Chapter #4

Study of Impurities Deposited on Tokamak Flange

In the present chapter, qualitative and quantitative analysis of the impurities deposited on the exposed surface of the flange (Figure 4.1) of Aditya Tokamak has been performed using laser induced breakdown spectroscopy. LIBS can be used as a diagnostic tool for characterization of the wall conditioning and coating on wall of tokamak vacuum vessel. It can be performed under ultrahigh vacuum conditions and the existing toroidal magnetic field [1]. For depth profile analysis, the intensity variation of spectral lines of impurity elements with successive number of laser shots has been studied. The concentrations of elements present in successive laser shot (1\textsuperscript{st} to 12\textsuperscript{th}) have been determined using CF-LIBS technique.

Figure 4.1: Photograph of the Tokamak Flange.

4.1 Experimental Setup

The experimental setup with other parameters as discussed in chapter 3 is used to record the LIBS spectra of the flange of the tokamak at different depths and different locations. The laser pulse energy was optimized and the best signal to background ratio and signal to noise ratio were observed with energy of 15 mJ. Laser pulse energy was measured with an energy meter (Genetec-e model UP19K- 30 H-VM-DO) [2-4]. LIBS spectra have also been recorded by allowing successive number of laser shots at same points of the flange surface and similar experiment have been repeated for 10 different points of a concentric circle on its contaminated surface.
4.2 Results and Discussion

4.2.1 Qualitative analysis of the flange

Figure 4.2 (a-c) represent the typical LIBS spectra of exposed surface of the flange. The wavelength of the atomic lines of the different elements appearing in the LIBS spectra of flange have been identified using the National Institute of Standards and Technology (NIST) atomic spectroscopic database [5] and W.R. Brode, Chemical Spectroscopy [6]. Similar to the optical window (in chapter 3), spectral signatures of Cr, Fe, Ni, Mo, Mn, Cu, C, Ca and Mg are also seen in the LIBS spectra of exposed surface of the flange as shown in Figure 4.2(a-c).

![Figure 4.2: LIBS spectra of impurity present on the exposed surface of the flange in different spectral range](image)

To study the different layers of the flange sample, successive laser shots were focused at a point of the exposed side of the flange and the LIBS spectrum of each laser shot was recorded. The intensity of the spectral lines of the elements present in the
deposited layers (Cr, Fe, Ni, Mo, Mn, Cu, C, Ca and Mg) of the flange were measured for every laser shot (i.e. one laser shot, two laser shot and so on up to 12 laser shot at a point).

The tokamak wall and flange are constructed by the same material (SS316L) [7-10]. The impurity deposited layer is obtained due to eroded material from the wall (SS316L) through the tokamak plasma-wall interaction. Therefore the constituents of deposited layer and the flange material are nearly same. Thus it is difficult to identify the deposited impurity layer and the flange material whose compositions are similar. As discussed in chapter 3 that the tokamak is made up of stainless steel material (SS316L), whose elemental composition is Cr, Fe, Ni, Mo, Mn, Cu and C and the spectral signature of these elements are also found in the LIBS spectra of unexposed surface of the flange, hence it is also made up of the same material. It is clear from Figures 4.2(a-c) that the elements present in the LIBS spectrum of the deposited layer i.e. in the 1st laser shot are same as the constituents of the flange or tokamak wall materials. Figure 4.3 shows the variation of intensity of the spectral lines of the elements Cr (428.9 nm) and Fe (438.3 nm) with number of laser shot at the same point of the flange sample. It is clear from the Figure 4.3 that the integrated intensity of these elements decreases with increasing number of laser shots. But, the intensities of chromium (Cr) and iron (Fe) spectral lines do not become zero on increasing laser shots; instead it becomes constant after 5th or 6th laser shot.

![Figure 4.3: Intensity variations of spectral lines of (a) Cr 428.9 nm & (b) Fe 438.3 nm with increasing number of laser shots.](image)
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One may think that in first 1-6 laser pulses, it modifies the surface of a homogenous substrate (change of roughness, optical properties) and only after these initial pulses equilibrium is reached. So to remove the above confusion, we have performed the experiment and recorded the LIBS spectra of the unexposed surface of the flange at different points with successive number of laser shots, but we do not see any considerable change in the spectral intensities of flange material.

Thus, we conclude that the changes occur in the intensity of spectral line with successive laser shots, due to removal of impurity layer in first 5 laser shots. After 5th or 6th laser shot (Figures 4.3a & b) the ablated material contains the flange constituents similar to the impurity material and for further laser shots the laser faces the same matrix and therefore the spectral intensities becomes constant. The colour due to interference of the reflected light from the two opposite surfaces of the thin film of deposited layer on the surface of the flange is reddish brown, so it is clear from the interference of thin films that the thickness of deposited layer is in the order of micrometer. To study such variation in spectral intensity, the concentration of these elements (Cr, Fe, Ni, Mo, Mn, Cu, C, Ca and Mg) in the laser induced plasma of 1st laser shot and 12th laser shot is calculated using CF-LIBS technique.

4.2.2 Calculation of concentration of constituents of deposited layer using CF-LIBS

After detecting the impurities deposited on the surface of the flange, the concentration of these elements is calculated. One can calculate the concentration of sample constituent either using calibration curve method or CF-LIBS method. But, in the present work the reference material for drawing the calibration curve is not available; therefore the traditional calibration curve method [11] is not useful in the present study for estimating the concentration of constituents. Thus, the calibration free LIBS (CF-LIBS) technique [12-13] for estimating the concentration of above elements is used. As discussed in chapter three, before using the intensity of the spectral lines for quantitative analysis, the laser induced plasma should satisfy three conditions/assumptions [14-15] and these assumptions are verified as discussed below.

4.2.2.1 Stoichiometric ablation

Similar to optical window, 15 mJ laser energy is used to record the LIBS spectra of the flange. Therefore, for this laser energy, the calculated value of fluence and
irradiance of the laser will be $3.75 \times 10^3$ J/cm$^2$ and $9.37 \times 10^{11}$ Wcm$^{-2}$ respectively. Thus, laser irradiance is greater than $10^9$ Wcm$^{-2}$ and hence the condition for stoichiometric ablation is satisfied [16].

### 4.2.2.2 Local thermal equilibrium

The plasma is said to be in LTE condition, if it satisfies the necessary condition and sufficient condition which are stated below.

**Necessary condition:** The electron number density calculated using LIBS spectra of the plasma in LTE condition must satisfy the McWhirter criteria [14-15].

**Sufficient condition:** If the ionization temperature calculated using Saha-Boltzmann equation and excitation temperature using Boltzmann equation coincide within standard deviation of 15%, the plasma is said to be in LTE condition [14-15, 17].

![Boltzmann plot for the LIBS spectra of (a) 1st laser shot & (b) 12th laser shot.](image)

As discussed in chapter three, Boltzmann plot $\ln \frac{B_i}{A_{kd\gamma k}}$ vs $E_k$ is plotted and shown in Figure 4.4 (a-b). From the slope of the plots (Figure 4.4a-b), the plasma temperatures for 1st and 12th laser shot LIBS spectra are calculated and are equal to $(16928 \pm 948)$ K and $(18283 \pm 407)$ K respectively. Thus the plasma is characterized by single temperature, which is known as Boltzmann excitation temperature.
Experimentally the electron density can be calculated by measuring the FWHM (Δλ) of the Stark broadened spectral line (Figure 4.5) using equation 3.4.

Figure 4.5: Lorentzian profile of Ca 422.6 nm spectral line in the LIBS spectra of upper surface of the flange.

Figure 4.6: Saha-Boltzmann plot of LIBS spectra of upper surface of the flange using impurity element Fe.
The measured value of electron density is equal to $1.04 \times 10^{18} \text{ cm}^{-3}$, which is greater than the value of electron density ($1.97 \times 10^{16} \text{ cm}^{-3}$) for McWhirter limit given by equation 3.3. The above result clearly satisfies the necessary condition for LTE.

Using Saha-Boltzmann relation (equation 3.5), Saha-Boltzmann plot for iron is plotted and is shown in the Figure 4.6. Ionization temperature is calculated using this plot and its value is equal to (19098 ± 481) K. This value is very close to excitation temperature (16928 ± 948) K with the difference of ~11%. Thus the necessary as well as sufficient conditions hold in the present experiment and satisfy the LTE condition of the laser induced plasma.

### 4.2.2.3 Optically thin plasma

As discussed in chapter three, intensity ratios for spectral lines of Ni, Cr, Cu and Mg and value of $A_{1g_1} \lambda_2/A_{2g_2} \lambda_1$ have been calculated and tabulated in Table 4.1.

<table>
<thead>
<tr>
<th>Element</th>
<th>Intensity ratio$(I_1/I_2)$</th>
<th>$A_{1g_1} \lambda_2/A_{2g_2} \lambda_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-II (217.4/220.6)</td>
<td>1.34</td>
<td>1.29</td>
</tr>
<tr>
<td>Cr-I (359.3/360.5)</td>
<td>1.37</td>
<td>1.30</td>
</tr>
<tr>
<td>Cu-I (324.7/327.4)</td>
<td>2.22</td>
<td>2.03</td>
</tr>
<tr>
<td>Mg-II (279.0/279.8)</td>
<td>0.55</td>
<td>0.56</td>
</tr>
</tbody>
</table>

The intensity ratios $(I_1/I_2)$ of two spectral lines are approximately equal to the values of $A_{1g_1} \lambda_2/A_{2g_2} \lambda_1$ (Table 4.1), satisfying the condition for optically thin plasma. In this way all the three basic assumptions are verified, thus equation (3.2) can be used for calculating the relative concentration of the constituents/elements present in the flange.

### 4.2.2.4 Calculation of concentration

For calculating the concentration of elements present in the deposited impurity layer and in the matrix of flange, we have used the average intensity of spectral lines of 32 LIBS spectra of 1st laser shot and average intensity of the spectral lines of 32 LIBS spectra of 12th laser shots. To calculate the concentration, intercept values of constituent’s elements species in the Boltzmann plot shown in Figure 4.4(a-b) are used, we follow the following steps
(i) Calculations of area under curve of spectral lines of elements present in the LIBS spectra using OOI LIBS 2000+ software.

(ii) Calculation of temperature using Boltzmann plot.

(iii) Measuring the intercept of Boltzmann plot for each species.

(iv) Calculation of partition functions for each species.

(v) Calculation of experimental parameter F.

(vi) Calculation of concentration of species of elements.

The calculated percentage concentration of elements present in the laser induced plasma of the 1st and 12th laser shot is tabulated in the Table 4.2. The main body of Aditya Tokamak is constructed from SS316L, whose major constituent is Fe (61-68%) and other minor constituents are C (<0.03%), Cr (16-18.5%), Ni (10-14%), Mo (2-3%), Mn (<2%), Si (<1%), P (<0.045%), S (<0.03%), N (0.1%) [9-10].

Table 4.2: Relative concentration of elements present in deposited layer (1st laser shot) and matrix of the flange (12th laser shot)

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe (%)</th>
<th>Cr (%)</th>
<th>Ni (%)</th>
<th>Mo (%)</th>
<th>Mn (%)</th>
<th>Cu (%)</th>
<th>C (%)</th>
<th>Ca (%)</th>
<th>Mg (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Concentration in deposited impurity layer (%) (1st laser shot)</strong></td>
<td>57.65±0.27</td>
<td>14.68±0.35</td>
<td>9.95±0.01</td>
<td>2.26±0.03</td>
<td>1.77±0.02</td>
<td>0.61±0.01</td>
<td>0.67±0.01</td>
<td>11.07±0.29</td>
<td>1.35±0.24</td>
</tr>
<tr>
<td><strong>Concentration in matrix (%) (12th laser shot)</strong></td>
<td>61.37±0.58</td>
<td>17.30±0.13</td>
<td>14.93±0.36</td>
<td>2.33±0.11</td>
<td>2.20±0.19</td>
<td>1.15±0.01</td>
<td>0.71±0.01</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td><strong>Constituents of SS316L (%)</strong></td>
<td>61-69</td>
<td>16-18</td>
<td>10-14</td>
<td>2-3</td>
<td>2</td>
<td>----</td>
<td>0.03</td>
<td>----</td>
<td>----</td>
</tr>
</tbody>
</table>

From Table 4.2, it is clear that the concentration of elements present in the deposited layer (1st laser shot) and that of the matrix (12th laser shot LIBS spectra) of the flange are found to be similar to each other, in spite of the different intensities of spectral lines in the LIBS spectra of the 1st and 12th laser shot. The reason for such anomalous behavior is due to different matrices seen by 1st and 12th laser shots, because, the matrix of thin layer of impurities and the flange (SS316L) material are different from each other.
In the case of the flange material (12th laser shot), the matrix is hard compared to the impurity deposited layer (1st laser shot), therefore the fixed amount of laser energy ablates greater amount of impurity material giving the larger spectral intensity in the LIBS spectra of the 1st laser shot. In the 12th laser shot, the laser ablates the flange material having hard matrix compared to deposited layer and same amount of energy of the laser can ablate less amount of the flange material and hence smaller spectral intensity compared to the deposited layer.

4.2.3 Hardness of the matrix in 1st and 12 laser shot on deposited layer

To verify the presence of two different matrices seen by 1st and 12th laser shots, we have calculated the hardness of these matrices using LIBS spectra. As the speed of the shock front depends on the hardness of the sample and a positive relationship exists between the speed of the shock front and the ionization rate of the ablated atoms. In harder matrix the population of atoms in higher ionization state will be greater and thus the intensity of ionic spectral line emitted from the plasma is high [18]. Hence, the intensity ratio of the ionic and atomic spectral lines can be used to examine the hardness of the material [14, 18].

Table 4.3: Ionic to atomic intensity ratio of the matrix in 1st and 12 laser shot in the deposited layer of the flange

<table>
<thead>
<tr>
<th>Wavelength of atomic and ionic spectral lines of Fe in LIBS spectra</th>
<th>Ionic to atomic integrated intensity ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic (λ₁ nm)</td>
<td>Ionic (λ₂ nm)</td>
</tr>
<tr>
<td>----------------</td>
<td>--------------</td>
</tr>
<tr>
<td>252.2</td>
<td>234.3</td>
</tr>
<tr>
<td>271.9</td>
<td>238.2</td>
</tr>
<tr>
<td>278.8</td>
<td>239.5</td>
</tr>
<tr>
<td>344.0</td>
<td>240.4</td>
</tr>
<tr>
<td>358.1</td>
<td>249.3</td>
</tr>
<tr>
<td>438.3</td>
<td>275.5</td>
</tr>
<tr>
<td>404.5</td>
<td>274.9</td>
</tr>
<tr>
<td>385.9</td>
<td>273.9</td>
</tr>
<tr>
<td>382.0</td>
<td>261.1</td>
</tr>
<tr>
<td>375.8</td>
<td>259.8</td>
</tr>
</tbody>
</table>
It has been observed that to produce the plasma in hard material the total threshold energy required is less in comparison with the soft material [16]. Thus the available energy of the later part of laser pulse is more at hard matrix, which causes more heating of the plasma. Thus the temperature of the plasma will be higher in harder matrix.

Therefore, in case of harder material, the ionic to atomic intensity ratio will be higher. It is clear from Table 4.3 that the ionic to atomic intensity ratios in 12th laser shot is greater than the 1st laser shot. Due to this, the matrix of the flange present in 12th laser shot is harder compared to the matrix seen by 1st laser shot. Thus the present study demonstrates the ability of LIBS to identify the different matrices of impurity layer, deposited on the flange.

4.3 Conclusion

The present chapter reveals that a thin layer of impurity elements like Fe, Cr, Ni, Mo, Mn, Cu, C, Ca and Mg are deposited on the exposed surface of the tokamak flange. Most of these impurities are coming from the erosion of tokamak wall material and limiters due to plasma wall interaction and plasma limiter interaction. As the laser reaches to the substrate after 5th or 6th laser shot, the spectral intensity of elements decreases with successive number of laser shots and becomes constant after 5th or 6th laser shot. The concentrations of elements in deposited layer, calculated using CF-LIBS, are in good agreement with concentrations of the constituents of tokamak wall material. The differences in the intensities of the spectral lines of the elements in 1st and 12th laser shots are due to two different matrices i.e. deposited layer having loose matrix and the bulk of the flange having hard matrix.

Present study clearly demonstrates the capability of CF-LIBS to study the two different natures of the samples but having similar relative concentration of the constituents. An idea of the thickness of the deposited material by measuring the variations of their spectral intensities with successive number of laser shot was also employed. Elemental composition in the different layers of impurity and flange was evaluated using CF-LIBS approach.
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References:


