Spectrochimica Acta Part B 60 (2005) 1392 – 1401

SPECTROCHIMICA ACTA PART B

www.elsevier.com/locate/sab

Effect of laser pulse energies in laser induced breakdown spectroscopy in double-pulse configuration

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Received 20 April 2005; accepted 15 August 2005
Available online 10 October 2005

Abstract

In this paper, the effect of laser pulse energy on double-pulse laser induced breakdown spectroscopy signal is studied. In particular, the energy of the first pulse has been changed, while the second pulse energy is held fixed. A systematic study of the laser induced breakdown spectroscopy signal dependence on the interpulse delay is performed, and the results are compared with the ones obtained with a single laser pulse of energy corresponding to the sum of the two pulses. At the same time, the crater formed at the target surface is studied by video-confocal microscopy, and the variation in crater dimensions is correlated to the enhancement of the laser induced breakdown spectroscopy signal. The results obtained are consistent with the interpretation of the double-pulse laser induced breakdown spectroscopy signal enhancement in terms of the changes in ambient gas pressure produced by the shock wave induced by the first laser pulse.

Keywords: LIBS; Laser; Spectroscopy; Double pulse; Confocal microscopy

1. Introduction

The laser induced breakdown spectroscopy (LIBS) performed in double-pulse (DP) configuration is a promising development of the traditional well-known LIBS, which makes use of a single laser pulse (SP) for the ablation of the sample. In the DP configuration a pair of pulses, delayed the one with respect to the other by a temporal gap of the order of 1–10 μs, is used for the ablation of material from the target surface and consequent formation of a plasma plume; the analysis of the plasma emission, acquired in a suitable temporal window, allows qualitative and quantitative information on the elemental composition of the sample.

The DP configuration maintains the benefits of the LIBS technique, such as the fastness, the absence of chemical pretreatment and the ability of in situ applications; however, it has been demonstrated that DP LIBS improves the limits of detection of the different chemical elements by one to two orders of magnitude, by increasing the discrete optical emission of the plasma plume.

Several DP configurations have been studied, differing on the geometrical configuration, the wavelength and the temporal order of the two laser beams. Mainly, the so-called parallel or collinear configuration is often used, where both the beams are directed perpendicularly to the target surface [1–5], but also the orthogonal configuration has been tested, where the first pulse (pre-pulse scheme) [6–10] or the second one (re-heating scheme) [11,12] is directed parallel to the target surface and focused in the ambient gas in front of it, while the other is perpendicular and ablates the target.

In spite of the numerous works dedicated to the DP LIBS configuration, the reason (or the concurrent reasons) of the signal improvement is still not completely clear.

In our previous works, all devoted to the study of DP LIBS in parallel configuration, we have presented a phenomenological model of the different ablation characteristics of the DP LIBS, using a time- and space-resolved emission analysis of the plume [13] and a study of the emission obtained at different ambient gas pressures and different interpulse delays with spectroscopic [14] and imaging techniques [15].

The present work is aimed to the study of the effect of the pulse energy on the LIBS signal enhancement in collinear configuration, to add another element to the comprehension of

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0584-8547/$ - see front matter
doi:10.1016/j.sab.2005.08.007

the physical processes involved in DP LIBS. In particular, since we hypothesized in the previous works that the benefits of double-pulse configuration are due to the effect of the first pulse, which "prepares" the ambient conditions where the second pulse can produce an optimal ablation, we focused our study on the effect of the first pulse energy on LIBS signal. In order to account for the different signal enhancements obtained with the different laser energies, we studied the thermodynamical parameters of the plasma and the mass ablated from the target.

The few previous works on this subject [12,16] were carried out in different experimental setups: Ray et al. [16] studied the effect of the energy of the first laser pulse in a DP LIBS experiment on a liquid jet while Gautier et al. [12] reported a study on both laser pulse energies but in the orthogonal DP configuration (both in the re-heating and in the pre-pulse schemes).

2. Experimental setup

The experimental setup used in this work is sketched in Fig. 1. The measurements were performed using a new dual-pulse mobile LIBS instrument (MODI—MObile Dual-Pulse Instrument) produced by Marwan Technology s.r.l. (Italy) in collaboration with our laboratory. The instrument incorporates a dual-pulse laser, constituted by a double-rod resonator pumped by a single flashlamp, emitting two collinear laser pulses of about 10 ns duration (FWHM) with energy per pulse variable between 50 and 150 mJ at a maximum repetition rate of 10 Hz. The interpulse delay can be set from 0 (single pulse) to 60 μs. The laser pulse energies can be varied independently for the two beams.

The energies of the pulses were calibrated by means of a Scientech thermopile and then monitored during the experiment by sending a small fraction of the laser beams to a fast photodiode coupled to a digital oscilloscope.

An aluminum target (Al 99%, Mn 0.3%, Mg 0.6%), with the surface perpendicular to the laser beams, was mounted inside the MODI experimental chamber, on a motorized table for positioning at the optimal lens-to-sample distance. The sample surface was previously polished and cleaned to increase the reproducibility of measurements.

The two beams were focused on the target surface by means of a 100-mm focal length lens; the lens to sample distance was set to 5 mm less than the lens focal length (95 mm), in order to avoid the air breakdown in front of the target [17] and to improve the stability of the plasma [18].

The space-integrated LIBS signal was collected through an optical quartz fiber (diameter = 600 μm, N.A. = 0.22), placed at 45° with respect to the beam axis at a 3-cm distance from the target surface, and sent to the MODI Echelle spectrometer ($\lambda/\Delta\lambda = 7500$) coupled with an intensified CCD camera, which provided for each acquisition a full spectrum in the range 200–900 nm.

All the experimental operations, including sample movement, settings of the laser (energy of the beams, delay between the pulses, repetition rate) and setting of the spectral acquisition parameters (number of spectra averaged, acquisition delay, CCD measurement gate and gain), were controlled by the MODI personal computer.

The delay between the laser pulses was changed between 0, corresponding to single pulse, and 50 μs. A delay time of acquisition of 700 ns was chosen in order to allow the decay of continuum, due to Bremsstrahlung radiation and free-bound electronic recombination; an acquisition gate of 500 ns was also chosen, which guaranteed well-visible emission signals in all the different experimental conditions analyzed, but still allowing a meaningful calculation of the

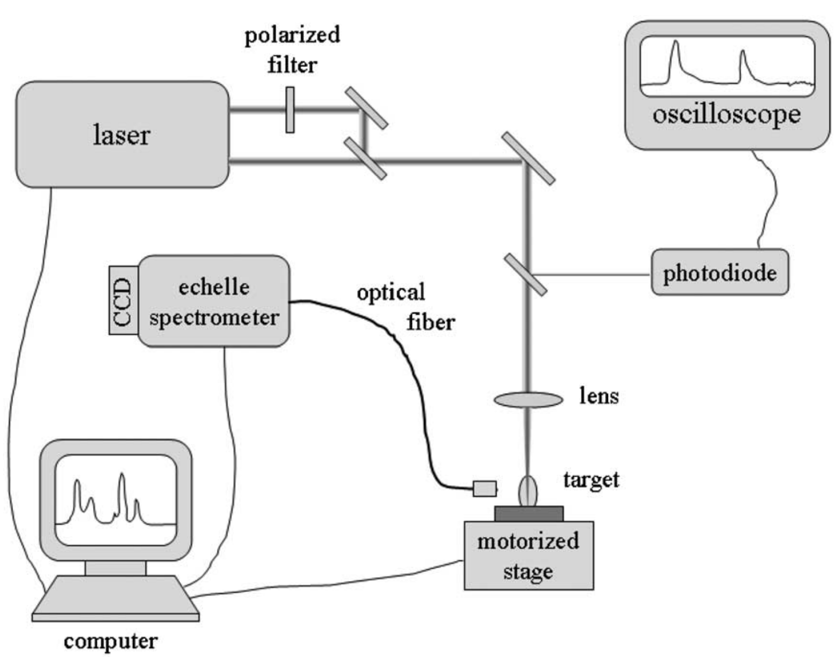

Fig. 1. Experimental setup used for spectroscopic analysis.