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Research of hydrogen diffusion in a material with various types of traps

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ABSTRACT

A model of the process of hydrogen diffusion over the crystal structure in solids is presented. A defect-free and defective structure are considered. This study is relevant for the process of hydrogen embrittlement, which can lead to premature destruction of the material. A hypothesis about the creation of a surface layer upon pre-charging a sample with hydrogen is considered, which is necessary for further study of the hydrogen desorption process. The effect of the surface layer on the extraction curves is studied, and the simulated extraction curves are compared with the experimental ones. The results obtained make it possible to better understand the interaction of hydrogen atoms with the structure of a solid.

KEYWORDS

hydrogen diffusion • hydrogen charging • hydrogen traps • hydrogen desorption • diffusion equation

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Introduction

In the process of hydrogen sorption in the material, changes in the crystal structure in solids are possible. As a consequence, such effect can negatively affect the strength properties of the material. One of the most dangerous effects is hydrogen embrittlement of the material. This effect can lead to premature destruction of the material. To study the effects, the method of thermal desorption mass spectroscopy (TDS) is used [1–5]. The TDS method makes it possible to determine the binding energy of hydrogen in the crystal lattice in solids and crystal lattice defects [6,7]. This method is based on pre-charging the sample with hydrogen and further desorption of hydrogen from the sample when it is being heated. The flux of desorbed hydrogen is recorded by sensors, and extraction curves are plotted. The pre-charging of the sample with hydrogen and, as a consequence, hydrogen distribution over the sample is of great importance in obtaining the extraction curves. Under laboratory conditions, various methods of pre-charging a sample with hydrogen are used, such as: in gaseous hydrogen [8], in electrolyte solutions when a potential difference is applied [9–11] and in saline solutions [12,13].

When studying the process of hydrogen desorption, it is usually assumed that after charging the sample with hydrogen, the hydrogen concentration is uniformly distributed over the sample. Therefore, the distribution of hydrogen over the sample is often not studied in experimental papers, and sometimes the concentration after charging is not even measured [14–17]. However, it was experimentally observed that during laboratory saturation, hydrogen is not distributed uniformly [18,19], but instead forms a surface

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layer, beyond which it almost does not penetrate [13,20]. This hypothesis is to be investigated.

The diffusion process is described by taking into account defects in the crystal lattice, which can affect the hydrogen diffusion process; these defects are called traps, [21–24]. The most popular traps model of hydrogen transport was proposed by Mac Nabb and Foster [25] and Oriani [26]. The models describe the capture of hydrogen in traps. The description of the process is based on Fick's first and second laws.

Oriani introduced a “phenomenological” diffusion coefficient, which in this paper will be called "effective diffusion coefficient" to considerate the effect of hydrogen trapping. Further on, on the assumption of local equilibrium between the concentration of hydrogen atoms in the crystal lattice of the sample and in the traps, Oriani derived an equation for describing the process of hydrogen diffusion with allowance for traps. Oriani's work investigated the effect of a single trap on the diffusion process. Fisher [14] generalized relations for several traps.

In the present paper to describe the diffusion process, we rely on the Oriani hypothesis of local equilibrium and calculate the effective diffusion coefficient for several traps following Fisher's equations. Fischer carried out simulations at a constant temperature of the sample in his work. In the present paper, the effect of thermal conductivity is taken into account when the sample is placed in a heated chamber.

The purpose of this article is to derive equations for the diffusion process taking into account traps, to show the effect of the presence of a boundary layer on extraction curves, and to argue for the hypothesis of the presence of a boundary layer.

Analytical description of the diffusion process in a defect-free structure

Consider a soled with a defect-free crystal lattice. Below is Fick's first law for the diffusion of hydrogen atoms in a defect-free lattice:

$$j = -D_L \, grad(c_L), \tag{1}$$

where D_L is the diffusion coefficient of hydrogen in a defect-free lattice, c_L is the concentration of hydrogen atoms at a given point, j is the hydrogen flux.

According to Arrhenius's law, the diffusion coefficient D_L can be represented as follows:

$$D_L = D_0 \exp\left(-\frac{U_L}{kT}\right), \tag{2}$$

where D_0 is the diffusion constant, U_L is the binding energy of hydrogen atoms with the crystal lattice, k is the Boltzmann coefficient, T is the absolute temperature.

For a homogeneous body structure, D_0 and U_L are constant for the whole body, therefore the diffusion coefficient D_L depends only on the temperature at the considered point of the body.

According to Fick's second law:

$$\Delta c = \frac{1}{D_L} \frac{\partial c}{\partial t}. \tag{3}$$

Equation (3) establishes the relationship between the spatial and temporal changes in the concentration of hydrogen. Equation (3) is rewritten in the form of a difference scheme, then the finite element method with specified boundary conditions makes it possible to simulate the process of hydrogen diffusion. Further, according to Fick's first

law, it is possible to find the dependence of the hydrogen flux from the sample on time, that is, the extraction curves that are compared with the experimental ones.

Analytical description of the diffusion process in a defect structure

Almost any solid has defects at the molecular level, which can create obstacles for the diffusion of hydrogen atoms. These defects are called traps. The traps are divided into sorts that correspond to a certain binding energy with hydrogen atoms. Dislocation cores can serve as an example of a trap. For this sort of trap, hydrogen diffusion will proceed along the dislocation lines.

We consider m sorts of traps. Each sort of trap can be a new hydrogen diffusion channel with a corresponding diffusion coefficient. As a special case, the diffusion coefficient for some kind of traps can be zero. This means that hydrogen atoms do not move through traps of this sort. They can get out of the trap, move along the crystal lattice of the body and fall into the trap at another point in the body.

Since a new sort of traps can be represented as an additional diffusion channel, we rewrite Fick's first law (1) taking into account the influence of traps:

$$j = -D_L\, grad(c_L) - \sum_{k=1}^{m} D_{Tk}\, grad(c_{Tk}), \tag{4}$$

where j is the total diffusion flux of hydrogen atoms, D_{Tk} is the diffusion coefficient of hydrogen in traps of sort k, c_{Tk} is the concentration of hydrogen in a trap of sort k.

A closed system is considered. We introduce the following parameters: N_L is possible number of moles of hydrogen in the positions of defect-free crystal lattice of the body; N_{Tk} $(k = 1,\ldots,\mathrm{m})$ is the number of moles of positions of traps of sort k in the sample; y_L is the amount of hydrogen distributed in the lattice; y_{Tk} is the amount of hydrogen distributed in the trap of sort k.

Suppose that when a mole of hydrogen atoms is captured, the total energy of the system decreases by the value ΔE_k. Then the total Gibbs energy of the system can be written as:

$$G = G_0 + RT\left([y_L \ln y_L + (1-y_L)\ln(1-y_L)]N_L + \sum_{k=1}^{m}\left\{[y_{Tk}\ln y_{Tk} + (1-y_{Tk})\ln(1-y_{Tk})]N_{Tk} - \frac{\Delta E_k}{RT} y_{Tk} N_{Tk}\right\}\right), \tag{5}$$

where R is the gas constant, T is the absolute temperature.

The parameter ΔE_k can be written as a difference between the binding energies of hydrogen in a crystal lattice and a trap of sort k:

$$\Delta E_k = U_k - U_L\,. \tag{6}$$

According to the law of conservation of mass in a closed system:

$$N_L\, y_L + \sum_{k=1}^{m} N_{Tk} y_{Tk} = \mathrm{const}\,. \tag{7}$$

The Oriani hypothesis about the local equilibrium between the concentration of hydrogen atoms in the crystal lattice of the body and in the traps corresponds to the minimum of function (5) with respect to the variables y_L and y_{Tk}, taking into account

relation (7). We will use the Lagrange multiplier method and find the minimum of function (8):

$$F = G + \lambda\left(N_L y_L + \sum_{k=1}^{m} N_{Tk} y_{Tk} - \text{const}\right), \tag{8}$$

where λ is the Lagrange multiplier.

The minimum of function (8) corresponds to the following system:

$$\begin{cases} \dfrac{\partial F}{\partial y_L} = RT[\ln y_L - \ln(1-y_L)]N_L + \lambda N_L = 0, \\ \dfrac{\partial F}{\partial y_{Tk}} = RT[\ln y_{Tk} - \ln(1-y_{Tk})]N_{Tk} - \Delta E_k N_{Tk} + \lambda N_{Tk} = 0, \qquad (k = 1, \dots, m). \end{cases} \tag{9}$$

System (9) can be reduced to the following expression:

$$\frac{y_L(1-y_{Tk})}{y_{Tk}(1-y_L)} = \exp\left(-\frac{\Delta E_k}{RT}\right) = K_k, \tag{10}$$

where K_k is the equilibrium constant.

We express y_{Tk} from Eq. (10):

$$y_{Tk} = \frac{y_L}{K_k + y_L(1-K_k)}, \qquad (k = 1, \dots, m). \tag{11}$$

We introduce the variables V_{Tk} and V_L are volumes corresponding to one mole of hydrogen in traps of sort k and in the lattice, respectively.

Then the concentration of hydrogen in the lattice can be written as:

$$c_L = \frac{y_L}{V_L}. \tag{12}$$

The concentration of hydrogen in traps of sort k, taking into account Eq. (11), can be represented as:

$$c_{Tk} = \frac{y_{Tk}}{V_{Tk}} = \frac{y_L}{V_{Tk}} \frac{1}{K_K + y_L(1-K_k)}. \tag{13}$$

Using Eq. (12), we get:

$$c_{Tk} = \frac{V_L}{V_{Tk}} \frac{1}{(K_k + V_L c_L(1-K_k))} c_L. \tag{14}$$

Then the total concentration of hydrogen can be written:

$$\begin{aligned} c = c_L + \sum_{k=1}^{m} c_{Tk} &= \frac{y_L}{V_L} + \sum_{k=1}^{m} \frac{y_L}{V_{Tk}} \frac{1}{K_K + y_L(1-K_k)} \\ &= \left(1 + \sum_{k=1}^{m} \frac{V_L}{V_{Tk}} \frac{1}{K_K + V_L c_L(1-K_k)}\right) c_L. \end{aligned} \tag{15}$$

The parameters V_L, V_{Tk}, D_L, D_{Tk}, $(k = 1, \dots, m)$ are considered constant over the sample volume.

Let's return to Eq. (4) and write down the gradient:

$$j(x,t) = -\left(D_L \left.\frac{dc_L}{dc}\right|_{x,t} + \sum_{k=1}^{m} D_{Tk} \left.\frac{dc_L}{dc}\right|_{x,t} \left.\frac{dc_{Tk}}{dc_L}\right|_{x,t}\right) \text{grad}(c) = -\widehat{D}\,\text{grad}(c), \tag{16}$$

where

$$\widehat{D} = \left(D_L + \sum_{k=1}^{m} D_{Tk} \left.\frac{dc_{Tk}}{dc_L}\right|_{x,t}\right) \left.\frac{dc_L}{dc}\right|_{x,t}. \tag{17}$$

The parameter $\widehat{D}$ will be called the effective diffusion coefficient. This parameter shows the effect of hydrogen diffusion along the crystal lattice and traps.

The derivatives on the right side of Eq. (17) are calculated for a given spatial position and a given time. The derivative $\frac{dc_L}{dc}$ follows from Eq. (15):

$$\frac{dc_L}{dc} = \left[1 + \sum_{k=1}^{m} \frac{V_L}{V_{Tk}} \frac{K_k}{(K_k + V_L c_L (1 - K_k))^2}\right]^{-1}. \quad (18)$$

The expression for the derivative $\frac{dc_{Tk}}{dc_L}$ follows from Eq. (14) as:

$$\frac{dc_{Tk}}{dc_L} = \frac{V_L}{V_{Tk}} \frac{K_k}{(K_k + V_L c_L (1 - K_k))^2}. \quad (19)$$

Then Fick's second law corresponds to Eq. (16) in the form:

$$\Delta c = \frac{1}{\widehat{D}} \frac{\partial c}{\partial t}. \quad (20)$$

Thus, Eqs. (17) – (19) allow us to find the dependence $\widehat{D}(c_L)$. To find the dependence $\widehat{D}(c)$, it is necessary to solve the nonlinear Eq. (15) and express c_L in terms of c.

As a result, we obtain the dependence $\widehat{D}(c)$ and by representing Eq. (20) in the form of a difference scheme and writing the boundary conditions, we are able to simulate the process of hydrogen diffusion using finite element methods, taking into account different sorts of traps.

Experiment

To study the process of hydrogen diffusion, the following experiment was carried out. The sample was pre-charged with gaseous hydrogen and then placed in a preheated chamber. Then, using sensors, the flux of desorbed hydrogen from the sample surface was measured. Thus, we obtained experimental extraction curves showing the dependence of the desorbed hydrogen flux on time.

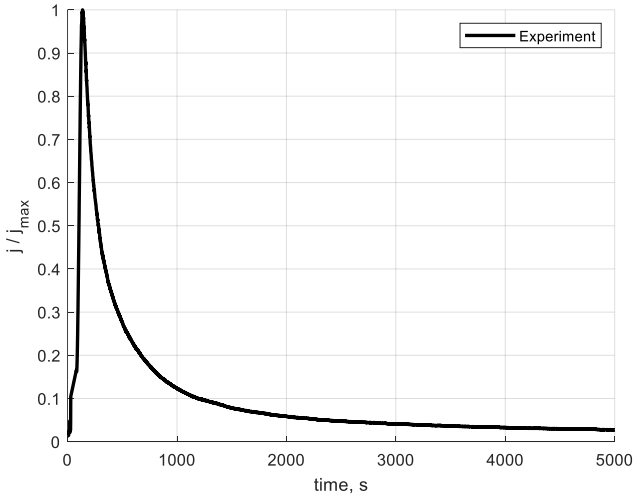


Fig. 1. Experimental extraction curve

Cylindrical billets made of BT16 titanium alloy are considered as samples. The radius of the samples under consideration is $R = 11$ mm, $0 \leq r \leq R$, and the height is 11 mm. It was experimentally found that after pre-charging the sample with hydrogen, the internal hydrogen content corresponds to 23 ppm. This content corresponds to a hydrogen concentration of 179.4 mol/m^3. The temperature of the heated chamber, in which the sample was placed, was 750 °C. The experimental normalized extraction curve is shown in Fig. 1.

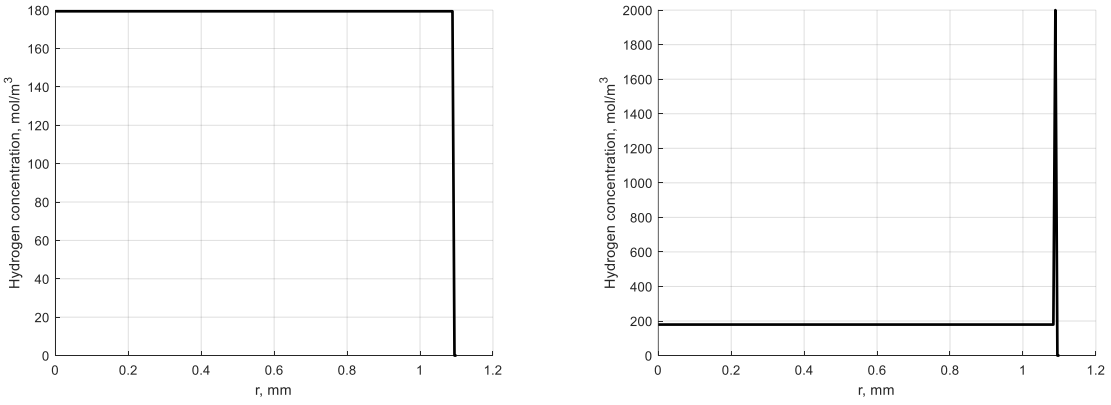
Modeling and discussion of the results

The modeling is qualitatively compared with the experimental extraction curves. The crystal lattice parameters are taken as follows: $D_0 = 3.1081 \cdot 10^{-9}$ m^2/s; $U_L = 0.1$ eV; $k = 8.62 \cdot 10^{-5}$ eV/K; $T = 750$ °C = 1023 K; $V_L = 4.9 \cdot 10^{-6}$ m^3/mol.

Then, according to Eq. (2): $D_L = 10^{-9}$ m^2/s. Consider a one trap with parameters: $V_{T1} = 6 \cdot 10^{-5}$ m^3/mol; $\Delta E_1 = 25$ kJ/mol; $K_1 = 1.6 \cdot 10^{-5}$.

Below are the boundary conditions for modeling the process of hydrogen desorption: $t = 0, \quad c =$179.4 mol/m^3, $t > 0, \; r = R; \; c = 0$.

Figure 2 shows the distribution of the initial hydrogen concentration along the radial coordinate of a cylindrical sample without taking into account (Fig. 2(a)) and taking into account (Fig. 2(b)) the surface layer of hydrogen.



(a) (b)

Fig.2. The form of the distribution of the initial hydrogen concentration without and taking into account the surface layer of hydrogen

First, we have investigated the process when the diffusion coefficient over a trap of the sort under consideration is zero: $D_{T1} = 0$.

Figure 3 shows how the presence and size of the initial surface layer of hydrogen affects the qualitative behavior of the modeled extraction curve. According to Fig. 3, it can be concluded that an increase in the surface layer leads to a qualitative convergence of the modeled curve and the experimental curve.

Then we have studied the process when the diffusion coefficient for a trap of the sort under consideration is $D_{T1} = 10^{-13}$ m^2/s. Figure 4 shows how the presence and size of the initial surface hydrogen layer affect the qualitative behavior of the modeled extraction curve in the case of a nonzero diffusion coefficient in the trap. According to

Fig. 4, it can be concluded that with a nonzero coefficient of hydrogen diffusion through the traps, an increase in the surface layer also leads to a qualitative convergence of the modeled curve and the experimental curve. Convergence occurs at a smaller surface layer than at a zero diffusion coefficient over the traps.

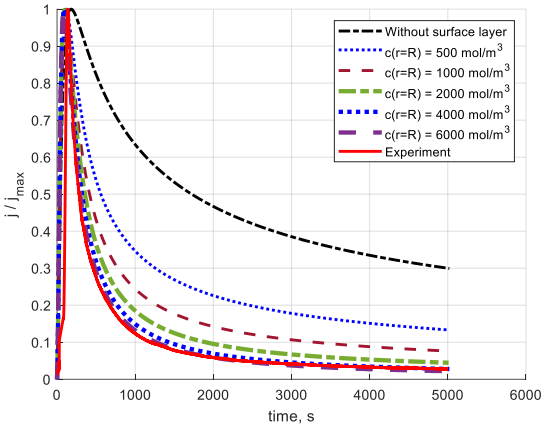


Fig. 3. Extraction curves at zero diffusion coefficient over traps

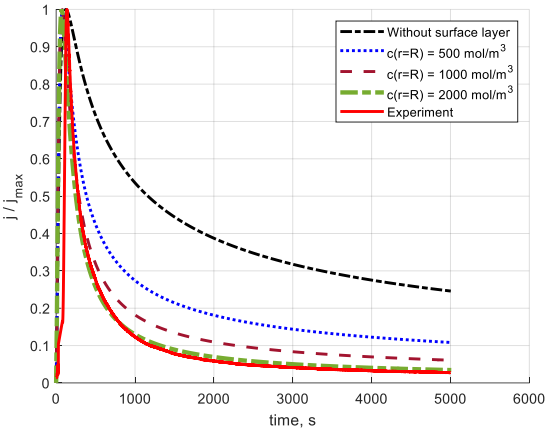


Fig.4. Extraction curves for a nonzero diffusion coefficient over traps

It can be concluded that the presence of a boundary layer changes the shape of the extraction curve and qualitatively brings it closer to the experimental one. Under the assumption of an initial uniform distribution of hydrogen, extraction curves were obtained, which, even at a qualitative level, did not agree with experiment. Including the nonzero coefficient of hydrogen diffusion through traps into consideration changes the shape of the extraction curve, but the presence of a boundary layer again brings the simulation closer to experiment.

Conclusions

In this paper, we considered the hypothesis of the presence of a surface layer when the sample is charged with gaseous hydrogen. A hydrogen diffusion model was presented for a defect-free body structure and for a body structure with traps. According to the described model, the diffusion process was modeled and the effect of the surface layer of hydrogen on the extraction curves was investigated. It was shown that the presence of a surface layer qualitatively changes the shape of the extraction curve and brings the simulated curves closer to the experimental ones. The diffusion coefficient over traps was investigated at zero and non-zero values. In both cases, the presence of a surface layer brought the simulation closer to experiment. This study is to be carried out for traps of other varieties and transfer from a qualitative description to a quantitative one.

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