, $c_0 = 3.72 \cdot 10^{15}$ at.H/cm^3.

Then the parameters of the models are recorded, and a series of computational experiments are carried out for both models (changes in the thickness of the wafer, heating rate, initial saturation concentration, heating law, etc.). The accumulated computational material makes it possible to understand which of the additional experiments should be carried out in order to finally select the model and then carry out its parametric identification.

Fig. 2 shows the numerical spectra. The model — is the sum of two fractional-order reactions. Fig. 2, *a* shows the changes as the heating rate varies. Then, the energies of peak activation were calculated from the temperatures of the flow maxima in the Kissinger coordinates (see the inset in Fig. 2, *a*). Despite the fact that the model peaks correspond to a fractional order of reaction (other than unity), it was possible to recover the activation energies of the peaks quite accurately. The points in Kissinger's coordinates are almost in a straight line. Fig. 2, *b* shows the change in spectra as the initial uniform total concentration varies. The fractions of desorbed hydrogen at the peaks remain unchanged. Likewise — when varying the thickness of the plate. The temperatures of the maxima of the resulting total spectrum practically do not change.

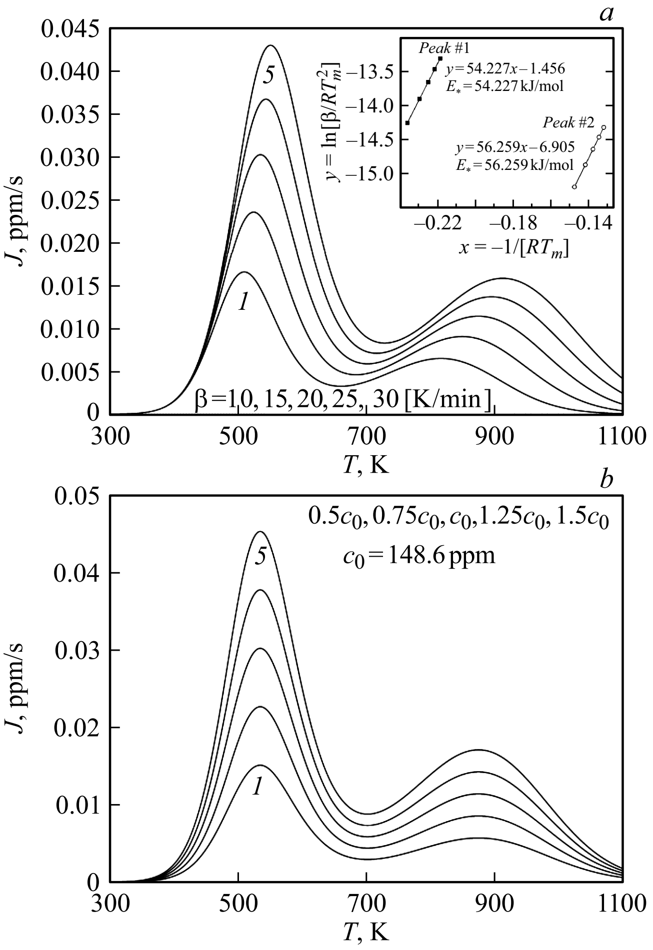

Figure 2. Model for average concentration, sum of two reactions.

Fig. 3 shows the effect of parameters in the model boundary value problem (2). Fig. 3, *a* shows the spectra of thermal desorption when varying the heating rate. Qualitatively, the spectra are the same as in Fig. 2, *a*. The numerical spectrum in the boundary value problem reflects the interaction of processes in the volume and on the surface, and therefore the „participation" share of these processes in peaks may alter with changes in the heating rate. Note that in this model, too, the points in Kissinger's coordinates are located almost in a straight line. Therefore, it cannot be assumed that the arrangement of the temperatures of the maximum peaks in Kissinger coordinates on the same line indicates limitation by diffusion alone.

Fig. 3, *b* shows the change in spectra with varying of the initial uniform concentration. The temperatures of the maxima of the resulting total spectrum shift slightly as the initial concentration changes. We note that when the initial concentration decreases (curve *1* in Fig. 3, *b*), the high-temperature peak is practically indistinguishable against the background of the maximum of the low-temperature peak.

Fig. 3, *c* shows the dynamics of the spectra when varying the thickness of the sample. There have been revealed qualitatively different behavior of peaks. The low-temperature peak associated with surface processes does not change. When the thickness (volume of the sample) changes, the proportion of the high-temperature peak (associated with diffusion processes in the volume) changes. For a high-temperature peak, there is a gluing of ascending fronts.

Let us summarize the conclusions based on the numerical simulation results. Both models (superimposition of 1–2 reactions of orders in terms of average concentrations of hydrogen trapped in the volume and the nonlinear boundary value problem considering the dynamic interaction of the

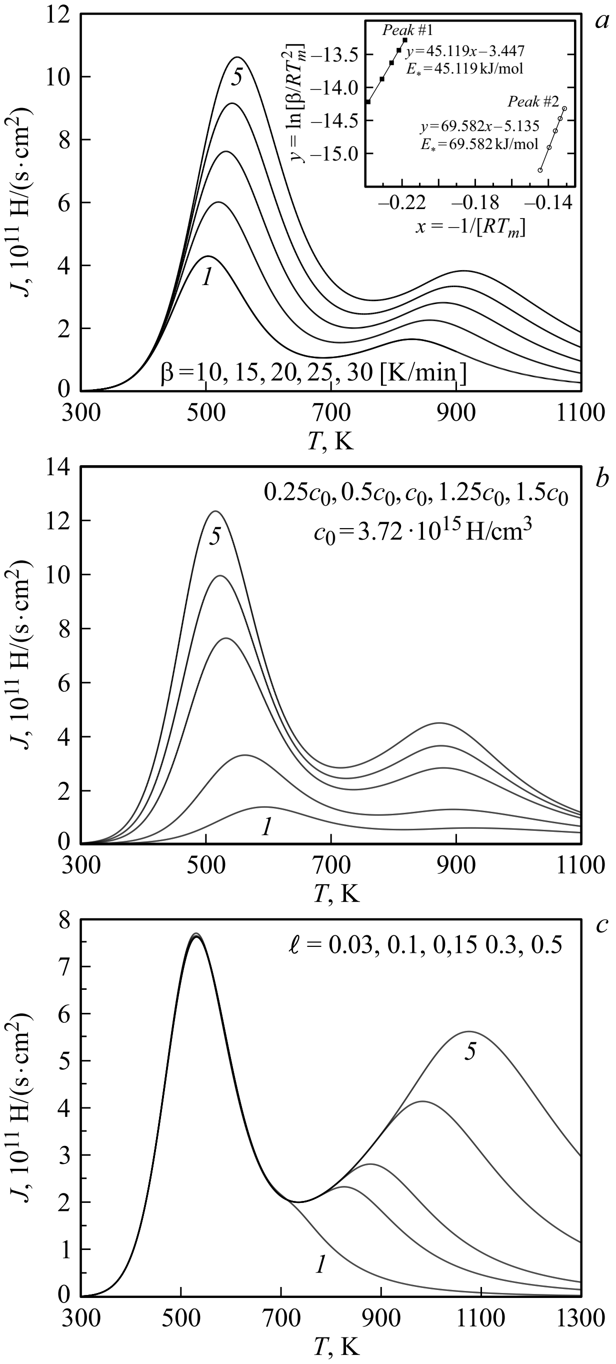

Figure 3. A model in the form of a boundary value problem. Parameter Effect.

surface–volume) allow a fairly accurate approximation of the experimental spectrum. Varying the heating rates and the initial saturation level does not reliably give preference to one of the scenarios. An additional experiment should be performed on a sample of a different thickness. If the commensurability of the peaks (the areas below them) remains, then the explanation in terms of volume capture with different binding energies (e.g., for „porous" materials) is preferable. If the first peak remained almost in place, and the second one increased markedly with increasing thickness, then this is the interaction of the surface with the volume, and not the capture with different binding energies.

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Conflict of interest

The authors declare that they have no conflict of interest.

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