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Hydrogen retention studies on Lithiated Tungsten exposed to Glow Discharge Plasmas under varying lithiation environments using Thermal Desorption Spectroscopy and Mass Spectrometry

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Abstract

For the design of a Fusion Reactor based on a liquid lithium divertor target and a tungsten first wall at high temperature, the interaction of the wall material with plasmas of significant lithium content must be assessed, as issues like fuel retention, tungsten embrittlement and enhanced sputtering may represent a showstopper for the selection of the first wall material compatible with the presence of liquid metal divertor.

In this work we address this topic for the first time at the laboratory level, hot W samples (100°C) have been exposed to Glow Discharges of H₂ or Li-seeded H₂ followed by *in situ* thermal desorption studies (TDS) of the uptake of H₂ on the samples. Pure and pre-lithiated tungsten was investigated in order to evaluate the differential effect of Li ion implantation on H retention. Global particle balance was also used for the determination of trapped H into the full W wall of the plasma chamber. A factor of 3-4 lower retention was deduced for samples and main W wall exposed to H/Li plasma than that measured on pre-lithiated W.

1. Introduction

Tungsten has been selected as the Plasma Facing Material (PFM) for the ITER divertor [1] and is the basic material taken into account for the PFM selection in the design of a future fusion reactor as DEMO [2]. Its selection is motivated by the good thermal properties of tungsten that has the highest melting point among metals, its low sputtering yield under particle/ion bombardment and the low hydrogenic isotope retention of tungsten compared with other studied materials as carbon. Despite these advantages, the nominal heat loads on the divertor region (5-20 MW/m²) during plasma operation and even more the extreme conditions expected during transient events such as ELMs or disruptions can induce permanent damage and irreversible degradation on this solid material that would seriously limit its lifetime.

On the other hand the use of liquid lithium as PFM offers unique advantages in terms of heat handling capabilities and plasma performance improvement [3, 4]. Furthermore its use as a liquid metal would avoid the problems related with induced permanent damage on solid materials exposed to burning plasma and the renewable surface of a liquid material could suppress its disintegration and the dust formation during plasma operation, increasing the lifetime of the Plasma Facing Components (PFC). Hence, lithium is considered as the favorite liquid metal PFM for future fusion devices, but its high H retention [5] makes the associated Tritium inventory a possible showstopper.

The lithium research as an alternative PFM has been addressed in a wide variety of experiments involving hot plasma devices [3-9], linear plasma facilities [10, 11], laboratory configurations [12, 13] and innovative concepts for future fusion devices [14, 15], showing promising results in respect of improved plasma performance, power exhaust handling and

the possibility of control and decrease the lithium hydrogen uptake. In addition some studies about the interaction of W-Li hybrid layers with linear plasma have been performed. Neff et al [10] studied the D retention in W-Li coatings exposed to a high fluence linear deuterium plasmas in Magnum PSI device and reported the inhibition of Li-D-O complex formation responsible of the enhanced fuel retention on the coatings when the deuterium linear plasma is seeded with helium. Other experiments involving lithiated tungsten samples exposed to Magnum PSI linear plasma [17] have shown the possible saturation in the deuterium retention and the inhibition of blistering on the W surface due to the protective effect of the Li coating. However, the possible effect that a simultaneous irradiation with hydrogenic species and lithium on W-Li layers (conditions that can be expected in a fusion reactor environment with W-Li PFM), can have in multiple Plasma Wall Interaction (PWI) phenomena as T global retention, redeposition, material erosion and mixing is unavoidable. Under this scenario a specific investigation involving PWI and Material Science topics in terms of fuel retention, surface erosion and material compatibility are clearly necessary. In this work dedicated experiments and analysis oriented to quantify the H retention on several W-Li samples exposed to H₂ Direct Current (DC) Glow Discharge (GD) plasmas under different environments have been performed by using Thermal Desorption Spectroscopy (TDS) in order to induce the in situ hydrogen desorption from the W-Li layers and Mass Spectrometry to quantify it.

2. Experimental setup and procedure

The experiments were carried out in a full W wall device designed at CIEMAT and similar to the one previously used and described [17]. An overview of the setup can be visualized

in Figure 1. The primary vessel consists on a cylindrical stainless steel vacuum chamber that acts as the grounded cathode where the irradiation with the H₂ GD plasmas is carried out. The plasma chamber (V= 5.4 L) has its inner wall totally covered with high purity cold rolled tungsten (A=0.14 m²) and is pumped out by using a unit that consist on a set of turbomolecular-rotary pump that decreases the base pressure until 10⁻⁵ Pa approximately. The pressure during the plasma operation and the lithiation process is measured with a capacitance manometer (0.1-100 Pa). Inside this chamber a cylindrical, stainless steel oven (3 cm of diameter and 6 cm of height) filled with high purity (>99%) lithium is placed to produce the evaporation of lithium for the *in situ* lithiation of the samples and the main W wall, by the effusion of the evaporated Li atoms through a circular hole (~1 cm of diameter) placed on the top of the oven. An AC power supply is used to heat up the oven. The temperature of the lithium is measured during the evaporation by a thermocouple type K that is placed inside the oven, in direct contact with the lithium. Before the lithiation process the lithium placed in the oven is outgassed by heating it until 300°C of temperature during 30 minutes approximately inducing the hydrogen, water and impurities desorption from the lithium bulk.

On the top of the plasma chamber and open to it, a small chamber intended to harbor the *in situ* TDS analysis on the W-Li samples is located. To measure the H retention during the desorption process, a Residual Gas Analyzer (RGA) Mass Spectrometer (SRS 100) is connected to this chamber. A manipulator that contains a holder for the W-Li samples and a pure resistive filament (fed with a direct current and 60 W of total heating power) in order to heat up the samples by radiation and induce the H desorption, is placed on the top of this TDS chamber. The temperature evolution on the sample during the TDS analysis is

measured by using a type K thermocouple welded on the holder and that is in direct contact with the sample. The manipulator can move the samples from the plasma chamber to the TDS chamber without breaking the vacuum conditions after the H₂ GD plasma irradiation. In this way the possibility of contamination and hydrogen release from the samples before the TDS analysis can be excluded.

The samples consist on a cold rolled, high purity tungsten pieces with dimensions of 12.6±0.2 mm of width, 21.7±0.2 mm of height and 0.1 mm of thickness with a surface area exposed to the plasma of 273±7 mm². These samples are introduced in the holder and are outgassed by heating previously to the plasma exposure. Before the H₂ irradiation one of the samples was exposed to a previous in situ lithiation by Li evaporation at 500°C-550°C during 30 minutes, (Li evaporation rate of $1.36 \cdot 10^{18}$ atoms/cm²·s and total evaporation of 0.2 g approximately) under a H₂ flow (~ 4 Pa of total pressure) atmosphere. Another sample was exposed directly to a H₂ GD plasma in a lithium evaporation environment (Li at 500°C-550°C during 30 minutes as in the pre-lithiated case), producing a Li-seeded H₂ GD plasma in order to study the hydrogen retention under simultaneous irradiation of Li and H on the W sample. Finally a pure W sample was also irradiated with pure H₂ GD plasma in order to compare the hydrogen retention with the two cases previously described.

Between the plasma and the TDS chamber a stainless steel grid with boron nitride insulation pieces are placed to limit the plasma in this region and assure that the plasma does not touch any part of the TDS chamber, excluding in this way the possibility of contamination of the TDS analysis by the desorption of hydrogen from other parts non exposed in principle to the plasma. Additionally and also connected to the plasma chamber a differentially pumped analysis chamber is placed to monitor, with a Residual Gas

Analyzer (RGA) Mass Spectrometer (Pfeiffer Vacuum Prisma QMS 200), the plasma operation. This analysis chamber is pumped down with another turbomolecular-rotary pump set until a base pressure around 10^{-7} Pa, being this pressure measured with an Ionization Gauge. All the experiments were carried out after a wall conditioning on the main W wall and samples that assures the reproducibility of the experiments and a fresh/clean surface prior to the lithiation/irradiation processes. This wall conditioning consists on pure DC-GD Helium plasma during 20 minutes in order to desorb and clean by sputtering the impurities present on the sample and main wall surface.

To produce the discharge, the high purity (>99.999%) gases (H_2 and Helium for the wall conditioning) are introduced into the chamber by an electronic mass flow controller. The plasma characteristics of the H_2 irradiation are: ~ 4 Pa of total pressure, a discharge voltage between 100-250V, plasma current (300-350 mA) and total ionic fluence up to $7.5 \cdot 10^{22} \text{ m}^{-2}$ (being the dominant plasma ions at a pressure of 4 Pa a mixture of H_2^+ and H_3^+ [18]), with a total duration of 30 minutes. During the irradiation the main W wall and the samples were not heated up externally, but due to the plasma bombardment the surface temperature was increased until 90-100°C approximately. To complete the measurements during the plasma operation an Optical Emission Spectroscopy (OES) diagnostic was also used to measure the intensity of the lines related with Li I (670.7 nm) and $H\alpha$ (656.3 nm) transitions. The OES diagnostic consists of a focusing lens that directs the plasma emitted light to a monochromator (Oriel 77250) in order to select the registered wavelength during the plasma operation (performing a 650-675 nm wavelength scan) and a photomultiplier, (Hamamatsu R3896) with high efficiency spectral response for the 400-700 nm wavelength

range, that amplifies the signal measured from the plasma emission collected through an optical window situated in the main plasma chamber.

After the H₂ GD plasma irradiation the treated sample is moved to the TDS chamber by using the manipulator and the hydrogen uptake on the samples is measured by TDS assisted mass spectrometry. The filament that induces the heating of the sample and the hydrogen desorption is fed with a DC power supply with a nominal voltage of 12 V and a maximum current of 5 A. Finally, an absolute calibration work that relates the single RGA peak at 2 amu/e signal with its associated H₂ partial pressure was performed in order to quantify the hydrogen retention on the samples and on the full W wall.

3. Experimental results and discussion

3.1 Hydrogen uptake on a W sample lithiated under a H₂ atmosphere and exposed to H₂ GD plasma irradiation.

In figure 2, the TDS analysis of the pre-lithiated sample in a H₂ environment and later exposed to H₂ GD plasma irradiation is presented. The heating ramp of the sample during the first part of the TDS analysis is approximately linear with a mean value of 5 K/s. A clear desorption peak is visible for the signal at 2 amu/e (directly related with hydrogen) at a sample temperature of 400°C, in agreement with previous studies performed on TJ-II Stellarator that consisted on the exposure of a Liquid Lithium Limiter (LLL) to hot plasma [ref TDS TJ-II??]. The signal at 18 amu/e related with water keeps approximately constant during the measurement, around a value that is at least an order of magnitude lower compared to the 2 amu/e signal. In this way the amount of hydrogen desorbed that could occur from water decomposition can be considered as negligible. The figure 3 shows an

optical emission spectroscopy measurement registered during the irradiation with H₂ GD plasma (red line). The H α (656.3 nm) and Li I (670.7 nm) lines are clearly visible, showing the presence of lithium in the plasma as a consequence of its sputtering from the plasma chamber walls. The visual inspection of the sample during its replacement for a new one also shows the presence of lithium on the surface. Hence the interaction between the impinging hydrogen from the plasma and the W-Li surface during the irradiation process seems evident.

3.2 Hydrogen uptake on a W sample exposed to H₂ GD irradiation under a Li evaporation environment

The TDS analysis of this sample is shown in figure 4. The heating ramp of the sample until it reaches 400°C can be approximated as linear with a mean value around 10 K/s, (double compared to the previous case) suggesting with the lower area of the H desorbed spectrum that the amount of hydrogen present on the surface is quite lower in comparison with the previous sample. There are two main peaks in the H desorption spectrum located at 400°C and 560°C of sample temperature, being the second one located at a slightly higher temperature compared to hydrogen desorption peaks observed in gas exposure laboratory experiments with lithium [13]. The contamination of the measured hydrogen desorption with residual hydrogen related to water decomposition, could be rejected as the water level during the TDS analysis remains at least an order of magnitude lower. The OES spectrum also shows the presence of lithium in the hydrogen plasma (Figure 3, blue line). In this case the intensity of the Li I line is 10 times higher compared to the previous case while the intensity of H α line remains at the same level, hence suggesting the presence of Li in the plasma as a main component not as an impurity that enter in the plasma as a result of the

plasma wall interaction processes. Hence, in this case the sample was irradiated simultaneously with mixed plasma of lithium and hydrogen due to the ionization of the evaporated atoms of lithium in the plasma. After finishing the analysis the presence of lithium layers on the sample surface was also clearly visible.

3.3 Hydrogen uptake on a pure W sample

The corresponding TDS spectra of a pure W sample irradiated with a H₂ GD plasma is shown in figure 6. This analysis allows the direct comparison among the Li-W hybrid layers and the pure W material in terms of hydrogen retention. The heating rate of the sample exhibits a similar behavior during the initial step of the heating, compared to the case of the sample irradiated simultaneously with hydrogen and lithium. The hydrogen desorption spectrum does not show a well-defined peak, instead of it, the spectrum presents a plateau between 400°C and 520°C in the sample temperature. In this range of temperatures the most of the hydrogen present on the sample is desorbed. The contribution in the desorbed hydrogen from the possible water decomposition during the measurement could also be considered as negligible as the level of the registered water signal is kept much lower than the registered signal of hydrogen.

3.4 Quantification of the global and local hydrogen retention

The absolute calibration work allows us the quantification of the local hydrogen retention on the samples desorbed in the TDS analyzes. Furthermore by using the differentially pumped mass spectrometer to monitor the evolution of the 2 amu/e signal during the plasma operation, the global hydrogen uptake on the W wall of the plasma chamber can be estimated by particle balance calculations taken into account the depleted hydrogen from

the gas phase during the GD plasma exposition. A comparison between the local H retention measured by TDS on the samples and the concomitant global retention in the plasma chamber W wall is presented in Table 1 for the experimental cases previously detailed.

The calculated global H retentions for the W wall used in the experiments exhibit a clear difference among the studied cases. For the irradiation of the pure W without previous lithiation or Li evaporation during the plasma exposure a value around $2.1 \cdot 10^{21}$ H atoms/m² is obtained by particle balance for the global hydrogen retention, being in agreement with previous results [19, 20]. On the other hand for the case of the W lithiated before its H₂ GD irradiation with H₂ GD the global H retention obtained is $2.2 \cdot 10^{22}$ H atoms/m², a factor 10 higher compared to pure W. Finally for the experiment with Li-seeded H₂ GD irradiation on W, the global retention calculated is $5.2 \cdot 10^{21}$ H atoms/m², being this value approximately 4 times lower compared to the global retention calculated for the pre-lithiated W case. This difference between the both Li-W cases could be caused by the implantation of Li on W during the simultaneous irradiation in the Li-seeded H₂ plasma, assuming in this way that the H uptake by the implanted lithium atoms is much lower compared to the H uptake in just deposited Li. The local H retention on the W samples obtained by the integration of the H₂ desorption rate over the time during the TDS measurement exhibit a similar trend, being the H retention for the pre-lithiated W sample ($6.1 \cdot 10^{22}$ H atoms/m²) 3 times higher compared to the sample exposed to Li-seeded plasma ($1.9 \cdot 10^{22}$ H atoms/m²) and ~8 times higher than the retention on the pure W sample only exposed to H₂ GD plasma ($8.4 \cdot 10^{21}$ H atoms/m²). This result also points to the difference in terms of H retention between the implanted Li and the deposited Li on the samples

previously commented. However the obtained values are systematically a factor 3-4 higher compared to the global retention values. This discrepancy between the global and local measurements could be caused by a non-homogeneous distribution of the plasma inside the chamber as well as differences in the distribution of lithium deposition/implantation on the W surfaces.

4. Conclusions

Local hydrogen retention has been measured on W samples at a temperature of $\sim 100^\circ\text{C}$ by TDS assisted mass spectrometry. The results show a hydrogen uptake in the case of tungsten irradiated with Li-seeded H_2 GD plasma approximately 3 times lower compared to the case of pre-lithiated W irradiated with H_2 GD plasma.

The estimations of the global hydrogen retention on the W wall ($T_{\text{surface}} \sim 100^\circ\text{C}$) of the plasma chamber, calculated by particle balance from differentially pumped mass spectrometry measurements, also exhibit a hydrogen uptake 4 times lower for the Li-seeded H_2 GD plasma experiment, a similar factor compared to the observed for the measurements of the local H retention on the samples.

OES measurements show the presence of Li as a main component of the plasma, suggesting that the W surfaces are simultaneously bombarded by H and Li ions in the case of Li-seeded H_2 GD plasma, causing the Li implantation on the surfaces that could explain the lower H retention observed in this case.

This scenario with simultaneous Li-H bombardment on the surfaces could be expected in future reactor configurations that would combine W and lithium as PFM. These results may represent an approximation to this topic but it is necessary to keep in mind that the

conditions and results in a hot and fully ionized plasma existing in a fusion reactor could be different. A further research involving hot and linear plasmas exposure is necessary to understand the behavior of implanted Li in terms of associated fuel retention.

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Figure captions

Figure 1: General view of the setup: 1. Mass-Flow controllers (gas inlet), 2. Anode, 3. Lithium oven, 4. Sample holder, 5. Heating filament, 6. Isolation grid, 7. Manipulator, 8. Sample position during TDS, 9. Mass spectrometers, 10. Capacitance manometer, 11. W wall (plasma chamber), 12. Ionization Gauge, 13. Gate valve, 14. Collimator (differential pumping), 15. Optical window, 16. Focusing Lens, 17 Monochromator, 18. Photomultiplier, 19. Pumping units.

Figure 2: TDS measurement on a W sample irradiated with H₂ GD after its lithiation under a H₂ flow environment. A desorption peak of hydrogen is clearly visible at a sample temperature of approximately 400°C.

Figure 3: OES measurement during the H₂ irradiation of the samples previously lithiated under a H₂ flow atmosphere (red line) and exposed to H₂ GD plasma during Li evaporation (blue line). The presence of lithium in the plasma for the first case is related with its sputtering from the walls. For the second one the intensity of the Li I line is an order of magnitude higher compared to the previous case showing the presence of Li as a plasma component not only as an impurity.

Figure 4: TDS measurement on the W sample exposed to a simultaneous H₂-Li plasma. Two peaks of desorbed hydrogen are registered at 400°C and 560°C.

Figure 5: TDS analysis of a pure W sample irradiated with H₂ GD plasma. The spectrum does not present a well-defined peak of desorbed hydrogen. Instead of it a plateau appears between 400°C and 520°C of sample temperature

Figure 1

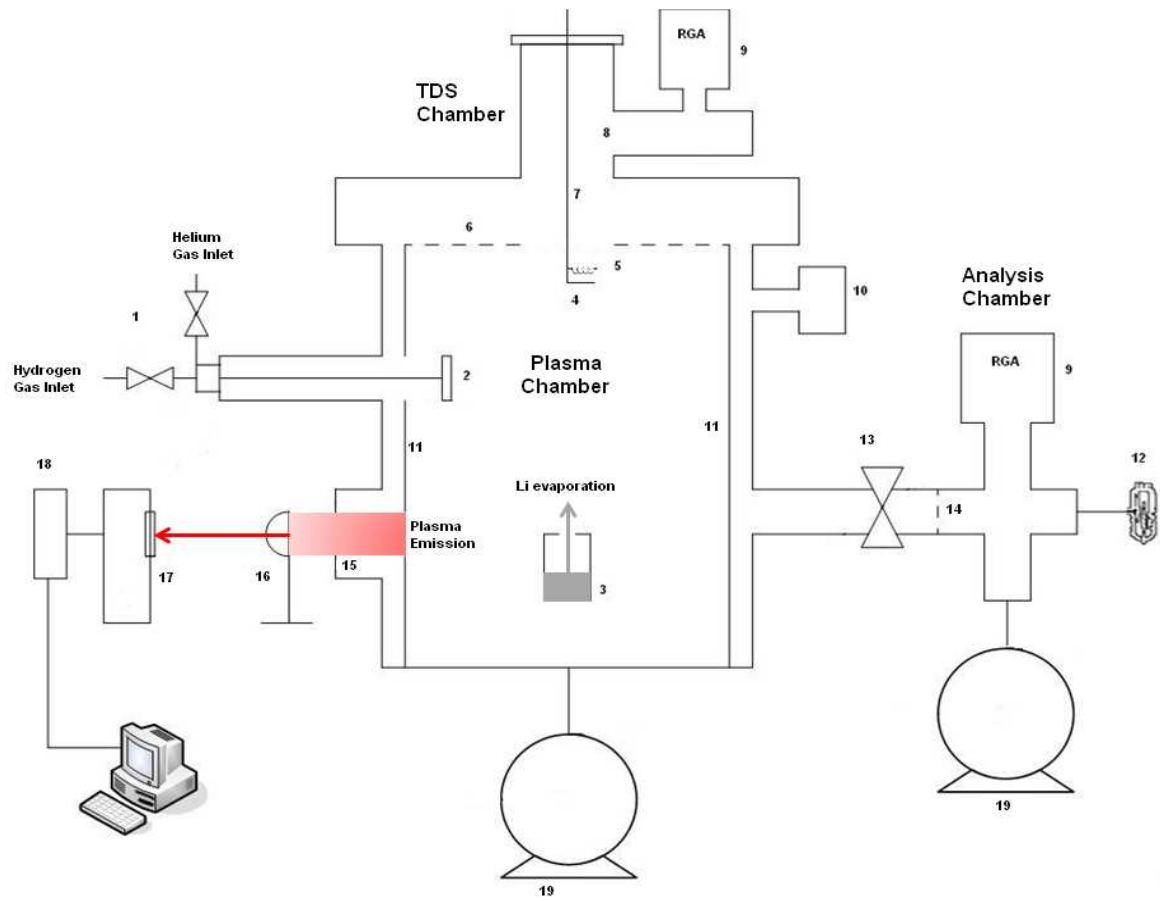


Figure 2

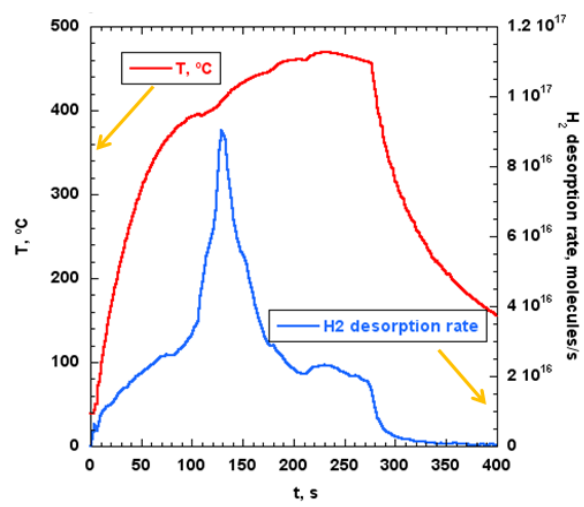


Figure 3

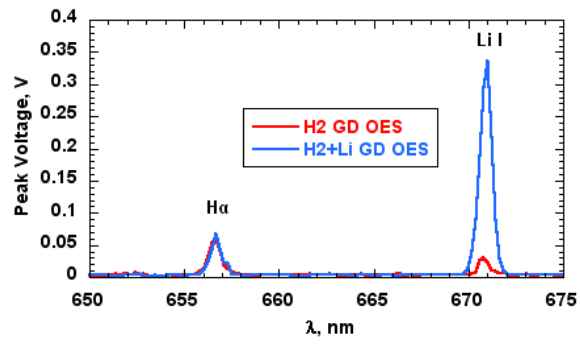


Figure 4

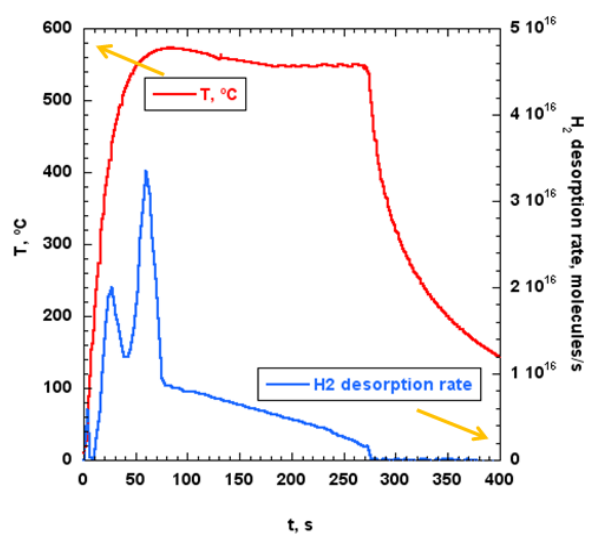


Figure 5

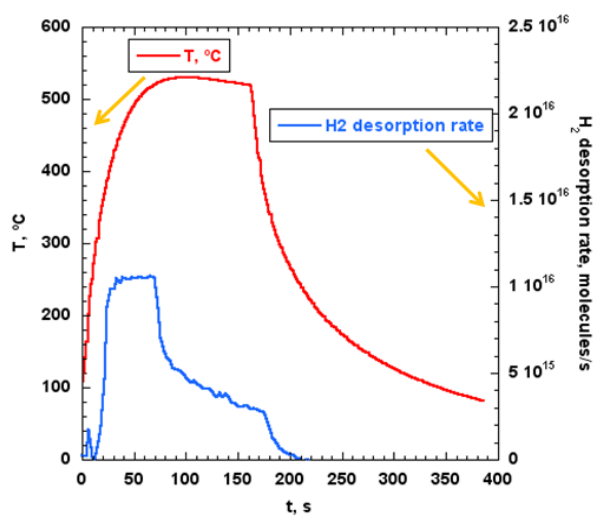


Table captions

Table 1: Summary of the global (W wall) and local (W samples) hydrogen retention obtained for the different experimental cases. A hydrogen retention 3-4 times lower is obtained for Li-seeded H₂ GD irradiation in comparison with H₂ irradiation on the prelithiated W in both global and local retention measurements.

Table 1

Li-W Wall and sample state	Discharge Voltage, V	Global H retention (Wall), H atoms/m²	Local retention (sample), H atoms/m²
Pure W irradiated with H ₂ GD	250	2.10E+21	8.40E+21
pre Li W irradiated with H ₂ GD	110	2.20E+22	6.10E+22
W irradiated with Li-seeded H ₂ GD	120	5.20E+21	1.90E+22