

## INFLUENCE OF POROSITY ON EROSION BEHAVIOR AND HYDROGEN PERMEABILITY OF TUNGSTEN FILMS

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The erosion characteristics of dense and porous W-films deposited on Pd substrates were measured under impact of mirror Penning discharge nitrogen plasma. It is shown that the erosion rate of high porous tungsten films (up to 45% porosity) is similar to that for dense (1 – 3% porosity) tungsten films. At the same time hydrogen permeation through porous tungsten films essentially higher than for dense W coatings and in some cases it approaches to values as for bare Pd. The activation energies of hydrogen permeability measured for two-layer Pd-W systems with high porosity are higher than for dense W-films on Pd (15.44 kJ/mol and 12.8 kJ/mol, accordingly), but these values much lower than the ones for bulk W under gas-driven permeation experiments. The possible reasons of such erosion and permeation behavior are discussed.

### INTRODUCTION

It was reported in [1] that an erosion coefficient of vacuum-plasma deposited (VPD) and chemical vapor deposited (CVD) dense W-films on Pd is near to that for bulk tungsten, but hydrogen permeability of such two-layer systems is much lower (up to two orders of magnitude for CVD W-films) than for bare palladium. To create more effective diffusion system, it is needed to increase hydrogen penetration through W films and the increasing their porosity is the possible way for this. It was also presented in [1] the effect of the W erosion rate decrease in 2 – 5 times under nitrogen plasma impact for Pd-W system in hydrogen saturated state, in compare with non-saturated state. It has been suggested to explain such effect by selective hydrogen sputtering. To confirm the reality of such mechanism it was necessary to examine the erosion behavior of such diffusion system under impact of plasma discharges in nitrogen-hydrogen mixtures, the more so as such discharges have perspective to be used for wall conditioning in plasma devices [2]. So, in this work it were studied the influence of porosity and hydrogen admixture to nitrogen on an erosion behavior of W films on Pd and the influence of porosity on kinetics of hydrogen penetration through such two-layer systems.

### EXPERIMENTAL AND RESULTS

The experimental setup used in the **erosion experiments** was the device DSM-1 [3.] with steady state mirror Penning discharge, which was ignited at magnetic field 0.05 T and at work gas pressure about 0.2 Pa. Plasma characteristics measured by multigrid and single Langmuir probes (central and peripheral discharge regions, accordingly) are presented in tabl. 1, where  $U$  is discharge voltage,  $I$  is discharge current,  $T_e$  and  $n_e$  are electron temperature and electron density,  $\phi$  is plasma potential,  $E_i$  – ion energy for maximum of distribution function,  $\Delta E_i$  – half-width of distribution function.

Table 1

Nitrogen plasma characteristics in discharges with porous W cathodes

Discharge voltage and current		Edge plasma characteristics for porous/dense cathodes			Central plasma characteristics	
$U$ , keV	$I$ , mA	$n_e \cdot 10^{10}$ , part./cm <sup>3</sup>	$T_e \cdot 10^4$ , K	$\phi$ , B	$E_i$ , eV	$\Delta E_i$ , eV
0.8	0.8	0.03/0.1	0.62/0.90	9/7	0.62	50
1	2.2	0.05/0.15	0.48/0.71	12/9	0.85	60
1.2	5	0.13/0.17	0.37/0.67	12/13	0.93	75
1.5	8	0.15/32	0.32/0.52	15/13	1.15	93
1.7	10	0.22/65	0.30/0.35	14/15	1.32	110
2	16	0.31/93	0.30/0.28	16/16	1.57	132

The samples for studies were W films vacuum-plasma deposited on palladium foils of 25mm diameter (for erosion experiments) or on the 99.98% pure Pd tubes of 6 mm diameter, 0.25 mm thickness and 190 mm length (for permeation studies). To produce dense tungsten coatings (1 – 3% porosity), the deposition was carried out at high vacuum or at argon pressure lower than  $\approx 0.6$  Pa. The porous W-coatings (about of the 45% porosity) were deposited at argon pressure higher than 10 Pa. Coating thicknesses were measured by two different methods: by weighting of probes before and after deposition and by optical measurements on metallographic sections. Porosity level was estimated as the difference among thicknesses determined by different methods. Metallographic and electron microscope investigations show the large number of pores in tungsten films (fig. 1).

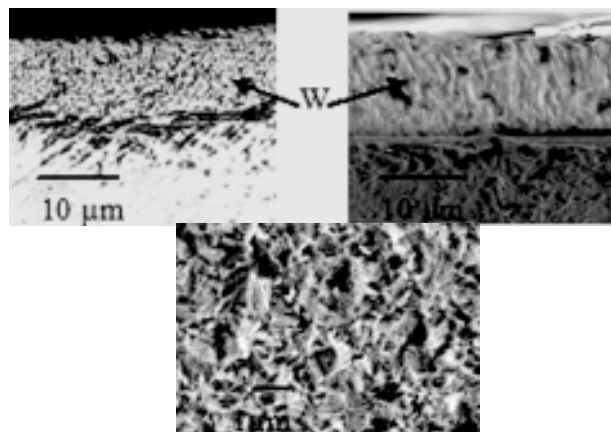


Fig. 1. The metallographic microscopic sections (left, center – before and after annealing) and surface morphology (right) of 15  $\mu\text{m}$  W film deposited at Ar pressure of 10.4 Pa.

Erosion coefficient values were measured by weight loss method reviewed in details in [1, 3]. The main results on erosion are presented in fig. 2 and fig. 3. It is seen, that erosion rate of

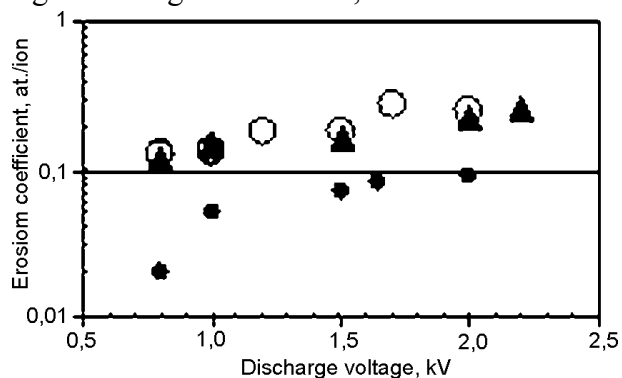


Fig. 2. Erosion coefficient dependence on nitrogen ion energy for Pd-W systems:  $\blacktriangle$  – dense W film,  $\circ$  – W film of the 45% porosity,  $\bullet$  – experimental data for hydrogen saturated W films [2].

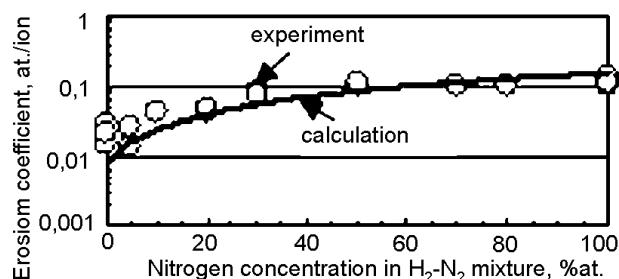


Fig. 3. Tungsten erosion coefficient versus nitrogen concentration in hydrogen: experimental data for 1.2 keV ion irradiation ( $\circ$ ), curve is the calculated data.

porous tungsten films is similar to that for dense tungsten films prepared by W sputtering in high vacuum and that W erosion rate weakly depends on hydrogen admixture to nitrogen up to 40% concentration (fig. 3).

The scheme and methods of **hydrogen permeation experiments** were similar to the used in the previous works [1, 3]. The dependencies of specific hydrogen flow (permeation rate)  $\phi$  through membrane on inlet hydrogen pressure  $p$  and on membrane temperature  $T$  are shown in fig. 4 and fig. 5. From the data of temperature dependencies of hydrogen permeation, the activation energy values  $E$  of hydrogen permeability were calculated to be for two-layer Pd-W systems with high tungsten porosity  $E = 15.44$  kJ/mol (for 9  $\mu\text{m}$  and 14  $\mu\text{m}$  W film thickness). This value of activation energy is higher than for bare palladium (11 kJ/mol) and higher than for dense VPD 4 $\mu$  W-films (11 kJ/mol). But, in any case,

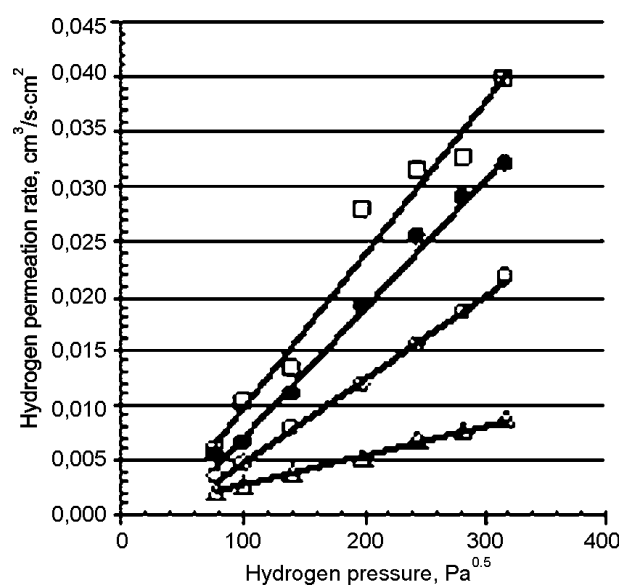


Fig. 4. Hydrogen permeation rate at 973 K temperature versus pressure: bare palladium ( $\square$ ); high porous 14  $\mu\text{m}$ , 9  $\mu\text{m}$  W film on Pd ( $\Delta$ ,  $\blacktriangle$ ); 4  $\mu\text{m}$  dense W film on Pd ( $\circ$ ).

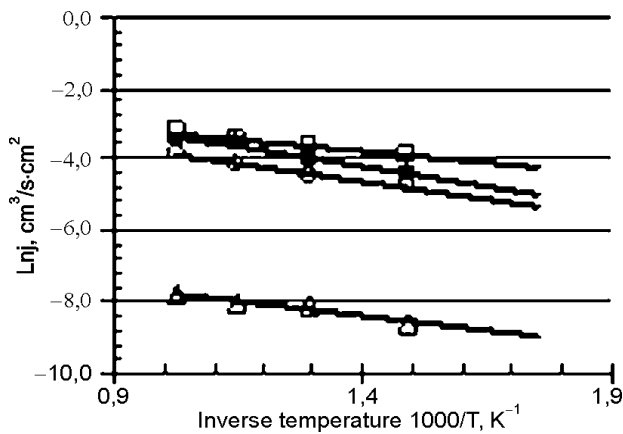


Fig. 5. Temperature dependencies of specific hydrogen flow through two-layer Pd-W systems at  $10^5$  Pa  $H_2$  pressure: bare palladium ( $\square$ ); high porous 14  $\mu\text{m}$  and 9  $\mu\text{m}$  W film on Pd ( $\Delta$ ,  $\blacktriangle$ ); 4  $\mu\text{m}$  dense W film on Pd ( $\circ$ ).

the values of activation energy of hydrogen permeation through W-Pd bimetallic systems are much lower than the one (131.67 kJ/mol) for the bulk W under gas-driven permeation experiments reviewed in [4].

## DISCUSSION

High porous materials have usually very extended surface, so higher erosion rate would have been expected for high porous tungsten films due to possible angle dependence of erosion. Moreover, heavy gas argon could be adsorbed in pores and it could influence on the erosion rate. The absence of an essential influence of W porosity on its erosion behavior (fig. 2) is very encouraging result for creation of plasma facing diffusion system. To explain such erosion behavior one can suppose the strong influence of redeposition processes, when large number of sputtered tungsten atoms deposits on nearest surfaces of W film pores. Note also, that the preliminary measurements of outgassing from high porous Pd-W systems have shown the absence of argon release.

It is seen in fig. 3, that the sputtering weakly depends on hydrogen admixture to nitrogen up to the 40% concentration. Such dependence can be easily explained on the base of mass dependence of erosion rate, according to equation [3]:  $\alpha = \alpha(H^+) \cdot I_H/I + \alpha(N^+) \cdot I_N/I$ , where  $\alpha(H^+)$  and  $\alpha(N^+)$  are the erosion coefficients under hydrogen and nitrogen ion bombardment, respectively;  $I$  is the total ion current;  $I_H$  and  $I_N$  are hydrogen and nitrogen ion currents, respectively. If to

suppose that ion currents are proportional to gas partial pressures, and to take into account that  $\alpha(H^+) \sim 0.01$  [5] we will obtain the curve in fig. 3 which is in close agreement with the experimental points. The visible deviation for pure hydrogen is explained by impurity flow from cathodes during initial stage of discharges as it is earlier shown in [3].

So, hydrogen addition to the main working gas (nitrogen) could not be the reason for reported in [1] and above mentioned effect of an erosion coefficient decrease of hydrogen saturated W. And the physical mechanism, suggested in [1] to explain this effect, is, most likely, hydrogen selective sputtering, similar to the reported in [6] for deuterium saturated lithium under helium ion bombardment.

Hydrogen permeation flow through W-Pd membranes is near to  $j(P) \sim P^{0.5}$  for both dense and porous W-films (see fig. 4). But the unusual film thickness dependence of hydrogen flow is observed: hydrogen flow through 14  $\mu\text{m}$  tungsten layer is higher than through W film of 9  $\mu\text{m}$  thickness. It could be explained by the fact that not only film open porosity increases with thickness increase due to Lifshits-Slyozov-Wagner pore coalescence theory [7, 8], but the porosity of the initial coating layers increases with the deposition time duration increase. The latter seems as unlikely. At the same time the change of film-Pd interface state can take place at the increase of film thickness and heating time increase. Investigations of substrate-film interface have shown that transition layer forms of W solid solution in Pd in Pd-W samples produced at more than 873 K (see fig.1). The additional heating can change transition layer state (width, composition, etc.) and can lead to increase of its role in hydrogen permeation process. Note, the preliminary investigations of the influence of long time baking of dense W-films on hydrogen permeation rate have shown its essential (up to one order magnitude) increase with baking time increase [fig. 6]. The activation energy values increase, too.

Hydrogen flows through porous W-films essentially higher than for micron dense coatings (fig. 4, fig. 5). For 14  $\mu\text{m}$  porous W film the hydrogen permeation rate at high temperatures can be near to that for bare Pd. To recognize the

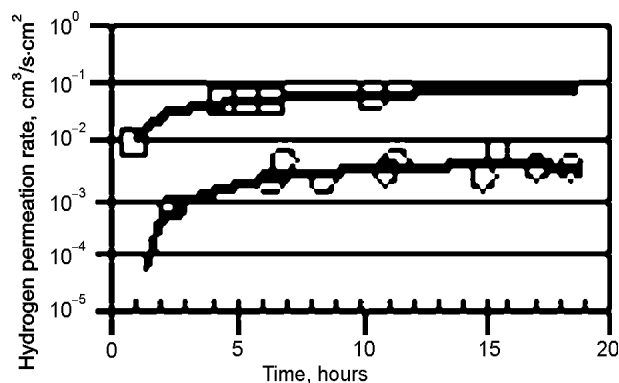


Fig. 6. Hydrogen permeation rate measured at 973 K temperature and at hydrogen pressure of  $10^5$  Pa versus time of baking at 973K temperature:  $\square$  – 4  $\mu\text{m}$  VPD W-film on Pd,  $\circ$  – 300  $\mu\text{m}$  CVD W-film on Pd.

physical reasons for such extremely high hydrogen flows it is necessary to determine the limiting stage of hydrogen penetration. It was analyzed and reported in previous work [1] that hydrogen diffusion in rather dense micron W films is the limiting stage of permeation process in Pd-W two-layer systems. Very low values of activation energy were explained by the two reasons: (i) the inverse dependence of hydrogen concentration on the Pd-W interface and (ii) the anomalous hydrogen diffusion along the network formed by communicating pores. The former provides the significant increase of hydrogen pressure on the inlet side of W-film with temperature decrease and strongly influences on the temperature dependence of hydrogen permeability and, correspondingly, on flow and activation energy values. The latter reduces barrier height for diffusing atoms and also causes the activation energy decrease. Aforesaid reasons can act on hydrogen permeability of Pd-W system with high porous W film, too. Film porosity increase and, especially, open porosity increase provides high hydrogen flows through such films. In this case diffusion in W film can not be the limiting stage, taking also into account the observed permeation inverse dependence on film thickness. Hydrogen solution in Pd and diffusion in Pd bulk can not also be the limiting stage. So the diffusion in transition layer on the Pd-W interface could be the limiting stage. If so, one can explain high hydrogen permeation with film thickness and heating time increase as “interface opening”. Really, it is likely to suppose that an interdiffusion during baking leads to increase of transition layer

width, and to enhancing of its role in permeation process. Of course, in order to get a direct evidence of such mechanism favorability, additional investigations are needed.

If to analyze the results on Pd-W system erosion behavior together with the data on hydrogen permeation, it is came into clear that high porous tungsten films are very convenient material for plasma facing diffusion system creation. Being of high erosion resistant, such films can provide high hydrogen flows through them. These properties could be useful not only for hydrogen recycling control but for tungsten erosion decrease and tritium extraction in future fusion systems.

## CONCLUSION

Erosion coefficients of porous vacuum-plasma deposited W films on palladium are similar to that for dense VPD tungsten films, and there is not essential influence of W porosity on its erosion behavior. It could be caused by the strong influence of redeposition processes, when large number of sputtered tungsten atoms redeposes on nearest surfaces of W film pores.

Hydrogen admixture to nitrogen (up to 40% atom.) does not essentially influence on the W erosion rate. This confirms the hydrogen selective sputtering as the main physical mechanism explaining the early observed effect of W erosion coefficient decrease in hydrogen saturated Pd-W system.

Hydrogen permeation rate through Pd-W systems with high-porous W-films and activation energy of hydrogen permeability for such systems are higher than for Pd-W two-layer systems with dense W coatings. These results could be explained if to suppose the diffusion in transition layer on the Pd-W interface as the limiting stage of Pd-W two-layer system permeation process.

## ACKNOWLEDGMENTS

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### ВПЛИВ ПОРИСТОСТІ НА ЕРОЗІЙНУ ПОВЕДІНКУ І ВОДНЕВУ ПРОНИКНІСТЬ ПЛІВОК ВОЛЬФРАМУ

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Зміряні ерозійні характеристики щільних і пористих плівок вольфраму на паладії при дії азотної плазми відбивних розрядів Пеннінга. Показано, що швидкість ерозії високопористих плівок вольфраму (пористість близько 45%) практично не відрізняється від такої для щільних плівок W (пористість 1 – 3%). У той час проникнення водню крізь високопористі плівки вольфраму багато вище, ніж крізь щільні покриття W і в деяких випадках величини проникності можуть бути близькі до такої для Pd без покриття. Енергії активації водневої проникності зміряні для двошарових систем Pd-W з високою пористістю W вище, ніж для щільних W-плівок на Pd (15,44 кДж/моль і 12,8 кДж/моль, відповідно), але в обох випадках ці величини багато нижче, ніж для масивного W в умовах проникнення з молекулярної фази. Обговорюються можливі причини такої поведінки ерозії і водневої проникності.

### ВЛИЯНИЕ ПОРИСТОСТИ НА ЭРОЗИОННОЕ ПОВЕДЕНИЕ И ВОДОРОДОПРОНИЦАЕМОСТЬ ПЛЕНОК ВОЛЬФРАМА

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Измерены эрозионные характеристики плотных и пористых пленок вольфрама на палладии при воздействии азотной плазмы отражательных разрядов Пеннинга. Показано, что скорость эрозии высокопористых пленок вольфрама (пористость около 45%) практически не отличается от таковой для плотных W пленок (пористость 1 – 3%). В то же время проникновение водорода через высокопористые пленки вольфрама много выше, чем через плотные W покрытия и в некоторых случаях величины проницаемости могут быть близки к таковой для Pd без покрытия. Энергии активации водородопроницаемости измеренные для двухслойных Pd-W систем с высокой пористостью W выше, чем для плотных W-пленок на Pd (15,44 кДж/моль и 12,8 кДж/моль, соответственно), но в обоих случаях эти величины много ниже, чем для массивного W в условиях проникновения из молекулярной фазы. Обсуждаются возможные причины такого поведения эрозии и водородопроницаемости.