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Kinetics of Hydrogen Penetration into Palladium in Stationary Mode

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It is proposed to use the idea of the rate of hydrogen crossing the metal boundary for the calculation of the hydrogen permeability of palladium-containing membranes. The corresponding kinetic coefficient of proportionality between the hydrogen flux density and the hydrogen chemical-potential jump at the metal boundary is introduced. Criteria for distinguishing between diffusion-limited and surface-limited regimes based on the introduced kinetic coefficients are established. This coefficient is amenable to relatively simple experimental determination by a bending–rebending study of a palladium cantilever. The hydrogen flux density through the membrane is calculated as a function of the diffusion coefficient, membrane thickness, and kinetic coefficients at the entrance and exit surfaces. As revealed, the hydrogen flux density and concentration profile within the membrane are influenced by membrane thickness and the rates of hydrogen penetration at the input and output surfaces. Furthermore, it is proposed a simple scheme for calculating the hydrogen permeability of palladium-containing membranes, providing insights for membrane design and optimization. The concentration of atomic hydrogen at the inlet and outlet of the membrane is determined. The results of hydrogen-permeability calculation converge with relevant literature data. This study sheds light on the factors governing the hydrogen permeability in palladium membranes and offers valuable insights for the

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development of high-performance hydrogen-separation technologies.

Key words: hydrogen, palladium, diffusion, concentration, hydrogen stresses, bending–rebending, penetration.

Запропоновано використовувати ідею швидкості переходу Гідрогену через межу металу для розрахунку водневої проникності паладійових мембран. Введено відповідний кінетичний коефіцієнт пропорційності між густиною потоку Гідрогену та стрибком хемічного потенціалу Гідрогену на межі металу. На основі введених кінетичних коефіцієнтів встановлено критерії розмежування дифузійно-обмеженого та поверхнево-обмеженого режимів. Цей коефіцієнт піддається відносно простому експериментальному визначенню за допомогою дослідження вигину та розпрямлення паладійового кантилевера, закріпленого з однієї сторони під час взаємодії з Гідрогеном. Густина потоку Гідрогену через мембрану розраховується як функція коефіцієнта дифузії, товщини мембрани та кінетичних коефіцієнтів на вході та виході поверхонь. Результати показують, що на густину потоку Гідрогену та профіль концентрації всередині мембрани впливають товщина мембрани та швидкість проникнення Гідрогену на вхідну та вихідну поверхні. Крім того, пропонується проста схема для розрахунку водневої проникності мембран, що містять паладій, надаючи розуміння дизайну й оптимізації мембран. Визначено концентрацію атомарного Гідрогену на вході та виході з мембрани. Результати розрахунку водневої проникності збігаються з відповідними літературними даними. Дане дослідження проливає світло на чинники, що визначають проникність Гідрогену в паладійових мембранах, і пропонує цінну інформацію для розробки високоефективних технологій розділення водню.

Ключові слова: Гідроген, паладій, дифузія, концентрація, водневі напруження, вигин, проникнення.

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1. INTRODUCTION

In light of the rapid development of hydrogen energy and a number of high technologies in various industries, the interest in efficient ways of producing pure hydrogen has increased. One of the most promising, productive and economically profitable ways to produce high-purity hydrogen from industrial gas mixtures containing more than 30% hydrogen is diffusion through metal membranes made of palladium alloys whose permeability for other gases is extremely low (10^{-10} – 10^{-8} cm·s⁻¹·Pa^{-1/2} [1–3]).

The main characteristics of palladium membranes for hydrogen extraction from gas mixtures are the rate of hydrogen penetration through the membrane, their selectivity and stability under working conditions [4–10].

The use of thermodynamically open Pd–H systems is in demand not

only because of palladium's unique hydrogen permeability, but also because of the relative simplicity of its phase diagram [11–13]. This allows the use of palladium as a model material to study the basic interactions of hydrogen with metals. However, the use of pure palladium is limited to temperatures below 300°C and pressures up to 2 MPa and to hydride phases, the transitions between which lead to the destruction of diffusion membranes after several cycles of heating and cooling in a hydrogen atmosphere [13, 14].

The problem of creating industrial membrane separators has not yet been solved, since there are no high-performance palladium alloys that have high selectivity for hydrogen, low ability to expand when saturated with hydrogen, high resistance to corrosive gases and durability in operation above 300°C [15–20]. Given that the membranes are foil and microtubes, the alloys must have high plasticity [21–24]. Therefore, the task of studying the hydrogen permeability of the palladium membrane is topical [25–28].

Our work consists of studying the kinetics (specifically, finding the rate) of the process of hydrogen passing through the membrane [29]. To do this, it is necessary to know the corresponding kinetic coefficients. For the first time, we introduced a clearly defined kinetic γ coefficient, which can be found from a detached experiment.

2. EXPERIMENTAL DETAILS

According to the classical scheme of membrane permeability by hydrogen, the process consists of the following stages [6, 7]: 1) dissociation and chemical adsorption of hydrogen on a metal surface (in our case, palladium), 2) overcoming the surface energy barrier, 3) diffusion flux of atomic hydrogen from the inlet to the outlet surface, 4) transition of hydrogen atoms across the outlet surface, 5) the union of hydrogen atoms into molecules and the desorption of molecular hydrogen from the outlet surface.

In a phenomenological description of hydrogen permeability, we can interconnect processes 1) and 2) at the input surface, as well as 4) and 5) at the output surface. This integration is based on the notion that the hydrogen flux density is proportional to the jump $\mu_{\text{H}_2}/2 - \mu_{\text{H}}$ of the chemo potential at the transition across the interface. Here, μ_{H_2} is the chemo potential of molecular hydrogen, μ_{H} is the potential of atomic hydrogen.

In turn, this jump is proportional to the difference $c_e - c_s$, where c_e is the equilibrium of atomic hydrogen at given pressures and temperatures, c_s is the current concentration of atomic hydrogen immediately below the surface on the metal side.

According to these notions, the hydrogen flux density j through the inlet surface of the membrane (index 1) is

$$j_1 = \gamma_1(c_{e1} - c_1), \quad (1)$$

where γ_1 is the kinetic coefficient of velocity dimensionality, which depends on temperature, surface condition (impurities, defects, roughness), *etc.*, c_{e1} is the equilibrium concentration of hydrogen at the inlet surface of the membrane, c_1 is the current concentration of the atomic immediately below the inlet surface.

This coefficient determines the rate at which two processes occur simultaneously: the separation of hydrogen molecules into atoms on the input surface (or recombination on the output surface) and the penetration of hydrogen atoms through the input surface (passage through the output surface).

The coefficient γ can be called the rate of hydrogen penetration through the surface. Its role and possibilities of experimental determination will be discussed later. The hydrogen flux density through the outlet surface of the membrane is written similarly to (1):

$$j_2 = \gamma_2(c_2 - c_{e2}), \quad (2)$$

where γ_2 is the penetration rate at the exit surface, c_2 is the current concentration on the output side, c_{e2} is hydrogen concentration at the outlet surface.

In the general case with different structure and defectiveness of the input and output surfaces, $\gamma_1 \neq \gamma_2$.

The flux density of hydrogen inside the metal is determined by diffusion processes. In the stationary mode, the flux density is

$$j_i = \frac{D(c_1 - c_2)}{h}, \quad (3)$$

where D is the effective diffusion coefficient of hydrogen, h is the thickness of the membrane.

The above relationship is illustrated by a scheme (Fig. 1) that comes from Wang's classical scheme [30], but it differs significantly from it in the introduction of concentration jumps on the inlet and outlet sides of the membrane and their analytical description.

If hydrogen does not accumulate in the metal, then, all three fluxes j_1 , j_2 and j_i in the stationary mode, should be equal to each other:

$$j_1 = j_2 = j_i, \quad (4)$$

$$\gamma_1(c_{e1} - c_1) = \gamma_2(c_2 - c_{e2}) = \frac{D(c_1 - c_2)}{h}. \quad (5)$$

From the set of equations (5), we find the total flux j , as well as the concentrations c_1 and c_2 of hydrogen on the inlet and outlet surfaces, respectively,

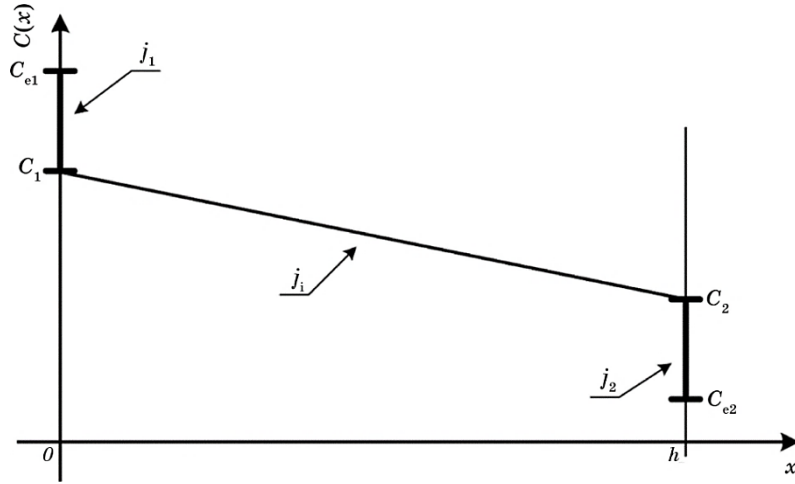


Fig. 1. Concentration profile of hydrogen in the membrane in the stationary-state mode.

$$c_1 = c_{e1} - \frac{c_{e1} - c_{e2}}{\gamma_1(h/D + 1/\gamma_1 + 1/\gamma_2)}, \quad (6)$$

$$c_2 = c_{e2} + \frac{c_{e1} - c_{e2}}{\gamma_2(h/D + 1/\gamma_1 + 1/\gamma_2)}, \quad (7)$$

$$j = \frac{c_{e1} - c_{e2}}{h/D + 1/\gamma_1 + 1/\gamma_2}. \quad (8)$$

3. RESULTS AND DISCUSSION

First of all, note that the equilibrium concentrations, according to Sieverts' law [6, 7], are proportional to the square root of the corresponding pressure [31]:

$$c_{e1} = f(T)P_1^{1/2}, \quad (9)$$

$$c_{e2} = f(T)P_2^{1/2}, \quad (10)$$

where P_1 is the inlet pressure of molecular hydrogen, P_2 is the output, $f(T)$ is a temperature-dependent inverse Sieverts' constant having the dimensionality [$\text{Pa}^{-1/2}$].

From formula (8), we see that the flux density is determined by three parameters: D/h and two permeability rates, γ_1 and γ_2 . If

$$\gamma_1 h / D \gg 1 \text{ and } \gamma_2 h / D \gg 1, \quad (11)$$

then,

$$j = \frac{D}{h}(c_{e1} - c_{e2}) = \frac{D}{h}f(T)(P_1^{1/2} - P_2^{1/2}). \quad (12)$$

If, in the experiment [4], hydrogen is pumped from the outlet side, and the inlet pressure is $P_1 = P$, then, the flux density:

$$j = \frac{D}{h}f(T)P^{1/2}, \quad (13)$$

that is the classical form of Richardson [31] in the DRL (diffusion-limited regime).

In the reverse limiting case, when at least one of two parameters ($\gamma_1 h/D$, $\gamma_2 h/D$) much less than one the SRL mode (surface limited regime) is realized:

$$\frac{\gamma h}{D} \ll 1, (\gamma_1 \rightarrow \gamma), \quad (14)$$

flux density

$$j = \gamma f(T)P^{1/2}, \quad (15)$$

where γ is the smaller of the two (γ_1, γ_2) parameters.

In both limiting cases, the flux density is proportional to $P^{1/2}$, and the proportional coefficients, which can be called hydrogen permeabilities, are determined by different parameters: in the case of DRL, the hydrogen permeability is equal to $(D/h)f(T)$, and, in the case of SRL, it is equal to $\gamma f(T)$.

In general terms, the above reasoning and conclusions are known (see *e.g.*, [30, 32]). However, we found criterion (12) and formula (13), which includes the rate of hydrogen passing through the boundary (γ). The physical meaning and experimental determination of this parameter are discussed in detail in our works [32–36]. In particular, a method for determining the hydrogen penetration rate in palladium from simple bending–unbending experiments of a palladium cantilever is indicated.

Under the conditions of our experiment, maximum bending is achieved in $t_s = 21$ s. The coefficient γ is calculated by the simple formula:

$$\gamma = h / t_s,$$

where $h = 0.27 \cdot 10^{-3}$ m is the thickness of the plate. In the way, we get $\gamma = 1.3 \cdot 10^{-3}$ m/s.

We tested a series of experiments on the bending and unbending of a palladium cantilever at temperatures from 110°C to 350°C. At these temperatures, a solution of hydrogen in palladium is a pure α -phase.

The difference for different temperatures in this range is only in the duration of the experiment and the convenience of recording the results. In this regard, a temperature of 180°C is representative.

The test sample in the form of a thin plate with dimensions (68×5.5×0.27 mm) made of pure palladium (99.98%) was annealed at 700°C for 60 minutes and cooled in a furnace. One side of the annealed sample was electrolytically coated with copper.

In the working chamber of the hydrogen–vacuum installation, the sample was fixed into the holder with one end so that the side of the sample with copper coating was at the top. To remove residual stresses, the fixed sample was subjected to low-temperature vacuum annealing directly in the working chamber: it was slowly heated to the experimental temperature at a rate of 3°C/min and then cooled in the furnace.

The experiments were carried out in the following order. The sample was slowly (3°C/min) heated to 180°C and kept at this temperature for 20 min. After this, under isothermal conditions, diffusion-purified hydrogen was supplied to the working chamber to a given pressure, thus saturating the plate to the alloy composition $\alpha\text{-PdH}_n$, where n is the equilibrium concentration of hydrogen in palladium. Then it was kept in such conditions until the plate returned to its original state. From the start of hydrogen supply ($t = 0$ s), changes in the cantilever deflection through a quartz window in the working chamber were recorded using a cathetometer and a video camera. The resulting video recordings were analysed frame by frame in the Sony Vegas program, which makes it possible to obtain the dependence of the sample deflection arrow on time.

It turned out, for example, that at a temperature of 180°C, palladium plate thickness $h = 0.27 \cdot 10^{-3}$ m and concentration $c_e = 9 \cdot 10^{-3}$ the permeation rate $\gamma = 1.3 \cdot 10^{-5}$ m/s. For such a membrane thickness and for this temperature, with a diffusion coefficient $D = 10^{-9}$ m²/s, $\gamma h/D = 3.5$, that is, criterion (9) is satisfied, and hence Richardson's formula works.

For a specific numerical determination of hydrogen permeability, it is necessary to know the inverse Sieverts' coefficient. In estimating it, we used the values of the enthalpy of hydrogen dissolution in palladium $\Delta H = 4620$ cal/mol [6, 7] and the residual entropy $\Delta S = 25.5$ cal/(K·mol) [6]. As a result, we obtained that:

$$f(T) = 0,53 \cdot 10^{-5} \cdot 10^{502/T} \text{ Pa}^{-1/2}, \quad (16)$$

where T is the temperature in Kelvin's degrees.

For the hydrogen permeability in the SLT mode, using the results we obtained earlier [32–36] for γ , we obtain:

$$\gamma f(T) \approx 10^{-7} \text{ cm} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1/2}.$$

The corresponding flux density at a pressure of 10^4 Pa is of 10^{-5} cm/s, which is close in order to the flux density for the coated sample [4] studied in [4, 32–36].

Thus, the calculated and experimentally obtained [32, 33] values of the rate γ of hydrogen penetration through the palladium–molecular hydrogen interface make it possible, using our model, to estimate with the accepted accuracy the hydrogen permeability of palladium-containing membranes. It seems to us that our scheme can also be applied to calculate the hydrogen permeability of other metallic membranes.

Let us consider further, the distribution of hydrogen over the membrane thickness in the stationary-state mode. For certainty, let us consider the case when hydrogen is pumped out of the working chamber from the side of the outlet surface. In this case, $c_{e2} = 0$. The inlet and outlet concentrations of atomic hydrogen, according to (6) and (7), have the form, respectively:

$$c_1 = c_{e1} \left(1 - \frac{1}{\gamma_1(h/D + 1/\gamma_1 + 1/\gamma_2)} \right), \quad (17)$$

$$c_2 = \frac{c_{e1}}{\gamma_2(h/D + 1/\gamma_1 + 1/\gamma_2)}. \quad (18)$$

From formulas (17) and (18) it is clear, that at low permeation rates through the outlet surface of the membrane ($\gamma_2 \rightarrow 0$) both concentrations c_1 and c_2 , are close to c_{e1} . This means that atomic hydrogen fills the entire membrane with a concentration close to the equilibrium concentration at a given pressure of molecular hydrogen at the inlet. If $\gamma_1 \rightarrow 0$, however, the hydrogen concentration in the membrane is close to zero, *i.e.*, hydrogen hardly penetrates the membrane. In both of these cases, the hydrogen permeability of the membrane is small in proportion to the smallness of γ_1 or γ_2 .

In the symmetric case, when $\gamma_1 = \gamma_2 = \gamma$, that is, when both surfaces have the same permeability, the hydrogen flux density:

$$J = \frac{c_{e1} - c_{e2}}{h/D + 2/\gamma} = \frac{D}{h} \frac{c_{e1} - c_{e2}}{1 + 2D/\gamma h}. \quad (19)$$

The multiplier $1/2$ appears in the criterion for the applicability of the Richardson formula, that is, the DLT mode,

$$\gamma h / 2D \gg 1. \quad (20)$$

In the reverse limiting case, in the SLT mode, with $\gamma_1 = \gamma_2 = \gamma$, it follows from formulas (17) and (18) that the concentrations c_1 and c_2 are close to each other. If, in addition, hydrogen is pumped from the outlet

side, *i.e.*, $c_{e2} = 0$, then $c_1 \approx c_2 \approx (1/2)c_{e1}$. This means that the hydrogen concentration is homogeneous over the thickness of the membrane, and that only half of the hydrogen approaching the inlet side penetrates the metal.

4. CONCLUSION

1. A simple scheme for calculating the hydrogen permeability of palladium-containing membranes based on the notion of the rate of hydrogen penetration through the hydrogen–metal interface has been proposed.
2. The hydrogen flux density and hydrogen concentration profile in stationary-state mode as a function of membrane thickness, diffusion coefficient, and hydrogen penetration rates through metal boundaries were calculated. Formulas have been introduced that quantify the increase in hydrogen permeability and membranes with the increase in the coefficients we introduced, γ_1 and γ_2 .
3. It is indicated that it is quite possible to use the results of calculations and experiments on bending–rebending of palladium cantilevers outlined in our papers to determine the penetration rate.
4. It was found that the hydrogen concentration in the metal, in the stationary mode, is close to zero, when the penetration rate of the input surface is low and close to the equilibrium concentration when the crossing rate of the output surface is low.
5. The criteria for the implementation of the DLT (diffusion limited regime) and SLT (surface limited regime) modes are written using the kinetic coefficients we introduced, such as the hydrogen crossing rates of metal surfaces.

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