Plasma properties of 355 nm and 532 nm laser-ablated molybdenum target at atmospheric pressure

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Abstract. This paper presents the results obtained in Mo laser ablation experiments performed in air. Two lasers were used: one Nd:YAG AVIA 355-X emitting pulses with 0.205 mJ energy and 25 ns duration in 355 nm, and one Quantronix Hawk-532-40-M emitting pulses with 2.05 mJ energy and 110 ns duration in 532 nm. The Mo targets were fixed to a XY table, controlled by a computer program which moves permanently the table in order to avoid cratering. The plume was imaged by a 4x telescope and the light emission was collected at the image position by a fiber-optic and coupled to a Triax 550 Jobin-Yvon spectrometer. The spectra analysis was performed assuming the Local Thermal Equilibrium approximation and calculating the plasma temperature by using the Boltzmann plot method using neutral Mo spectral lines. The plasma temperature was obtained for different positions along the expansion axis, which allowed obtaining the electron population distribution as a function of the distance from the target. The plasma temperature along the expansion axis allowed evaluating the evolution of the excited states population when the plume expands.

1. Introduction
Currently, laser ablation has been used in applications in which accuracy and fine tuning of parameters are needed, such as in Medicine (as instrument on gastroenterological and orthoplastic surgery through ablation of tissues and organs [1-2]) or in the industry (in material processing [3-8], thin film deposition and isotopic separation [9]) for example.

On the other hand, nuclear medicine applies radioactive materials for diagnostic and treatment of patients. Radioisotopes are used like tracers in image medical diagnostics due to some propitious physical properties such as radiation emission and time decay. When radioisotopes are combined with chemical compounds of specific metabolic, biochemical and biological characteristics, they become radiopharmaceuticals. SPECT (Single Photon Emission Computed Tomography) is one of the techniques which use the radiation emitted by radiopharmaceuticals, mainly $^{99m}$Tc, to produce images for medical diagnostics [2, 10-11]. Molybdenum-$^{99}$ is the only reliable source for the production of technetium-$^{99}$m, accounting for 80% of nuclear medicine diagnostics. Table 1 shows the production mechanisms of molybdenum-$^{99}$, however these processes present low efficiency due to the losses, the variety of reaction sub-products and the high cost. So, it is necessary to develop ways to optimize the molybdenum-$^{99}$ production, to meet the market demand for diagnostics imaging.
Table 1. Reactions of production of $^{99}$Mo.

| Production mechanisms | Reaction | Physical Principle |
|-----------------------|----------|--------------------|
| Cyclotron             | $^{96}$Zr($\alpha$,n)$^{99}$Mo | Neutron zirconium activation |
|                       | $^{100}$Mo(p,pn)$^{99}$Mo | Proton bombardment of 100 molybdenum |
|                       | $^{100}$Mo(d,dn)$^{99}$Mo | Deuteron bombardment of 100 molybdenum |
| Reactor               | $^{98}$Mo(n,$\gamma$)$^{99}$Mo | Neutron activation of 98 molybdenum |
|                       | $^{235}$U(n,f)$^{99}$Mo | Uranium fission |

According to the research line developed at IEAv (Institute for Advanced Studies) on isotopic separation, it is intended to separate the molybdenum-$99$ through laser ablation of irradiated molybdenum metal target followed by selective photo ionization. To this end, a nanosecond pulsed Nd:YAG laser focuses on a molybdenum target and generates a plasma plume that is composed of neutral and ionized atoms. The part of the plume related to neutral atoms must be separated from the ionized part and, after that, an arrangement of laser beams is applied to separate the isotopes according their ionization energies (selective photo ionization) [12-15].

In this paper, it is discussed the molybdenum plasma plume production and characterization. An important goal in this process was to determine the proportion of neutral and ionized atoms on the material resulting of ablation and the population of neutral atoms excited states. The characterization of plasma plume was made by Optical Emission Spectroscopy [16-20] and the spectra were acquired for different positions along the expansion axis. Doing so, it was possible to quantify parameters such as plasma temperature, through Boltzmann plot method, to compare theoretical and experimental spectra considering the relevance of some physical processes (blackbody radiation, recombination, bremsstrahlung radiation), and to calculate the population of excited states of the plasma.

2. Laser ablation

Laser ablation consists in material removal from a target by incidence of a laser, commonly a pulsed laser. This process results from focusing a laser beam onto a surface inducing heating, ejection and ionization of the material and forms a plasma jet. For metallic samples, most of the energy of laser beam, nearly 40%, is transferred to superficial layers of the sample, which corresponds to $1/\varphi$, known as optical absorption length, in which $\varphi$ is optical absorption coefficient. For molybdenum, optical absorption length is 14 nm. The heat flows into the material, thus, it is important to define the thermal diffusion length ($L_D$), equation (1).

$$L_D = \sqrt{4t_p \alpha}$$

where, $\alpha$ is thermal diffusivity and $t_p$ is laser pulse duration ($t_p = 25$ ns and 110 ns). For molybdenum, thermal diffusion length is nearly 2.0 $\mu$m.

Figure 1 shows the interaction between laser and the material. The sample is reached by a sequence of laser pulses and the surface temperature increases due energy absorption. The process following the surface heating is phase transition of part of the solid forming a liquid region. After that, laser beam continues focused at same portion of the target until it absorbs sufficient energy to reach latent heat of evaporation. Considering that laser pulse duration is too short, the sample volume that was melted and evaporated does not suffer displacements and heat does not conduct into the target. The vapor reaches
very high temperature, increasing the collision rate between vapor particles leading to ionization. The interaction between laser and the sample, considering the ionized atoms, free electrons and neutral particles in vapor, sustain the plasma and increase its density [21-24].

Figure 1. Interaction between laser and solid. At (a) fusion process is represented; at (b) evaporation and at (c) thermo ionization.

After the end of the laser pulse, the density of ejected material is approximately $10^{21}$ atoms/cm$^3$, comparable to solid density, and is strongly ionized. At this point, the energy exchange between the plasma particles is due to collisions. The plasma plume behaves like a fluid and its expansion is ruled out by a hydrodynamic model. At a certain distance of the target, the plasma achieves local thermal equilibrium.

3. Plasma spectroscopy
Spectroscopy allows non intrusive methods for the measurement of species population and plasma temperature [21, 24-25]. However, it is required that the plasma is in Local Thermal Equilibrium (LTE), such that the intensity of emitted light for a given transition is proportional to transition upper state population.

3.1. LTE requirement
The radiation emitted by the plasma escapes from the material and thus there is a deviation from Planck’s equilibrium. However, when the energy exchange is dominated by collisions the resulting stationary state can be described for the same laws of complete thermal equilibrium, with exception for the emitted radiation. This plasma is in LTE [26] which is characterized by:

- The electron population density in each state is determined for collision processes.
- The velocity distribution of free electron is maxwellian.
- The electron population distribution of the states is determined for Boltzmann distribution while, to ionization cases, it is determined for Saha distribution.

The criterion for the electron density ($N_e$) required for a local thermal equilibrium between two states separated in energy by $\Delta E$ [eV] is a function of electronic temperature $T_e$ [K], given by equation (2):

$$N_e[cm^{-3}] \geq 1.6 \times 10^{12} (T_e[K])^{\frac{1}{2}} (\Delta E[eV])^{\frac{3}{2}}$$

3.2. Temperature measurement
Electron temperature can be determined using Boltzmann distribution, equation (3), through a method developed by Griem [25-26], that consider the ratio of intensities between two emission lines of spectrum. Equation (3) shows the emitted spectral line intensity ($I_{\text{em}}$) that is a measure of the population of the corresponding energy in the plasma, under LTE approximation.
\[
I_{nm} = \frac{hc}{4\pi \lambda_{nm}^2} A_{nm} g_n \frac{1}{U(T)} e^{-\frac{E_n}{k_B T}}
\]  
(3)

where \(\lambda_{nm}\), \(A_{nm}\) and \(g_n\) are wavelength, transition probability and statistical weight of the upper level, \(E_n\) is the energy of the level \(n\) and \(U(T)\) is the partition function. Using the ratio of two emission lines (1 and 2), the electron temperature can be calculated, equation (4).

\[
\frac{I_1}{I_2} = \frac{g_1 A_1}{g_2 A_2} \frac{e^{-\frac{E_1}{k_B T}}}{e^{-\frac{E_2}{k_B T}}}
\]  
(4)

4. Experimental setup

This work presents molybdenum optical emission spectra for experiments performed in air, using two Nd:YAG lasers: Avia 355-X and Hawk-532-40-M, the first one, emitting pulses with 0.205 mJ energy and 25 ns duration in 355 nm, and the second, emitting pulses with 2.05 mJ energy and 110 ns duration in 532 nm.

The Mo targets were fixed to a XY table, controlled by a computer program which moves permanently the table in order to avoid cratering. The plume was imaged by a 4x telescope and the light emission was collected at the image position by a fiber-optic and coupled to a Triax 550 Jobin-Yvon spectrometer. Figure 2 presents a scheme of experimental setup [27-31].

5. Results and discussion

The theoretical spectra construction, figure 3, begins with data files generated through fundamental data obtained at NIST (National Institute of Standards and Technology) website [32]. A table that contains wavelengths of emission lines, \(\lambda\), related with transition probabilities (which are given by Einstein coefficient, \(A\)), degeneracy of energy levels, \((2J+1)\), energy values of the levels involved on transitions and electronic configurations is used to assign an intensity to the emission lines. So, using data acquired at NIST on equation (3), theoretical spectra are constructed.

In figure 3, it can be seen that emission at 400-450 nm is due de-excitation of neutral atoms while emission at ultraviolet region is due de-excitation of ionized atoms. For selective photo ionization, the plume must be neutral and monatomic and this explains the choice of interest region in 400-450 nm.
Figure 3. Theoretical molybdenum spectra. (a) Emission lines for neutral atoms; (b) emission lines for singly ionized atoms and (c) emission lines for doubly ionized atoms.

Quantitative data were acquired assuming Local Thermal Equilibrium approximation and excitation temperature was calculated through intensity ratio between two emission lines, equation (4). Two neutral molybdenum emission lines were considered for each 5 nm spectral range and the measurement was made for five different positions along the expansion axis.

Figure 4 and figure 5 represent the excitation temperature along the plasma plume. Despite the large error bars, it can be seen that the behavior of the values of temperature does not change for two lasers: the value of temperature has a maximum at the center and is minimum at the ends of the plume, that agree with literature [33]. The average temperature is 15000 K.

Another point that should receive attention is the electron population distribution. Figure 6 and figure 7 show the evolution of electron population for 4d4 5s 6s state. In the first portion of the plot, Boltzmann distribution was considered. After it, the plasma reaches a non-collision regime, in which the intensity of emission light decreases and it can be attributed to spontaneous emission.

During the experiments, other important results were also obtained:

- The height of plume was measured and is nearly 2mm.
- Plasma “survives” just a short period after the laser pulse ends. The plasma lifetime is, approximately, 250 ns.
- The target must move relative to the laser avoiding cratering. This movement produces instability in spectra amplitude, but does not affect the intensity ratio of emission lines.
Figure 4. Excitation temperature along the plasma plume for 355 nm laser.

Figure 5. Excitation temperature along the plasma plume for 532 nm laser.

Figure 6. Electron population distribution for 4d\(^{5}\)5s\(6\)s state. For 355 nm laser.

Figure 7. Electron population distribution for 4d\(^{5}\)5s\(6\)s state. For 532 nm laser.

6. Conclusions

In this work, optical emission spectroscopy of laser-ablated molybdenum was performed in air. The generated plasma was considered at local thermal equilibrium, so that plasma temperature and electron population distribution were determined by Boltzmann distribution. The average temperature is 15000 K, and it has a maximum at the center of the plasma plume and a minimum at the ends. Through electron population distribution, it was observed that, near the target surface, both atoms and ions are in excited states and tends to decay to the ground or metastable state as the plume expands.

Future work will be devoted to improve the accuracy of the measurements and to demonstrate, more precisely, the molybdenum plasma properties in air. Moreover, it is necessary to establish the optimal experimental conditions for evaporation and data acquisition for subsequent measurement in vacuum.

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