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Comparison of plasma parameters and line emissions of laser-induced plasmas of an aluminum target using single and orthogonal double nanosecond/picosecond pulses

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ABSTRACT

The emission of laser-induced plasma on aluminum targets in air was investigated with nanosecond- and picosecond-pulsed Nd:YAG laser emitting at the fundamental wavelength. Orthogonal double pulse in pre-ablation and reheating configurations was also performed where the picosecond laser was employed to ablate the target. Ablation fluences were kept fixed at 100 J cm^{-2} regardless of the laser pulse duration. Time integrated emission spectroscopy was employed to determine the plasma emission; thus, picosecond laser ablation provided larger figures than the nanosecond one. The emission was further enhanced when double pulse schemes were used. This enhancement was analyzed as a function of interpulse delays. Electron density and temperature evolutions were determined from time delays of 150 ns after the ablation plasma onset. Results are discussed in terms of the ablation rate.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is an analytical technique to determine the composition of solid, liquid or gaseous samples [1], where elemental analysis can be performed onsite with practically null sample preparation. However, the main weakness of the LIBS resides on its low sensitivity and relatively low reproducibility when compared with other established techniques such as inductively coupled plasma-mass spectrometry. The limit of detection (LOD) typically ranges from the high numbers of parts per billion (ppb) to hundreds of parts per million (ppm) for most elements [1]. To increase the LIBS sensitivity two or more laser pulses have been used in orthogonal and collinear double-pulse (DP) arrangements [2–9]. In the former DP configuration, one laser ablates the target while the other produces background gas plasma near the ablation location. The goodness of this setup is that the processes involved in the emission enhancement can be separately investigated since only one laser ablates the target. On the other hand, the collinear configuration is simpler to implement for remote analysis onsite, for instance. Several works have been published ([2] and references therein), during the last decade by using DP-LIBS achieving large signal enhancement values; especially when ablation is performed under low fluence regimes [10]. Thus, several experimental arrangements have been tested to investigate the best way to produce such an enhancement: laser wavelength and fluence [6,8,11–13], time delay between pulses [14] and timing parameters for detection [14–16] among others. As a result, a decrease of LOD in different DP arrangements has been reported [9,17,18].

On the other hand, to increase the LIBS signal reproducibility, picosecond and femtosecond pulsed lasers have also been employed [19–21]. Under these regimes, most of the laser energy is coupled into the material causing a fast transition from solid to vapor phase prior to plasma expulsion [22]. However, for pulse lengths shorter than a few picoseconds, observed transitions are weaker and shorter in duration compared with nanosecond laser ablation. Several works have investigated the pulse duration effect for laser drilling and ablation efficiency [23–25], the effect of sample temperature [26], the background atmosphere [27] and signal emission and plasma properties [28–31]. A reduction of background continuum, fewer matrix effects and higher shot-to-shot stability have been reported. Most of these works were performed under different experimental conditions of laser deposited energy, fluence and spot diameters making comparison between different conditions a difficult task. Le Drogoff et al. [32–34] investigated the influence of laser pulse duration, from ps to fs lengths, on the LIBS detection sensitivity and the plasma properties by using the same energy laser pulses and spot diameters. Results show that the excitation temperature increases with the pulse duration. Moreover, detection sensitivity using picosecond laser ablation is up to two-fold enlarged in comparison with fs produced plasma. To improve the detection sensitivity using short laser pulses, double pulse configuration has also been investigated using different geometrical approaches, pulse wavelengths and durations [35–43]. These works reported on plasma characteristics and the LIBS signal enhancement, including in some of them comparisons with experiments using

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nanosecond laser pulses. However, these assessments were performed for different ablation energies and, again, comparison becomes difficult.

The goal of this work is to compare the emission properties achieved with picosecond, nanosecond and orthogonal double pulse ps laser ablation, in reheating and pre-ablation configurations, keeping constant the ablation pulse energy and fluence. Ablation plasmas were studied by time-resolved emission spectroscopy in the sub-microsecond timescale. Results are discussed in terms of the electron density, electron temperature and laser drilling performance.

2. Experimental

The basic orthogonal configuration of double-pulse LIBS using sub-nanosecond laser ablation is outlined in Fig. 1. The ablation laser was a mode-locked Nd:YAG (Continuum, Leopard) with a pulse length of 50 ps and was operated at 1064 nm, 10 Hz and 50 mJ/pulse. This beam was focused ~1.5 mm underneath the target surface at atmospheric pressure by a 15 cm plano-convex lens, so the ablation plasma emission was maximized avoiding air breakdown. The plasma produced in air was generated by a Nd:YAG (Continuum, Surelite III) emitting at 100 mJ, with 5 ns pulse duration and operated at a fundamental wavelength of 1064 nm. The emission of this laser was focused parallel to the target surface, at a distance of 1 mm, by a 15 cm focal length plano-convex lens. Lasers and the diagnostics system were synchronized through an 8-channel pulse/delay generator (Berkeley Nucleonics, 575-8C). Nanosecond single-pulse laser ablation was performed by using the same energy, fluence and repetition rate as the picosecond ablation. Experiments were performed onto commercial aluminum based alloy (Al 6463) to produce ablation craters of 250 μm in diameter, which were measured by using a confocal microscope (Olympus, FV1000) at the target surface plane. The target was mounted on a translation stage to allow having a fresh surface every acquisition. Besides, both focusing lenses were mounted on independent translation stages, to adjust the relative position of the produced plasmas.

The whole plasma emission was collected using a quartz optical fiber bundle 10 cm away from the ablation crater and at about 45° with respect to the target surface. The fiber was coupled to a 50 cm focal length spectrometer (Acton Research, Spectra Pro 2500) with a 1800 groves mm^{-1} diffraction grating. The entrance slit of the spectrometer was ~5 μm wide, providing an instrumental broadening of 0.3 Å. The dispersed light was collected by an intensified charge-coupled device (ICCD) camera (Princeton Instruments, PiMAX 1024 × 1024). Time integrated spectra for single pulse experiments were taken 200 ns after the plasma onset and using an acquisition time of 30 μs to maximize the LIBS signal. For double pulse experiments, acquisitions started 200 ns after the second pulse. Spectra taken with this time delay resulted in a signal-to-noise ratio well above one for all observed transitions. To get all integrated spectra, the ICCD gain was set to zero. Time resolved spectra were acquired by gating the ICCD camera at different time delays with respect to the ablation pulse using a gate width of 30 ns in all experiments. The target was mounted on a 2-D translation stage so each spectrum acquisition could be obtained from an undamaged surface. Spectra were taken by accumulating 20 shots after cleaning the surface with 15 ablation laser shots. Then, the target is ablated by 35 laser shots before it is displaced to a new region for the next spectrum acquisition. Acquired spectra included ionic and neutral transitions from Al, Mg, Si, Fe and Cr to study the behavior of both matrix and minority species under different ablation conditions. Thus, three different spectral regions, centered at 281, 308 and 358 nm, were studied; additionally a fourth region centered at 656 nm was employed to follow the evolution of the H_α transition from the water vapor within the atmospheric air and used to determine the plasma electron density.

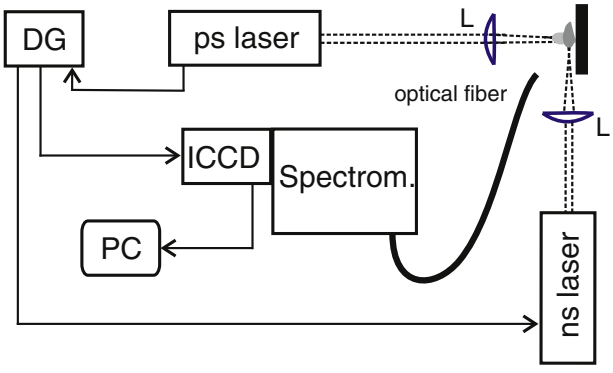

Fig. 1. Diagram of the experimental setup employed for the orthogonal double pulse configuration. L: lens, DG: time/delay generator, ICCD: intensified CCD.

3. Results and discussion

3.1. Spectroscopy results

From an analytical point of view, the comparison between different LIBS arrangements should be considered fair when the best signal to noise ratio (S/N) from each experimental configuration is compared [3]. In this work, to facilitate the comparison between experiments of different pulse lengths, the fluence was kept constant at 100 J cm^{-2} by using the same laser energy of 50 mJ.

Fig. 2 shows time-integrated spectra obtained from the single pulse (SP) ablation made with the nanosecond laser pulse (SP-ns hereafter) and the picosecond laser pulse (SP-ps hereafter). Under the experimental conditions described above the SP-ps spectrum is more intense than the SP-ns, while the background level and the noise from the signals are similar. In general, the emission of all observed transitions from different species, either ions or neutrals, is enhanced roughly a factor of three on average. Although the fluence in both experiments was kept fixed, the deposited irradiance (W cm^{-2}) was 2 orders of magnitude higher in the SP-ps than in the SP-ns. In another work comparing the ablation performed with different pulse lengths and using the same fluence [34], the longer pulse produced plasma (270 ps) was more intense than the shortest one (80 fs).

To gain more insight on the temporal evolution of the LIBS signal, time-resolved spectroscopy following several transitions was performed. One way to determine accurately the LIBS sensitivity for different configurations is by measuring the transition signal to noise ratio. Here, the signal comes from subtracting the spectrum background to the peak maximum intensity; while the noise is obtained by getting the standard deviation from the background signal nearby the studied transition. The

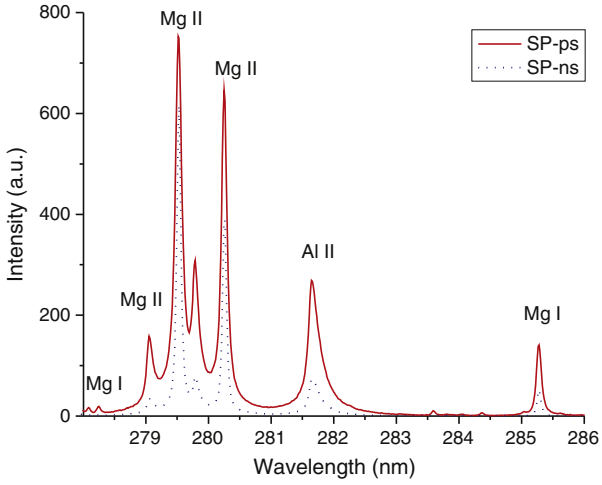

Fig. 2. LIBS spectra obtained by picosecond (solid) and nanosecond (doted) pulses.