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Analysis of LiSn alloy at several depths using LIBS

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Abstract

The difference between the composition of the surface and the inner part of the LiSn sample was studied using Calibration Free Laser Induced Breakdown Spectroscopy (CF-LIBS) method. The sample was analysed under the low pressure (1 330 Pa) in Ar atmosphere. The spectra were recorded using Echelle spectrometer (Mechelle ME5000). Gate delay and gate width was optimised and set to 300 ns. In order to analyse depth profile the LIBS spectra was recorded after each laser shot. The electron density analysed by laser induced plasma was determined separately for each laser shot, which means for each ablated layer of investigated sample. The differences between the individual shots taken at distinct sites of the sample are shown. The CF-LIBS method was used to determine the elemental composition near the surface and in the central part of the LiSn sample.

1. Introduction

The study of plasma-wall interactions is crucial for the design of fusion reactors as well as the development of novel materials suitable in such environments. Compatibility between the plasma and the wall material is one of the main challenges in designing a fusion reactor. The parts exposed to the plasma are designed to be heat resistant, thermally conductive, resistant to physical and chemical erosion, and of low fuel retention [1]. Such materials are either of high or low atomic numbers (Z).

Materials of low Z elements such as beryllium (Be) are easy to erode. These elements make bonds with hydrogen isotopes-deuterium (D) and tritium (T) and can form deposited layers. In contrast with the low Z materials, the materials of high Z elements are significantly more difficult to erode. This results in less contaminated plasma due to the effect of sputtering of the wall materials. However, even a marginal presence of high Z elements, such as of tungsten (W), causes the plasma to be easily extinguished due to the energy loss associated with Bremsstrahlung. The conventional choice for the walls of the reactor is Be for the first wall and W for the divertor [2, 3]. Another concept of increasing popularity is that the wall remains liquid under operation (i.e. the liquid wall). This proves to be a twofold advantage. Firstly, the liquid state prevents the creation of nano-cracks and other local defects. Secondly the wall can easily be purged from the retained fuel (D,T) by heating.

This the low Z liquid alternative for material of the divertor is likely formed of Li or Li based alloys (e.g. LiSn, LiPb), which exhibit suitable thermophysical properties, such as low melting point (180 °C for Li, 180-783 °C for LiSn, 180-730 °C for LiPb), low vapour pressure, resistance to the high heat and neutron fluxes. Due to Li breeding being an important source of T for the fusion reaction, the future power plants are proposed to have a certain minimal Li content in the alloys (Sn–20at.%Li, Pb–
The advantages of LiSn alloys over LiPb alloys are better thermal conductivity and heat capacity [4, 5].

Recently, several studies were focused to deepen the understanding of the properties of suitable candidates (elements and associated alloys) for the formation of the liquid wall in fusion application. Dynamical and structural properties of liquid metals, as Pb and Li, were studied by Embedded Atom Method [6]. The research was also conducted on the static and thermodynamic properties resulting in the calculations of entropy and free energy. Allain et al performed an experimental study of the surface chemistry of Li based materials. It has been found that when Li atoms are bound to deuterium (D) or an impurity, the amount of energy needed for breaking the surface bond increases [7].

Recently some studies [8-12] were dedicated to a direct application of different Li based liquid metals for plasma facing components in fusion devices. A preliminary study of the liquid plasma facing components [12], together with the design of liqid wall facility [11] contributes to the liquid wall approach. Due to aforementioned properties, LiSn was introduced as a divertor material [9], and its corrosion behavior was further studied as a part of a design determination of a fusion reactor [10]. Li based limiter was also considered, and its main limitations were identified to be: liquid metal splashing and heat removal [8].

The LIBS method has been used before as an investigative method for fusion relevant materials, mainly for W and W based deposits [13-17]. Recently, the focus of LIBS studies in fusion research is put to the D retention studies in pure materials as well as mixed deposited layers which could be formed during the operation of a fusion device. In present paper we concentrate only on LIBS studies of materials containing Li. Analysis of W and lithiated W using LIBS method was presented in the study [18], where the main focus was lithiated W interaction with D plasma (the effect of lithiation on D retention, the profile of elemental distribution and the chemical state of lithiated W). The results show that after D plasma exposure, the D retention can be saturated in the lithiated layer and lithiation can inhibit the blistering on the W surface. The Li in lithiated layer is chemically bound to D which is why an amount of D retention could be maintained throughout several laser shots for lithiated W. It also explains why the amount of D was larger for lithiated W than for a pure W. The LIBS method was also used for the investigation of D concentration ratio and Li-D co-deposition distribution in the depth profile of the divertor tiles in the study [19]. The results of this work show that the depth profile behaviours of Li and D were quite similar, and it indicates that D retention came from Li-D co-deposition during the deuterium discharge in tokamak. These results have proven LIBS measurements suitable for monitoring D retention and Li-D co-deposition in tokamak.

The lack of studies using CF-LIBS on such alloys motivates the focus of this article. This study aims to implement the CF approach to determine and compare the concentration of the sample at two sites (on the surface and in the centre) based on the spectra measured by LIBS. Associated calculations necessary for CF method include the calculation of electron density and electron temperature.

2. Method

The LIBS is a method of optical emission spectroscopy which allows qualitative and quantitative analysis of the sample of all states of matter. The main principle of the method is a material sampling using laser ablation followed by an analysis of the recorded spectra. The method allows for a simultaneous detection of several elements ranging across all groups of the periodic table. Moreover the fired sample remains intact, which is referred as quasi-nondestructivity, and the process can be done remotely i.e. stand-off analysis. The quantitative analysis can be approached by calibration and CF methods. In the calibration method the measured spectrum is contrasted with the so called
calibration curves that are obtained from an analysis of like samples of known concentration, also referred as calibration standards. Then a relationship is established between given elemental concentration and the intensity of particular peaks. Usually the calibration method involves the estimation of the calibration curves based on samples of standard concentration. Particularly, for a sample such as LiSn the calibration standards have not been measured extensively, hence the CF approach was developed [20, 21]. As demonstrated in [22] CF LIBS is applicable across concentrations of several orders of magnitude, ranging from major concentration to trace element analysis. For the CF approach, two physical quantities are necessary to be determined. The first one, the electron density, is determined from the Stark broadening of the H-alpha spectral line. The second one, the electron temperature, is determined from the slope of the Saha-Boltzmann plot [23].

3. Experimental setup and measurement

The sample of Li-Sn alloy (20:80 in weight %, from Princeton Scientific Corp.) was analysed with the LIBS measurements at the pressure of 1330 Pa in the argon atmosphere. Firstly the vacuum chamber was decompressed to the minimal pressure followed by an inclusion of argon. Our LIBS experimental setup is shown in Figure 1.

The source of the LIBS plasma was a Q- switched Nd: YAG laser operating at the fourth harmonic (266 nm, CFR, Quantel, 80 mJ). The maximal pulsing frequency is 10 Hz and laser pulse duration was 9 ns. The emitted light was collected by optical fibre and guided into an Echelle spectrometer (ME5000, Andor Technology, resolution λ/Δλ = 4000, range 230-975 nm) coupled with an iCCD camera (iStar DH743, Andor Technology, temporal resolution 5 ns). The gate delay and spectral gate width delay were kept to an identical value, which was varied to find an optimum. The optimal value, found to be 300ns, was the one where lines from different ionization states have the largest signal to noise ratio.

![Figure 1. Schematic experimental setup used in our experiment, which contains of laser, mirrors, lens, vacuum chamber with sample and pumping/inserting gas windows, fibre holder (objective), fibre and Echelle spectrometer](image)

The sample was broken in order to expose its inner structure. The site of this defect is referred to as “the inner part”. So in addition to the conventional surface measurements a set of measurements focused at the inner part was performed. Both of those location types were fired 20 shots out of which first three were analysed. The laser pulse is locally destructive so the consecutive measurements unveil the structure at increasing depths. For the sake of avoiding a random error the surface was shot at five distinct locations and the spectra of like order (depth) were averaged.

4. Results and analysis

The analysis of LiSn sample was based on CF LIBS approach. For this method the determination of electron density and electron temperature is necessary.
Determination of the electron density

The electron density \( n_e \), was calculated from Stark broadening of hydrogen alpha (656.25 nm) spectral line using formula:

\[
FWHA = 0.549 \text{nm} \left( \frac{n_e}{10^{17} \text{cm}^{-3}} \right)^{0.67965} \tag{1}
\]

where FWHA is the full width at half area [24]. Determined \( n_e \) was verified by McWhirter criterion:

\[
n_e \geq 1.6 \times 10^{12} T^{1/2} (\Delta E)^3 \tag{2}
\]

It is used to test, whether the plasma is in local thermodynamic equilibrium.

Determination of the electron temperature

The electron temperature, T, was determined from the Saha-Boltzmann plot using the Saha equation:

\[
\frac{N_{i+1}}{N_i} = \frac{Z_{i+1}}{Z_i} \left( \frac{2\pi m_e k T}{\hbar^2} \right)^{3/2} e^{-\frac{\epsilon_i}{kT}} \tag{3}
\]

where \( N_i \) and \( N_{i+1} \) are the populations of the ionization states \( i \) and \( i+1 \), respectively, \( Z_i \) and \( Z_{i+1} \) are the partition functions of these states, \( n_e \) is the electron density calculated from Stark broadening of H alpha spectral line, \( m_e \) is mass of the electron, \( k \) is the Boltzmann constant, \( h \) is the Planck constant and \( \epsilon_i \) is the ionization energy.

T was determined for every analysed shot. In case of the Sn, the neutral and singly ionized lines were taken from the spectra recorded by the Echelle spectrometer. In case of the Li, only neutral spectral lines were observed and used in the analyses. Few rules were used for the spectral line selection in order to improve accuracy. The spectral lines were selected such that no interference with neighbouring spectral lines occurred; no resonant spectral line was taken into account. Spectral data were taken from the NIST [25], Harvard [26] databases and for some spectral lines of Sn from [27]. In Figure 2 is shown ion abundance for \( n_e = 5.36 \times 10^{17} \text{cm}^{-3} \) with highlighted area of T, corresponding to our values in experiment. One of the computed Saha-Boltzmann plots is shown in Figure 3. In Table 1. are shown determined values for T and \( n_e \).

![Figure 2. Ion abundance for Sn (black for singly and red for doubly ionized state) and Li (pink for singly and blue for doubly ionized state) calculated for electron concentration 5.36 x 10^17 cm^3. Highlighted region represents values of T, which corresponds to our experimental conditions (1st shot, analyses of the surface).](image-url)
Table 1. Determined values of $T$ and $n_e$ for the first, second and third shots at the surface and at the inner part of the sample

<table>
<thead>
<tr>
<th></th>
<th>$T$ (eV)</th>
<th>$n_e$ (cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Surface</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1$^{st}$ shot</td>
<td>1.91</td>
<td>5.36E+17</td>
</tr>
<tr>
<td>2$^{nd}$ shot</td>
<td>1.53</td>
<td>6.10E+17</td>
</tr>
<tr>
<td>3$^{rd}$ shot</td>
<td>1.72</td>
<td>8.05E+17</td>
</tr>
<tr>
<td><strong>Inner part</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1$^{st}$ shot</td>
<td>1.16</td>
<td>7.10E+17</td>
</tr>
<tr>
<td>2$^{nd}$ shot</td>
<td>1.31</td>
<td>4.35E+17</td>
</tr>
<tr>
<td>3$^{rd}$ shot</td>
<td>1.30</td>
<td>2.93E+17</td>
</tr>
</tbody>
</table>

Figure 3. The Saha-Boltzmann plot for the first laser shot of LIBS analysis. The black squares represent results from the surface of the sample and the blue squares represent the inner part of the sample (mechanically broken sample).

In Figures 4 - 6 the LIBS spectra of the first, the second and the third shot, taken at the surface and inner part respectively, are shown. The most intense spectral lines are the ones identified in all figures. Unfortunately only neutral Li spectral lines are observed due to the very high potential energy of upper states of ionic Li spectral lines. Figure 7 depicts are shown the results from CF approach and comparison between determined concentration from the surface and the inner part of the sample.

Figure 4. The comparison between average spectra recorded from the first shots (black colour) at the surface of the sample and the first shots at the inner part of the sample (red colour). The less intense part of the spectra is showed in the inner plot.
Figure 5. The comparison between spectrums recorded from the second shot (black colour) at the surface of the sample and the second shot at the inner part of the sample (red colour). The less intense part of the spectra is shown in the inner plot.

Figure 6. The comparison between spectrums recorded from the third shot (colour) at the surface of the sample and the third shot at the inner part of the sample (red colour). The less intense part of the spectra is shown in the inner plot.

Figure 7 depicts the results from approach and comparison between determined concentration from the surface and the inner part of the sample.
5. Discussion and conclusion
The main aim of this work was to test the CF-LIBS method for analyses of the LiSn alloy. This work shows that CF-LIBS method is suitable for such an analysis. The separates figures demonstrate main differences between individual shots and between the two sites of the sample (centre and surface). From figures 4-6 it is clear, that the most intense spectral line from the chosen non-resonant spectral lines of Li and Sn is neutral Li spectral line at 610 nm. From the first shot (figure 4), this Li line is more intense in the case of the inner part. In the following shots (see figure 5-6), the intensity of this line is approximately the same for the inner part and on the surface.

Comparing the intensity of neutral and singly ionized Sn spectral lines, the biggest difference between inner part and the surface is in the first shot of LIBS spectra (figure 4). Both spectral lines are more intense in the LIBS spectra from the surface of the sample. Figures 5 and 6 suggest that the spectral lines of Sn behave differently, i.e. the neutral Sn spectral lines are more intense in the inner part of the sample and the singly ionized Sn spectral lines on the surface. This character of the Sn LIBS spectra could be explained by the difference of the electron temperature between the inner part (T~1.2 eV) and on the surface (T~1.7 eV). In fact the ion abundance diagram (figure 2) shows the decrease of neutral degree of ionization of Sn by one order of the magnitude for the corresponding increase of the temperature. In the case of singly ionized Sn spectral lines, there is practically no difference in ionic abundance with respect to increasing temperature, because Sn forms the majority of more than 99%. On the other hand the increase of electron temperature (from 1.2 to 1.7 eV) leads to an increase of upper state population of corresponding Sn II lines.

The intensity of H-alpha spectral line, observed in all three shots at both sites of the sample (on the surface and in the inner part), decreases with each additional shot. The presence of this spectral line in the LIBS spectra is due to the surface pollution from the atmosphere.

The concentration which was determined using CF LIBS method (Li:Sn = 40:60 in weight % for surface of the sample and Li:Sn = 35:65 in weight % for inner part of the sample) demonstrates the heterogeneity of LiSn alloys. The difference between the composition evaluated by CF LIBS and the composition provided by the producer can be explained by relying solely on the neutral spectral lines of Li in the CF LIBS analysis (as Li ionic spectral lines were not observed). Further investigation and an improvement of accuracy of Li density determination in alloys is under progress. Finally the LIBS method proves to be suitable for depth profiling of Li in the alloys.

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