Eurasian Chemico-Technological Journal 21 (2019) 25–28

https://doi.org/10.18321/ectj783

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

T.V. Kulsartov, Zh.A. Zaurbekova*, Ye.V. Chikhray, M.T. Gabdullin

Kazakh-British Technical University, 59, Tole bi str., Almaty, Kazakhstan

Article info

Received:
04 September 2018

Received in revised form:
18 October 2018

Accepted:
28 November 2018

Keywords:
hydrogen
accumulation
chemical traps
diffusion, simulation

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.

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:

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

here 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:

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

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

here 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}); k_d 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:

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

---

*Corresponding author. E-mail: zzha@mail.ru

$$C(L,t) = S\sqrt{P_0} \tag{5}$$

here $S = S_0 \exp\left(-\frac{E_s}{RT}\right)$ is the solubility (mol/(m^3·Pa$^{1/2}$)); S_0 – pre-exponential factor in Arrhenius dependence (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 experimental chamber is changed, due to absorption of the gas part, the described problem has no analytical 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.

To do this, note that the introduction of the substitution C=C1exp(-kt) into this equation takes it to the usual form:

$$\frac{\partial C1}{\partial t} = D\frac{\partial^2 C1}{\partial x^2} \tag{6}$$

Then the general solution will look like this:

$$C = k \cdot \int_0^t C1\exp(-kt)\,dt + C1\exp(-kt) \tag{7}$$

here, C1 is the solution of the classical diffusion equation, which for the selected boundary conditions and initial concentration distribution C(x,0)≠0 will look like [7]:

$$C1(x,t) = S\sqrt{P0}\left(1 + \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{\cos(n\pi)-1}{n}\sin\frac{n\pi x}{L}\exp\left(-\frac{n^2\pi^2 Dt}{L^2}\right)\right) + \\ + \frac{2}{L}\sum_{m=0}^{\infty}\sin\frac{n\pi x}{L}\exp\left(-\frac{n^2\pi^2 Dt}{L^2}\right)\int_0^L C1(\xi,0)\sin\frac{m\pi}{L}\xi d\xi \tag{8}$$

Using the Eqs. 7 and 8 in the MathCAD14 environment, a model was developed for calculating the rate of gas absorption by a sample from the experimental chamber under conditions of uncompensated pressure. The calculation scheme was as follows:

- Initially, the time interval (in which the absorption process is carried out) is divided with an interval Δt, and also the thickness distribution of the sample is divided with ΔL;
- After that the concentration distribution is calculated in the first time step (Eqs. 7 and 8).
- Next, the new pressure in the chamber is recalculated, taking into account the amount of hydrogen absorbed by the sample during the time Δt.
- Then, in the second step, the solution (Eq. 8) is again used for the new boundary and initial conditions, 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 hydrogen isotopes that have been carried out earlier 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 vanadium 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 composition 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 saturation experiments was carried out at another investigated temperature.

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

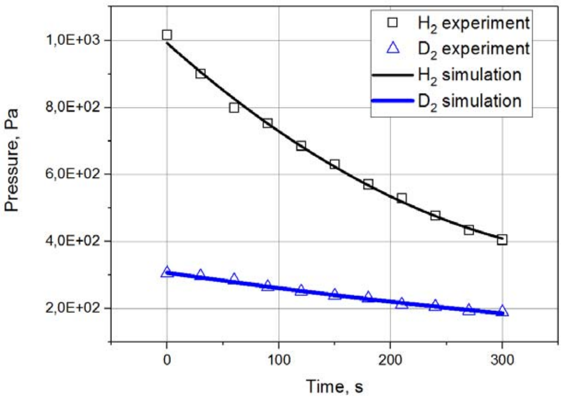

Fig. 1. Results of pressure drop simulation of hydrogen isotopes in experimental chamber during sorption experiment at 393 K.

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

The parameters of the rate constant for the capture of hydrogen isotopes in a vanadium alloy V4Cr4Ti

	H	D
k_0, s^{-1}	3.1E-02	1.4E-02
E_k, kJ/mol	2.1	3.5

The time variation of the gas (hydrogen) concentration over the sample's thickness is shown in Figs. 2 and 3.

As can be seen from Fig. 2, despite the fact that the near-surface concentration of hydrogen decreases (due to a reduction in the gas pressure in the chamber and, accordingly, on the sample surface), the total amount of hydrogen in the sample increases.

In addition, there is an accumulation of hydrogen isotopes in traps (Fig. 3).

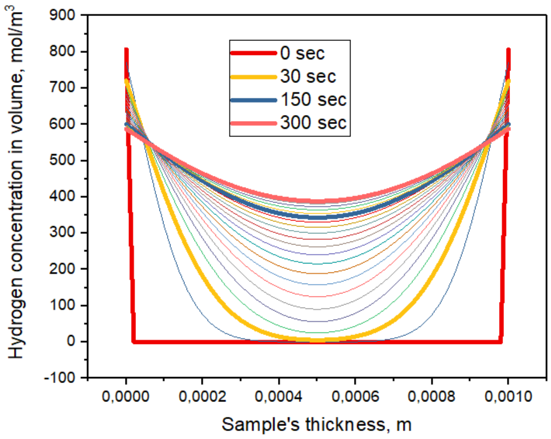

Fig. 2. Free hydrogen concentration change over sample's thickness in absorption process.

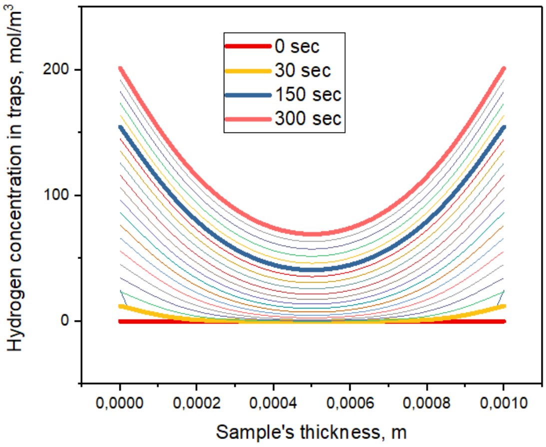

Fig. 3. Hydrogen concentration change in traps over sample thickness in absorption process.

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.

Acknowledgments

The work was carried out within the framework of the program # BR05236800 of the Ministry of Education and Science of the Republic of Kazakhstan.

References

[1]. P.V. Danckwerts, *Trans. Farad. Soc.* 47 (1951) 1014–1019. DOI: 10.1039/tf9514701014

[2]. I.N. Bekman, Mathematics of diffusion. Schoolbook. M.: OntoPrint, 2016. 400 p.

[3]. L. Li, B. Song, J. Cheng, Z. Yang, *Int. J. Hydrogen Energ.* 43 (2018) 17353–17363. DOI: 10.1016/j.ijhydene.2018.07.110

[4]. T. Schaffner, A. Hartmaier, V. Kokotin, M. Pohl, *J. Alloy. Compd.* 746 (2018) 557–566. DOI: 10.1016/j.jallcom.2018.02.264

[5]. W.T. Geng, V. Wang, J. Li, N. Ishikawa, H. Kimizuka, K. Tsuzaki, S. Ogata, *Scripta Mater.* 149 (2018) 79–83. DOI: 10.1016/j.scriptamat.2018.02.025

[6]. Z. Zhang, K.L. Moore, G. McMahon, R. Morana, M. Preuss, *Corros. Sci.* 146 (2018) 58–69. DOI: 10.1016/j.corsci.2018.10.019

[7]. T. Kulsartov, V. Shestakov, Ye. Chikhray, I. Kenzhina, S. Askerbekov, Yu.N. Gordienko, Yu. Ponkratov, Z. Zaurbekova, *Fusion Eng. Des.* 113 (2016) 303–307. DOI: 10.1016/j.fusengdes.2016.09.006

[8]. G. Schaumann, J. Völki, G. Alefeld, *Phys. Stat. Sol.* 42 (1970) 401. DOI: 10.1002/pssb.19700420141

[9]. D.J. Pine and R.M. Cotts, *Phys. Rev. B 2*8 (1983) 641. DOI: 10.1103/PhysRevB.28.641

[10]. D.J. Pine and R.M. Cotts, Diffusion of hydrogen in vanadium-based BCC alloys”, in Electronic Structure and properties of hydrogen in metalls, plenum Press, New York, (1983) 465 p.

[11]. D.T. Peterson and H.M. Herro, *Metall. Mater. Trans. A* 18 (1987) 249–254. DOI: 10.1007/BF02825705

[12]. H. Bleichert, H. Wenzl, *Phys. Stat. Sol. B* 144 (1987) 361–373. DOI: 10.1002/pssb.2221440132

[13]. M.D. Dolan, K.E. Lamb, J.B. Evtimova, D.M. Viano, *Int. J. Hydrogen Energ.* 42 (2017) 24183–24188. DOI: 10.1016/j.ijhydene.2017.07.185

[14]. A.A. Smirnov. Teorija diffuzii v splavah vnedrenija [Theory of Diffusion in Embedding Alloys] Kiev, Naukova Dumka, 1982, 168 p. (in Russian).

[15]. T. Schober and W. Pesch, *Z. Phys. Chem.* 114 (1979) 21–28. DOI: 10.1524/zpch.1979.114.114.021

[16]. J.F. Smith, D. T. Peterson, *J. Phase Equilib. Diff.* 3 (1982) 49. DOI: 10.1007/BF02873411

[17]. Y. Lu, M. Gou, R. Bai, Yixin Zhang, Zheng Chen, *Int. J. Hydrogen Energ.* 42 (2017) 22925–22932. DOI: 10.1016/j.ijhydene.2017.07.056

[18]. M.L. Martin, A. Pundt, R. Kirchheim, *Acta Mater.* 155 (2018) 262–267. DOI: 10.1016/j.actamat.2018.06.011