

First Wall Monitoring by LIBS: Options and Limitations

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The development of laser induced breakdown spectroscopy (LIBS) for characterisation of plasma facing components (PFC) of fusion reactors, is under study in numerous scientific laboratories [1, 2]. A feasibility study showed that *in situ* LIBS is applicable at JET [2]. Many problems, met in application of LIBS at fusion-related studies (like those connected with single shot and remote recording, methods of quantitative analysis) are characteristic to LIBS in general [3, 4]. At the same time LIBS for fusion has its peculiarities. The thermal and ablation properties of ITER-relevant materials (Be, W) differ considerably. Due to the plasma action the surface morphology and phase structure of PFC changes [5] which could alter the ablation rate. In situ LIBS for first wall testing assumes the measurements in vacuum. In vacuum the plasma plume expands rapidly and compared with atmospheric pressure background, the charged particle concentrations and plasma temperature are considerably lower.

Most of LIBS groups tested samples where Al has been used as a proxy for Be. LIBS studies with Be-containing samples were carried out only in [6]. Elemental depth profiling of samples surface, built on the basis of LIBS measurements, showed a qualitative matching with results obtained by different surface characterisation methods.

The most straightforward way for quantitative finding of unknown concentrations by LIBS is the using of calibration curves. This method assumes the knowledge of elemental composition of samples. Another method, called calibration-free LIBS (CF LIBS), is free from this limitation [4]. It is based on the theoretical relationship between the concentration N of an element in the plasma plume and the integral intensity of its spectral line. Reliable estimation of concentrations could be reached when there are a number analytic lines with a small self-absorption, Stark widening is large enough for determination of electron density, LTE conditions for plasma is fulfilled, etc. Only few papers dealt with the application of CF LIBS for W-containing samples [7, 8].

Recently a method for a rough estimation of relative concentration has been proposed [1]. The method compares the spectral line intensity of an element of unknown concentration with that

of the bulk material. The aim of the present study was to clarify the limits of the applicability of this method.

Our main measurements were carried using 1064 nm wavelength of Nd/YAG laser. Time-gated single shot LIBS spectra were recorded with Mechelle 5000 spectrometer and ICCD camera. Spectra of samples which had W/Al/C and Be/W coatings were compared with those of bulk materials. Spectra were recorded at different values of laser fluence Φ .

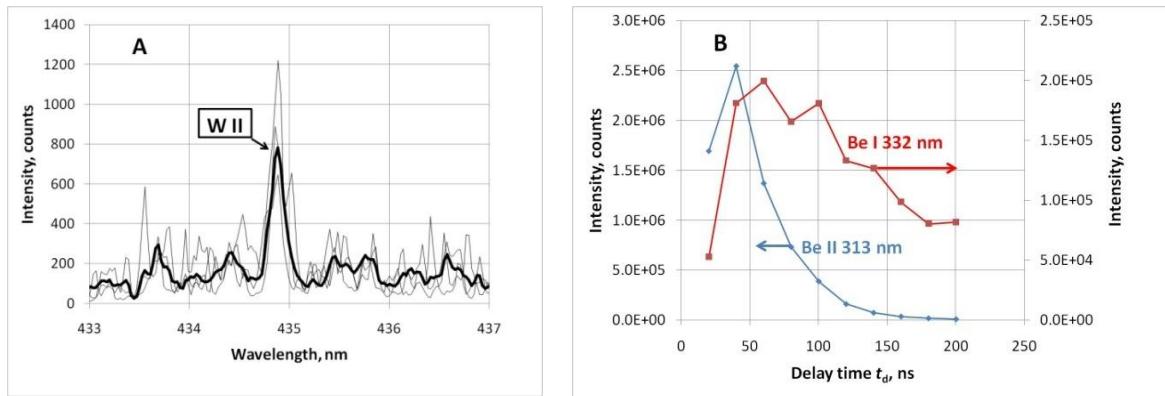


Figure 1. A – a part of W spectrum, bulk material ; thin lines – three single-shot spectra; thick line – the average of 8 spectra, $\Phi = 20 \text{ J cm}^{-2}$. B – intensity of spectral lines as a function of delay time from the laser pulse, Be coating on stainless steel, $\Phi = 5 \text{ J cm}^{-2}$.

In case of W there were a very limited number of spectral lines which had acceptable values of signal-to-background, S/B, ratio (Figure 1A) and small enough self-absorption. Besides the instrumental noise and continuous spectrum, partly overlapped numerous weak W lines gave a remarkable contribution to the background signal. Figure 1B shows that optimum delay times in vacuum are considerably shorter than at atmospheric pressure [3]. From shot-to-shot the intensity of a spectral line fluctuates remarkably and the cumulative intensity much better brings out the sample properties (Figure 2A). It should be pointed that the slope of the cumulative intensity is nothing else but the average intensity. When the matrix effects are negligible, the ratio of the slope of a sample's element to the slope of the corresponding bulk material should give the relative concentration (Figure 2B). We studied 18 Al lines and selected lines of negligible self-absorption. Relative concentrations of Al, [Al], obtained for selected spectral lines matched well with those measured by the nuclear reaction analysis (NRA - [Al] = 0.5, LIBS - [Al] = 0.45). The similar good result was found also for Be. At the same time even for those W lines which had a minor self-absorption, the slopes' ratio depended on fluence and gave values of the relative concentrations different from that of NRA (NRA - [W] = 0.19, LIBS - [W] = 0.5 (at $\Phi = 20 \text{ J cm}^{-2}$)).

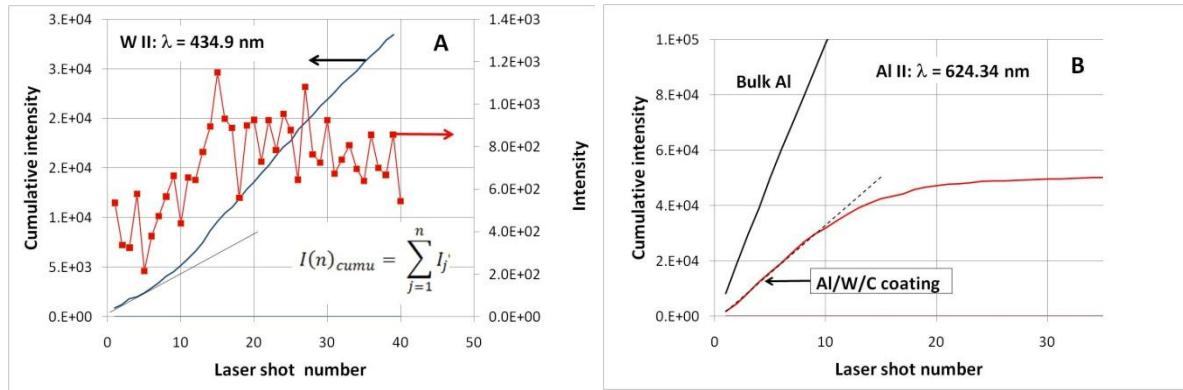


Figure 2. W/Al/C coating on W, $\Phi = 20 \text{ J cm}^{-2}$. Intensity and cumulative intensity of W as a function of laser shot number. B – comparison of cumulative intensities of Al.

In the case of W, we relate the failure of the slopes method to the considerably different ablation/thermal properties of the coating components as well as to those of the coating and the bulk material.

Fractionated ablation of the coating components could cause a difference in concentrations' ratio in the sample and in the plasma plume [4] and the ratio of components' intensity should depend on the fluence. According to Figure 3 the ratio, $I_{\text{Al}}/I_{\text{W}}$, is independent of the fluence. Thus, the fractionation of the coating components is not the likely reason of the failure of the method.

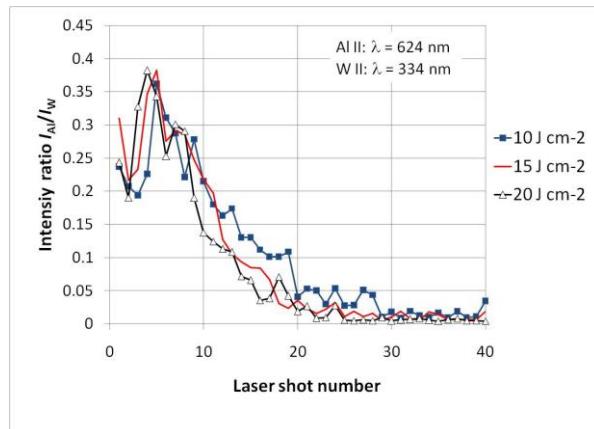


Figure 3. W/Al/C coating on W. Intensity ratio of Al and W spectral lines as a function of laser shot number.

Another reason which could lead to the failure of the slopes method is the difference between the ablation rate (atoms per pulse) of the coating and that of the bulk material. As a result, the W relative concentration, coating/ bulk, in plasmas does not equal to that in the sample. Likely the ablation rate of W bulk is lower and thus the ratio of slopes gave a value which exceeds that of relative concentration. The discrepancy between the slopes ratio and the actual value of the W relative concentration could be further enhanced by the plasma-absorbed laser radiation which leads to the temperature difference between the coating and bulk plasmas.

We speculated that the slopes method will work better when the branching of the laser energy between the ablation and the plasma excitation will be redistributed. It could be realised using a shorter laser wavelength where both metals reflectivity and the absorption coefficient of plasma (absorption coefficient by inverse bremsstrahlung $\propto \lambda^3$) are lower. Thus, at a shorter wavelength an energy redistribution takes place, more energy is absorbed by the solid material and the laser radiation passes less energy to the plasma plume. It means the plasma temperature will be lower. It leads to a lower excitation rate of energy states and for compensation of the temperature fall higher values of fluence should be used.

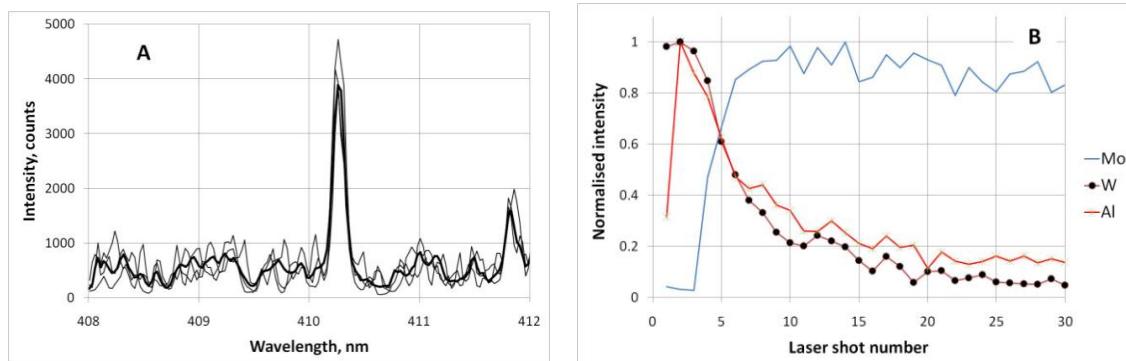


Figure 4. W/Al coating on Mo; $\lambda = 266$ nm; $\Phi \approx 75$ J cm $^{-2}$. A – a part of spectrum with W line; thin lines – three single-shot spectra; thick line – the average of 8 spectra. B – depth profiles; averages of 5 different sites.

To check the validity of presented considerations we carried out a preliminary testing at 266 nm wavelength (Figure 4). As it was supposed, the same intensity of a spectral line as at $\lambda = 1064$ nm, was reached at higher fluence values and the ablation rate increased more than two times. As a considerable improvement of S/B ratio took place, a larger number of W lines which could be used as analytic ones, were detectable.

Positive trends found at $\lambda = 266$ nm, are the basis to hope that the slopes method will give better results at this wavelength.

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