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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 (1330 Pa) in Ar atmosphere. The spectra were record 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 difference 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 nanocracks 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–17at.%Li). 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

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plasma facing components [12], together with the design of liqid wall facility [11] contributes to the liquid wall approach. Due to forementioned 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 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-nondesctructivity 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 Fig. 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 collecting by optical fibre and guided into an Echelle spectrometer (ME5000, Andor Technology, resolution $\lambda/\Delta\lambda = 4000$, range 230–975 nm,) coupled with an iCCD camera (iStar DH743, Andor Technology, temporal resolution 5 ns).

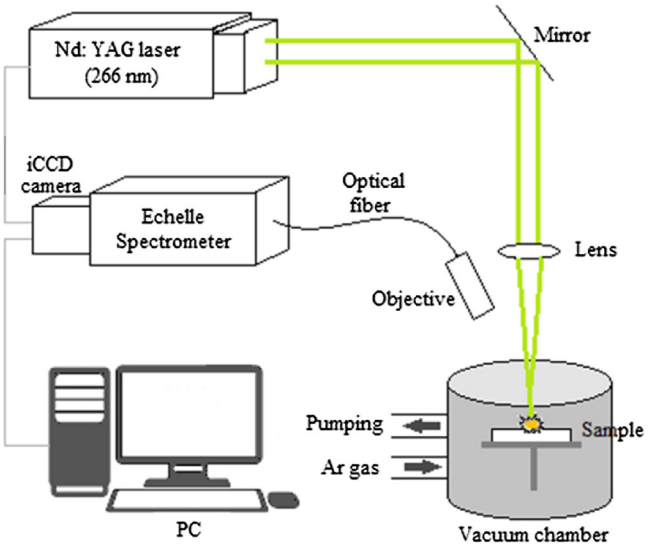

Fig. 1. Schematic experimental setup used in our experiment, which contains of laser, mirrors, lens, vacuum chamber with sample and pumping/inserting gas windows, fibre holder (objective), fibre and Echelle spectrometer.

The gate delay and spectral gate width were kept to an identical values, which was varied to find an optimum. The optimal value, found to be 300 ns, was the one where lines from different ionization states have the largest signal to noise ratio. 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.

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