Spectrochimica Acta Part B 125 (2016) 103–110

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

journal homepage: www.elsevier.com/locate/sab

Laser induced plasma expansion and existence of local thermodynamic equilibrium

Miloš Skočić*, Srdjan Bukvić

University of Belgrade, Faculty of Physics, Studentski Trg 12-16, Belgrade 11000, Serbia

ARTICLE INFO

Article history:
Received 4 February 2016
Received in revised form 21 July 2016
Accepted 18 September 2016
Available online 24 September 2016

Keywords:
Laser induced plasma
LIBS
LTE
Monte Carlo simulation
Radially resolved spectroscopy

ABSTRACT

In this paper we present a simple model of the laser induced plasma (LIP) expansion in a low pressure surrounding atmosphere. The model is based on assumption that expansion process is dominantly governed by kinematics of the heavy particles. The model is accompanied with a simple, yet effective, Monte-Carlo simulation. Results of the simulation are compared with spectroscopic measurements of the laser induced copper plasma expanding in low pressure (200 Pa) hydrogen atmosphere. We found that characteristic expansion time of the LIP is proportional to the linear dimension of the initial volume heated up by the laser. For sufficiently large initial volume copper plasma remains in *local thermodynamic equilibrium* on the submicrosecond-microsecond scale. It is shown that diagnostics based on the spectral lines of the hydrogen atmosphere is not suitable for characterization of the core of the copper plasma. We have demonstrated importance of radially resolved spectroscopic measurements as a key step for correct diagnostics and understanding of laser induced plasma.

1. Introduction

The laser induced plasma (LIP) is generated by focusing beam of a high power pulsed laser on gas or metal surface. Power required for creation of LIP is in the range of 10^5–10^{10} W/cm^2. The electron density typically ranges between 10^{22} and 10^{25} m^{-3} while the electron temperature is in the interval 5000–40,000 K [1,2]. The laser induced plasma is extremely non-homogeneous with cylindrical geometry in respect to the axis defined by the laser beam. The LIP lifetime mainly depends on type and pressure of surrounding atmosphere. For surrounding gas pressure of a few millibars laser induced plasma exists on the microsecond scale, while for pressures close to atmospheric lifetime of the plasma extends up to hundred of microseconds [1]. The lifetime of LIP prolongs as the molecular mass of surrounding gas increases. The emission spectrum of the plasma, obtained by illuminating solid surfaces, contains predominantly lines of the material from which the target is made of. This feature provides a way for distant characterization of materials, the methodology employed by NASA mission on Mars [3,4]. Besides, LIP is an extremely interesting spectroscopic source, with the great potential in studying the spectral lines shapes [5–9].

Number of studies point out that interaction of electromagnetic radiation with a metal surface is a very complex and depends on the intensity and duration of the laser pulse [10]. A typical, simplified, scenario for nanosecond lasers includes heating of the metal target and evaporation in the early stage, and ionization of the metal vapor accompanied by the rapid increase in temperature with intensive expansion [11,12] in the second stage. Investigation of LIP is commonly based on spectroscopic data. The easiest way to estimate the electron density, the electron temperature, the amount of energy radiated by the laser induced plasma, etc., is to rely on spectroscopic diagnostic techniques. On the other hand existence of local thermodynamic equilibrium (LTE) is a common assumption for number of spectroscopic diagnostic techniques [13]. Due to strong gradients and rapid expansion laser induced plasma could departure from LTE, thus the use of these techniques needs additional attention in case of LIP. This issue is discussed in details in [14].

Systematic investigation of the laser induced plasma expansion shows that light emission has different distribution for metal and gas emitters, see Fig. 1. This feature of LIP depends on the metal target type and sort and pressure of the surrounding gas [15]. Reason for such behavior of the plasma plume could be due to large gradients of the electron density and electron temperature along the radius and axis. Different distributions of the metal and gas atoms/ions within the plasma plume should be also considered as a possible cause for mentioned observation. Intention of this paper is to provide systematic measurements of this feature as well as to propose a simple and sufficiently general model able to explain our experimental findings. Another goal of the model is to provide an additional understanding regarding existence of LTE in LIP plasma at low ambient pressures.

* Corresponding author at: Studentski Trg 12, Belgrade,Serbia.
E-mail address: skocic@ff.bg.ac.rs (M. Skočić).

http://dx.doi.org/10.1016/j.sab.2016.09.011

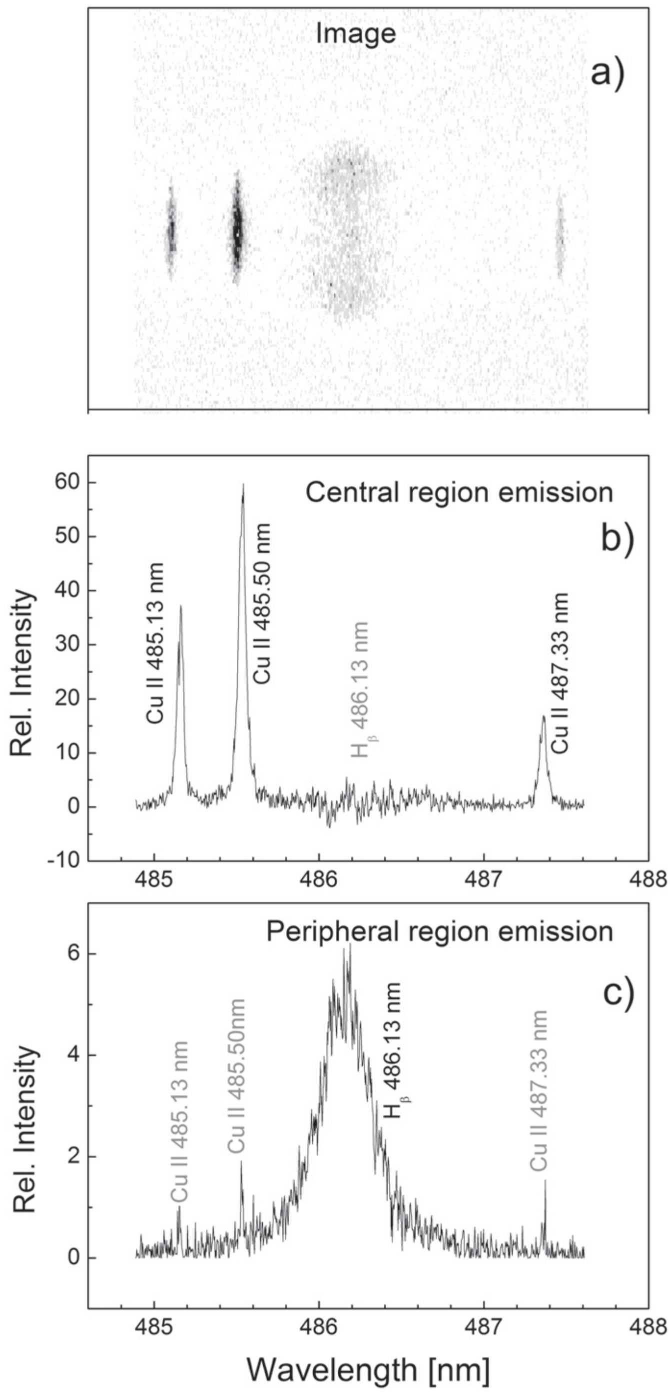

Fig. 1. Panel a: unprocessed image of the LIP spectrum at the 486 nm. Negative gray scale is applied - dark pixels are more illuminated. The wide grainy feature is hydrogen H_β. Narrow black strokes are Cu II lines. Panel b: intensity of the emission from the central region of the plasma obtained by the inverse Abel transform [16], Cu II lines are intense while H_β is below detection limit. Panel c: emission from the peripheral region of the plasma, Cu II lines are very weak whereas H_β is clearly present. The image is recorded 0.5 mm far from the target surface at 120th nanosecond after the laser pulse with 20 ns exposure. The hydrogen pressure was 200 Pa.

2. Experiment

In this paper we conduct measurement of the plasma emission along the radius (the radial profiles) for H_β and chosen Cu I and Cu II spectral lines.[1] This set of radial profiles recorded at the same axial position, at different times, provides the base for developing our model. We emphasize that radial profiles are independent on the plasma state, i.e. the assumption regarding existence of LTE is not necessary to evaluate the radial profiles from the recorded data.

As a light source we employed the Nd:YAG laser, EKSPLA NL 311, operating at 532 nm. Duration of the laser pulse was 5 ns, with repetition rate of 1 Hz and output energy reduced to 35 mJ. Sample made from the high purity copper (99.9%) was placed inside the home made chamber which ensures controlled pressure and quality of the surrounding atmosphere. Measurements presented in this work are conducted in hydrogen atmosphere at 200 Pa pressure. The detection system is based on the Andor DH740-18F-03 iStar intensified CCD camera, cooled down to -20°C and mounted on McPherson model 209 spectrograph (1.33 m focal length) equipped with a holographic grating of 2400 grooves/mm. The image of the plasma is collected side-on and projected onto a 50 μm wide entrance slit with unit magnification. Details regarding radiometric and wavelength calibrations are given in [8].

3. Model

Most of researchers use hydrodynamic approach in modeling LIP expansion [17–19]. Even though the limits of validity of the model are not strictly defined, it is assumed that the hydrodynamic approach is valid when the Knudsen number[2] (Kn) is less than 0.01 [20]. During the evolution of the plasma Kn changes, and after a certain time it becomes greater than the limit value and the hydrodynamic approach becomes inadequate. Possible alternatives are particle models [21,22] or a combination of the hydrodynamic and particle approaches [23]. Particle models can be applied at any stage of evolution, but in the early stages they are extremely inefficient due to the large number of particles which are needed to properly describe the system.

3.1. The model

Within the framework of the proposed model the heavy particles (atoms and ions) and electrons are considered in a different way. Each heavy particle is represented by its mass, position and velocity vector, at a given time. Movement and *elastic* collisions of the heavy particles are monitored in detail. However, details regarding motion of the electrons are ignored completely, the free electrons are represented only by the local density and temperature. Concentrations of the heavy particles are related to the electron density and temperature via Saha equation, supposing existence of LTE. In this way all *inelastic* collisions are substituted by the Saha equation. *Elastic* collisions of electrons are maintained separately.

Therefore, plasma expansion is dominantly governed by kinematics of the heavy particles which is fairly insensitive on details of the plasma state, i.e. whether the plasma is in LTE or not. In this way some important features, for example characteristic time of the plasma expansion, do not depend on internal plasma state, while the electron density, the electron temperature, degree of ionization, population of the excited states, etc., are evaluated relying on hypothesis that the plasma is in LTE.

Given the assumption that the target is homogeneous and that the distribution of the intensity of the laser beam along the radius is Gaussian (zero mode), one can expect that the LIP has an axial

[1] **The choice of copper-hydrogen is motivated by the fact that hydrogen is a very convenient gas in spectroscopic diagnostics, while high purity copper is inexpensive and easy to find.**

[2] Knudsen number (Kn) is a dimensionless number defined as $Kn = \lambda/L$ (λ is the mean free path and L is a characteristic length of the system.).