Spectrochimica Acta Part B 63 (2008) 746–754

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

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

Double pulse laser ablation and laser induced breakdown spectroscopy: A modeling investigation

Annemie Bogaerts *, Zhaoyang Chen, David Autrique

University of Antwerp, Department of Chemistry, Research Group PLASMANT, Universiteitsplein 1, B-2610 Wilrijk-Antwerp, Belgium

ARTICLE INFO

Article history:
Received 1 February 2008
Accepted 7 April 2008
Available online 20 April 2008

Keywords:
Double pulse
Laser ablation
Laser induced breakdown spectroscopy
Numerical modeling
Plume expansion

ABSTRACT

A numerical model, describing laser–solid interaction (i.e., metal target heating, melting and vaporization), vapor plume expansion, plasma formation and laser–plasma interaction, is applied to describe the effects of double pulse (DP) laser ablation and laser induced breakdown spectroscopy (LIBS). Because the model is limited to plume expansion times in the order of (a few) 100 ns in order to produce realistic results, the interpulse delay times are varied between 10 and 100 ns, and the results are compared to the behavior of a single pulse (SP) with the same total energy. It is found that the surface temperature at the maximum is a bit lower in the DP configuration, because of the lower irradiance of one laser pulse, but it remains high during a longer time, because it rises again upon the second laser pulse. Consequently, the target remains for a longer time in the molten state, which suggests that laser ablation in the DP configuration might be more efficient, through the mechanism of splashing of the molten target. The total laser absorption in the plasma is also calculated to be clearly lower in the DP configuration, so that more laser energy can reach the target and give rise to laser ablation. Finally, it is observed that the plume expansion dynamics is characterized by two separate waves, the first one originating from the first laser pulse, and the second (higher) one as a result of the second laser pulse. Initially, the plasma temperature and electron density are somewhat lower than in the SP case, due to the lower energy of one laser pulse. However, they rise again upon the second laser pulse, and after 200 ns, they are therefore somewhat higher than in the SP case. This is especially true for the longer interpulse delay times, and it is expected that these trends will be continued for longer delay times in the µs-range, which are most typically used in DP LIBS, resulting in more intense emission intensities.

1. Introduction

Laser induced breakdown spectroscopy (LIBS) is a well-known analytical technique for the analysis of solid, liquid, gaseous and aerosol samples (e.g., [1,2]). It suffers, however, from low sensitivity, in comparison with other spectrometric methods [2]. One of the approaches to overcome this limitation is the double (or dual) pulse (DP) configuration (e.g., [3–27]. In this way, the LIBS sensitivity is improved due to a better coupling of the laser energy to the target and ablated material.

Also for laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), the DP technique has been applied, by Russo et al., to break the ablated mass into a finer aerosol, which is more readily transported to and digested in the ICP [28]. Moreover, for the application of laser machining of metals, Forsman et al. observed an enhancement of material removal rates when applying the DP technique [29], and Zhang et al. reported high quality laser ablation (i.e., smooth surfaces due to reduced debris deposition) of fused quartz, when applying double pulses with 30 ps–4 ns interpulse delay times [30]. Finally, for pulsed laser deposition (PLD) the DP technique has proved to be capable for large-area, uniform film growth due to increased plume expansion and higher plasma temperatures [31].

An excellent review paper on the topic of DP LIBS, by Babushok et al., has recently been published in this journal [3]. An overview was given on different configurations, including collinear, orthogonal pre-ablation, orthogonal re-heating and dual pulse crossed beam modes. In addition, the effects of combining laser pulses with different wavelengths (e.g., UV and IR [8]), energies, pulse durations (e.g., femtosecond (fs) and nanosecond (ns) [24]) and interpulse delay times were reviewed. Enhancement effects are reported for a wide variety of parameters, including ion yield, kinetic energy of ions, plasma temperature, plume expansion velocity, size and shape of the plasma volume, emission line intensities,… (see Ref. [3] for a detailed overview). Most often, interpulse delay times in the microsecond range are applied, because this gives most pronounced enhancements in the LIBS emission intensities (e.g., [4–21]). However, enhancements (e.g., for the material ablation rate) were reported also for interpulse delay times in the ns-range or even ps-range, for instance by Russo and coworkers [14,28], as well as other researchers [29–32].

The review paper by Babushok et al. also gives an overview of the possible mechanisms behind the DP effect, both with respect to the

* Corresponding author.
E-mail address: annemie.bogaerts@ua.ac.be (A. Bogaerts).

0584-8547/$ – see front matter
doi:10.1016/j.sab.2008.04.005

ablation processes and the vapor plume/plasma [3]. Furthermore, another recent review paper also discusses the emission enhancement mechanisms in DP LIBS [25]. It is mentioned in this paper that the enhancements are clear, but the mechanisms behind it are still not so well understood. There exist several explanations, depending on the interpulse delay time, such as an increased pulse-plasma coupling (reflected in the higher plasma temperature and electron densities), an increased sample heating, yielding more ablation, and ambient gas rarefaction (see Ref. [25] for more details and corresponding references).

To obtain more insight in these DP effects, several research groups have experimentally investigated the mechanisms of DP LIBS enhancements. Cristoforetti, Tognoni and colleagues have studied the DP effects by spectroscopic analysis, measuring line intensities (emission enhancements), but also electron densities and temperatures in the plume [4–7,19,26] as well as the evolution of the plume by shadowgraphic analysis [6,19]. In Ref. [6] a three-dimensional analysis of the laser-induced plasma was made by spectrally, temporally and spatially resolved measurements and a deconvolution algorithm. Moreover, in Ref. [4] the crater was studied by video-confocal microscopy, and the variation in crater dimensions was correlated to the enhancements in the LIBS signals. Recently, they presented a very interesting spectroscopic study of the factors concurring to intensity enhancements in DP LIBS [26]. This study provided an easy check of the temperature in the plasma. The approach is able to discriminate between the effects of re-heating of the plasma by the second laser pulse, and enhance ablation, and to assess the contribution of these effects to the observed enhancements.

Noll et al. [11] also studied the dynamics of the expanding laser-induced plasma by a high-speed electro-optic camera. A Mach–Zehnder interferometer was applied to detect the spatio-temporal changes of the refractive index of the plasma. The same group measured the material ablation rates, electron density and temperature and line intensities, and reported enhancements for all these quantities when using double pulses [12]. Colao at al. [13] used spectroscopic diagnostics of the plasma to determine the electron densities and plasma temperatures. They observed a lowering in the second pulse-plasma threshold and an overall enhancement in the line emission, for an interpulse delay time of 40–60 μs. Gautier et al. investigated the influence of the interpulse delay time (in the range of 0.2–5 μs) from temporal and spectral analysis [9,10].

A very interesting study on the effect of interpulse delay time (in the range of 1 ns–10 μs) was performed by Russo et al. [14]. They observed an abrupt increase in the plasma properties (plasma temperature and electron density) and crater dimensions between 100 and 200 ns, which they attributed to a phase explosion mechanism. Forsman et al. [29] also observed a higher mass removal rate when the interpulse delay time was increased in the range of 30–150 ns, and this was explained by a mechanism of ablation of the target by heated ejecta. The latter were produced by the first laser pulse, and subsequently heated by the second laser pulse.

In general, several authors have reported a reduction in ambient gas density as a result of the first laser pulse, which yields a faster vapor plume expansion (and hence a larger plasma volume) and less effective shielding of the second laser pulse [4–7,9,11,17–19]. The same effect was also observed when varying the ambient gas pressure in single pulse LIBS [5]. Also, the measured increase in the plume temperature in the DP configuration can explain why lines originating from higher excited levels are more enhanced than other lines [4,8,9]. In a very interesting study of enhanced LIBS signals using a combination of 1064 nm and 266 nm laser pulses, St-Onge et al. [8] observed also larger signal enhancements for ionic lines than for atomic lines, which were also correlated with a higher plume temperature. Moreover, the optimum interpulse delay time appeared to be around 100 ns for atomic lines and about 3 μs for ionic lines. A similar observation was made by Cristoforetti et al. [5] and by Gautier et al. [10].

Recently, De Giacomo et al. [27] were able to shed a new light on the expansion dynamics in SP and DP LIBS, by means of spectrally resolved imaging. Based on temporal and spatial maps of the emission signals of atomic and ionic lines, a very interesting information was obtained on the plume expansion dynamics, for instance the recombining character of a SP laser-induced plasma, and the fact that the DP laser-induced plasma expands in a hotter environment, thereby keeping its energy for longer times. This results in a higher ionization degree during longer times and a more stable signal. The spatial and temporal maps of TiI and TiII intensities showed maximum values which were quite similar, but the position and time of the maxima were different, i.e., in the DP case, the maximum was obtained later in time and further away from the target. Hence, in this way the authors could demonstrate that the enhancement is connected to the detection time and the optical configuration. It is concluded that the most important feature of DP LIBS is the possibility to increase the detection time window and the emission volume, thus obtaining a more stable and intense emission signal. This experimental work was complemented by simple modeling of the expansion dynamics (by Euler equations), including the chemical kinetics. The same research group has also applied experimental and modeling techniques to investigate DP LIBS under water [15,16]. The laser-induced bubble, produced by the first pulse, was simulated to clarify the effect of interpulse delay time. It was established that the dynamics of the plasma by DP LIBS was strongly affected by the chemical reactions between the plasma species and the background environment inside the bubble. A hydrodynamic theoretical expansion model was also used in Ref. [31] to yield radial thickness profiles of the deposited films in DP laser deposition.

In our paper, we will try to obtain a deeper understanding of the mechanisms behind DP LIBS, by a more comprehensive model, describing also the laser–solid interaction (ablation), besides plume expansion and plasma formation. Moreover, the plume expansion dynamics is modeled by the full Navier–Stokes equations, taking into account also the interaction terms (viscosity, diffusion, thermal conductivity) between vapor plume and background gas.

2. Brief description of the model

The model applied for this study was developed before in our research group [33]. It is a one-dimensional model, describing (i) the laser–metal interaction by a heat conduction equation, yielding heating, melting and vaporization of the metal target, (ii) the vapor plume expansion in a background gas by fluid dynamics equations, including interaction terms between vapor and gas (see above), (iii) the plasma formation, assuming local thermal equilibrium (LTE) conditions, hence using Saha equations to calculate the ionization degree in the vapor and the background gas, and (iv) the laser–plasma interaction by inverse Bremsstrahlung and photo-ionization, resulting in plasma shielding. More details about this model, the input data and the solution methods, can be found in Ref. [33].

The model was already applied to expansion in vacuum [34] and in a background gas with varying pressure [35], for a range of different laser operating conditions (irradiance, pulse duration and wavelength) [36], background gases [37] and metal targets [38], but always for a single laser pulse.

Because the model is only one-dimensional, it assumes vapor plume expansion in the forward direction. This is fine for the first (few) 100 ns, but afterwards, the expansion in the radial direction cannot be neglected anymore. Furthermore, the model assumes the plasma to be in LTE conditions, which becomes also questionable for longer simulation times, due to the growing importance of electron-ion recombination upon cooling of the vapor plume. Finally, particle formation by condensation in the expanding (cooling) vapor plume then starts to become important as well. For these reasons, we have applied the model here for only 200 ns, and therefore, the interpulse