

PLASMA DYNAMICS AND PLASMA WALL INTERACTION KINETICS OF HYDROGEN PERMEATION THROUGH W-Pd BIMETALLIC SYSTEMS

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The experimental investigations had been carried out of the kinetics of hydrogen permeation through W-Pd bimetallic systems. The possible mechanisms had been suggested and analyzed to explain the observed anomalies in the hydrogen permeation behavior of such systems, on the assumption of measured isotherms and isobars of hydrogen permeability, energy state of hydrogen in W-Pd system, and theory of hydrogen diffusion in the systems, which contains large number of closed and interconnecting pores.

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1. INTRODUCTION

Knowledge of performances of hydrogen isotope behavior in materials, in particular, of hydrogen isotope permeability, is necessary for control of hydrogen isotope recycling and inventory in controlled fusion devices [1], estimation of construction material state, etc. For tungsten what is one of the most perspective material for manufacture of some plasma facing components in a future fusion reactor, the available data on hydrogen isotope behavior are very limited. Especially it applies to data on the hydrogen permeation process when hydrogen diffuses through tungsten from bulk of others materials to vacuum chamber of plasma devices. To simulate this process in the wide range of hydrogen concentration, one can use palladium, as the bulk metal for tungsten-film. The permeation data in such researches obtained could be also useful for creation of diffusion membrane for active control of hydrogen isotope recycling [2], atomic and hydrogen energy, etc.

2. EXPERIMENTAL AND RESULTS

The scheme of the experiment is clear from Figure 1. Samples for study were the 99.98% pure palladium tubes of 6mm diameter and of 0.25mm thickness coated by W-films manufactured by vacuum-arc method (vacuum-plasma deposition, VPD, method) and chemical vapor deposition (CVD) method. During VPD the conditions were: potential on the Pd-substrate was -20V, arc current was 170A, deposition rate was 10 $\mu\text{m}/\text{h}$, substrate temperature was 500°C. Thickness of VPD W-films was $\approx 2 \mu\text{m}$ and 4 μm and there were some amount of droplets on the coating surface. Under CVD the conditions were: substrate temperature was 700°C, tungsten hexacarbonyl pressure was 0.1 Pa, deposition rate was 10 $\mu\text{m}/\text{h}$. The thickness of CVD films was from 0.2 to 10 μm . The outer surface of the membrane-pipe was presented to the vacuum chamber, which was pumped by turbomolecular pump, while the inner surface was in contact with hydrogen over the pressure range from 1 to 760 Torr. The membrane was heated by directly running the current through it. The temperature was controlled by a Chromel-Copel thermocouple located inside the Pd-pipe.

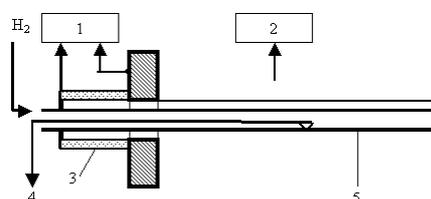


Fig. 1. Scheme of the experiment for measurement of hydrogen permeation rate in W-Pd systems: 1 – system of sample heating, 2 – pumping system, 3 – isolator, 4 – thermocouple, 5 – diffusion membrane (W-Pd)

The specific hydrogen flow (permeation rate) j through membrane was measured by constant pressure method. During the experiments, first the vacuum chamber was pumped out to a pressure of about 5×10^{-6} Torr, then the membrane heating at highest possible temperature $T=973\text{K}$ started. After pumping out the gases, membrane-desorbed due to heating, the pressure in the measurement chamber settled again at a value of about 5×10^{-6} Torr and the fixed hydrogen pressure P over the pressure range 1-760 Torr was supplied to the inner side of the Pd-pipe. Hydrogen pressure in the vacuum chamber increased for different samples over the range from 5×10^{-6} Torr to 5×10^{-2} Torr. When the gas flow to vacuum chamber eventually attained a steady-state value p , the latter was measured. Knowing this pressure and pumping speed S one can calculate hydrogen permeation flow, or specific hydrogen permeation flow through membrane, according to equation $j = pS/F$, where F is the membrane surface area. The typical pressure dependencies of hydrogen permeation flow (isotherms) through bare Pd and through bimetallic W-Pd system are shown in Fig. 2. Figure 3 shows the temperature dependencies (isobars) of hydrogen permeation through W-Pd systems. For comparison, the permeation data are also presented for bare Pd. The activation energy E of hydrogen permeability was determined from the slope of $\ln(j) = -b - E/RT$ straight lines as functions of the inverse temperature (Fig.3). For bare palladium the activation energy E was calculated to be (10.4 ± 0.52) kcal/mol that is higher than 3-4 kcal/mol reported in [3-5].

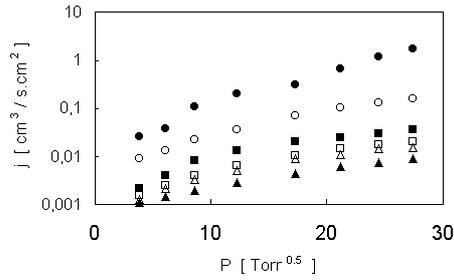


Fig. 2. Permeability isotherms: closed and open circles – Pd (700°C and 400°C), closed and open squares – (2µm W)-Pd (700°C and 400°C), open and closed triangles – (4µm W)-Pd (700°C and 400°C)

It could be explained by higher carbon concentration on the inner surface of Pd-pipes and non-activated state of palladium [5]. The activation energy of hydrogen permeability for W-Pd systems was calculated to be (2.9 ± 0.15) kcal/mol and (2.85 ± 0.14) kcal/mol for 2 µm and 4 µm W-film thickness, accordingly. The similar values had been obtained for W-films manufactured by CVD method.

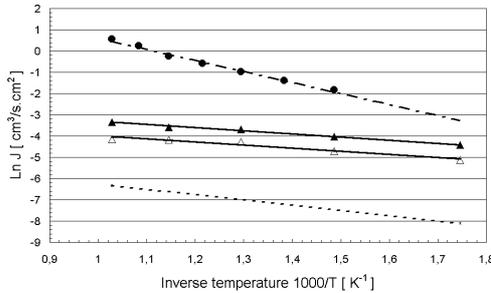


Fig.3. Permeability isobars (hydrogen pressure $P=760$ Torr): closed circles – bare Pd, closed triangles – (2µm VPD W)-Pd, open triangles – (4µm VPD W)-Pd, dash line – calculated curve of hydrogen permeation of (4 µm W)-Pd system at the 5×10^{19} at.H/cm³ (760 Torr) hydrogen concentration on the inlet side of tungsten film

3. DISCUSSION

It is seen in Fig.2 that absolute values of hydrogen flows through W-Pd membranes in two orders lower than that for bare Pd-membranes. The measured values of relative permeability (the ratio of specific hydrogen permeation flow through the W-coated membrane to the one through bare Pd-membrane) $j/j_0 \approx 1\%$. It is the lowest value among the earlier examined materials (Ti, Zr, Nb, Cr, Ni, stainless steel, Cu, Mo, TiN and others [2]) under low pressure molecular hydrogen. This confirms the fact that tungsten is the one of the most hydrogen permeation resistive materials not only for molecular hydrogen but for active hydrogen which diffuses from palladium bulk (hydrogen in palladium is in the activated, atomized and partially ionized state, similar to plasma state [6, 7]). The dependence of hydrogen permeation flow through W-Pd membranes is near to $j(P) \sim P^{0.5}$ with some deviations at high temperatures and pressures. The permeation flow inverse dependence on W-film thickness is also realized. It means that the hydrogen permeation through W-film determines the permeation process in whole W-Pd

system. The hydrogen diffusion could be the limiting process, but as it can be seen in the Fig.3 and from the table, presented below, the values of activation energy of hydrogen permeation through W-Pd bimetallic systems E are much lower than that the ones E_m for the bulk W under gas-driven permeation experiments reviewed in [1,8]. Moreover, these values are even lower than the ones for activated Pd. What are the reasons of such behavior?

Membrane material	E, kcal/mol	E_m , kcal/mol	Ref.
2µ PVD W-Pd	2.9	31.5; 33	[1]; [8]
4µ PVD W-Pd	2.85	31.5; 33	[1]; [8]
4.5µ CVD W-Pd	2.7	31.5; 33	[1]; [8]
9µ CVD W-Pd	2.65	31.5; 33	[1]; [8]
Pd	10.4	3.74; 3.7; 3.7	[3]; [4]; [5]

The activation energy of hydrogen permeation through metal is summarized as $E = E_s + E_D$, where E_s is the activation energy of solubility and E_D is the activation energy of diffusion. Even if to put $E_s = 0$, and $E = E_D$, one would have expected higher values of activation energy of hydrogen permeation in W-films.

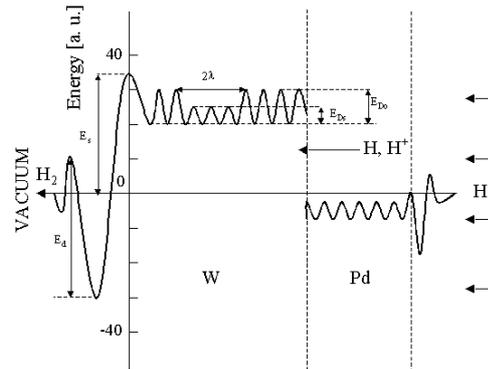


Fig. 4. Potential diagram of hydrogen interaction in W-Pd system: E_d is the activation energy of desorption and recombination, E_s is the activation energy of solution, E_{D0} is the activation energy of hydrogen diffusion in W-film bulk, E_{Ds} is the activation energy of hydrogen diffusion in the subsurface layer of thickness 2λ

For specific hydrogen flow through W-films one can write the next equation: $j = K_0 l^{-1} F^{-1} c(T) e^{-(E_D + E_s)/RT}$, where K_0 – hydrogen permeability constant for tungsten, l – W-film thickness. Note, that instead of usually used $P^{0.5}$, the term $c(T)$ -hydrogen concentration in Pd had been put in the equation. Under temperature change from 700°C to 300°C hydrogen concentration in the palladium increases in two times from 0.8 to 1.6 at.% [9]. It is sufficiently high hydrogen concentrations as 10^{21} H/cm³ and 2×10^{21} H/cm³ instead of 5×10^{19} H/cm³ in the molecular hydrogen at 1 atm. pressure. So, Pd-substrate plays in the W-Pd system the role of the original “compressor”, which provides the significant increase of hydrogen pressure (H-atoms and ions) on the inlet side of W-film (20 and 40 atm. instead of 1 atm.). In this case the inverse temperature dependence of hydrogen concentration on the W-Pd interface strongly influences

on the temperature dependence of hydrogen permeability and correspondingly, on activation energy value. If to put hydrogen concentration on the inlet side of W-film to be 5×10^{19} H/cm³ (1atm.) and its independence on the temperature, then we will get much lower hydrogen flow and higher values of activation energy (dash line in Fig.3). Nevertheless, these values essentially lower than the literature data for molecular hydrogen penetration through W. So, not only increase of hydrogen pressure, but also the above mentioned active state of hydrogen (atoms/ions) on the inlet side of W-film can play the important role in permeation process.

The next reason to explain the extremely low E values could be an anomalous diffusion of hydrogen along the network formed by communicating (non-through/closed) pores [10]. The following expression had been obtained for the effective diffusion coefficient $D_{\text{eff}} = (\pi/2)\lambda\rho_0D_s$, where D_s is the diffusion coefficients in the subsurface layer of thickness 2λ , the diffusion in the latter being easier; ρ_0 is the length of network lines per cm². The D_{eff}/D_0 , where D_0 is diffusion coefficient in the metal bulk, was estimated in [10] to be in the range $10^{-10} - 10^{-2}$. This model of anomalous diffusion in the system with a network of interconnecting pores makes it possible to explain decrease in the activation energy in comparison with the bulky specimens (E and E_m in the table, presented above). The activation energy is given by the barrier heights in migration of diffusing atoms; it can be reduced in the 2λ subsurface layer owing to an increased density of defects (vacancies, dislocations, etc.). So the flow density of hydrogen atoms (ions) in this layer will depend only slightly on the temperature (the activation energy is low).

4. CONCLUSIONS

Hydrogen permeation flow through palladium coated by micron W-films in two orders of magnitude lower than that through bare palladium. It confirms the fact that tungsten is the one of the most hydrogen permeation resistable metal not only for molecular hydrogen but for activated hydrogen (atoms/ions), too. The limiting stage

of hydrogen permeation through W-Pd bimetallic system, seemingly, is diffusion in W-film. But the strong influence is exerted on this process by the inverse temperature dependence of hydrogen concentration in the range of film-Pd interface, the activated state of hydrogen in Pd, and anomalous diffusion in the system with a network of interconnecting pores in W-films. These factors leads to decrease of activation energy of hydrogen permeability in more than one order of magnitude in comparison with bulk tungsten under molecular hydrogen driven permeability (2.9kcal/mol, instead of ≈ 33 kcal/mol).

To understand more exactly the reasons of anomalous behavior of hydrogen permeability in W-Pd systems the additional investigations are needed including examination of others bimetallic systems.

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КИНЕТИКА ПРОНИКНОВЕНИЯ ВОДОРОДА ЧЕРЕЗ W-Pd БИМЕТАЛЛИЧЕСКИЕ СИСТЕМЫ

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Проведены экспериментальные исследования кинетики проникновения водорода через W-Pd биметаллические системы. Предложены возможные механизмы для объяснения обнаруженных аномалий в поведении водородопроницаемости таких систем, исходя из измеренных изотерм и изобар водородопроницаемости, энергетического состояния водорода в системе W-Pd и теории диффузии в системах с большим количеством замкнутых и сообщающихся пор.

КИНЕТИКА ПРОНИКНЕННЯ ВОДНЮ КРИЗЬ W-Pd БИМЕТАЛІЧНІ СИСТЕМИ

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Проведено експериментальні дослідження кінетики проникнення водню через W-Pd біметалічні системи. Запропоновано можливі механізми для пояснення виявлених аномалій у поведженні воднепроникнення таких систем, виходячи з обмірюваних ізотерм і ізобар проникнення водню, енергетичного стану водню в системі W-Pd і теорії дифузії в системах з великою кількістю замкнутих і сполучених пор.