INHIBITION OF HYDROGEN PERMEABILITY BY TiN: EVALUATION OF KINETIC PARAMETERS

Popov V.V.*, Denisov E.A.(1)
Institute of Applied Mathematical Research of Karelian Research Centre of
Russian Academy of Sciences, Pushkinskaya str. 11, Petrozavodsk, 185910 Russia
(1) St.Petersburg State University, V.A. Fock Institute of Physics,
Ulyanovskaya str. 1, St. Petersburg, 198504 Russia
* *Fax: +7(814-2) 76-63-13 E-mail: popov@krc.karelia.ru*

Introduction

Wide use of hydrogen-metal systems during the recent years demands effective protective coats that inhibit hydrogen permeability. The influence of thin-film coat of titanium nitride (TiN) to hydrogen permeability of a metal membrane was investigated in [1]. This coat has good protective properties and can be used for considerable reduction of penetration and accumulation of hydrogen inside construction materials. The aim of this work is to identify the hydrogen permeability model parameters. The model describes hydrogen permeability of stainless steel membrane (brand 12X18H10T) with titanium nitride (TiN) protective coat.

Experiment, model

Here we describe the method of permeability. Membrane with titanium nitride protective coat divides an evacuated vessel into two parts. The temperature of the sample is constant. At titanium nitride side a constant pressure of molecular hydrogen is provided. At the other side of membrane (output side) gas is pumped out by a vacuum system. Hydrogen is adsorbed at the TiN surface, diffuses through the protective coat and the membrane, and desorbs from the output side into vacuum. Hydrogen pressure at the vacuum vessel is measured with a mass-spectrometer. The desorption flux density is calculated using the measured pressure, and is used for parameters identification. Model parameters are Arrhenius with respect to the temperature; therefore kinetic constants can be obtained using parameters’ values for different temperatures.

The following model describes hydrogen transfer in metal membrane with protective coat:

$$c_t(t,x) = D_1 c_{xx}(t,x) - a_{11}c + a_{12}z, \qquad (1)$$

$$z_t = a_{11}c - a_{12}z, \quad (t,x) \in (0,t^*) \times (0,\ell_1), \qquad (2)$$

$$c(0,x) = \varphi_1(x), \quad z(0,x) = \psi_1(x), \qquad (3)$$

$$\mu s_1 p_0 - b_1 c_0^2 = -D_1 c_x(t,0), \quad c_0 = c(t,0), \qquad (4)$$

$$D_1 c_x(t,\ell_1) = D_2 u_x(t,0), \qquad (5)$$

$$k_1 c(t,\ell_1) - k_2 u(t,0) = -D_1 c_x(t,\ell_1), \qquad (6)$$

$$u_t(t,x) = D_2 u_{xx}(t,x) - a_{21}u + a_{22}w, \qquad (7)$$

$$w_t = a_{21}u - a_{22}w, \quad (t,x) \in (0,t^*) \times (0,\ell_2), \qquad (8)$$

$$u(0,x) = \varphi_2(x), \quad w(0,x) = \psi_2(x), \qquad (9)$$

$$\mu s_2 p_{\ell_2} - b_2 u_{\ell_2}^2 = D_2 u_x(t,\ell_2), \; u_{\ell_2} = u(t,\ell_2). \qquad (10)$$

Here: (1), (2), (7), (8) are the diffusion equations with reversible hydrogen capture by the traps at the membrane layers; (3), (9) are initial conditions; (4), (10) are non-linear boundary conditions of the third kind (Neumann conditions); (5), (6) are mating of layers condition; $c(t,x)$, $u(t,x)$ are concentrations of dissolved atomic hydrogen; $z(t,x)$, $w(t,x)$ are concentrations of hydrogen captured by traps; D_1, D_2 are the diffusion coefficients; μ is a kinetic constant; s_1, s_2 are the shiking probabilities of hydrogen molecules to the surface; b_1, b_2 are the desorption coefficients; a_{11}, a_{12}, a_{21}, a_{22} are the coefficients of hydrogen capture and release by the traps; p_0, $p_{\ell_2}(t)$ are for pressures of molecular hydrogen at input and output sides of the membrane; k_1, k_2 are the rates of hydrogen exchange at the layers joint; ℓ_1, ℓ_2 are the thicknesses of the layers; $J(t) = b_2 u_{\ell_2}^2(t)$ is the output desorption flux density. The hydrogen pressure at the output side is lower than at the input side to 8-9 orders of value. Therefore we may neglect hydrogen return at the output side: $\mu s_2 p_{\ell_2}(t) \approx 0$.

It is necessary to determine the coefficients of the protective coat $D_1, b_1, s_1, a_{11}, a_{12}$ and the joint coefficients k_1, k_2 assuming that the hydrogen permeability coefficients of stainless steel are known.

Identification of parameters

Firstly the coefficients D_2, b_2, s_2, a_{21}, a_{22} of stainless steel were determined using experimental data by the identification algorithm based on Fourier series [3, 4] for the concentration pulses method [2]. Identification of the protective coat coefficients D_1, b_1, s_1, a_{11}, a_{12} and the joint coefficients k_1, k_2 is described below.

We can get the following equalities from the model equations (all time derivatives are zero) for the mode of stationary hydrogen permeability:

$$c(t^*,\ell_1)=\left(k_2u(t^*,0)+\bar{J}\right)/k_1,\ \ u(t^*,0)=\bar{J}\ell_2/D_2+\sqrt{\bar{J}/b_2},$$
$$c(t^*,0)=\bar{J}\ell_1/D_1+c(t^*,\ell_1),\quad c(t^*,0)=\sqrt{\left(\mu s_1p_0-\bar{J}\right)/b_1}.$$

Let us equate two last expressions and rewrite them for different values of input pressure p_{0i} and corresponding stationary output flux densities $\bar{J}_i$:

$$A_{1i}X_1+A_{2i}X_2=B_i,\ \ i=\overline{1,n},$$
$$A_{1i}=\bar{J}_i,\quad A_{2i}=\bar{J}_i\ell_2/D_2+\sqrt{\bar{J}_i/b_2},\ \ B_i=\sqrt{\mu s_1p_{0i}-\bar{J}_i},$$
$$X_1=\sqrt{b_1}\left(\ell_1/D_1+1/k_1\right),\quad X_2=\sqrt{b_1}\left(k_2/k_1\right).$$

This is a system of linear equations for unknown X_1,X_2, where right-hand member depends on s_1. We can get $X_1^1(s_1),X_2^1(s_1)$ choosing a pair of pressures and solving these equations for different values of s_1. Another pair of $X_1^2(s_1)$, $X_2^2(s_1)$ is received similarly for a second different pair of pressures. Then $s_1=\arg\min(X_2^1(s_1)-X_2^2(s_1))$. For the known s_1 we determine the values $X_1=X_1^1(s_1)$, $X_2=X_2^1(s_1)$.

Coefficients a_{11},a_{12} define only flux evolution and don’t influence on the stationary flux value. From this we get two limitations $X_2=\sqrt{b_1}\left(k_2/k_1\right)$, $X_1=\sqrt{b_1}\left(\ell_1/D_1+1/k_1\right)$ for the parameters D_1,b_1,k_1,k_2, which determinate stationary flux value.

The values s_1, X_2 under the assumption $\bar{c}_0\ge\bar{u}_0$ $\left(\bar{u}_0=u(t^*,0),\ \bar{c}_0=c(t^*,0)\right)$ give us the estimations:

$$b_1\le\bar{J}_{inp}/\bar{u}_0^2,\ \ k_2/k_1\ge\sqrt{\left(X_2\bar{u}_0\right)^2/\bar{J}_{inp}},\ \ \bar{J}_{inp}=\mu s_1p-\bar{J}.$$

The simulation of experimental fluxes allows determining the values of D_1,b_1,k_1,k_2. The limitations and estimations for the coefficients and the concentrations inside the membrane layers were taken into account. This considerably restricted the region of parameters. The coefficients a_{11}, a_{12}, a_{21},a_{22} of hydrogen capture and release by the traps were used to obtain the typical dynamics of reaching the stationary flux level. The kinetic constants were determined using the parameter values for different temperatures.

Results

Let us describe some results of processing the experimental data. The experimental data were given by V.A. Fock Institute of Physics at Saint-Petersburg State University.

Kinetic constant for titanium nitride (TiN).

	D_1	b_1	s_1
preexponential factor	3.74E-6	2.07E-20	3.66E-4
activation energy ($kJ/mole$)	22.44	37.69	78.87

The TiN coefficients (first layer) and layers joint.

T	p_0	D_1	b_1	s_1	a_{11}	a_{12}	k_2/k_1
^0C	$Torr$	cm^2s^{-1}	cm^4s^{-1}		s^{-1}	s^{-1}	
380	20,1	6,00E-08	1,00E-23	1,80E-10	2,00E-02	7,00E-05	2,5
380	126	6,00E-08	3,30E-23	1,80E-10	2,00E-02	6,50E-04	2,5
380	249	6,00E-08	2,17E-23	1,80E-10	1,58E-02	6,89E-04	2,5
600	3	1,30E-07	1,30E-22	7,00E-09	1,24E-01	1,50E-03	2,5
600	9	1,70E-07	1,15E-22	7,00E-09	9,50E-02	2,00E-03	2,5
600	20	1,76E-07	1,00E-22	7,00E-09	1,20E-01	2,40E-03	2,5

The stainless steel (12X18H10T) coefficients (second layer).

T	p_0	D_2	b_2	s_2	a_{21}	a_{22}
^0C	$Torr$	cm^2s^{-1}	cm^4s^{-1}		s^{-1}	s^{-1}
380	20,1	1,50E-06	4,25E-21	1,50E-06	3,50E-03	3,50E-03
380	126	1,50E-06	4,25E-21	1,50E-06	7,00E-03	6,00E-03
380	249	1,50E-06	4,25E-21	1,50E-06	8,10E-03	6,50E-03
600	3	5,77E-06	5,16E-19	7,38E-05	2,20E-01	7,00E-02
600	9	5,77E-06	5,16E-19	7,38E-05	7,40E-02	2,40E-02
600	20	5,77E-06	5,16E-19	7,38E-05	1,00E-01	5,00E-02

Conclusions

Studying hydrogen permeability of TiN and mathematical processing of experimental data allow to determine the kinetic constants of volumetric and surface processes of hydrogen interaction with the coat. The coefficient of shiking probability of hydrogen molecules to the TiN is 4 order of value lower compared to that of stainless steel. This means that adsorption to the surface of TiN is the limiting stage. The low rate of adsorption agrees with the physical conceptions of surface processes and may be explained by peculiar properties of TiN electronic structure. TiN takes place between metals and semi-conductors. The probability of hydrogen molecule dissociation on the surface of TiN is much less than for stainless steel due to low concentration of free charge carriers (it is 3 order of values less at TiN than at metals) and due to the low density of electronic states on Fermi level.

References

1. I.E.Gabis, V.A.Dubrovsky, E.A.Denisov et. al. Hydrogen permeability of titanium nitride. I International Workshop "Interaction of Hydrogen Isotopes with Structural Materials". 2001: 75-82.
2. I.E.Gabis Method of concentration pulses for studying hydrogen transfer in solids. Journal of tech. physics 1999; 69, №1: 99-103 (in Russian).
3. Yu.V.Zaika Parametric regularization of hydrogen permeability model with dynamic boundary conditions. Mathematical modeling 2001; 13, N11: 69-87 (in Russian).
4. Popov V.V., Gabis I.E., Sidorov N.I., Zaika Yu.V. Studying hydrogen permeability by method of concentration pulses. Journal of Alloys and Compounds 2005 (at press).