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Double pulse laser induced breakdown spectroscopy with Gaussian and multimode beams

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ABSTRACT

Single vs multimode laser beams were compared for double pulse laser ablation, plasma properties and laser induced breakdown spectroscopy (LIBS) analytical capabilities. Laser beams with Gaussian and multimode profiles were generated within the same Nd:YAG laser in single and double pulse regimes. Gaussian beam produced a small and deep crater while multimode beam formed a wide shallow crater. Greater double pulse enhancement of ablated material and plasma volume were observed for Gaussian beam sampling. The higher intensity for atomic/ionic lines in the plasma spectra was observed for multimode beam sampling due to greater laser pulse energy and larger ablated mass. Interestingly, spectra line intensity enhancement for double pulse ablation was 2–3 times greater for Gaussian than for multimode beam ablation. Background emission decreased for plasma induced by multimode beam when using double pulse mode while for Gaussian beam an opposite dependence was observed. Surprisingly, higher peak fluence at sample surface for Gaussian beam didn't provide higher plasma temperature and electron density for double pulse ablation. Analytical capabilities of LIBS method were compared for double pulse plasma induced by Gaussian and multimode beam in terms of precision, sensitivity and linearity of calibration curves. It was observed that Gaussian beam sampling leads to improvement of analysis precision while sensitivity was element dependent.

1. Introduction

Laser induced breakdown spectroscopy is a technique for express multi elemental quantitative analytical of samples in different states (solid, liquid, gas) [1–3]. Any sample that can be reached by photons can be analyzed by LIBS. This feature initiated unique applications for online analysis in numerous applications like molten steel analysis [4,5], radioactive [6–8] and explosive [9] materials detection, space exploration missions [10,11].

Double pulse method represents a very effective approach to improve analytical performance of LIBS [12–14]. According to this technique, laser ablation is induced by two consecutive laser pulses with short delay between them in 100 ns–200 μs range. Several terms are widely used in LIBS literature to describe laser ablation with sequential laser pulses: double pulse, dual pulse and multipulse techniques. According to Oxford dictionary the meaning of the adjective 'double' can be expressed as 'consisting of two equal, identical, or similar parts or things'. This definition is slightly different from the one given by 'dual': 'consisting of two parts, elements'. Here we will use the term 'double' pulse method due to the similarity of laser pulses characteristics (the same wavelength, duration of pulse). In case of substantial difference in laser pulses properties (wavelength, duration, etc.) the term 'dual pulse' should be used.

First experiments for laser ablation with double pulses were carried out in the beginning of 1970-s by Piepmeier et al. [15] and by Scott et.al. [16] but the results obtained were of low reproducibility due to low quality of the laser systems at that time. Maher and Hall [17] studied double pulse ablation with two microsecond laser pulses (~20 μs, CO_2 laser) and explained the difference in second plasma dynamics by gas media change after first laser pulse. However "renaissance of double pulse" method was initiated by Cremers et.al. [18] for bulk water analysis. They used the first laser pulse to create a water bubble while the second laser pulse was used to induce plasma inside this bubble. Surprisingly this study remained unnoticed by LIBS community despite the remarkable improvements: several hundred increase of atomic/ionic lines intensity in the spectra; improvement of signal-to-noise ratio and longer plasma lifetime. For solid samples in the air first experiments with nanosecond double pulse LIBS have been carried out by Pershin et al. [19–21]. An increase of atomic/ionic lines in plasma spectra for sample elements and depletion of lines for elements from gas

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was observed. The authors proposed possible mechanism of intensity improvement with major factors attributed to increased ablated mass and changes of condition for plasma initiation and expansion. Two years later Uebbing et al. [22] suggested using second laser pulse to reheat plasma and to increase spectra intensity. Sattmann et al. [23] used multiple laser pulses for steel analysis and observed improvements of analytical results. The same group uses double pulse method for several unique implementation of LIBS systems in industry [23,24]. Several groups have been focused on double pulse method fundamental studies and a number of different applications. Stratis et al. [25,26] proposed pre-ablation double pulse method when the first laser pulse (femto or nanosecond) was used to produce air spark above the sample and the second pulse (femto/nano) was used for ablation. Different schemes of double pulse sampling were used by Palleschi and co-workers to study double pulse method in different conditions and schemes [27–29]. St-Onge et al. systematically studied two pulse ablation with UV and IR laser pulses [30,31]. A detailed review of double pulse LIBS can be found in excellent reviews [12,14].

Laser ablation is a complex phenomenon which strongly depends upon laser pulse characteristics (energy, wave length, etc.). Influence of laser pulse properties (i.e. laser wave length [32], laser fluence [33], pulse duration [34] and burst of pulses [12,35]) has been extensively studied for double pulse LIBS [12,14]. However laser beam profile or laser beam quality is rarely described in LIBS papers and to the best of our knowledge hasn't been discussed in the literature on double pulse LIBS [2,36]. Different laser beams profiles will provide different fluence (energy density) profiles in focal spot that will result in difference of laser plasma characteristics: size, temperature, electron density. Plasma properties influence the analytical performance of LIBS, thus laser beam quality (beam parameter product M^2) should be known prior to experiment beginning.

Previously we have compared Gaussian and multimode laser beams for ablation process, plasma properties and analytical performance of single pulse LIBS [37]. It was shown that optimal laser beam (and optimal lasing mode) should be chosen depending on LIBS analysis. If highest sensitivity for additives analysis is the primary goal then multimode beam should be used. For all other goals of LIBS analysis (better precision, better lateral resolution in mapping applications) laser sampling by Gaussian beam provides better results including higher plasma temperature, smaller influence of surface defects and improved precision and accuracy. In this paper we continue our study and present a comparison of laser beam influence on double pulse effect and LIBS analysis.

2. Experiment

The detailed description of experiments setup can be found elsewhere [37] and here will be given briefly. Laser plasma was generated in air by focusing a Nd:YAG laser pulse (1064 nm, 10 ns) normally onto the sample surface. The focusing lens, of 90 mm focal length, was placed 89 mm from the sample surface to improve reproducibility of sampling. Solid state Nd:YAG laser with flash lamp pumping could be operated in two lasing regimes: single transverse mode TEM_{00} (Gaussian beam) and multiple transverse mode (multimode beam). Lasing modes were controlled by introduction of a pin-hole diaphragm into the laser cavity (single mode lasing - with diaphragm, multimode - without diaphragm). A home designed electronics for Pockel's cell Q-switch provides one (single pulse) or two (double pulse) high-voltage opening pulses. A pair of laser pulses was generated with 45 μs delay and 1:3 ratios for pulse energies. Laser characteristics are summarized in Table 1. Laser plasma emission was transferred to the spectrograph slit with 1:1 magnification by quartz lens ($F = 120$ mm). Spectrograph (Andor Shamrock SR – 303i) was equipped with ICCD (Andor iStar) for time resolved spectra measurements.

High-alloy steel samples (BAM, Germany) were used in the study (Table 2). According to our LIBS measurements sample's composition was rather uniform: spectral line intensities reproducibility in 10 different spots on samples surface was equal to reproducibility in single spot sampling. In order to increase stability of laser sampling and to diminish surface defects influence all samples were polished with sandpaper before every measurement (ISO grit designation P 2400). Laser crater profiles were measured with white light interferometer microscope Zygo (NewView 6000).

Table 1
Single mode (Gaussian) and multimode laser beam parameters in double pulse mode.

Parameter	Single mode laser beam	Multiple mode laser beam
Laser beam (near field):		
Energy for first (E_1) and second (E_2) pulses, mJ/pulse	$E_1 = 1.1$ $E_2 = 3.2$	$E_1 = 25$ $E_2 = 65$
Energy reproducibility (RSD[a]), %	1.8	1.9
Laser beam profile, dimensions, mm	Gaussian, round, 1.1 × 1.1	Multimode ellipse, 4.8 × 4.3
Laser beam quality, M^2	9	220
Laser beam spot (far field):		
Spot dimensions measured by CMOS (1/e2 amplitude), μm by single shot crater, μm	100 × 100 130 × 130	520 × 480 550 × 500
Energy density:		
At maximum, J/cm^2	90	25
CMOS average, J/cm^2	43	20
Crater average, J/cm^2	51	20

[a] Relative standard deviation.

3. Results and discussion

3.1. Laser beam profile in far and near fields

Laser beam profile measurements at laser output (near field) and focal spot (far field) were carried out with CCD camera (DragonFly2, PoinGreyResearch) equipped with neutral optical filters. Camera exposure time was set to 100 ms thus the image obtained was a sum of two consecutive laser pulses. The laser beam profiles and its fluctuation for Gaussian and multimode beams are compared in Fig. 1.

Single mode beam profile can be described as nearly Gaussian beam while the measured beam parameter product M^2 [38] was rather poor compared to single pulse TEM_{00} beam (Table 1). To estimate fluctuation of beam profiles we used the following procedure: ten successive images of laser beam were acquired to measure the average and standard deviation of fluence (z coordinate in Fig. 1) at every point of beam profile (*x* and *y* were the same for single *z* coordinate). Relative standard deviation (RSD) of laser beam profile was significantly better for Gaussian beam: Gaussian beam fluctuation didn't exceed 2% while multimode beam variability was about 10% especially for numerous peaks. We've compared these results with our previous beam profile study for single pulse ablation [47]: switching to double pulse lasing resulted in poor

Table 2
Elemental composition of reference high-alloy steel samples, wt.% (BAM, Germany).

Samples	C	Si	Mn	Cr	Ni	Mo	Co
C1	0.092	0.46	0.74	12.35	12.55	–	–
C2	0.0103	0.374	0.686	14.727	6.124	0.0138	–
C3	0.0345	0.463	0.722	11.888	12.85	0.0304	–
C4	0.019	0.270	1.400	18.46	10.20	0.265	0.116
C5	0.086	0.57	0.791	25.39	20.05	–	0.054
C6	0.066	0.405	1.380	17.31	9.24	0.092	0.053
C7	0.0141	0.480	1.311	17.8	10.20	2.776	0.0184
C8	0.143	1.41	1.70	17.96	8.90	–	0.018
C9	0.050	0.21	0.89	14.14	5.66	1.59	0.22
C10	0.0201	0.537	1.745	16.811	10.72	2.111	0.0525