

# HYDROGEN PERMEATION THROUGH VPD AND CVD TUNGSTEN FILMS ON PALLADIUM

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Isobars and isotherms were measured for hydrogen permeation through porous tungsten films on palladium, activation energy values were calculated for various Pd-W systems. The analysis of the obtained data and its comparison with the ones for dense tungsten coatings are carried out.

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## 1. INTRODUCTION

It was reported in [1] that an erosion coefficient of vacuum-plasma and chemical vapor deposited dense W films on Pd is near to that for bulk tungsten, but such two-layer system hydrogen permeability is much lower than that for bare palladium. One can increase hydrogen penetration through W films by increasing their porosity. So in this work the investigations were carried out of hydrogen permeability of W-Pd two-layer systems with high porous W-films.

## 2. EXPERIMENTAL AND RESULTS

Samples for studies were W films vacuum-plasma deposited (VPD) and chemical vapor deposited (CVD) on the 99.98 % pure Pd tubes of 6 mm diameter, 0.25 mm thickness and 190 mm length. To produce dense VPD 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 (Fig. 1). Under CVD process the mostly dense films (19.12-19.2 g/cm<sup>3</sup>) were deposited at 973-1073 K temperatures, at pressures lower than 5 Pa. Low density and, accordingly, porosity up to 10-18% was realized at 773-873 K temperatures and 30-50 Pa pressure of vapor-gas mixture. But pressure increase leads not only to W film density decrease, but at the same time leads to impurity concentration increase in films. So, in permeation investigations we used only dense CVD W-coatings. Coating thicknesses were measured by two different methods: by weighting of probes before and after deposition and by measurements on metallographic sections. Porosity level was estimated as the difference among thicknesses determined by different methods.

The scheme (Fig. 2) and methods of hydrogen permeation experiments were similar to the used in the previous works [1, 2].

Permeation rate  $j$  through membrane was measured by the constant pressure method, and was calculated by the equation  $j = PS/F$ , where  $P$  is the increased hydrogen pressure in the vacuum chamber,  $S$  is the pumping speed of hydrogen,  $F$  is the membrane surface area.

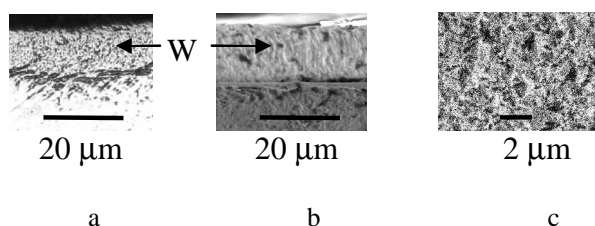


Fig. 1. The metallographic microscopic sections (a, b - before and after etching) and surface morphology (c) of 15  $\mu$ m W film deposited at Ar pressure of 10.4 Pa

The activation energy  $E_p$  of hydrogen permeability was determined from the slope of  $\ln(j) = -b - E/RT$  straight lines as a function of the inverse temperature. The experimental accuracy for specific hydrogen flow and activation energy of hydrogen permeation was about 10% and 5%, accordingly.

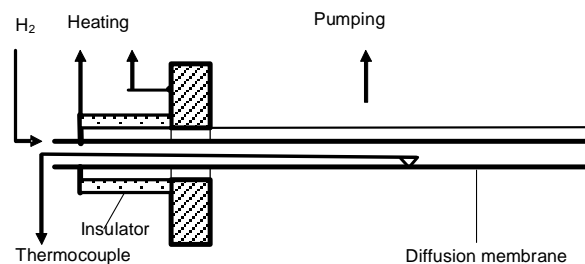


Fig. 2. Experimental scheme of hydrogen permeation experiments

The dependencies of specific hydrogen flow (permeation rate) through membrane on inlet hydrogen pressure and on membrane temperature  $T$  are shown in Fig. 3-6. From the data of temperature dependence of hydrogen permeation the activation energies  $E$  of hydrogen permeability were calculated. For dense CVD/VPD W-films these values are very low  $E = (11.9-13.04)$  kJ/mol as for bare Pd ( $\sim 11$  kJ/mol). For two-layer Pd-W systems with high porous tungsten films  $E=15.44$  kJ/mol (9  $\mu$ m and 14  $\mu$ m W film thickness). Note, that these values are much lower than for bulk tungsten in molecular driven permeation (134 kJ/mol, [3]).

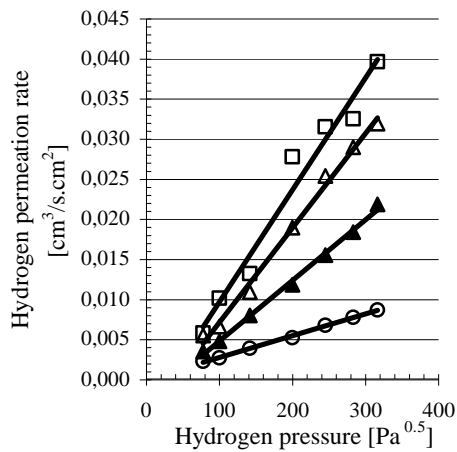


Fig. 3. Hydrogen permeation rate at 973K temperature versus pressure: bare palladium (○); high porous 14 μm and 9 μm VPD W film on Pd (◻, ▲); 4 μm dense VPD W film on Pd (Š)

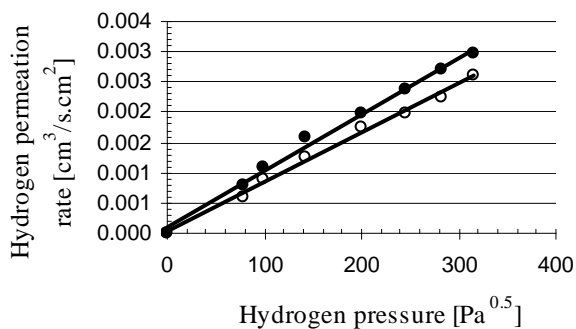


Fig. 4. Hydrogen permeation rate at 973K temperature versus pressure: 130 μm dense CVD W film on Pd (●); 300 μm dense CVD W film on Pd (Š)

### 3. DISCUSSION

The pressure dependence of hydrogen permeation flow through dense both VPD and CVD W-Pd membranes is near to  $j(P) \sim P^{0.5}$ . The inverse dependence of the permeation flow on the W film thickness is fulfilled. So hydrogen permeation through the W film governs the permeation process in the whole W-Pd system and the hydrogen diffusion in the dense W films is most likely the limiting process. The dependence of hydrogen permeation flow through porous W films on Pd is near to  $j(P) \sim P^{0.5}$ , too. But the unusual thickness dependence of hydrogen flow is observed for porous films: for tungsten 14 μm layer (white triangles) hydrogen flow is higher than for W film thickness of 9 μm (black triangles).

It could be explained by the fact that 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.

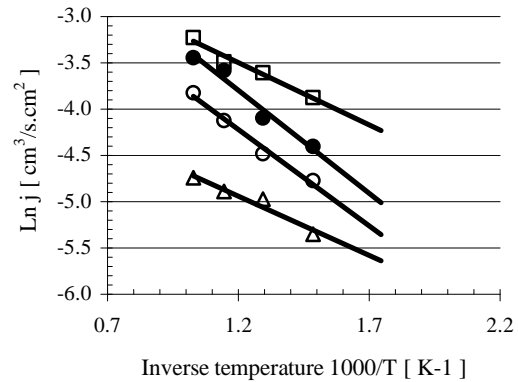


Fig.5. Temperature dependencies of specific hydrogen flow through two-layer Pd-W systems at  $10^5$  Pa  $H_2$  pressure: bare palladium (○); high porous 14 μm and 9 μm VPD W film on Pd (●, Š); 4 μm dense VPD W film on Pd (◻)

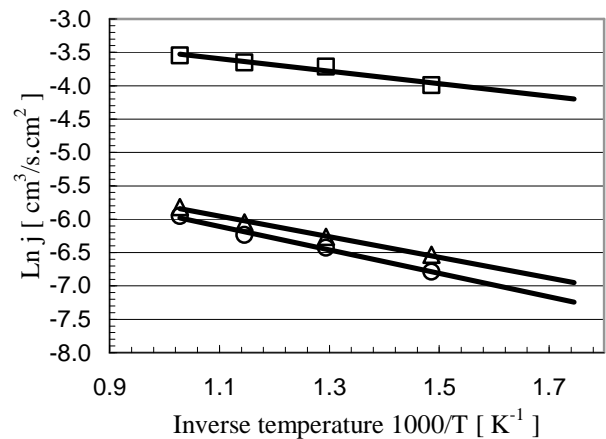


Fig.6. Hydrogen permeation rate temperature dependence ( $10^5$  Pa hydrogen pressure): bare palladium (○); 130 μm dense CVD W film on Pd (◻); 300 μm dense CVD W film on Pd (Š)

When film porosity increases and, especially, open porosity increases, it 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. Of course, in order to get a direct evidence of such mechanism favorability, additional investigations are needed.

### 4. CONCLUSION

Hydrogen permeation 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.

## ACKNOWLEDGEMENTS

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## ПРОНИКНОВЕНИЕ ВОДОРОДА ЧЕРЕЗ ВАКУУМНО-ДУГОВЫЕ И ГАЗОФАЗНЫЕ ПЛЕНКИ ВОЛЬФРАМА НА ПАЛЛАДИИ

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Представлены результаты исследований изобар и изотерм проникновения водорода через пористые пленки вольфрама на палладии, определены величины энергии активации водородопроницаемости в различных системах Pd-W. Проведен анализ полученных данных и сравнение с данными для плотных вольфрамовых покрытий.

## ПРОНИКНЕННЯ ВОДНЮ КРИЗЬ ВАКУУМНО-ДУГОВІ І ГАЗОФАЗНІ ПЛІВКИ ВОЛЬФРАМУ НА ПАЛАДІЇ

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Представлено результати дослідження ізобар та ізотерм проникнення водню крізь пористі плівки вольфраму на паладії, визначені величини енергії активації водневої проникності у системах Pd-W. Проведено аналіз одержаних даних і порівняння з даними що до щільних вольфрамових покриттів.