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Quantification of H/D content in Be/W mixtures coatings by CF-LIBS

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Abstract

In ITER, a remote handling laser-induced breakdown spectroscopy (LIBS) system is considered to be able to observe regions where deposition of thick layers is expected to occur and assess the retention of fuel on wall structures. The H and D contents of surface layers on divertor and first-wall materials have been intensely studied by LIBS but mostly by depth profile analysis of D. As far as we know, quantitative analysis of H/D in BeW mixed layer by calibration free-LIBS (CF-LIBS) has not been performed. Thus, the aim of this work is the quantification of the relative concentrations of D and H in Be-based material samples by CF-LIBS. The samples used were Be/W(67:33) as mixed homogeneous coatings (2 μm) on Mo substrates. Laser ablation was performed using a 1064 nm laser with 5 ns pulses. In order to enhance the resolution to distinguish H, D and in future T from each other, two different pressures were used: high vacuum and 0.5 mbar of Ar. Suitable Be and W spectral lines (without interferences and self-absorption) have been selected for precise evaluation of the electron temperature, T_e, of the plasma using the Boltzmann plots. The electron density, n_e, was extracted from the Saha equation using the average electron temperatures obtained from the Stark broadening of the H_α line. With these values, the D content of the samples has been calculated by CF LIBS as $\sim$4.7% $\pm$ 2.9%. These results are in a good agreement with thermal desorption spectroscopy measurements, which gives a 4–5 at% for the D content. In addition, the depth profile is similar to that recorded using secondary ion mass spectrometry.

Keywords: BeW, fuel retention, quantification, CF-LIBS

(Some figures may appear in colour only in the online journal)

1. Introduction

The study of plasma-wall interactions is crucial for the design and operation of fusion reactors as well as the development of novel materials suitable in such environments with high energy and particle fluxes from the main plasma [1, 2]. One of the most active research questions in this field is the avoidance of damaging plasma-facing components by erosion and polluting of the plasma itself by eroded impurity atoms [3]. But equally, if not more, important is understanding where the eroded particles are finally deposited together with various impurity atoms and particles from the plasma fuel.

In the last few years, many experiments have been conducted to find the best first-wall materials for fusion devices. These shall be designed to tolerate high heat and particle

loads as well as efficiently resist physical and chemical erosion, to exhibit long lifetime under neutron-bombardment, and to show low activation and retention of the fuel in them [4]. Such materials are either of high or low atomic numbers (Z). In contrast to low-Z materials, the materials of high-Z elements are significantly more resistant to erosion. This results in a less contaminated plasma due to the effect of sputtering of the wall materials. On the other hand, high-Z impurities are much more efficient radiators, so it has to be considered that burning plasma tolerates even smaller quantities of high-Z materials. The choice for the materials of the reactor at the international fusion device, ITER is Be for the first wall and W for the divertor [5, 6]. Materials of low-Z elements such as Be are easy to be eroded and co-deposition of tritium with the eroded Be is expected, as well as a significant fraction of impurities like N and O [2]. But, if Be atoms end up in the plasma, they will not lead to massive radiation losses. In addition, a Be wall getters O efficiently, thus reducing contamination of the plasma. Nonetheless, the beryllium-clad first wall is the material chosen for the initial phase of ITER, presently under construction [1, 7]. Thus, it is of great importance to understand how fuel (D, T) is retained in such an environment due to radiological safety reasons, especially in pure wall materials and various co-deposited layers or mixed materials that could appear in real nuclear fusion reactor in the divertor region.

The use of laser-induced breakdown spectroscopy (LIBS) as a multi-elemental analytical technique in fusion-relevant materials has become very popular recently [8, 9]. LIBS has proven to be a suitable experimental technique for real time diagnostics of deposition and retention processes [7] and compositional analysis of deposited layers in the divertor region [8]. In ITER, a remote handling LIBS system is considered for *in situ* monitoring and characterization of fusion relevant materials during maintenance breaks [3, 10].

The aim of this work is the quantification of H/D elemental content in Be-based material samples by calibration free LIBS (CF-LIBS), an approach of multi-elemental quantitative analysis of the qualitative LIBS spectra. The so-called CF-LIBS approach is well described in [11]. Even if the quantification by CF-LIBS is not as precise as with some other methods, it can be used *in situ*, which obviously is a benefit in comparison to, e.g. ion beam analysis.

2. Experimental setup

2.1. Samples

The samples with mixed coatings of Be/W with thicknesses of 1.5–2 μm were deposited on Mo substrates in the National Institute for Laser, Plasma, and Radiation Physics, Romania, by high power impulse magnetron sputtering (HiPIMS) in a high vacuum chamber pumped down to a typical base pressure lower than 10^{-4} Pa [5]. The target values for the atomic concentrations of Be and W were 67% and 33%, respectively, and the layers were produced both with and without D inclusions to simulate deposits in the divertor region of ITER.

2.2. LIBS set-up

LIBS experiments were carried out in a specially designed set-up in the Be-handling premises of VTT—the Technical Research Centre of Finland. The optical scheme and detailed description of the set-up are presented elsewhere [12, 13]. Briefly, a pulsed Nd:YAG laser (Brilliant B, Quantel), operating at 1064 nm with 5 ns laser pulses, was used to produce the LIBS plasma. The laser fluence was set to ~4.5 J cm^{-2}, which corresponds to the minimum pulse energy obtained from the laser without additional attenuators. The fluence was aimed to be kept low to keep the ablation rate of real co-deposited layers reasonable. As discussed in [12], the ablation rates of samples from JET have been observed to be significantly higher than those of laboratory-made coatings (compare to [13]), most likely due to their less crystalline structure. The created plasma emission was detected perpendicularly to the laser beam. The emitted light was collected by an off-axis parabolic mirror and guided onto the end of a fiber bundle (50 fibers with diameters of 50 μm) which delivered it to the entrance slit of the Andor SR-750 spectrometer equipped with an Andor iStar 340 T ICCD camera. Two different gratings were used in the spectrometer.

The LIBS spectra were measured in five pre-selected spectral ranges centered at 260 nm, 314 nm, 395 nm, 450 nm, and 518 nm, respectively, using a grating with 600 grooves mm^{-1} density blazed at 500 nm, giving 40 nm wide spectral windows. All these measurements were carried out at high vacuum (10^{-7} mbar) conditions with the delay time 80 ns. At such delay, both the ionic and neutral lines are visible while the continuum radiation due to the bremsstrahlung has already decayed sufficiently.

For recording the Balmer alpha lines of hydrogen isotopes at around 656 nm, a special grating with 1350 grooves mm^{-1} and blaze at 675 nm was used. The spectral resolution of the applied spectrometer with this grating was approximately 0.1 nm (experimentally verified by recording the HeNe laser line at 632.8 nm scattered from diffuser). This configuration with a spectral window of 20 nm enabled partly resolving D_α and H_α lines. The LIBS spectra recordings were done both in high vacuum and at 0.5 mbar Ar background pressures in order to enhance the signal-to-noise ratio by increased collisional excitation and thus improve the detectability and separation of the D_α and H_α lines. The recording delay at 0.5 mbar was 150 ns. A longer delay at higher pressure was selected for D/H studies than for Be/W to obtain narrower spectral lines with an easier distinction between the isotopes.

In all the experiments the width of the recording gate was 500 ns. This parameter was chosen after optimization to obtain the best signal-to-noise ratio. The removal rates for the coatings were estimated from the produced crater depths measured with a profilometer and were practically the same in both experimental conditions (high vacuum and 0.5 mbar pressure of Ar).

For each measurement point on the sample, 150 laser pulses were applied to be able to reconstruct the elemental depth profiles of the coating and reach the Mo substrate. For
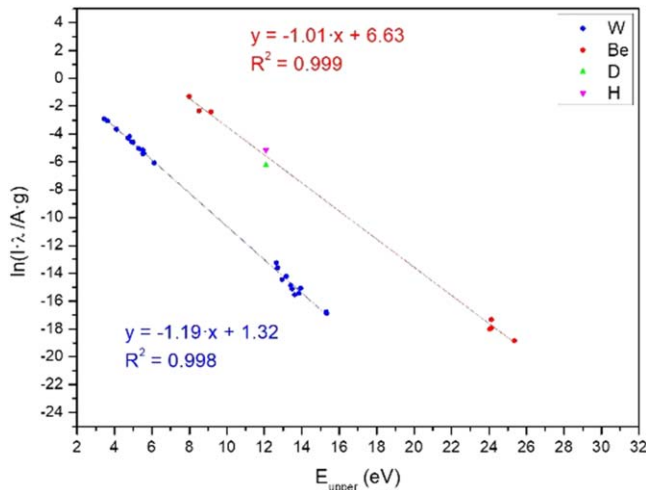
Figure 1. Saha–Boltzmann plot for W, Be, D and H for the first shot of BeWD LIBS analysis.

the 656 nm spectral window, averages of five depth profile series at five different fresh places were used. The spectral response curve of the entire optical system was evaluated for both gratings using a deuterium-halogen calibration lamp (Ocean Optics DH-2000-cal). For long wavelengths (above 400 nm), high passband filters with a transmittance of 90% were used in the desired spectral range. The filters were used to avoid the simultaneous detection of the second-order lines from lower wavelength ranges. All measured spectra were corrected to the spectral response curve and the presence of the filter.

3. Results and discussion

In all the measured spectra a set of interference and self-absorption free W I–II and Be I–II lines was selected by comparing the measured data with simulated spectral lines. From the experimental spectra it was clear that Mo lines start to appear from the 9th shot onwards, thus we concentrated on the first eight shots. For the general CF-LIBS method, the fulfillment of local thermodynamical equilibrium (LTE) requires a single value for the common electron temperature. Both at high vacuum and at 0.5 mbar Ar pressure conditions the density of the particles inside the plasma plume was much higher than density and pressure at surrounding gas due to the ablation process (vacuum: particle density $= 1.6 \times 10^{21}\,\mathrm{m}^{-3}$ and pressure $= 250\,\mathrm{Pa}$; 0.5 mbar Ar: particle density $= 2.3 \times 10^{22}\,\mathrm{m}^{-3}$ and pressure $= 3500\,\mathrm{Pa}$).

Figure 1 shows the Saha Boltzmann plot (SBP) of selected emission lines of W I–II, Be I–II and D I, H I lines for the first laser shot (the selected lines are collected in table 1). It is noticeable that the electron temperature can be quite reliably extracted from the W I–II lines, thus these lines were used also for the evaluation of the electron density by the Saha equation. For Be, not enough lines for precise temperature evaluation were obtained from the Be I and Be II Boltzmann plots separately, and the previously evaluated

electron density was used to calculate the electron temperature. The electron temperatures obtained this way were slightly different ($\sim$10%) from those determined using figure 1. Obtained electron density values from the Saha equation were verified by the Stark broadening of the D_{α} and H_{α} non-resolved line.

Figure 2 shows the electron temperature obtained from neutral and singly ionized tungsten spectral lines, as well as the average electron temperature. It can be observed in the figure that the electron temperature is practically constant until the Mo substrate is reached, around the 8th laser pulse. Also, both W I and W II lines show similar behavior.

Figure 3 shows the electron density values for each laser shot, being on average $2.7 \times 10^{22}\,\mathrm{m}^{-3}$ for the first 8 laser shots. As observed for the electron temperature (see figure 2), the electron density is constant (with a slight increase/dispersion). After the 8th laser pulse, the behavior of the electron density changes, probably due to the interference of Mo spectral lines of the substrate with the W lines used in the evaluation.

Figure 4 shows the resolved spectral lines belonging to D_{α}, H_{α}, and W at 656.1 nm, 656.3 nm, and 656.39 nm, respectively. This spectrum was obtained under 0.5 mbar Ar pressure as it was observed experimentally to have improved signal to noise ratio. The experimental spectra are partially resolved, showing two peaks that consist of the three above-mentioned spectral lines. To this end, a Lorentzian contour for the D_{α} and H_{α} with varying FWHM (blue lines) and a Gaussian contour for the W line with an FWHM of 0.1 nm (magenta line) have been used in the fitting procedure.

D'Ulivo *et al* [14] also deal with the deconvolution of hydrogen and deuterium lines in the LIBS spectrum. They performed a two-peak Lorentzian deconvolution of the spectra. In their case, the sample was in gaseous state and the electron density was an order of magnitude lower ($2 \times 10^{15}\,\mathrm{cm}^{-3}$).

Line broadening of hydrogen isotope in laser-induced plasma is caused dominantly by the Stark effect. The higher the electron density the larger broadening is observed. Thus it is difficult to resolve these lines at higher pressures, but at reasonably low pressure (0.5 mBar) it is possible. In our experiments, spectra obtained in vacuum showed narrower lines than in 0.5 mBar Ar background pressure, but the signals were very weak (also low S/N ratio) and reliable deconvolution of D and H based on these spectra was not possible.

The intensities of H_{α} and D_{α} lines obtained by fitting are shown in figure 5. In that figure, it can be observed that both H_{α} and D_{α} intensities decrease immediately after the first shot. The retained D_{α} is mainly on the surface of the plasma-facing material, and the extra high intensity of H_{α} in the first shots is due to surface water contamination.

As it was mentioned before, it is well-know that to perform CF-LIBS LTE is necessary. In this particular case, LTE is not completely achieved. Thus, we evaluated T_e separately for each element and compared the values with each other. For Be and W the difference is only $\sim$10%, thus no major errors are induced. Thus, we used different T_e for different elemental species found in the plasma. As can be observed in

Table 1. List of the spectral lines used in the Saha–Boltzmann plot for the T_e evaluation. The non-resolved lines that were fitted as one spectral line are presented in the table by black frames. The resolved lines that were fitted separately are presented each one inside one black frame.

Element	Wavelength (nm)	A_{ki} (s^{-1})	E_i (eV)	E_k (eV)	g_i	g_k
W (I)	272.268	2.85E + 08	1.857	6.409	5	5
	272.435	1.05E + 08	0.366	4.916	7	7
	272.463	2.57E + 07	0.771	5.320	9	9
	272.503	1.77E + 07	0.412	4.961	5	5
	307.328	7.66E + 06	0.771	4.805	4	4
	331.139	7.67E + 06	0.366	4.109	3	2
	377.370	3.35E + 07	1.708	4.993	2	3
	378.077	5.25E + 06	0.366	3.645	3	2
	383.851	1.52E + 07	1.508	4.737	4	3
	398.328	5.01E + 07	2.458	5.570	5	6
	400.875	1.72E + 07	0.366	3.458	3	4
	401.522	1.14E + 08	2.436	5.523	6	5
	402.213	2.14E + 07	2.422	5.504	5	6
	407.315	4.29E + 06	1.869	4.912	5	5
	440.828	1.56E + 08	3.308	6.120	5	5
W (II)	244.640	4.06E + 07	0.920	5.987	6	6
	247.780	3.20E + 07	0.762	5.765	10	10
	255.497	3.52E + 07	0	4.852	2	4
	258.916	1.69E + 07	0.762	5.550	10	10
	259.149	4.96E + 06	0	4.783	2	2
	274.080	6.89E + 07	2.951	7.474	8	10
	317.356	8.56E + 06	3.533	7.439	4	6
	334.246	5.80E + 06	1.856	5.564	6	8
	334.310	6.07E + 06	2.057	5.764	8	10
	334.342	4.81E + 06	1.842	5.549	10	10
	385.111	2.08E + 05	2.546	5.764	12	10
	385.156	3.04E + 06	1.633	4.851	2	4
	385.158	1.15E + 06	1.633	4.852	2	4
	391.547	6.70E + 06	2.908	6.074	6	4
H (I)	656.271	5.39e+07	10.199	12.088	2	4
D (I)	656.112	4.21e+06	10.202	12.091	4	2
Be (I)	319.383	5.08E + 06	5.277	9.158	3	5
	381.345	4.87E + 07	5.277	8.528	3	5
	457.266	7.62E + 07	5.277	7.988	3	5
Be (II)	319.710	6.82E + 07	12.157	16.034	4	6
	319.715	7.31E + 07	12.157	16.034	6	8
	327.458	1.41E + 07	10.939	14.725	2	4
	327.467	1.41E + 07	10.939	14.724	2	2
	436.066	9.09E + 07	11.964	14.806	2	4
	436.099	1.09E + 08	11.964	14.806	4	6
	467.333	2.07E + 08	12.157	14.809	4	6
	467.342	2.21E + 08	12.157	14.810	6	8

Note. E_i and E_k are the energies of the lower and upper levels, respectively, g_i and g_k the corresponding degeneracy of the levels, and A_{ki} the transition probabilities.
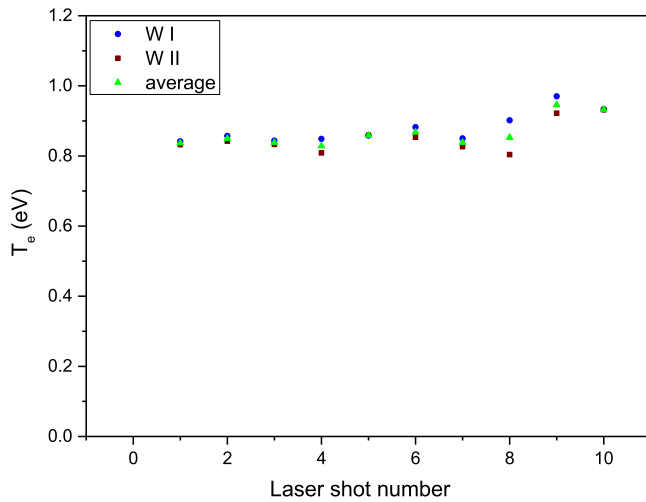
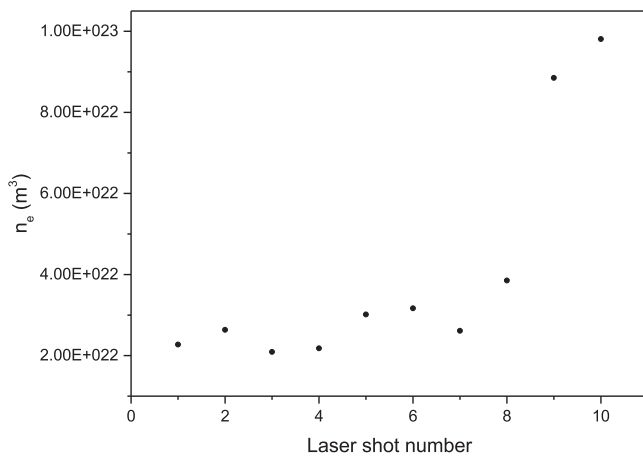**Figure 2.** Electron temperature of W I–II in the BeW sample profile as a function of the laser shot number.

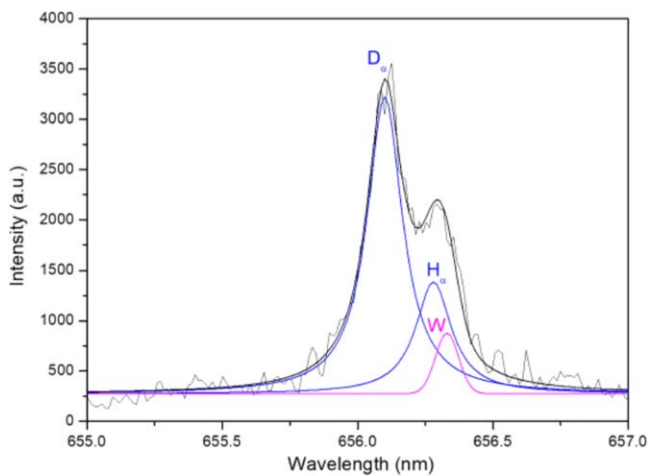**Figure 3.** Electron density of each laser shot as a function of the laser shot number.

Figure 4. D_α, H_α and W spectral lines, spectrally resolved by Lorentz and Gaussian fittings at 656.1 nm, 656.3 nm, and 656.39 nm, respectively, for the 4th laser shot.
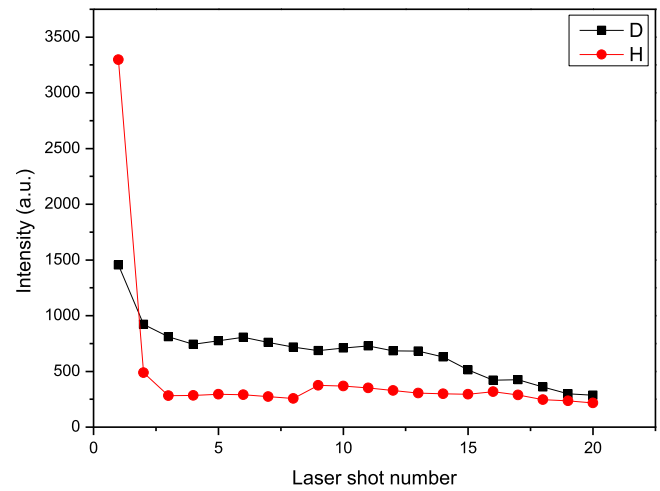

Figure 5. D_α and H_α intensities according to the laser shot number of the $Be_{33}W_{66}D$ sample.

the Saha–Boltzmann plot (see figure 1), a slightly different T_e (around 10%) can be evaluated from the W and Be curves. Each evaluated T_e was employed to quantify the respective element. Although for H/D, only 1 spectral line is observed in the spectrum, so only one point is represented in the SB plot. Thus, the T_e of some other element should be applied to quantify D content. As the chosen T_e can affect strongly the value of the estimated H/D content, three different approaches have been carried out in this work, using different evaluated averaged T_e: (1) from Be I–II and W I–II (the elements of the thin coating layer); (2) from Be I and W I (because neutral H line is observed); and (3) from Be I–II (because both H/D and Be are light elements). These temperatures and the corresponding D content for each laser shot in-depth profile mapping is presented in table 2. In the last line of the table, the final averaged value of the D content can be observed. According to the values in the table 2, the averaged D% value for each temperature ranges from 1.20% to 8.84%. Thus, we used the average of these three values to obtain the final D% from the first eight laser shots (belonging to the thin layer onto the surface).

Figure 6 shows the relative fractions of Be, W, D, and H in the BeW coating loaded with D during the first 8 laser shots of LIBS analysis. The CF-LIBS quantification was done in two steps. First, from the vacuum-based measurements, the quantities of Be, W and H + D were evaluated. At low-pressure conditions, the signal of H_α and D_α lines was relatively weak. To evaluate correctly the ratio between H and D, in the quantification process, other LIBS measurements at 0.5 mbar Ar pressure conditions were employed, and so the quantification of all 4 species (Be, W, D, H) was correctly performed. In general, all the obtained values are in agreement with the Be/W(67:33) coating, with the average value for Be being equal to 63.97% ± 11.42% (not taking into account the H isotopes).

Looking more in detail on the depth profile of the CF-LIBS quantification shot by shot, it can be seen that the lowest value was around 2%–3% (shots 1, 3 and 4) and the
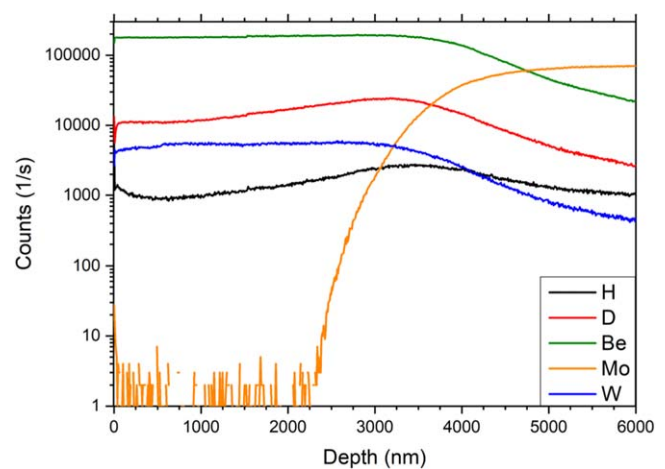
Table 2. Electron temperature (T_1 belongs to W I–II + Be I–II, T_2 belongs to W I + Be I, and T_3 belongs to Be I–II) and atomic percentages for W, Be, H and D.

Temperature (eV)	Laser shot number								
	1	2	3	4	5	6	7	8	
T_1	0.913	0.920	0.921	0.931	0.936	0.935	0.903	0.890	
T_2	0.971	0.878	0.917	0.940	0.895	0.859	0.923	1.046	
T_3	1.089	1.091	1.026	1.042	1.070	1.206	1.045	1.078	
									Average
D% for T_1	5.24	11.86	4.15	2.42	8.67	7.26	9.43	11.62	7.58
D% for T_2	2.63	19.30	4.33	2.14	14.34	18.89	7.27	1.79	8.84
D% for T_3	0.73	1.81	4.15	0.62	1.90	0.44	1.71	1.28	1.20
W %	24.54	39.35	23.72	16.15	32.16	28.63	29.94	22.29	27.1 ± 7.04
Be %	66.12	43.84	71.96	81.46	56.38	59.32	61.73	70.97	63.97 ± 11.42
H %	6.48	5.82	1.11	0.66	3.16	3.19	2.20	1.85	3.19 ± 2.11
D %	2.87	10.99	3.20	1.73	8.30	8.86	6.14	4.89	5.87 ± 3.28
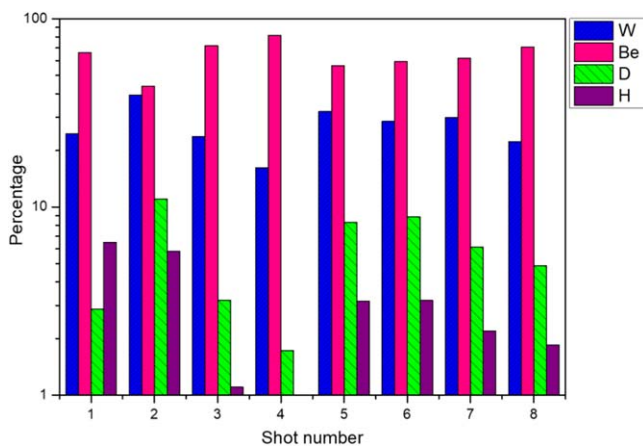
Figure 6. Percentage elemental concentration of the BeWD coating (first 8 laser shots into the surface of the sample).

Figure 7. SIMS depth profile of the BeWD/Mo sample for H, D, Be, Mo and W.

highest value was approx. 10% (shot 2). In the averaged first eight shots the error in the quantification by CF-LIBS was around 3.3%. The error in each concentration value shot to shot is a little bit higher than the error of the averaged concentration of the first eight laser shots, but we should point that the emission spectra for the quantification by CF-LIBS as a function of depth were measured in a number of spectral regions, changing the location for each region. This means that each laser-induced breakdown is a new event, so it could has slightly different plasma parameters (temperature and density) from shot to shot, resulting in slightly different elemental composition values finally. In our case, we aimed at the quantification performed on the basis of single-shot measurements in order to keep the possibility of depth profiling. This is of great importance when considering the real-world applications in fusion reactors to see the real limits of the method.

The quantification of the elements in the BeWD sample by CF-LIBS confirms the possibility to evaluate the correct Be/W ratio from a single-shot depth profile analysis with a depth resolution of 275 ± 35 nm. By enlarging the spectral range down to the UV region, a more precise temperature evaluation than in [15] and also a precise quantification of the

major elements is achieved. Here, for the first time, D and H are quantified in Be-based samples by the CF approach at low pressures, resulting in an estimated D concentration of 5.87% ± 3.28% (average value for the entire thickness of the BeW layer, 2 μm thickness).

These results are in good agreement with thermal desorption spectroscopy (TDS) measurements, which gives a 4–5 at% for D content. The advantage of CF-LIBS comparing with TDS is that measurements are performed only in a single place, removing nanograms of the surface, while in TDS, the whole surface of the sample is heated to remove the D that is contained in it. Some other techniques, e.g. Rutherford backscattering spectrometry (RBS) or nuclear reaction analysis (NRA) can also provide quantification information. Although, RBS can only perform analysis ex situ, while NRA can perform them *in situ* but the installation of its setup it is considerable more expensive than LIBS.

In addition, secondary ion mass spectrometry (SIMS) measurements were performed also to compare with the CF-LIBS approach. In this case, SIMS provides very good information regarding the depth profile but only qualitatively, as it can be observed in figure 7. In figure 7 it can be observed the

studied main elements of the sample (Be, W, Mo, H, and D), are observed. SIMS provides information about the thickness of the layer, as well as the laser ablation rate per laser shot layer (once an absolute profilometry analysis on the final crater is done). At the same time, it gives information on the H/D ratio in the layer. SIMS indicates that the D levels in the samples are several at%. This supports the LIBS and TDS findings.

4. Conclusions

In this work, the depth profile quantification of the elements present in the BeWD sample has been performed by CF-LIBS. The enlargement of the spectral range to the UV part allows evaluating the electron temperature and density more precisely. Thus, this leads to a more accurate quantification by CF-LIBS. Besides, the measurements performed by a high-resolution spectrometer provide the possibility to separate by a Lorentzian and Gaussian fittings the D_α, H_α and W spectral lines at around 656.3 nm. This allows quantifying D and H separately by CF-LIBS. The obtained concentration, in percentage, of Be and W, are in agreement with the target composition of the analyzed sample (67:33), and the D concentration has been evaluated to $5.87\% \pm 3.28\%$ for D. This value is also in very good agreement with the TDS measurements (4–5 at% for D content). Although, the advantage of LIBS of measuring in only one place and not on the whole surface as in the TDS case makes this methodology more suitable for online analysis. LIBS and SIMS depth profile analyses were also in good agreement.

Acknowledgments

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