Spectrochimica Acta Part B 94–95 (2014) 63–70

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

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

Theoretical study of the formation mechanism of laser-induced aluminum plasmas using Nd:YAG fundamental, second or third harmonics

Vincent Morel, Arnaud Bultel

CORIA — UMR 6614, Normandie Université, CNRS — Université et INSA de Rouen, Campus Universitaire du Madrillet, 76800 Saint-Etienne du Rouvray, France

ARTICLE INFO

Article history:
Received 30 July 2013
Accepted 5 March 2014
Available online 21 March 2014

Keywords:
Aluminum
Collisional-Radiative model
Laser-induced plasma
Non-equilibrium plasma
Multiphoton ionization
Inverse Bremsstrahlung

ABSTRACT

The Collisional-Radiative model CoRaM-Al is implemented in a 0D numerical code in the purpose of describing the formation of the plasma resulting from the interaction between a 4 ns Nd:YAG laser pulse and an aluminum sample in vacuum. The influence of the first three harmonics at 355 nm, 532 nm and 1064 nm is studied. In each case, the fluence value is set equal to the threshold above which a phase explosion takes place. The sample surface temperature is therefore limited to the critical temperature (6700 K). The solid → gas transition is classically treated by using the Hertz–Knudsen law. The species considered in CoRaM-Al are Al, Al^+, Al^{2+}, Al^{3+} and free electrons. They are in thermochemical non-equilibrium at different temperatures. Each state behaves freely owing to electron impact induced excitation and ionization, elastic collisions, Multiphoton Ionization (MPI), Inverse Bremsstrahlung (IB), thermal Bremsstrahlung, and spontaneous emission.

The results show that MPI and IB play a complementary role in the heating process of electrons. In the ultraviolet and visible cases, the increase in electron temperature is mainly due to multiphoton ionization before the maximum irradiance. The electron temperature does not exceed 9000 K. The heavy particle temperature mainly results from the surface temperature. Conversely, in the infrared case, electron temperature strongly increases after the maximum irradiance owing to inverse Bremsstrahlung. Electrons then give a part of their energy for the benefit of heavy particles, which leads to the increase in their temperature. The electron number density reaches its maximum during the laser pulse with a value of the order of 10^{25} m^{-3} and the electron temperature exceeds 13,000 K. A maximum of the ionization degree close to 0.2 is thus obtained at 1064 nm.

1. Introduction

The laser-induced plasmas are characterized by strong radiative losses and by high expansion velocities. This is due to the pulse duration and to the characteristic diameter over which the pulse is usually focused. As a result, these plasmas can be in strong non-equilibrium. The question of the thermodynamic equilibrium is therefore open.

If the plasma departs from thermodynamic equilibrium, two important consequences can be derived. First, its modeling is much more complex than for the case of a plasma at equilibrium. Indeed, the equation of state is no longer valid and considering at least the first excited states of the neutrals and of the ions as independent species is required. Second, optical emission spectroscopy experiments performed on these plasmas do not allow the determination of the ground state number density. Indeed, the ground and excited states number densities do not fulfill the Boltzmann distribution.

In this context, the elaboration of Collisional-Radiative (CR) models is mandatory. In the past, some CR models have been elaborated for different elements and for different conditions [1–9]. Most of them have been elaborated in the framework of Laser-Induced Breakdown Spectroscopy (LIBS) experiments [10]. The main goal is to show how the plasma reaches equilibrium. In particular, the time required to reach thermodynamic equilibrium can be obtained. This time can help the implementation of a calibration-free technique [11,12] for the determination of the composition of a sample by LIBS.

Our work is focused on the ignition process of the plasma, therefore on the first 100 ns. Our objectives are to estimate the departure from thermodynamic equilibrium at the end of the ignition phase in order to assess the consequences of this departure on the subsequent evolution of the plasma. As a result, our work is not limited to the frame of LIBS, but extends to the field of the laser-matter interaction. In the past, we have elaborated a model in thermal and chemical non-equilibrium for the formation of laser-induced plasmas on aluminum samples at a wavelength $\lambda = 532$ nm [1]. The related paper will be referred to as paper I in the upcoming sections. Since the formation only concerns early times, a simplified 0D aerodynamic approach was developed. The present paper reports an extension of the former model essentially in terms of elementary processes taken into account and in terms of temperature reached by the sample surface. This new

E-mail address: morel@coria.fr (V. Morel).
URL: http://www.coria.fr (V. Morel).

http://dx.doi.org/10.1016/j.sab.2014.03.003
0584-8547/

model can now treat the case of samples reaching the critical temperature $T_c = 6700$ K, whereas the former model was able to treat the case of a surface temperature lower than 3000 K. The model is therefore used to its maximum capacity with respect to its assumptions. We are then closer to the experimental conditions of the LIBS technique, even if modelings have pointed out that the related regime is often supercritical [13]. In addition, this model can work for various wavelengths.

In Section 2, the conditions of the test-case (wavelength, fluence) are given. We treat the case of the first three harmonics of classical nanosecond Nd:YAG laser pulse interacting with an aluminum sample reaching its critical temperature. In Section 3, the model is briefly described. The description is focused on the updating of the former Collisional-Radiative model. The new CR model is now called CoRaM-Al (Section 3.2). In Section 4, the results are discussed. The behavior of the heavy particle temperature and electron temperature (denoted T_A and T_e, respectively) is analyzed during the plasma formation. Population densities are also discussed. Characteristic (excitation and ionization) temperatures are calculated and the time required to reach the chemical equilibrium is derived.

2. Test-case

The present paper deals with the interaction between nanosecond Nd:YAG laser pulses at the wavelengths $\lambda = 355$, 532 and 1064 nm and an aluminum target set in vacuum. The characteristic time τ for the laser pulse is supposed equal to 4 ns whatever the considered wavelength.

As far as we know, the sample surface temperature T_S has never been measured during the laser pulse. T_S is a fundamental limit condition for the plasma since this temperature drives the main part of the evaporation process. In modeling works, the surface temperature is sometimes calculated [13]. But these calculations are based on constant [14] or averaged [2] thermophysical properties of the sample. The surface can reach a temperature higher than 15,000 K during the laser pulse. In addition, the absorption coefficient at the laser wavelength is totally unknown in these thermal conditions. If $T_S > T_c$, the regime is supercritical, and a correct description of the explosion phenomenon requires one to consider a two-phase flow [15]. Today, no CR model reported in the literature with $T_S > T_c$ respects this requirement. The surface temperature calculated in these works is therefore questionable. The only way to be sure of the surface temperature and of the resulting evaporation process is to choose an irradiance corresponding to the threshold between the classical evaporation mechanism and the phase explosion. The surface then reaches the critical temperature T_c.

1. At 1064 nm, Porneala and Willis [16] have obtained a threshold of 5.2 J cm^{-2}. Cabalín and Laserna [17] have obtained 5.3 J cm^{-2} for pulses of 5 ns. For a pulse of 10 ns, Cao et al. have indicated a fluence threshold higher than 5 J cm^{-2} [18].
2. In the visible spectral range, Fishburn et al. [19] have obtained a threshold of 7 J cm^{-2} at 544 nm for pulses of 30 ns and Cabalín and Laserna [17] have obtained a value of 6.6 J cm^{-2} at 532 nm for pulses of 5 ns.
3. In the UV spectral range, the threshold has not been clearly determined. However, Amoruso et al. [20] have reported a fluence threshold at least equal to 3.24 J cm^{-2} for pulses of 6 ns at 355 nm. Cao et al. have mentioned in ref. [18] that the threshold is higher than 5 J cm^{-2} at 266 and 355 nm for pulses of 10 ns. As far as we know, no value of the fluence threshold for 355 nm has been reported in the literature.

We have assumed that the fluence threshold linearly depends on the wavelength. This assumption is approximately verified in the case of silicon as discussed by Yoo et al. [21]. Therefore, the retained values for the fluence threshold are $F_{1064} = 5.1$ J cm^{-2} at 1064 nm, $F_{532} = 6.8$ J cm^{-2} at 532 nm. This assumption leads to a value of $F_{355} = 7.4$ J cm^{-2} at 355 nm.

3. Description of the model

As mentioned in the Introduction, the present 0D model is based on the model published in paper I. The translational energy of heavy particles and electrons is assumed to follow a Maxwellian distribution at T_A and T_e, respectively. These particles gain energy owing to the laser pulse. The laser irradiance $\varphi_{las}(t)$ follows in time a Gaussian law

$$\varphi_{las}(t) = \varphi_{las}^{max} exp\left[-\left(2\frac{t-t_{max}}{\tau}\right)^2\right] \qquad \left[\mathrm{W\ m^{-2}}\right] \tag{1}$$

where t_{max} is the time corresponding to the maximum irradiance. t_{max} has been arbitrarily set equal to 10^{-8} s. The dynamics of the plasma does not depend on t_{max} and no significant phenomenon is observed in the interval $0 < t < 3 \times 10^{-9}$ s. In Eq. (1), φ_{las}^{max} is the maximum value of the laser irradiance defined as

$$\varphi_{las}^{max} \approx \frac{F_\lambda}{\tau} \qquad \left[\mathrm{W\ m^{-2}}\right] \tag{2}$$

where F_λ is the fluence threshold discussed in Section 2.

For copper, Bogaerts and Chen [13] have shown that the target surface temperature T_S decreases from 8000 K to 4500 K after the maximum irradiance over 15 ns in similar fluence conditions for $\lambda = 266$ nm. For aluminum, Amoruso [2] has shown that T_S decreases from 5000 K to 3500 K over 10 ns in similar fluence conditions for $\lambda = 355$ nm. In both cases, the decrease in T_S leads to a collapse of the ablation rate (i.e. the ejected particles from the sample per unit surface and per unit time). Actually, the ablation mainly occurs around the maximum irradiance. For irradiance considered in the present paper, the time evolution of the ablation rate shown by Amoruso can be correctly reproduced if T_S is assumed to evolve like the irradiance (1). We have therefore assumed that T_S evolves like the irradiance, even if the evaporation lasts later than the laser pulse ended. This late evaporation has no influence on the plasma since this evaporation corresponds to a weak ablation rate. In addition, the energy required to heat the surface from ambient temperature to the melting temperature T_f is negligible with respect to the energy necessary to heat the target until its maximum value. In addition, the equilibrium vapor pressure at T_f is negligible with respect to the one given by the equation of Alcock et al. [22] at higher temperature. We have therefore simplified the problem by assuming the initial temperature of the target equal to T_f. These assumptions lead to

$$T_S(t) = \left(T_S^{max} - T_f\right) exp\left[-\left(2\frac{t-t_{max}}{\tau}\right)^2\right] + T_f \qquad [\mathrm{K}] \tag{3}$$

where T_S^{max} is the maximum temperature reached by the surface. Since the maximum irradiance φ_{las}^{max} corresponds to the fluence threshold above which a phase explosion occurs, we have $T_S^{max} \equiv T_c = 6700$ K, the critical temperature of aluminum [23]. The plasma can be considered as a single-phase flow and the vaporization phenomena can be treated using the usual approach.

The particles ejected from the surface are treated like in [8]. The ablation rate respects the Hertz–Knudsen law [24], which depends on the equilibrium vapor pressure of aluminum at the surface temperature. The equilibrium vapor pressure respects the equation proposed by Alcock et al. [22]. The emerging particles are aluminum atoms in ground and first excited states, ions in ground state, and electrons. They are assumed in equilibrium at the target temperature.

The model accounts for 43 states of Al, 42 states of Al^+, 21 states of Al^{2+}, the fundamental state of Al^{3+}, and free electrons. The resulting 107 excited states are taken from our model reported in paper I. States of close energy are lumped together according to their core configurations to form a fictitious level. Each one is characterized by its statistical weight g, its azimuthal quantum number l and its total angular momentum quantum number J involved in the selection rules.