

# PALLADIUM EROSION BEHAVIOR UNDER LOW/HIGH LOCAL HYDROGEN RECYCLING IN STEADY STATE PLASMAS

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Sputtering experiments were carried out in steady state plasma of a mirror Penning discharge with cathodes made from hydrogen saturated/non-saturated palladium. For the both cases no difference in erosion behavior was found under hydrogen, helium or nitrogen plasma impact, in contrast to observed earlier erosion behavior of deuterium saturated/non-saturated lithium. Possible reasons are suggested and discussed to explain such erosion behavior.

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## 1. INTRODUCTION

One important problem associated with the interaction of hydrogen isotopes with structural materials in fusion devices is the change in hydrogen recycling coefficient during operation. It should be noted that in general case, studies of recycling process are important not only for hydrogen isotopes, but also for helium, oxygen, nitrogen, etc. This is of a great interest not only for fusion devices but also for numerous machines for plasma applications. In the latter, by the controlling of mentioned processes, one can provide, in particular, new conditions for material modification. Different material states (hydrogen saturated/non-saturated states) vary plasma properties and can also lead to change, under plasma irradiation, of material performances such as erosion rate, reflection coefficient, electron emission coefficient, etc. It was recently shown [1-3] that erosion rate of some materials (lithium, carbon, intermetallide,) decreases after hydrogen saturation up to high concentration. In particular, erosion of deuterium saturated solid lithium under  $\text{He}^+$  ion bombardment was observed in  $\approx 3$  times lower than that for non-saturated samples [1]. The physical mechanism of this phenomenon is not clear enough. It is incomprehensible also, if this effect will be working for other materials. Palladium is a unique material that can provide high hydrogen isotope concentration and high hydrogen flows, because hydrogen in Pd is in an active state and has high mobility. In this work, Pd was used as a convenient material to study the influence of both high and low hydrogen recycling regimes on material sputtering behavior under plasma impact. Such studies can be useful to understand erosion behavior of materials under plasma impact in high hydrogen recycling regime and for some applications, e.g., in connection with possible creation of erosion resistant plasma facing components on the base of bimetallic membranes containing palladium substrate for an active recycling control, as it was recently suggested [4, 5].

## 2. EXPERIMENTAL

The experimental setup used for plasma impact studies was DSM-1 device [6] with some modifications. The ground pressure in vacuum chamber before plasma experiments was about  $6.65 \cdot 10^{-4}$  Pa and determined by such residual gases as  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{CO}$ . Working gas (hydrogen, helium, or nitrogen) pressure in vacuum chamber was about 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  $U$  were in the range  $U = 1-2$  kV. The ion energy  $E$  in hydrogen discharges (0.8 keV-1.6 keV) had taken at the peak of the energy distribution, which equals  $E = 0.8eU$ , as it was shown earlier [6]. For comparison with literature data in the case of helium and nitrogen plasmas it were used energy values estimated similar to hydrogen plasma. As the weak energy dependence of erosion rate was observed in the above mentioned energy range for all kinds of working gases, so the error is believed not so large. Ion currents and doses were estimated in assumption that ion current to the cathode is 0.6 times the total measured current in hydrogen plasma discharge, and 0.8 times the total current in helium and nitrogen plasma discharge [7]. Ion current density values were in the range  $0.5 \text{ mA/cm}^2 - 5 \text{ mA/cm}^2$  for different discharge voltages and different working gases. Estimated irradiation doses were  $10^{18}-10^{19}$  ions/cm<sup>2</sup> and in this range it was not found the dose dependence of erosion coefficient. The samples for studies were mechanically cleaned and annealed in vacuum at temperature 600°C Pd (99.98 purity) foils without and with hydrogen saturation of concentration up to  $\text{H/Pd} \approx 0.65$ . It should be noted, that in the latter case, pressure during discharge increased up to 2.66 Pa due to hydrogen release from Pd targets (or from one target) and the high hydrogen-recycling regime was realized in this case for all kinds of working gas. Note, hereinafter we have in view so-called local hydrogen recycling process and local recycling coefficient determined by hydrogen sorption/release from targets only. After a few minutes of the operation at that regime, the working pressure decreased and reverted to the initial values. The similar experiments in diffusion regime, when back side of the target was in situ exposed to hydrogen at pressure of 2 atm., had been also carried out. In this case the working pressure during discharge increased to 0.29 Pa due to hydrogen diffusion through palladium target, and this pressure was constant during whole plasma experiment. The possibility existed to measure by thermocouple the temperature of the sample. The thermocouple was mechanically attached in the center of the sample back side. It was not found the difference between erosion rate under water cooled (50-100°C sample temperatures) and non-cooled cathode regimes. So, all presented results had been measured in non-cooled regime. In this case, the usual temperatures of the sample back side were 100-300°

C. With  $\pm 10\%$  temperature measurement accuracy it was not observed difference in the temperatures and in the erosion coefficients for Pd-samples made from thin or thick foils (foils were used of 0.2 mm, 0.3 mm and 1 mm thickness). It gives the reason to suppose that the real surface temperature of a sample was near to the measured one, and that sublimation did not influence on an erosion rate. Erosion coefficient values were measured by the weight loss method [6] and calculated by the equation:  $S = (P_1 - P_2) / 6.25 \cdot 10^{18} \cdot I \cdot t \cdot m$ , where  $P_1$  (grams) is the sample mass before exposure to plasma;  $P_2$  (grams) is the sample mass after exposure to plasma;  $I$  (Amperes) is the ion current;  $t$  (seconds) is exposure time;  $m$  (grams) is the mass of Pd atom. For hydrogen saturated samples,  $P_1$  means the mass before hydrogen saturation. Then the sample exposed in hydrogen at pressure of 2 atm. during 72 hours and hydrogen concentration was determined by the weighting on the VLR-20 analytic balance with sensitivity of  $10^{-5}$  g. After that, the sample was irradiated by plasma in erosion experiments. During plasma erosion

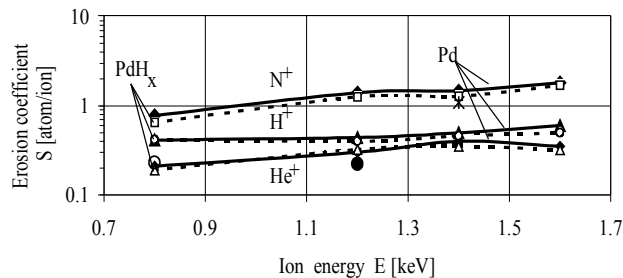


Fig.1. Energy dependence of palladium erosion coefficient under nitrogen, helium and hydrogen plasmas impact for hydrogen non-saturated samples (solid lines, Pd), for hydrogen saturated samples (dotted lines, PdH<sub>x</sub>); for diffusion regime: ○ - hydrogen plasma, ● - helium plasma, ✕ - nitrogen plasma.

experiments not all hydrogen released from the sample, so the irradiated sample 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 dissolved hydrogen. The weight of the sample after this baking is  $P_2$ . The all presented erosion coefficient values are the average of not less than three different measurements including measurements with samples of different thickness, and they are believed to be accurate with  $\approx 30\%$ . The main error  $\approx 25\%$  was determined by ion current measurements and caused by some current instability on the initial stage of discharges.

### 3. RESULTS AND DISCUSSION

The measured values of Pd erosion coefficient under hydrogen, helium or nitrogen plasma impact are presented in Fig. 1. One can see that erosion coefficient weakly depends on ion energy for all kinds of working gas. This is in agreement with numerous literature data [8], including Cu, Ni and stainless steel erosion behavior studies in the similar Penning discharges [6]. But practical independence of Pd erosion on hydrogen saturation up to concentration about H/Pd = 0.65 (in high hydrogen recycling regime) is unexpected result. The point is that in recent works [1-3] the decrease of some material erosion

was found after hydrogen/deuterium saturation to high concentration. The physical mechanism of that phenomenon is not clear enough. For example, in the work [1] erosion of deuterium saturated solid lithium (D/Li = 1) under He<sup>+</sup> ion bombardment was observed in  $\approx 3$  times lower than that for non-saturated samples. It had been explained as preferential sputtering for the lightest component (deuterium). So, the erosion rate decrease was expected for hydrogen saturated PdH<sub>x</sub> samples. In reality, the erosion coefficients for the non-saturated Pd samples (solid lines in Fig.1) are similar to those for hydrogen saturated PdH<sub>x</sub> samples (dotted lines in Fig.1), when a hydrogen flow of about 665 Pa-l/s from Pd targets is puffed due to the high hydrogen concentration in palladium (at 0.65 H/Pd concentration mainly hydrogen rich  $\beta$ -phase exists in Pd [9]). Such possible reason can be suggested to explain the obtained result. Hydrogen has very low binding energy in Pd lattice ( $\approx 0.15$  eV [10]) and high mobility at moderate and even at low temperatures [9]. Therefore, when hydrogen in metal lattice is strongly bound up with host atoms, 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 or preferential hydrogen sputtering can take place). In Pd case, hydrogen sub-system slightly bound up with host atoms, 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. In such conditions hydrogen receives thermal energy from Pd-lattice, and high hydrogen release during plasma impact could be caused by thermal diffusion and desorption processes, but not sputtering or radiation enhanced diffusion and desorption. In order to get direct evidence in favor of such mechanism, additional experiments are needed, in particular, using various coatings on plasma facing surface of palladium, including metals with low Z/high Z and high/low hydrogen couple energies, etc.

As seen in Fig.1 and the comparison with the literature data [8] shows that erosion coefficient of Pd under hydrogen plasma impact is extremely high. The control experiments with Cu and Kh18N10T stainless steel samples under hydrogen plasma impact had also shown enhanced erosion rates, which are in agreement with data in Ref. [6]. So it was difficult to expect for Pd another result. But, as for helium and for nitrogen the sufficient agreement was observed, it was supposed that explanation of the erosion increase used in Ref. [6] (self-sputtering) is not right in our case. If it were so one would have expected that erosion rate under nitrogen and helium plasmas would be essential higher. No traces of arcs were observed on sample surface. So, it is remained the influence of heavy impurity ions, such as N<sup>+</sup>, C<sup>+</sup>, O<sup>+</sup>. In the nitrogen plasma case the impurities (mainly C<sup>+</sup> and O<sup>+</sup> ions) have the nearest masses to nitrogen ion mass. So the influence of such impurities on erosion behavior under nitrogen plasma impact will be negligible. There are no literature data on Pd erosion under nitrogen ion bombardment. But obtained results are in a sufficient agreement with data [8] on Pd erosion under Ne<sup>+</sup> ion

bombardment ( $\approx 1.5$  at./ion at 1.5 keV ion energy). So the data on Pd erosion under nitrogen plasma impact one can consider as the hard data enough. We used this fact for calculation of the empirical coefficient “a” in the semi-empirical equation for mass dependence of erosion rate [8]:  $(Z_1 Z_2) \cdot m_1 / (Z_1^{2/3} + Z_2^{2/3})^{0.5} \cdot (m_1 + m_2)$ , where  $a = 0.31$  is constant,  $Z_1$  and  $Z_2$  are atomic numbers of bombarding ion and Pd-target, respectively,  $m_1$  and  $m_2$  are ion and Pd atom masses. In Fig.2 are presented the Pd erosion coefficients calculated by that equation for various atomic numbers  $Z$  of bombarding ions. The experimental results obtained under nitrogen, helium and hydrogen plasma impact and the data of ref. [8] obtained under  $H^+$ ,  $He^+$ , and  $Ne^+$  ions bombardment are shown in Fig.2, too. For nitrogen and helium plasmas the sufficient agreement with the literature data is observed. But, measured in hydrogen plasma, erosion coefficient is in 40 times higher than that for sputtering coefficient under hydrogen ions bombardment, i. e. overpowering influence of the impurities is observed. So the questions arises on the

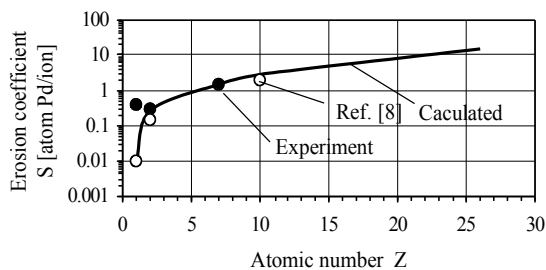


Fig.2. Experimental and calculated data on Pd erosion coefficient

possible impurity content and on the possible source of high impurity flow. As the ground pressure was  $6.65 \cdot 10^{-4}$  Pa and working gas pressure in plasma experiments was 0.266 Pa, the impurity content on the initial moment of the discharge was estimated as 0.25%. It is small value to be the reason of the observed erosion coefficient increase under hydrogen plasma impact. Really, for rough estimation of heavy impurity content one can use such equation:  $S(H) = S(H^+) \cdot I_H / I + S(N^+) \cdot I_N / I$ , where  $S(H)$  is the measured total erosion coefficient under hydrogen plasma impact;  $S(H^+)$  and  $S(N^+)$  are erosion coefficients under hydrogen and nitrogen ion bombardment, respectively;  $I$  is the total ion current;  $I_H$  and  $I_N$  are hydrogen ion and nitrogen ion current, respectively. To simplify a problem, only one heavy impurity ( $N^+$ ) was taken into account (it is not large error as ions  $C^+$  and  $O^+$  have masses near to  $N^+$  mass). If to put in equation measured values  $S(H) = 0.4$  and  $S(N^+) = 1.5$ , and taking into account that  $S(H^+) = 0.01$  [8]  $\ll S(N^+)$  it is obtained  $I_N / I \approx S(H) / S(N^+) \approx 0.25$ , i.e. 25% impurity content. The gas desorption from device walls cannot be the reason of such impurity flow as the pressure in vacuum chamber did not change during plasma experiment (in case of non-saturated Pd target). The possible reason could be impurity flow from targets. Really, if to suppose only one impurity monolayer on the sample surface before discharge (the experimental device is unbaked), we obtain  $3 \cdot 10^{15}$  impurity molecules could be desorpted from two samples. According to estimation, the number of working gas molecules in the plasma volume

(about  $60 \text{ cm}^3$ ) is  $\approx 10^{15}$  molecules. So, it could be more than 75 % impurity content on the initial stage of discharges. A life time of desorpted gases in the discharge is unknown, but if the current instability on the initial stage of the discharge (about a few minutes) is also caused by impurities, one can suppose the same time for impurity confinement in the discharge. On the next stage of the discharge the influence of the diffused and desorpted from Pd impurities could be observed (mainly C). As shown earlier [11], hydrogen irradiation is the more effective method for Pd surface cleaning (decarburation) in comparison with helium or argon ion bombardment and, consequently, one can expect more high impurity flow from Pd-target under hydrogen plasma impact.

For the diffusion regime, the downtrend of erosion coefficient values was observed (Fig.1). In the case of nitrogen plasma this effect is negligible, for helium plasma it is visible ( $\approx 25\%$ ), and for hydrogen plasma the erosion values in diffusion regime (high local hydrogen recycling coefficient) in 1.5 times lower than that for hydrogen saturated /non-saturated samples. It could be explained if to suggest the different impurity contents on the sample surface in different regimes.

## SUMMARY

The main intent of this work was to look an influence of hydrogen saturation of palladium on its erosion behavior. The measured values of Pd erosion coefficient are  $1.5 \pm 0.5$  at./ion under nitrogen plasma impact and  $0.3 \pm 0.09$  at./ion for helium plasma. For both cases the erosion rate independence was observed on hydrogen saturation of the samples up to concentration  $H/Pd = 0.65$ , in contrast to observed earlier [1] erosion behavior of lithium. It could be caused by difference in hydrogen binding energy values for both materials. In the case of hydrogen plasma impact, the measured erosion values are extremely high ( $0.4 \pm 0.12$ ) due to overpowering impurity influence, especially, on the initial stage of discharge, and additional experiments are needed to confirm the independence of Pd erosion behavior under hydrogen plasma impact on the hydrogen saturation (on the low/high recycling regimes).

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