In-situ LIBS and NRA deuterium retention study in porous W-O and compact W coatings loaded by Magnum-PSI

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Abstract

The purpose of this study is to investigate the applicability of in-situ laser induced breakdown spectroscopy (LIBS) for deuterium retention measurements in tungsten coatings with different morphology and oxygen content. These were exposed to a Gaussian beam of deuterium plasma in the Magnum-PSI linear plasma device. The deuterium line intensities determined by LIBS were compared with the deuterium content measured by nuclear reaction analysis (NRA).
Both LIBS and NRA results showed that higher deuterium retention was achieved in the coating region corresponding to the periphery of the plasma beam. This decreasing deuterium retention in the central region can be attributed to higher surface temperature. At the same time, the deuterium retention in different coating types assessed by LIBS D intensity was markedly different from the retention determined by NRA. Porous W-O coating with high oxygen content had the highest deuterium retention according to NRA while D intensity obtained by LIBS was an order of magnitude smaller when compared with other coatings. The deuterium retention in compact W coating and thick W coating was almost the same and LIBS D intensities were also comparable for these coatings. The results demonstrate the LIBS applicability and its limits in different coating types.

Keywords: ITER relevant tungsten coatings, deuterium retention, plasma exposure in Magnum-PSI plasma, in-situ NRA, in-situ LIBS

1. Introduction

Successful exploitation of the International Thermonuclear Experimental Reactor (ITER) requires the knowledge of the fuel retained in the reactor walls [1–3]. In order to comply to the safety regulations, the total retained tritium (T) in the reactor vessel should be monitored to assure that the amount of tritium in the ITER vessel does not exceed the limit of 700 g. ITER

will use two hydrogen isotopes, deuterium D and tritium T to fuel the fusion reaction. The fuel retention in ITER divertor walls exposed with plasma fluxes up to 10^{24} ions/m^2s can be systematically studied in the linear plasma devices with D plasma [4,5]. The retention is strongly influenced by the properties of wall materials, i.e. temperature, morphology, crystalline structure as well as elemental composition. ITER divertor walls are made from tungsten but during plasma exposure of the wall erosion and redeposition of wall material may change the surface material composition and the amount of retained deuterium [6–8]. It has been shown that D retention in coatings, which simulate these layers, increases markedly in polycrystalline, nanocrystalline and amorphous tungsten coatings [9–11]. Furthermore, the D retention is influenced by the co-deposition of additional elements, for example oxygen which is present in plasma as an impurity [12,13].

Laser Induced Breakdown Spectroscopy (LIBS) is a method where a short but powerful laser pulse is used to ablate a tiny amount of material from the surface, which results in the formation of a plasma plume of wall material. The spectrum of the light emitted from the plasma plume is used to determine the elemental composition of the ablated material. It has been demonstrated that LIBS can be used for remote in-situ determination of the hydrogen isotopes in the W based materials both in tokamaks [14–17] and linear plasma devices [18–22]. The determination of the absolute value of D content requires extensive calibration with different coatings. The calibration can be made by comparing the D intensity obtained by LIBS with the absolute D content obtained by other methods. One method which determines both the total amount of D and depth distribution is nuclear reaction analysis (NRA) [9,23–27].

Our previous ex-situ LIBS study [28] of D retention in nanostructured compact and porous W-O coatings loaded by Magnum-PSI plasma demonstrated the LIBS ability to obtain qualitative correspondence with D retention in the coatings. However, a disadvantage was that this study was made several months after D loading. The D intensity determined by LIBS was compared with the relative D content obtained by Secondary Ion Mass Spectroscopy (SIMS) and inherently the results were influenced by adsorbed water from surrounding atmosphere and possible outgassing of D. The H signal originating from the surface water vapor interferes with D signal, which has detrimental effect on the detection limit of D. More accurate D analysis requires experiments, which are made immediately after D loading without exposing the samples to ambient air. Furthermore, it is necessary to calibrate the LIBS signal with the absolute D composition. The ion beam diagnostic, which is installed on the Target Exchange and Analysis Chamber (TEAC) [4], enables to use NRA consecutively with LIBS in Magnum-PSI.

The aim of this study was the comparison of retention properties of samples with ITER like Wall (ILW) coatings of different composition and structure using in situ LIBS and direct comparison of LIBS results with these obtained with NRA. The investigated samples were compact W and porous W-O coatings which were exposed to deuterium plasma in Magnum PSI.

2. Experimental setup

2.1. Preparation of coatings

The investigated compact W coating and porous W-O coating were produced in the Micro and Nano Structured Materials Laboratory Department of Energy Politecnico di Milano and the samples consist of a Mo substrate of 30 mm diameter and 1 mm thickness coated with a W layer deposited by pulsed laser deposition. A ns laser pulse (wavelength 532 nm, pulse duration 5-7 ns, fluence 15 J/cm^2) was focused on a pure metallic W target in vacuum (10^{-3} Pa base pressure)[29] or 70 Pa argon pressure [30] to obtain respectively compact and porous coatings (Fig. 1). The deposited thickness was approximately 1.5 μm, assessed by SEM cross section analysis of identical films deposited on silicon substrates. A 150 nm adhesion interlayer of crystalline W was deposited in vacuum before the deposition of the porous coating to enhance film adhesion (see Fig. 1e in ref. 30). According to earlier studies [29] the compact coating contained about 1 at. % oxygen while porous coating contained 50 at. % oxygen as determined by EDXS [30]. In respect to their crystalline structure, compact W coating exhibits the crystallographically oriented growth along the (110) direction while porous W-O coating shows much lower crystallinity due to its cauliflower morphology.

In addition, a compact thick W coating was prepared by reactive high-power impulse magnetron sputtering (HIPIMS) method in National Institute for Laser, Plasma and Radiation Physics, Bucharest. The composition and thickness of the W coating was determined by Spectruma GDA 750 Glow Discharge Optical Emission Spectrometry (GDOES) and SEM. The thickness of this coating was approximately 10 μm (Fig. 1) with the uppermost 1 μm layer containing up to 20 at. % of oxygen. This coating has preferential growth along (211) plane according to an earlier study [31]. The schematic buildup of the samples with coatings and interlayers is shown in figure 1.

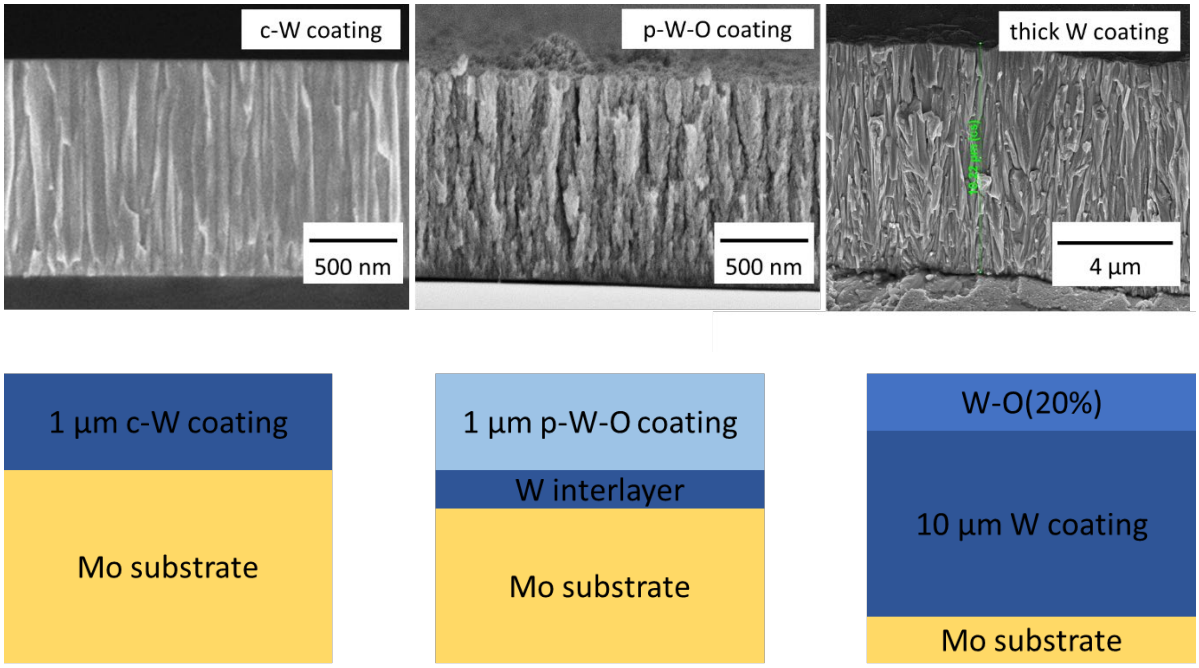


Figure 1. Upper panel - SEM figures of compact W coating, porous W-O coating and thick W coating. Lower panel - Schematic drawing of the sample composition for compact W (c-W) coating, porous W-O coating on W interlayer (p-W-O) and thick W coating with uppermost layer containing oxygen (W-O).

2.2. Deuterium loading in Magnum-PSI

The coatings were exposed to a deuterium plasma generated by the Magnum-PSI linear plasma generator of The Dutch Institute for Fundamental Energy Research (DIFFER) [5,32]. The exposure time was 2000 s. For all experiments, a D_2 flow of 5.0 slm was used at a plasma source current of 135 A and the plasma beam was confined by a magnetic field of 0.8 T. The Full Width at Half Maximum (FWHM) of the beam was 18 mm and 21 during plasma exposures of the porous W-O coating, thin compact W coating and thick W coating, respectively. The bias voltage of target was -40 V which results in an ion implantation energy of >15 eV. Thomson scattering [33] was used to measure the parameters of Magnum PSI plasma near the surface of the coating. The electron temperatures, electron densities, particle fluxes, fluences are shown in Table 1. Maximum values of surface temperature in the central zone of plasma beam were determined by IR camera and are also shown in Table 1.

Table 1. Characteristics of deuterium plasma exposure for c-W, p-W-O and thick W coating

	T_e, eV	n_e, m^{-3}	Flux, $m^{-2}s^{-1}$	Fluence, m^{-2}	T_{surf}, °C
1 µm c-W	1.4	$0.38 \cdot 10^{20}$	$2.5 \cdot 10^{23}$	$5.0 \cdot 10^{26}$	380

1 µm p-W-O	1.3	$0.35 \cdot 10^{20}$	$2.3 \cdot 10^{23}$	$4.6 \cdot 10^{26}$	390
10 µm W	1.2	$0.25 \cdot 10^{20}$	$1.6 \cdot 10^{23}$	$3.2 \cdot 10^{26}$	325

2.3. In-situ LIBS and NRA measurements

In order to perform LIBS and NRA measurements, the samples were transferred from the linear plasma device into the TEAC without breaking the vacuum. This allowed to minimize H_2O adsorption. The first series of LIBS measurements was made in vacuum approximately one hour after deuterium loading in the time interval of 15-20 minutes (first for thin compact W, then for thin porous W-O, finally for thick W coating). LIBS measurements were followed by NRA measurements 2-4 hours after loading (Fig. 2). Most of the LIBS measurements were performed in the following day in two series (Fig. 2) These LIBS measurements were made at a background pressure of 1 mbar argon because the LIBS signal obtained in vacuum was very weak. The final series of NRA measurements was repeated almost 2 days after loading to check for possible changes in deuterium concentrations (Fig. 2).

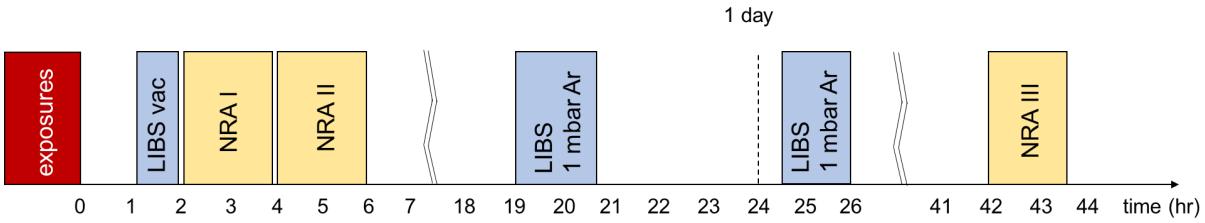


Figure 2. Time diagram showing different LIBS and NRA measurement series.

The description of the LIBS set-up can be found in earlier studies [20,34]. All parts of the LIBS set-up (laser, spectrometer and optics) were located outside the TEAC. The used Nd:YAG laser was operated at the fundamental wavelength of 1064 nm with pulse duration of 8ns. The laser beam was guided to the TEAC by mirrors of a 30 m long beamline and focused to the target by a lens with focal length of 1 m. The laser spot size corresponded to ≈ 1.65 mm^2 while the power distribution within the spot is approximately Gaussian. The fluence of the laser pulse at the target surface was kept at 20 J/cm^2 similarly to previous studies. The light emitted by laser plume was collected and imaged with a magnification of 1 onto a 0.8 mm diameter fiber by a 30 cm achromatic lens. A green alignment laser was used to align the recording fiber with a desired spot on the surface. The 30 m long fiber directed the light to a Czerny-Turner spectrometer with 1 m focal length and 1200 lines/mm grating coupled with an Andor iStar

ICCD camera (DG340T-18F-03). A 20 nm wavelength range was preselected for detection of D and H emission at 656 nm. The delay of the detection window, relative to the LIBS laser pulse was 1300 ns and a gate width of 2000 ns was used for detection of the emitted plasma light. The used delay time enabled the separation of H and D Balmer alpha lines.

D concentration profiles were determined by NRA analysis based on the nuclear reaction $D(^3He,p)^4He$ [35]. These measurements were performed after the LIBS measurements and without venting in the same TEAC chamber. Two ^3He beam energies were used: 1000 keV to obtain a detailed profile of the surface (about 50 nm depth resolution) and 2500 keV to probe about 3 microns deep in thick tungsten coating. The dimensions of the beam spot were 2.5x5.5 mm^2. The NRA detector was placed at a reaction angle of 172° with a solid angle of 7.9 msr. A 12.5 μm thick Mylar stopper foil was used to prevent that scattered ^3He particles could reach the detector.

3. Results and Discussion

The photos of samples exposed to a deuterium flux for 2000 s are shown in figure 3. The order of the craters resulting from the LIBS measurements is marked on the figure by yellow numbers. NRA measurements were made at 5 different points on a vertical line through the center of samples (marked with blue shaded rectangles). For thin compact W coating, there were clearly detectable darker rings on the coating surface while for porous W-O coating there was a slightly lighter region on the surface. The presence of these rings can be attributed to the location of central zone of plasma beam where the particle flux and temperature was highest. As the plasma beam was not deposited at the geometrical center of the samples, the faint contrast of the plasma treated region complicates the comparison between results obtained by NRA and LIBS. The thick W coating had small specks attributable to flaking off from most of the surface except for the region corresponding to the central part of plasma beam [28].

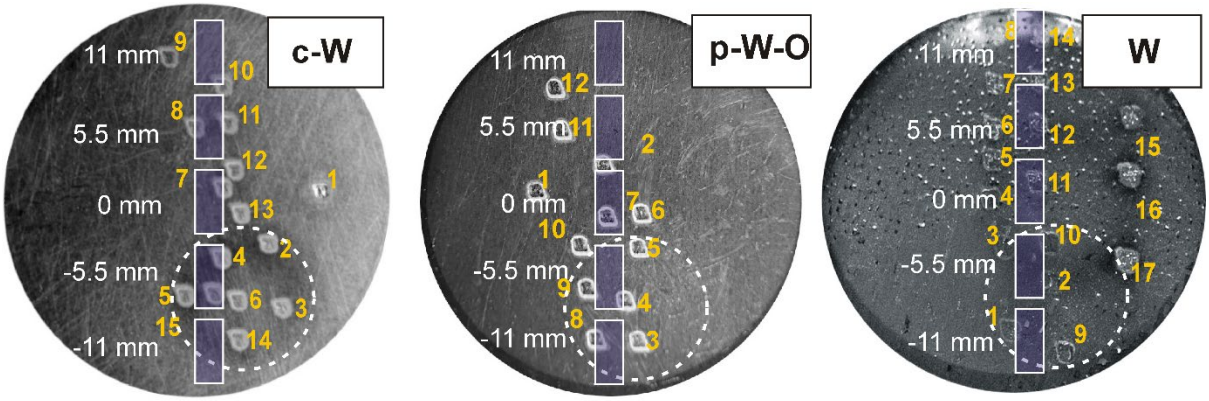


Figure 3. Photograph of the surface of W and W-O coatings exposed to deuterium flux for 2000 s. The blue shaded rectangles note the approximate locations for NRA measurements while yellow numbers denote the positions of laser produced crates. The region on the surface exposed to central zone of the plasma beam is depicted by a dashed ring.

3.1. D and H intensities and elemental depth profiles by in-situ LIBS

Figure 4 shows the LIBS spectra at central wavelength of 656 nm collected from the regions of c-W and p-W-O coatings which were outside from the central zone of plasma beam (spot 11 for both coatings). The spectra obtained from thick W coating were comparable with the spectra obtained from thin c-W coating. The partly overlapping peaks at 656.1 nm and 656.28 nm, corresponding to D_α and H_α lines, were clearly detectable during the first 2-3 shots. The integral intensities of these lines, I_D and I_H, were obtained by fitting the measured spectra with Lorentzian profile because Stark broadening is the main component of H_α and D_α line broadening at the used experimental conditions. According to figure 4, the use of Lorentzian profile allows reasonably good fitting of experimental results even when the apparatus function of spectrometer (0.05 nm) is of the same order of magnitude with the FWHM values of the lines. . The intensity of W 656.33 nm line was also considered in the fitting procedure. The intensity of H line, I_H, had a comparable value in all coatings while I_D was significantly higher than I_H in the case of thin c-W and thick W coatings but much smaller in the case of porous W-O coating.

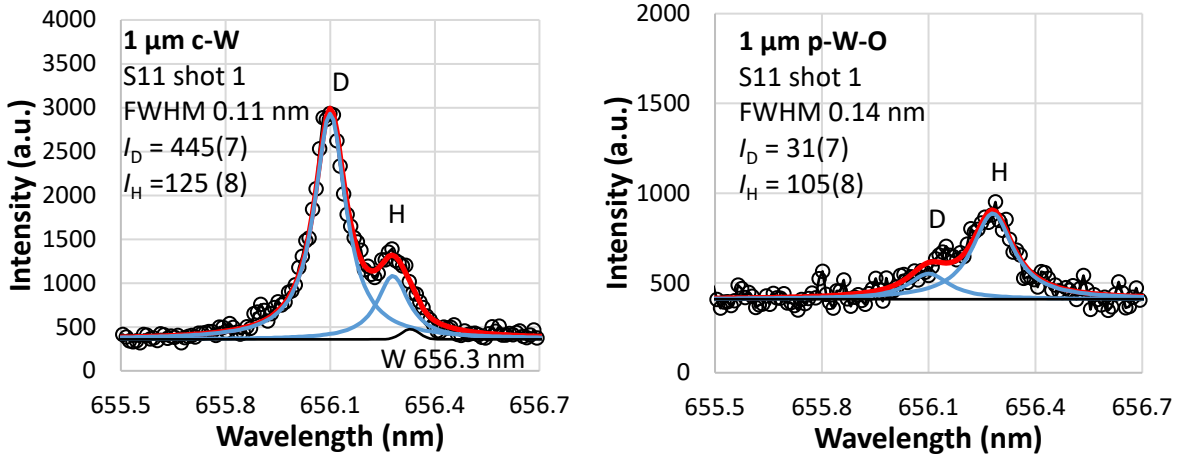
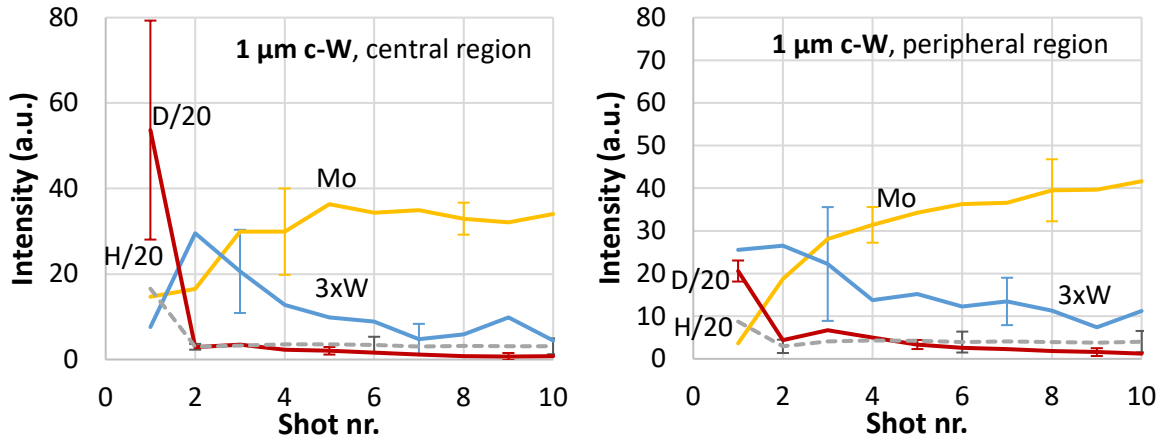


Figure 4. The in-situ LIBS spectrum of shot 1 recorded from spot 11 of c-W and p-W-O coating. These spots were corresponding to locations outside the central region of plasma beam. The FWHM values and integrated intensities of D and H Balmer alpha lines are shown together with the fitting error.

Examples of depth profiles of H, D, W, Mo line intensities corresponding to central and peripheral zones of plasma beam are shown in figure 5. Intensities of W and Mo lines, I_W and I_{Mo}, were obtained by fitting W 657.4 nm and Mo 661.9 nm lines by a Gaussian with the FWHM value corresponding to the apparatus function of spectrometer.



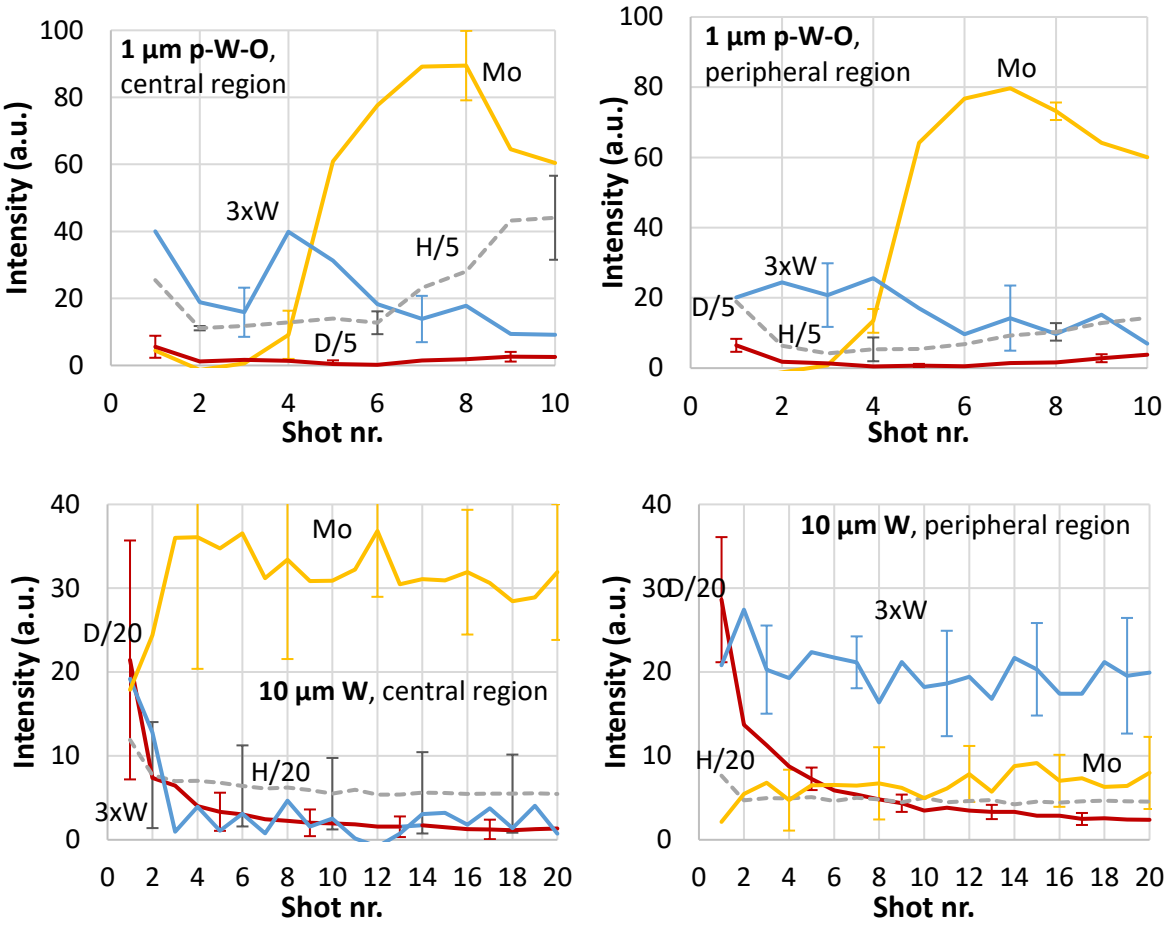


Figure 5. LIBS depth profiles of I_D, I_H, I_W and I_{Mo} values averaged over spots in central or peripheral regions of plasma beam. The values of I_D and I_H were divided by 5 or 20 and I_W was multiplied by 3 to use the same scale for all lines. Error bars are determined on the basis of the standard deviation of the average value over several laser produced craters.

The main observations for in-situ LIBS on thin c-W and p-W-O coatings are the following:

- I_W was clearly detectable on the signal of background during 3-4 shots for c-W coating and 4-5 shots for p-W-O coating. The decrease of I_W was accompanied with the increase of I_{Mo}, indicating that the Mo substrate was encountered.
- Much higher I_D was observed in the case of thin c-W and thick W coatings, when compared with the p-W-O coating. Both I_D and I_H were highest during the first shot. In the case of c-W coating, the I_D of first shot was higher in the region of coating exposed to the central zone of plasma beam while in case of p-W-O coating there was no clear correlation with the different regions on the coating similarly with our earlier study [28].
- During subsequent shots, corresponding to increasing depth in the material, the I_D remained above the noise level for 3-4 shots in the case of c-W coating while it reduced

to the noise level for p-W-O coating. I_H remained practically constant for c-W coating and somewhat increased for p-W-O coating. The noise level of approximately 10 a.u. was estimated from the standard error for line intensity and background signal.

- The ablation rates were determined by dividing the coating thickness with the number of laser shots required to reach the Mo substrate (3 shots for c-W coating and 5 shots for p-W-O coating). The resulting ablation rate was 460 nm/pulse for c-W coating and 320 nm/pulse for p-W-O coating.

The observed results obtained for c-W and p-W-O coatings are similar with our earlier ex-situ LIBS study with identical p-W-O coating and c-W-O coating containing 17% oxygen [28]. Similarity of the LIBS results obtained in present study for c-W coating and previous study for c-W-O coating suggests that the difference in oxygen content in these coatings does not affect the LIBS results. One of the main differences from our earlier ex-situ study is in H intensity which was previously considerably higher and thereby complicated the determination of D inside of the coating.

The elemental depth profiles of the 10 μm thick W coating are described separately from thinner c-W and p-W-O coatings because they were markedly different:

- I_D decreased approximately monotonically with increasing shot number and reached a stable value after about 15 shots. I_H was somewhat higher during the first shot and then remained nearly constant.
- I_W and I_{Mo} obtained from the W coating depended on the region of the coating. In at the central region of the plasma beam, I_{Mo} was higher than I_W even though the number of applied shots (20) was too small to reach the Mo substrate. In the peripheral region the I_W dominated and remained nearly constant during the applied 20 shots.

The origin of Mo in the W coating is unclear and requires additional studies. One possible explanation is the erosion of Mo substrate exposed by the flaking of W coating as suggested by figure 3. The eroded Mo is either implanted or deposited in the central zone of the plasma beam. To check the possible origin of Mo, an additional series of measurements was made with a bulk W sample, which was also exposed to deuterium plasma at similar conditions. In this case, the Mo signal was missing from LIBS spectra and the intensity of W lines remained same along the surface and through the depth profile. This result supports the proposed origin of Mo from the substrate of the coatings.

3.2. Comparison of LIBS D intensity depth profiles

Depth profiles of I_D are further compared for regions corresponding to central and peripheral zones of plasma beam in figure 6. With the exception of first laser shot, the I_D values obtained from the coating regions exposed to the central zone of plasma beam were consistently lower when compared to the ratios corresponding to peripheral zone. Highest I_D values were obtained in thick W coating followed by thin c-W coating. The I_D values of p-W-O coatings were the lowest and practically at the level of background noise with the exception of first shot. We checked that I_{Mo} originating from the substrate remained similar during different measurement series and did not depend on the region of the coating. Furthermore, I_{Mo} had comparable values for c-W and p-W-O coating. Therefore, the differences in LIBS I_D values reflect either differences in D concentration or in plasma properties and are not caused by differences in alignment of the LIBS spectral registration system relative to the laser induced plasma plume.

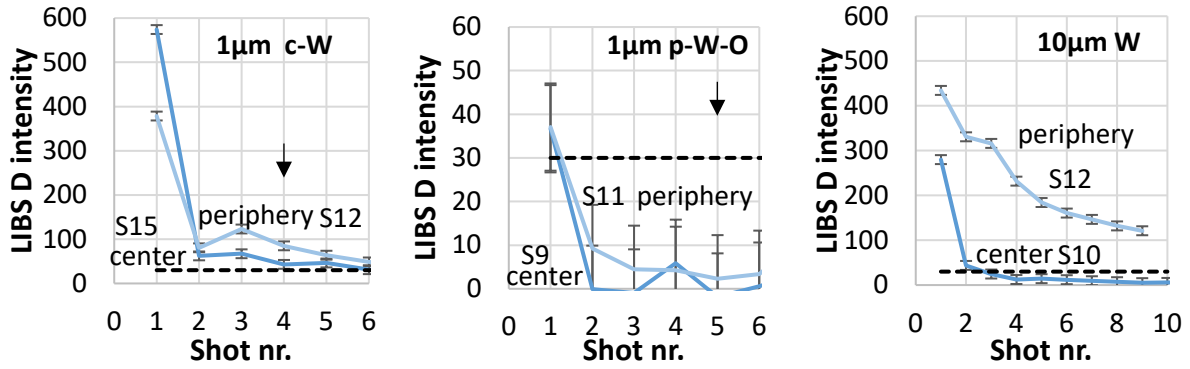


Figure 6. Depth profiles of I_D values obtained from different regions of plasma exposed coatings. Dark blue corresponds to the region exposed to the center of plasma beam while light blue corresponds to peripheral region. The arrows show the expected coating/substrate interface for thin W coatings while the dashed black line shows the limit of detection.

3.3. Deuterium depth profiles by in-situ NRA

NRA deuterium depth profiles measured 2-4 hours after the end of a D plasma exposure are shown in figure 7.

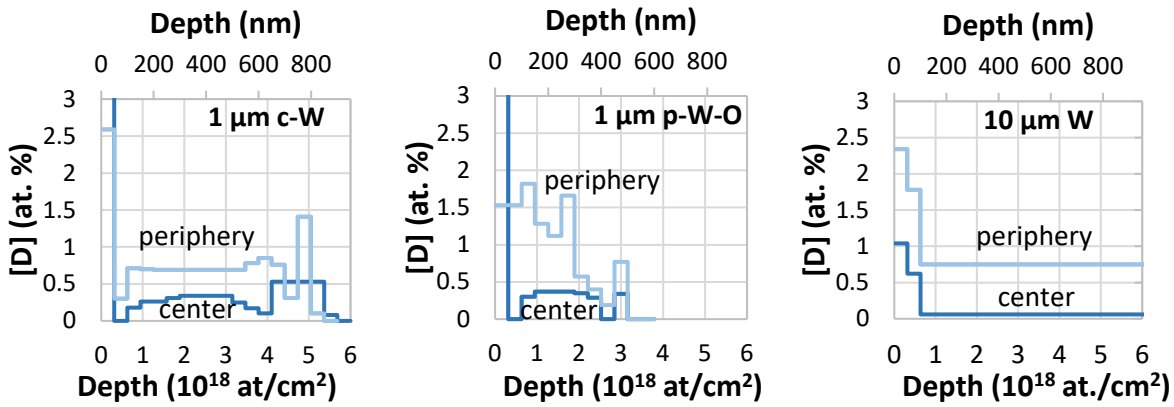


Figure 7. NRA deuterium depth profiles with at/cm^2 depth scale, in c-W, p-W-O and thick W coatings obtained at central and peripheral zones of plasma exposed coatings. For an impression of the actual depth, a scale in nm is added to the top axes assuming bulk W densities. Dark blue corresponds to the region exposed to the center of plasma beam (-5.5 mm) while light blue corresponds to peripheral region (5.5 mm). The y-axis is limited to 3 at. % to present more clearly D retention deeper in the coating.

Main NRA results are described below together with comparison with LIBS results:

- In general, the deuterium concentration was highest in the first 50-100 nm of the material and this surface concentration depended on the composition of the coating and the measurement location on the coating. Deuterium concentration in this thin surface layer varied between 2-10 at. % in the c-W coating, 2-4 at. % in the p-W-O coating and 1-3 at. % in thick W coating. Higher D surface concentration observed by NRA is consistent with the higher D intensity observed during the first LIBS shot. Highest D concentration in the surface layer of 50-100 nm was also observed in our earlier SIMS study carried out with similar c-W-O and p-W-O coatings exposed in Magnum-PSI [28].
- In the case of c-W coating, the highest surface D concentration was observed in the region corresponding to the central zone of plasma beam while for other coatings there was no clear correlation between surface concentration and the position on the coating. This tendency was also observed by LIBS.
- Deeper in the coating, the deuterium concentration remained below 2 at. % for all coatings and depended mostly on the coating region (Fig. 7). Consistently with the LIBS results, lower deuterium concentrations were found in the regions corresponding to the central zone of plasma beam.

- The main discrepancy between NRA and LIBS results was in the relative values of the average D content in different coatings. NRA showed comparable D concentration in the first 500 nm of all coatings while according to LIBS, p-W-O coating had an order of magnitude lower I_D when compared to other coatings. These results suggest that LIBS plasma plume parameters are considerably different in the case of porous W-O coating.
- The retention depth of deuterium was approximately 900 nm for c-W and 500 nm for p-W-O coating. It should be noted that the density of p-W-O coating is expectedly lower than bulk W density and its actual depth in nm is correspondingly larger. The D retention depth for thick W coating was at least 3 μm, which was the depth limit for NRA at 2.5 MeV. In the case of thin c-W and thick W coating the LIBS depth profiles of I_D comply with these D retention depths. In the case of p-W-O coating the I_D value was above the noise level only for the first shot while the ablation rate was approximately 300 nm/shot. One possible reason for this discrepancy is that the actual ablation rate of porous W-O layer of the coating is higher than the estimated ablation rate of full coating which includes the dense W interlayer. Another reason may be the temperature increase in the non-ablated part of the coating during the first laser shot which results in the D desorption. However, this should also influence the results of other coatings unless the D desorption is facilitated specifically by the porous material.
- Comparison of LIBS and NRA results allowed to estimate the sensitivity limits of LIBS in the used LIBS system. This limit depended on the coating material. In the case of thin and thick W coating, the LIBS signal was at least 3 times above the background noise level when D concentration was above 0.5 at. % according to NRA. The determined sensitivity of 0.5 at. % may be sufficient when compared to up to 5 at. % D found in JET [36].

3.4. D spatial distribution and retention by NRA

Spatial distribution of D concentration (in percentage) averaged over the first 200 up to 500 nm depth is shown in upper panel of figure 8. The results are shown for three NRA measurement series (Fig. 2), two series made in 2-6 hours interval after loading and third series 42-44 hours after loading. The results show that the outgassing of deuterium was not important in the used time-window as the deuterium retention remained the same in the limits of accuracy. This is in line with another study [21], where it was observed that most of the deuterium outgassing takes place during the first few hours after the loading.

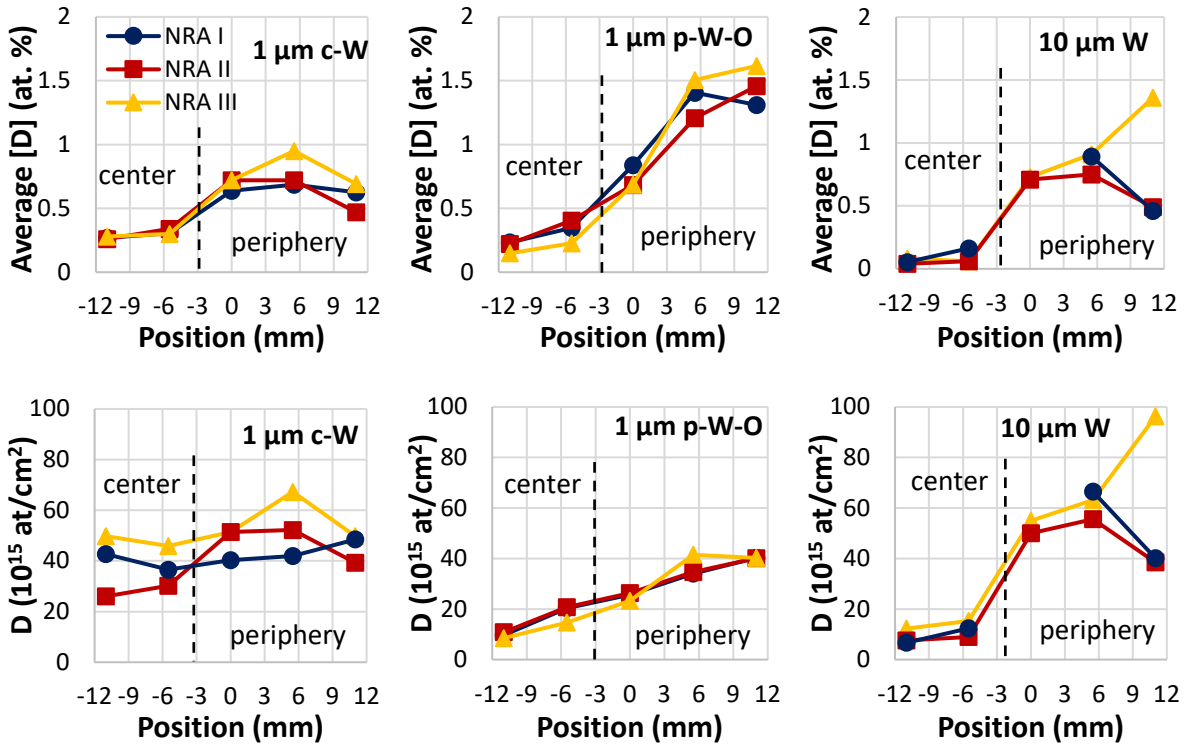


Figure 8. Spatial profiles of deuterium concentration integrated over 200 up to 500 nm depth (upper panel) and total retention of deuterium (lower panel) in c-W, p-W-O and W coatings. NRA I and II series were made 2-6 hours after deuterium loading while III series was made 42 hours later (Fig. 2).

The average deuterium content in the coatings was lower in the region exposed by the center part of the plasma beam. The difference between these regions was most notable for thick W and p-W-O coating. One reason for decreased D percentage in the coating region exposed to the central zone of plasma beam may be related to higher surface temperature in the central zone. Highest D retention is usually observed in the temperature range of 200-300°C while the retention decreases at higher temperatures [37]. In the present study, the maximum temperature in the central zone was 390°C. Earlier studies have shown that the temperature decreases towards the outer regions of the Gaussian plasma beam [38] and 200-300°C is therefore obtained outside of the center of the irradiation zone.

The total deuterium retention in 1 µm thick layer of coating is shown in the lower panel of figure 8. D retention in the peripheral coating regions had comparable value (40-60·10^{15} D at/cm^2) for all coatings regardless of the composition. This suggests that the presence of oxygen has only a small effect on the D retention at the conditions present in the peripheral

zone of plasma beam. In the region corresponding to the central zone of plasma beam, the D retention remained higher for c-W coating. This high retention can be partially explained by the increased D content in the uppermost 50 nm thick surface layer of c-W coating. Our previous study with c-W-O coating which had comparable LIBS results with the present c-W coating showed the formation of a 50-100 nm thick surface layer with nanosized voids in the central zone of plasma exposure [28]. It has been suggested that such layer may retain higher amount of D while decreasing the retention deeper in the coating [39].

4. Conclusions

For the present study, in-situ LIBS and NRA measurements of D retention in thin c-W, thick W and porous W-O coatings loaded with deuterium in Magnum-PSI linear plasma device were carried out. The aim was to compare the results of both methods.

According to NRA results, comparable deuterium retention was observed in all coatings. Except for 50-100 nm surface layer, higher D concentrations were determined in the regions of the coatings which were exposed to peripheral zone of plasma beam than in the region of the plasma beam. This is probably due to the lower surface temperature. The differences in retention were less pronounced for different regions of c-W coating because the surface layer had an order of magnitude higher D concentration in the region exposed to highest plasma flux in the central zone of plasma beam.

The results obtained by LIBS were partially in correlation with the NRA results. LIBS I_D depth profiles were similar with NRA D concentration depth profiles and also reflected the spatial distribution of D along the sample surface.

Clear differences between the results of LIBS and NRA methods were observed for coatings with different composition. According to LIBS, porous W-O coating had much smaller I_D values when compared with other coatings while according to NRA the differences in D concentrations of different coatings were considerably less pronounced. The difference is expectedly caused by different laser plasma plume properties for these coatings. In the future studies, the *D* intensity should be normalized by using intensities of elements which have known composition in the coating and give sufficiently strong intensity.

Acknowledgements

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