Simulation of Hydrogen Isotopes Accumulation Processes in Materials in the Presence of Chemical Traps

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Abstract

The accumulation of hydrogen inside a solids occurs in traps of a different nature. The following things are known in addition to finding hydrogen in interstitial sites: dislocation mechanisms of hydrogen storage, micropores and microcracks, sorption on the free surface of microdefects, chemical traps with the formation of hydrides and other compounds, both with matrix material and with impurities or components of alloys. It is established that each type of trap has its own binding energy of hydrogen, which can vary from 0.2 eV for hydrogen gas in microdefects to several eV for hydrogen chemically bound in traps. Measurements of the distribution of hydrogen concentration dissolved in a solid body over binding energies provide a clue as to the understanding of hydrogen impact on mechanical properties and to the development of technologies for controlling the materials properties during their production and operation. The paper presents the results of simulation experiments on hydrogen saturation of materials in the presence of chemical traps. The proposed model, based on the numerical solution of the diffusion equation in the presence of irreversible capture, made it possible to describe the absorption process and determine the activation energies of hydrogen interaction with the material.

Keywords: hydrogen accumulation, chemical traps, diffusion, simulation

1. Introduction

The results of numerous experiments on the gases diffusion in solids require the development of a theory that takes into account the properties of the diffusion medium when interacting with the diffusing impurity. The origin of the interaction can be explained by the existence of traps in the solid that capture the diffusing atom and, for some time, hinder their migration, or in general remove the diffusant from the migration process. Such traps can be micropores, gas bubbles, crystal or spherical edges, grain boundaries, inclusions of foreign phases, clusters, dislocations, radiation defects, etc.

In practice, this kinetics occurs in diffusion with the formation of hydrides, diffusion with a constant capture in nonequilibrium media, diffusion with radioactive decay [1–6]. The diffusion process in this one-dimensional case is described by the Eq. 1:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - kC \quad (1)$$

where $C(x, t)$ is the concentration of the diffusing gas (mol/m$^3$); $D$ is the diffusion coefficient (m$^2$/s); $k$ is the rate constant of the diffusing gas capture by traps (1/s).

The diffusion coefficient and the capture rate constant have an Arrhenius dependence:

$$D = D_0 \exp\left(-\frac{E_d}{RT}\right) \quad (2)$$

$$k = k_0 \exp\left(-\frac{E_k}{RT}\right) \quad (3)$$

where $D_0$ is the pre-exponential factor of the diffusion coefficient (m$^2$/s); $E_d$ is the diffusion activation energy (J/mol); $k_0$ is the pre-exponential factor of the capture rate constant (s$^{-1}$); $E_k$ is the capture activation energy of the traps (m$^2$/s); $R$ is the universal gas constant (J/(K∙mol)); $T$ – temperature (K).

It is assumed that the concentration in the near-surface regions (for a thin sample of thickness $L$) is equal to the equilibrium solubility:

$$C(0, t) = S \sqrt{P_0} \quad (4)$$

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$$ C(L, t) = S \sqrt{P_0} $$

(5)

de ep ora $ S = S_0 \exp\left(-\frac{E_s}{RT}\right) $ is the solubility (mol/(m$^3$·Pa$^{1/2}$)); $ S_0 $ – pre-exponential factor in Arrhenius depen
dence (mol/(m$^3$·Pa$^{1/2}$)); $ E_s $ – activation energy of
dissolution (J/mol); $ P_0 $ is the partial pressure of the
gas in the system (Pa).

Under conditions where the pressure in exper
imental chamber is changed, due to absorption of
the gas part, the described problem has no analyti
cal solution and may be described in the proposed
simulation below which is based on the sequential
solution of the diffusion problem (1) in desirable
time interval.

Using the Eqs. 7 and 8 in the MathCAD14 en
vironment, a model was developed for calculating
the rate of gas absorption by a sample from the
experimental chamber under conditions of uncom-
pensated pressure. The calculation scheme was as
follows:
• Initially, the time interval (in which the ab-
sorption process is carried out) is divided with an
interval $ \Delta t $, and also the thickness distribution of
the sample is divided with $ \Delta L $;
• After that the concentration distribution is cal-
culated in the first time step (Eqs. 7 and 8).
• Next, the new pressure in the chamber is re-
calculated, taking into account the amount of hy-
dergen absorbed by the sample during the time $ \Delta t $.
• Then, in the second step, the solution (Eq. 8)
is again used for the new boundary and initial con-
cditions, taking into account the pressure and gas
concentration along the thickness of the sample
calculated in the previous step.
• The last operation is repeated for the entire
time partition.

2. Results and discussion

With the help of the above-mentioned model,
were described the sorption experiments on the
saturation of vanadium alloy samples with hy-
dergen isotopes that have been carried out ear-
erly by the authors of [8]. Modeling experiments on
sorption by vanadium alloy respond the diffusion
conditions in the presence of traps with unlimited
capacity since the formation of hydrides occurs at
saturation below 473 K.

In the experiment the plate samples of vanadi-
um alloy V4Ti4Cr with dimensions of 1×20×25
mm was studied.

Studies on saturation of vanadium alloy samples
was carried out using the so-called integral method:
after high temperature degassing a predetermined
saturation temperature of samples was set and a
known quantity of the hydrogen and deuterium
mixture was supplied into the chamber with sample,
then, the self-saturation of sample among hydrogen
isotopes at a selected temperature was made. During
saturation the change of pressure and composi
tion of gas mixture in the chamber was registered.

The saturation was carried out successively at
different pressures of hydrogen and deuterium in a
gas mixture. At the end of a series of experiments
on sample saturation at one temperature, the gas
was evacuated and the samples were heated up to
973 K under conditions of continuous evacuation
of the chamber, after which a new cycle of satura
tion experiments was carried out at another inves
tigated temperature.

Using the literature data for solubility and dif
fusion coefficients in the vanadium alloy V4Cr4Ti
[9–14] and varying the parameters of the Arrhenius
dependence for the capture rate constant, model

To do this, note that the introduction of the sub-
stitution $ C = C_1 \exp(-kt) $ into this equation takes it to
the usual form:

$$ \frac{\partial C_1}{\partial t} = D \frac{\partial^2 C_1}{\partial x^2} $$

(6)

Then the general solution will look like this:

$$ C = k \cdot \int_0^t C_1 \exp(-kt) \, dt + C_1 \exp(-kt) $$

(7)

here, $ C_1 $ is the solution of the classical diffu
sion equation, which for the selected boundary
conditions and initial concentration distribution
$ C(x,0)$≠0 will look like [7]:

$$ C_1(x,t) = S \sqrt{P_0}(1 + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{\cos(n\pi)}{n} \sin \frac{n\pi x}{L} \exp \left(-\frac{n^2\pi^2 D t}{L^2}\right)) + $$

$$ + \frac{2}{L} \sum_{m=0}^{\infty} \sin \frac{m\pi x}{L} \exp \left(-\frac{n^2\pi^2 D t}{L^2}\right) \int_0^L C_1(\xi,0) \sin \frac{m\pi \xi}{L} \, d\xi $$

(8)
Fig. 1. Results of pressure drop simulation of hydrogen isotopes in experimental chamber during sorption experiment at 393 K.

dependences of the pressure decrease of isotopes in the chamber for different temperatures of a vanadium alloy V4Cr4Ti sample were obtained (see the example in Fig. 1).

As can be seen from the figure, the simulation allowed a good description of the process of hydrogen isotopes absorption by the sample and determine the optimal parameters of the hydrogen isotopes interaction with sample (see Table).

Main conditions and parameters of the conducted studies:
- Saturation pressure of hydrogen, deuterium in a mixture 100–1000 Pa;
- The investigated temperature of the samples 353, 393, 423 K;
- Number of saturation cycles at one temperature 3–5.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_k0, s^-1</td>
<td>3.1E-02</td>
</tr>
<tr>
<td>D_k0, s^-1</td>
<td>1.4E-02</td>
</tr>
<tr>
<td>E_k, kJ/mol</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
</tr>
</tbody>
</table>

The obtained data indicate the presence of an isotopic effect, which consists in the difference in the trapping constants of hydrogen by traps and, correspondingly, at different capture activation energies. This may be due to the fact that vanadium has unique properties with respect to hydrogen: protium atoms usually occupy octahedral interstitial sites in the bcc lattice of vanadium, while deuterium atoms are basically tetrahedral interstices [15–18].

3. Conclusions

Thus, with the help of the developed model describing the absorption of gas by thin samples, it was possible to describe perfectly the experimental results on the absorption of hydrogen isotopes mixture and to determine the interaction parameters of hydrogen isotopes with vanadium V4Cr4Ti alloy. In particular, the trapping constant of hydrogen isotopes was determined.
In the future, the proposed model can be used to calculate the accumulation of hydrogen in facilities of nuclear power plants, fusion reactors, petrochemical industries, fuel cells, etc.

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References


