

HYDROGEN SATURATION INFLUENCE ON EROSION BEHAVIOR OF THIN W-FILMS UNDER STEADY STATE NITROGEN PLASMA IMPACT

G.P. Glazunov, A.A. Andreev, D.I. Baron, E.D. Volkov, A. Hassanein*,
K.M. Kitaevskiy, A.L. Konotopskiy, V.I. Lapshin, I.M. Neklyudov, A.P. Patokin

NSC Kharkov Institute of Physics and Technology, Kharkov, Ukraine;

**Argonne National Laboratory, 60439 Argonne, IL, USA*

The erosion behavior of W-Pd bimetallic system was examined for both hydrogen saturated and non-saturated states under impact of steady state nitrogen plasma of a mirror Penning discharge. Possible physical mechanism is discussed to explain the essential decrease of erosion rate and damages of such systems (form change, macro-blistering and macro-flaking) caused by hydrogen saturation to high concentration.

PACS: 52.40.Hf, 79.20.R

1. INTRODUCTION

The interaction of hydrogen isotopes with structural materials in fusion devices leads to changes of material performances such as mechanical characteristics, erosion rate, arc ignition probability, reflection coefficient, electron emission coefficient, etc. In turn, the different material states (hydrogen saturated or non-saturated states) vary plasma properties due to the change of hydrogen recycling coefficient. The control of hydrogen recycling coefficient during work of fusion device is very important problem [1]. For such control it was suggested earlier [2] to use bimetallic (two-layer) diffusion systems, which comprise of a rather thick palladium substrate (it could be another material with high hydrogen diffusivity) and an erosion resistant coating on the plasma facing surface of substrate. The material for such coating could be, e.g., tungsten as the most erosion resistible material. To choose the optimal performances of tungsten-palladium bimetallic system, it is needed to carry out thorough investigations of its properties under plasma impact. In particular, it was of a great interest to look the erosion behavior of W-Pd bimetallic system in hydrogen saturated and in non-saturated states.

2. EXPERIMENTAL

The experimental setup DSM-1 (Diagnostic Stand of Materials) used for plasma impact studies was described in [3, 4]. Working gas pressure (during sputtering experiments it was nitrogen) in vacuum chamber was 0.266 Pa. A mirror Penning discharge was ignited at magnetic field $B \approx 0.05$ T that was produced by two pairs of coils. Cathodes potential values were in the range $U = 1-2$ kV. Irradiation fluence was $10^{18}-10^{19}$ ions/cm². The samples for studies were the 99.98% pure palladium foils coated by tungsten films of different thickness. Vacuum-arc sputtering method or vacuum-plasma deposition (VPD) [5], and method of chemical vapor deposition (CVD) [6] were used for W-film manufacture. The deposition of films by W-rod sputtering in situ in DSM-1 vacuum chamber was also applied. In the latter two symmetrical cathodes were connected by W-rod of 5mm diameter and so called "rodtron" configuration, similar to cylindrical magnetron-type discharge (CMD), was realized (Fig.1).

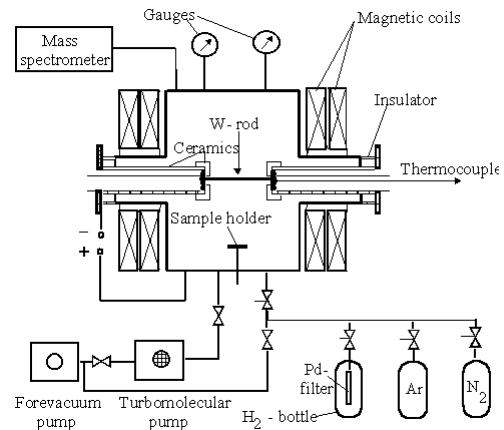


Fig.1. The experimental setup DSM-1 scheme during W-film deposition

Experimental technique for erosion rate measurement by weight-loss method had been described in detail in the previous works [3, 4]. It should be only noted, that erosion rate measurements for samples saturated to high hydrogen concentration were carried out by two ways. The first was, when to determine weight loss of the irradiated sample, it was placed in the special vacuum chamber and was baked at the temperature of 600°C in vacuum $1.33 \cdot 10^{-4}$ Pa during one hour to remove the residuary amount of dissolved hydrogen. The second one was, when the irradiated samples were exposed to hydrogen at pressure of 2 atm. during many hours to reach initial high hydrogen concentration in the Pd-substrate (usually about $H/Pd=0.65$). Erosion coefficients determined by these different methods were like with the experimental accuracy $\approx 30\%$. The main error was determined by ion current measurements ($\approx 25\%$) and was caused by some current instability on the initial stage of discharges due to impurity flow from cathodes.

3. RESULTS AND DISCUSSION

Erosion coefficient dependencies on fluence for W-films on Pd manufactured by different methods are shown in Figure 2. For comparison, the literature data for bare Pd[4] and bulk W[7], as well as our experimental results for rolled W-sheet of 0.1 mm thickness obtained in the

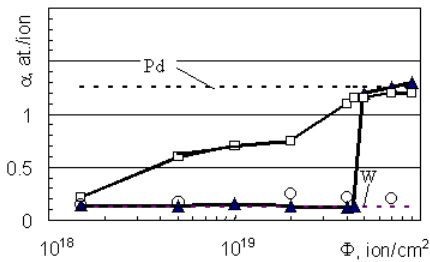


Fig. 2. Erosion coefficient dependencies on fluence Φ : dotted lines are the literature data for Pd [3] and W [8], empty circles are the present experiment data for 0.1 mm rolled W-sheet, empty squares are the experimental data for 0.1 μm W-films made in magnetron-type discharges, and solid triangles are the experimental data for 1.5 μm VPD W-films

similar conditions as for W-Pd system are presented in this figure, too. It is seen, that fluence dependencies are different for coatings made by different methods. For W-films made by VPD and CVD the erosion coefficient values are near to that for bulk tungsten presented in the work [7] ($\approx 0.15 \text{ at./ion}$, $E=1.2 \text{ keV}$), and it does not change up to the fluence Φ about $4 \cdot 10^{19} \text{ ion/cm}^2$ (for 1.5 μm W-film thickness).

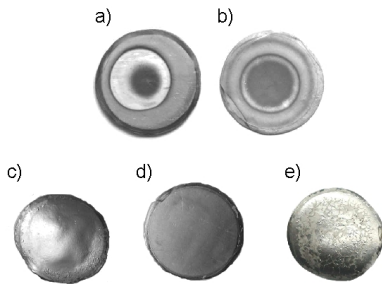


Fig. 3. W-Pd samples ($\times 0.6$) after nitrogen plasma irradiation with the fluence Φ about $7 \cdot 10^{19} \text{ ion/cm}^2$: (a) – 1.5 μm VPD W-film, (b) – 0.1 μm CMD W-film, (c) – form of (4 μm W)-Pd sample after hydrogen saturation to concentration $H/Pd=0.65$, (d) – the same one before saturation, (e) – (4 μm W)-Pd sample after repeated long time hydrogen saturation up to high concentration at room temperature

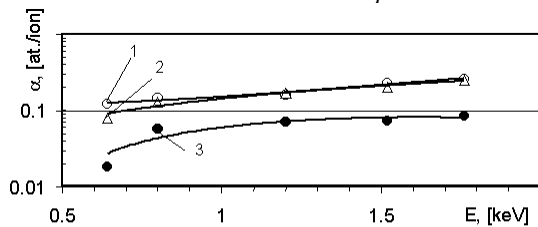


Fig. 4. Dependencies of erosion coefficient on nitrogen ion energy for W-Pd bimetallic systems in hydrogen saturated (1-VPD 4 μm W-film, 2- CVD 5 μm W-film) state and non-saturated (3) state

At the further fluence increase the sputtering rate extremely increases up to typical values for palladium (1.3 at./ion at 1.2 keV ion energy [3]) due to full film sputtering (Fig. 3a, 3b). In the case of W-coatings made in magnetron-type discharge in DSM-1, erosion coefficient monotone increases with an exposure time. Such erosion

behavior one can explain taking into account that VPD and CVD W-films were manufactured at a rather high substrate temperature (500°C and 800°C, accordingly), when film porosity is sufficiently low. The W-films manufactured in the cylindrical magnetron-type discharge in the DSM-1 are characterized by high porosity, including open porosity, because deposition was carried out at low substrate temperature ($\approx 50^\circ\text{C}$). So, taking into account small thickness, in this case it could be parallel erosion both W and Pd with permanently increasing of palladium part.

The erosion coefficient values measured depending on nitrogen ion energy for W-Pd systems in hydrogen-saturated and non-saturated states are shown in Fig. 4. It is seen that erosion of hydrogen saturated W-Pd samples under N^+ ion bombardment was observed in ≈ 2 -5 times lower than that for non-saturated samples. Note that during hydrogen saturation procedure the main amount of hydrogen is dissolved in palladium substrate. During plasma experiments with hydrogen saturated W-Pd samples, they are heated up to 200-300°C and hydrogen, diffusing from the Pd-substrate bulk through W-films, increases working pressure from 0.266 Pa to 0.29 Pa (it is the regime with high hydrogen recycling coefficient). The physical mechanism, similar to that described in [3], can be suggested to explain the obtained result. When hydrogen in metal lattice is strongly bound up with host atoms (in the case of hydrogen in W the binding energy is about 1.04 eV [1]), it is more probably, that bombarding ion gives its energy to large complex hydrogen-host atom. In this situation hydrogen atoms have good chance to be sputtered (selective hydrogen sputtering can take place). In palladium hydrogen has low binding energy ($\approx 0.23 \text{ eV}$ [1]) and high mobility at moderate and even at low temperatures. So hydrogen sub-system slightly bound up with host atoms, and, therefore it is more probably that bombarding ion gives its energy to large Pd atom than to small hydrogen atom/proton. In this situation Pd atoms have good chance to be sputtered and dissolved hydrogen has not an influence on the erosion behavior as it was earlier observed in the work [3]. Hydrogen saturation of W-Pd system leads not only to changes in sputtering yield values but to macro-damages of samples in kind of strong shape changes and shelling erosion, too. Shape changes (Fig. 3c and Fig. 3d) were observed as non-elastic residual form deformation from flat to convex after W-Pd sample two-sided exposure in hydrogen atmosphere at 2 atm. pressure and at room temperature during long time (usually more than 100 hours). At 0.2mm Pd-substrate thickness and of 20mm diameter the sample deflection was about 6mm. It is very large value in comparison with elastic and non-elastic deformation which was observed earlier for Pd [8], and for Cu-coated palladium after one-sided hydrogen saturation in the range of only α -phase hydrogen solution [9]. Behind of different scale of these effects, it seems reasonable guess to explain the observed strong shape change in our experiments similar, as it was described in above mentioned works, namely, as the affect of the dynamic fields of stresses caused by gradients of hydrogen concentration. It should be noted that even strong shape change caused by hydrogen

saturation does not lead at once to W-film disruption. But after repeated long time hydrogen saturation so called shelling erosion was observed, when large percent of W-coating surface was disrupted (Fig.3e). The possible mechanism of such disruption could be the next. Hydrogen diffusing from the palladium bulk segregates into those parts of W film-palladium interface, which have high defect concentration, e.g., into regions with lower adhesion. The hydrogen pressure in these zones increases and large size bags/voids (macro-blisters) are formed. At the further hydrogen pressure increase stressedly-deformed W-film breaks in the bag region, forming macro flakes. It should be noted that the nature and the scale of such damages are quite different from well known blistering and flaking, when blisters and flakes appears on the metall surface as the result of surface damage by implanted ions. The behavior and scale of the observed in this work damages more similar to shelling erosion of TiN-coating on stainless steel under impact of high-power pulsed plasma fluxes [10].

4. SUMMARY

In contrast to bare Pd, hydrogen saturation of W-Pd system to high concentration leads to decrease of erosion rate of W under nitrogen plasma impact in 2-5 times in compare with non-saturated state. Such hydrogen effect on the W erosion behavior could be explained by selective hydrogen sputtering due to high hydrogen binding energy in W. Long time hydrogen saturation of W-Pd systems at room temperature causes strong shape change in the form of non-elastic residual deformation from the flat form to the convex one. The possible reason could be the dynamic fields of stresses caused by gradients of hydrogen concentration. After repeated long time hydrogen

saturation at room temperature the strong shelling erosion of tungsten films on Pd was observed. High hydrogen diffusion from Pd-substrate bulk and segregation of hydrogen in the parts of W film-palladium interface, which have high defect concentration, forming hydrogen induced macro-blisters, could be the reason of such disruption of W-films.

REFERENCES

1. G. Federici et al. // *Nuclear Fusion*. 2001, v. 41(12R), p.1967-2137.
2. G.P.Glazunov et al. // *Hydrogen and Helium Recycling at Plasma Facing Materials*. (Ed. A.Hassanein) NATO Science Series II: Mathematics, Physics and Chemistry. 2002, v.54, p.163-176.
3. G. P. Glazunov et al. // *Physica Scripta*. 2003, v. T103, p. 89-92.
4. P.Ya. Burchenko et al. // *Sov. J. Tech. Phys.* 1985, v.55, No 11, p.2097-2288.
5. I.I. Aksyonov et al. *Ukrainian Physical Journal*. 1979, v.24, No 24, p. 515-525 (in Russian).
6. A.P.Patokin, A.P.Sagalovich. // *Sov. J. Phys. Chem.* 1976, v.50, p.630-634.
7. Y. Yamamura and H. Tawara . *Energy dependence of of ion-induced sputtering yields from monoatomic solids at normal incidence*. NIFS-DATA-23, Nagoya, Japan, 1995, p.114.
8. R.V. Kotelva and V.A. Goltsov. // *Proc. of the Int. Conf. "Precious and less-common metals-94", September 19-22, 1994, Donetsk, Ukraine*. p.52.
9. V.A.Goltsov et al. // *Int. J. Hydrogen Energy*. 1977, v.22, p.179-183.
10. G.P.Glazunov et al. // *J. Nucl. Mater.* 2001, v. 290-3, p. 266-270.

ВЛИЯНИЕ НАСЫЩЕНИЯ ВОДОРОДОМ НА ЭРОЗИОННОЕ ПОВЕДЕНИЕ ТОНКИХ ВОЛЬФРАМОВЫХ ПЛЕНОК ПРИ ВОЗДЕЙСТВИИ СТАЦИОНАРНОЙ АЗОТНОЙ ПЛАЗМЫ

*Г.П. Глазунов, А.А. Андреев, Д.И. Барон, Е.Д. Волков, А. Хассанейн,
К.М. Китаевский, А.Л. Конотопский, В.И. Лапшин, И.М. Неклюдов, А.П. Патокин*

Исследовалось эрозионное поведение W-Pd биметаллических систем в насыщенном водородом состоянии и ненасыщенном, при воздействии стационарной азотной плазмы отражательного разряда Пеннинга. Обсуждаются возможные физические механизмы, объясняющие существенное снижение скорости эрозии и повреждения таких систем (изменение формы, макро-блистеринг и макро-флэкинг), обусловленных насыщением водородом до высоких концентраций.

ВПЛИВ НАСИЧЕННЯ ВОДНЕМ НА ЕРОЗІЙНЕ ПОВІДЖЕННЯ ТОНКИХ ВОЛЬФРАМОВИХ ПЛІВОК ПРИ ВПЛИВІ СТАЦІОНАРНОЇ АЗОТНОЇ ПЛАЗМИ

*Г.П. Глазунов, А.А. Андреев, Д.И. Барон, Е.Д. Волков, А. Хассанейн,
К.М. Китаевський, О.Л. Конотопський, В.І. Лапшин, І.М. Неклюдов, О.П. Патокін*

Досліджувалося ерозійне поведіння W-Pd біметалічних систем у насиченому воднем стані і ненасиченому, при впливі стаціонарної азотної плазми відбивного розряду Пеннінга. Обговорюються можливі фізичні механізми, що пояснюють істотне зниження швидкості ерозії й ушкодження таких систем (зміна форми, макро-блістерінг і макро-флєкінг), обумовлених насиченням воднем до високих концентрацій.