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Abstract
Laser-induced breakdown spectroscopy (LIBS) is a promising method for quantifying the fuel content of the plasma-facing components of ITER both in between plasma discharges (in-situ) and after maintenance operations. The aim of the present study is to test the applicability of in-situ LIBS for monitoring deuterium (D) and helium (He) content of W samples exposed to fusion relevant plasma fluxes in the linear plasma device Pilot-PSI.

The D loading was performed during 1000 s of plasma exposure at low (200–300 °C) surface temperatures. Despite of low intensity and noisy LIBS spectra, H and D lines, at 656.1 and 656.3 nm, respectively, could be fitted with Lorentzian contours and reliably resolved at 1.2 mbar background pressure of argon.

In the case of He loading, the samples were also exposed to plasma during 1000 s while the surface temperature reached values up to 720 °C at the center. Already at 10−2 mbar residual pressure of the device, the He I line at 587.6 nm was visible for the first 2–3 laser shots.

We demonstrated that in-situ LIBS is a reliable method for detection of He and D retention in ITER-relevant materials. Nevertheless, for measuring relative and absolute concentrations of D and He in the ITER-relevant samples, further studies are needed.

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1. Introduction

Monitoring retention of hydrogen (H) isotopes on plasma-facing components (PFCs) will be a mandatory task during the operational phase of ITER to prevent the safety limit of 700 g of tritium (T) in the vessel from being exceeded. As ITER may start with helium (He) plasma, it is also necessary to monitor the amount of accumulated He in the PFCs: Large He inventories in the vessel may lead to the formation of nanoscale features on tungsten (W) wall components, which will further deteriorate their power-handling capabilities, enhanced erosion and dust formation in the vessel as well as strongly alter the fuel-retention characteristics of the PFCs [1].

Earlier studies have demonstrated that during exposure to fusion-relevant plasmas, fuel retention in W is strongly dependent on surface morphology and surface temperature [2–4] that are controlled by the flux and composition of the plasma [5]. D is mainly retained in the microcracks formed on the W surface [6] such that at low (~10−2 m−2s−1) D fluxes the retention rate is more efficient at moderate (200–300 °C) surface temperatures [4] while at higher fluxes (~10−3 m−2s−1) the retention characteristics are modified due to strong tendency for blister formation at high surface temperatures [4].

Laser-induced breakdown spectroscopy (LIBS) is a promising method for remote in-situ monitoring of the fuel retention in the reactor walls although most of the studies on ITER-relevant materials have been done under ex-situ conditions [7,8]. We have carried out in-situ LIBS investigations at the Magnum-PSI device [9] and a recent study [10] describes in-situ LIBS experiments at JET. Both the signal-to-noise ratio and the width of spectral lines for a specific laser shot depend on the delay time between the laser pulse and the beginning of the spectral recording (t0) and on the width of the recording time-gate Δt.

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Experimentally D detection and signal-to-noise ratios can be improved by carrying out the measurements at moderate background gas pressures (Ar or He at ~1 mbar) [11]. However, compared with vacuum conditions, the background gas increases the electron density in the laser-produced plasma plume. As a result, the broadening of spectral lines by the Stark effect increases which leads to a stronger overlapping of the closely-lying spectral lines of the different H isotopes. Therefore, both $t_d$ and $\Delta t$ have to be carefully chosen to resolve H, D, and finally T from each other [12–14]. He is widely used as background gas in LIBS experiments (for example in [15–17]). In spite of that, there is a very limited number of LIBS studies [18] dealing with He retained in W samples.

The aim of the present study is testing the applicability of in-situ LIBS for detection of He and D retained at the tungsten surface by different fluxes of Pilot-PSI plasma. To achieve this goal, the samples were exposed to Pilot-PSI plasma fluxes while applying different experimental parameters. These parameters are described in Table 1. After the Pilot-PSI plasma exposure the samples containing different amount of D and He were tested with in-situ LIBS to obtain information about the detection limits and other issues considering the LIBS method.

2. Samples and procedure

The samples with 1.5 mm thick W coatings on molybdenum (Mo) were prepared using the arc-discharge based DIARC® plasma coating method [19]. The thickness and diameter of the samples were 2.5 mm and 30 mm, respectively. Coatings were used instead of bulk W samples to ensure a known reference thickness for the LIBS measurements.

The samples were exposed to plasma at the Pilot-PSI linear plasma machine in the FOM Institute DIFFER (The Netherlands). A detailed description of the device and the properties of the formed plasma flux are available in [20]. A spectral pyrometer was used to measure the peak temperature of the sample surface ($T_s$) while the spatial distribution of the temperature was measured by an IR camera. Thomson scattering was applied to determine the electron density ($n_e$) and temperature ($T_e$) of the Pilot-PSI plasma near the sample surface.

The $T_s$ and $n_e$ were around 1 eV and $5 \cdot 10^{20}$ m$^{-3}$, respectively. For the peak particle and heat fluxes we obtained the following rough estimations: $10^{24}$ s$^{-1}$m$^{-2}$ and 5 MW m$^{-2}$, respectively. The targets were biased with $-40$ V, resulting in an ion energy of around 30 eV at the target. Experimental conditions describing the Pilot-PSI plasma and specific to samples are listed in Table 1. The axial magnetic field determined the full width at half maximum (FWHM) of the Gaussian plasma beam: at 0.4 T FWHM it was 25 mm and at 0.8 T some 12 mm. The temperature profile followed the particle flux and thus had also a Gaussian profile.

The exposure procedure was similar to that described in our previous work [21]. As the Pilot-PSI device was operated with plasma shots of $\approx 100$ s duration, 10 plasma shots resulted in a total exposure time of $\approx 1000$ s and an overall particle flux of $10^{22}$ m$^{-2}$.

In addition to the standard diagnostics an in-situ LIBS setup was installed (Fig. 1). This setup was similar to the one we used in our previous study [9]. Nd: YAG laser ($\lambda = 1064$ nm, pulse duration 8 ns) with the guiding laser applied for the LIBS measurements. The laser was at an approximately 20 m distance from the Pilot-PSI device. The laser beam was focused using a lens with a focal length of 1.5 m onto the sample. The laser pulse energy at the sample surface was 170 mJ and the area of the laser spot approximately 1 mm$^2$ corresponding to an average laser fluence of 17 J/cm$^2$. At this fluence value the ablation rate for W was typically around 100 nm per laser pulse [9]. The radiation of the laser-produced plasma was directed to the fiber end FE (Fig. 1) of 0.8 mm in diameter, using a plane mirror and a lens with a focal length of 30 cm. The magnification of the plasma image at the fiber end FE was close to unity. The approximately 20 m long fiber delivered the radiation to the spectrometer. The output end was coupled to a round-to-linear fiber optics bundle consisting of 50 fibers each 120 µm in diameter. The linear end of the bundle was used as an entrance slit of a 1 m Czerny-Turner spectrometer with a 1200 lines/mm grating.

For adjusting the recording system, we used a visible guiding laser beam whose spot at the sample surface coincided with that of the Nd: YAG laser beam. The fiber end FE was shifted to the position corresponding to the maximum of the guiding laser light scattered from the sample surface. Nevertheless, there was a noticeable uncertainty (about 0.5 mm) in the fiber end FE position corresponding to the maximum and thus the system response for the signal from different spots might alter. To overcome this problem, we assumed that after 40 subsequent laser shots the W coating was totally removed and the intensity of Mo (Mo was the substrate material of the samples) lines should be independent of the sample and the spot. This assumption is consistent with the ablation rate value. Thus, possible differences in the intensities of the Mo line for the 40th laser shot were related to adjustment issues and were taken into account by proper correction coefficients.

The spectrum was detected in a pre-selected 20 nm wavelength range by Andor ICCD DH340T-18F-03 (512 × 2048 pixels) camera; partial binning (500 pixels out of 512) was carried out for every wavelength. For the detection of D the range was centered near 656 nm while in the case of He the central wavelength was 587 nm. The instrumental half width of the recording system was less than 0.05 nm.

LIBS measurements were carried out at in-situ conditions about 20 min after the plasma exposure. Using Ar as a background gas, spectra were recorded at $10^2$ and 1.2 mbar pressures. Using the latter value of the pressure allows to increase the recording sensitivity [12]. Since D and He measurements were carried out at different background pressures of Ar (Table 1), the optimal parameters for recording of time-resolved spectra were also different. D was detected at $t_d = 200$ ns and $\Delta t = 3000$ ns, while for He the values were $t_d \approx 100$ ns and $\Delta t = 400$ ns. These values were chosen considering the general considerations about the LIBS plasma expansion at different background pressures [22,12] and the results the preliminary test measurements.

As the surface modifications induced by Pilot-PSI plasma were different at different sites on the sample surface, LIBS spectra as a function of the laser shot number were recorded from various

<table>
<thead>
<tr>
<th>Regime</th>
<th>Plasma</th>
<th>Surface temp, $T_s$, °C</th>
<th>FWHM, mm</th>
<th>Exposure, s</th>
<th>Background pressure &amp; gas</th>
<th>Result of LIBS detection</th>
</tr>
</thead>
<tbody>
<tr>
<td>Previous study</td>
<td>2-step process: Ne/D &amp; D</td>
<td>1100 &amp; 200–300</td>
<td>12 &amp; 25</td>
<td>300 &amp; 370</td>
<td>1.2 mbar Ar</td>
<td>Reliable D-line detection</td>
</tr>
<tr>
<td>1</td>
<td>Ne/D</td>
<td>1100</td>
<td>12</td>
<td>300</td>
<td>1.2 mbar Ar</td>
<td>No reliable D-line detection</td>
</tr>
<tr>
<td>2</td>
<td>2-step: He &amp; D</td>
<td>770 &amp; 400–500</td>
<td>12 &amp; 25</td>
<td>600 &amp; 640</td>
<td>1.2 mbar Ar</td>
<td>No reliable D-line detection</td>
</tr>
<tr>
<td>3</td>
<td>D</td>
<td>200–300</td>
<td>25</td>
<td>910</td>
<td>1.2 mbar Ar</td>
<td>Noisy but resolved D &amp; H lines</td>
</tr>
<tr>
<td>4</td>
<td>He</td>
<td>720</td>
<td>25</td>
<td>1010</td>
<td>Both 10$^{-2}$ mbar &amp; 1.2 mbar Ar</td>
<td>He 587 nm line is easily detectable</td>
</tr>
</tbody>
</table>
spots (Fig. 2a). The laser beam was directed onto a desired spot with the help of a scanning mirror (Fig. 1). The system was aligned as described above. At each spot, spectra from 40 subsequent laser shots were recorded.

Recently (paper submitted to Journal of Nuclear Materials) we used a 2-step process for D-loading of the samples (Previous study in Table 1). We assumed that during the first step Ne ions, which simulate heavy impurities in the tokamak plasma, introduced the necessary morphology changes for efficient D loading which was implemented in phase 2. To check the validity of these assumptions, in the present study we first exposed the samples to Ne/D plasmas at high surface temperatures (regime 1 in Table 1).

Next we applied a 2-step process (regime 2 in Table 1) where the exposition to He plasma was followed by D to test the effect of the He induced changes of the W surface morphology to the D retention and detectability by LIBS.

As described above, in our previous study we achieved a strong D signal with LIBS from W samples exposed to Ne/D plasma. This plasma caused strong changes in the W coatings structure. To test the applicability of LIBS for D detection from samples without strong changes we exposed W coating to D plasma at 200–300°C surface temperature (regime 3 in Table 1).

For He detection experiments we exposed W coating to He plasma at surface temperature around 700°C (regime 4 in Table 1).

To characterize the sample surface, scanning electron microscopy (SEM) measurements were carried out using a Helios NanoLab 600 device.

3. Results and discussion

As expected, from the sample exposed to Ne and D plasma mixture (regime 1 in Table 1) the D signal was not detectable with LIBS i.e. at higher surface temperatures the D retention is not effective.

The 2-step process (regime 2 in Table 1) where the exposition to He plasma was followed by D flux gave a similar negative result as could be expected according to [23].

When exposing samples to pure D plasmas at low surface temperatures (Table 1 regime 3) resulted only in small visual changes at surface (Fig. 2a) while SEM images show the appearance of randomly distributed specks of ~100 nm size (Fig. 2b, c). The structure is similar to the one achieved in [4] using similar D plasma parameters. These findings confirm that the sputtering yield of D has a low value [24]. Nevertheless, due to moderate surface temperature (200–300°C) a noticeable amount of D was retained. Near 656 nm LIBS signal with a low signal-to noise ratio was recorded. H and D lines were fitted by Lorentzian profiles with the same half-width FWHM = 0.13 nm (Fig. 2b, c). The relative standard deviation of the different fits belonging to the first laser shots was ~10%, but starting from the second shot the D peak (λ = 656.1 nm) was at the noise level, while the H line (λ = 656.28 nm) was detectable during all the laser shots. Thus, due to the plasma action most of the D was accumulated within the topmost 100 nm (assuming ablation rate around 100 nm per laser shot). Similar depth profile for D is described in [25]. An alternative explanation is that the first laser shot heat the sample near the LIBS crater, thus causing outgassing and the D signal becoming undetectable. At the same time the H0
line was persistent during all laser shots, therefore not caused by the water vapor on the surface that is reported in several works [11]. It is likely that hydrogen originated as a contamination from the background Ar gas. The other possible explanation is that the hydrogen content originates from the sample preparation procedure. This experiment shows that LIBS is suitable for detecting D from samples with relatively high D content (compared to the less effective loading conditions).

As a result of the He plasma (regime 4 Table 1), in the central region of the sample a filament-like network was observed (Fig. 3c), similarly to what has been observed under similar conditions in [26]. The first LIBS measurements were carried out at an Ar background pressure of 1.2 mbar, giving a clear and strong He signal at 587.6 nm. Further LIBS testing was done at a lower pressures (10^-2 mbar). The He signal was still easily detectable in regions with the clearest filament structures (Figures 4a and b). Further away from the center the He signal was almost non-existent (Fig. 4c). The He signal was detectable for the first two laser shots but the line intensity of the second shot was nearly 10 times lower than that of the first one. It could be assumed that He is retained mainly in the filament structure and not much deeper in the coating.

Compared to [27] we can say that the He concentration around 4 at. % in W samples is easily detectable with in-situ LIBS even at low (less than 10^-2 mbar) background pressures. This result is somewhat unexpected since the calculated (assuming excitation temperature in LIBS plasma around 1 eV) intensity for the 656.1 nm line of D should be orders of magnitudes larger than for the 587.6 nm line of He. The energies for the upper states of the transitions are 12.1 eV and 23.7 eV for D and He, respectively. The D0 line consists of 7 transitions with probabilities (gσA0) in the range of 10^7-10^8 s^-1, while the He line consists of 5 transitions with similar probabilities [28]. Nevertheless, it is not possible to say more about the differences in the line intensities, since we do not know the actual concentrations of D and He. Further work include ex-situ surface analyses, such as nuclear reaction analysis (NRA) and time-of-flight elastic recoil detection analysis (TOF-ERDA) to quantify the composition of the surface layers.

**4. Conclusions**

In this study we loaded tungsten coatings with deuterium and helium in the Pilot-PSI linear plasma machine. After the plasma exposure we carried out in-situ LIBS measurements to determine the amount of D and He retained in the samples. As previous studies suggest, the efficiency of deuterium loading depends strongly on the sample surface temperature. For the plasma fluxes used in this work the loading was efficient at low surface temperatures. In this case we reliably detected D signal at 1.2 mbar background pressure. He retention was efficient at regions were a filament-like structure had been formed. He signal was easily detectable at 10^-2 mbar background pressure.

Thus we demonstrated that in the applied conditions LIBS is a suitable in-situ tool for deuterium and helium detection from tungsten samples. In this study we have introduced a proper LIBS setup and measurement procedure for linear plasma machines monitor erosion of samples during their plasma exposure and the accumulation of plasma fuel on them.

To relate results directly to the ITER conditions, the limits of LIBS detection for deuterium and helium have to be determined with more sophisticated post-mortem methods, such as nuclear reaction analysis (NRA), time-of-flight elastic recoil detection analysis (TOF-ERDA), and secondary ion mass spectroscopy (SIMS).
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