



## Boosting persistence time of laser-induced plasma by electric arc discharge for optical emission spectroscopy



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### ABSTRACT

Plasma induced by nanosecond laser ablation is re-excited by a pulsed electric discharge and the parameters and optical emission of the plasma are measured. The discharge is a low-voltage and high-current electric arc that is triggered by the laser-induced plasma and slowly decaying with time. The optical emission of such combined plasma lasts up to several milliseconds which is much longer than without re-excitation ( $\mu\text{s}$  range). The emission spectra of re-excited plasma measured on different sample materials show higher line intensities than spectra measured by conventional laser-induced breakdown spectroscopy (LIBS). Moreover, emission lines of fluorine (spectral range 683–691 nm) and sulfur (range 520–550 nm) not detected by conventional LIBS become easily detectable with the combined plasma. The concentration of major components in metallurgical slags, as determined by calibration-free LIBS, agrees very well to the reference data evaluating the spectra taken from re-excited plasma.

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### 1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is an analytical technique that basically detects most chemical elements in solid, liquid, gaseous, and particulate materials [1–4]. The unique strength of LIBS is its applicability to field measurements under harsh conditions [5–9]. The limit of detection (LOD) for trace impurity elements is in the range of 1–30 ppm, typically, depending on the chemical element, the matrix material, and the experimental parameters. The detection is limited mainly by the transient nature of the laser-induced plasma (plasma lifetime in air  $\sim 10 \mu\text{s}$ , typ.), the small amount of sampled material (mass of ablated material  $< 1 \mu\text{g}$  per laser shot, typ.), the relatively low plasma temperature (energy  $\leq 1 \text{ eV}$ , depending on time), and the ablation of non-luminous particles. Various approaches have been undertaken to improve the LOD by employing a second (“auxiliary”) excitation to the laser-induced plasma. Double and multiple laser pulse excitation of plasma [10–13], resonant laser irradiation of plume [14–17], and coupling of microwave [18–20] and radiofrequency [21,22] radiation to the plasma, for example, have been reported to increase the optical emission spectroscopy (OES) signals for different materials. Another method employed for plasma re-excitation is the combination of

laser ablation with an electric discharge between electrodes that are positioned close to the laser-induced plasma. This combination has been studied already very early after the invention of the laser [23,24]. Pioneering experiments have been performed by P. Franken [25], F. Brech and L. Cross [26], R.C. Rosan, M.K. Healy and W.F. McNary, Jr [27], H. Moenke and L. Moenke-Blankenburg [28,29], and others, and commercial instruments had been developed by companies Jarrell-Ash and VEB Carl Zeiss Jena [29]. In recent years the interest in a combined excitation of plasma for spectrochemical analysis renewed. Glow discharges (GD) have been reported to improve the depth resolution of LIBS [30] and to detect laser ablated particles in gas/liquid background [31]. The employed GD electrode voltages and measured discharge currents were  $U \leq 1 \text{ kV}$  and  $I \leq 100 \text{ mA}$ , respectively. High voltage spark discharges (SD) have been reported to enhance the optical line emission, signal-to-background ratio (SBR), and signal-to-noise ratio (SNR) [32,33] and to improve the LOD values [34,35]. SD electrode voltages of  $U \geq 2.5 \text{ kV}$  were employed and the rapidly alternating discharge currents of  $I \leq 2 \text{ kA}$  decayed within several microseconds [32–34]. Electric discharges at low voltage and with high current, on the other hand, have not been used to re-excite laser-induced plasma for analytical applications.

Here, we report on the combination of laser ablation and low-voltage high-current arc discharges and on the properties and optical emission of the laser-induced and re-excited plasma. Plasma expansion was measured by time-resolved photography and the time-dependent discharge voltages and currents were recorded. Emission spectra of various materials were measured and the plasma parameters were

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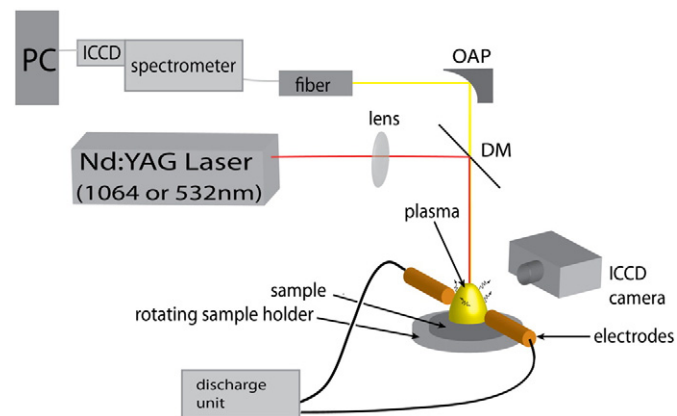
URL's: <http://www.jku.at/lad>, <http://www.jku.at/applphys> (J.D. Pedarnig).

determined. The spectra of steel slag samples were evaluated by a calibration-free analysis method.

## 2. Experimental

### 2.1. Experimental setup

Fig. 1 shows the experimental setup for time-resolved photography and optical emission spectroscopy of plasma. The radiation of a Nd:YAG laser (Quantel, Brilliant, wavelength  $\lambda_L = 1064$  nm, pulse duration  $\tau_L \approx 6$  ns, pulse energy  $E_L \leq 360$  mJ, repetition rate  $f_r \leq 20$  Hz) or of a frequency-doubled Nd:YAG laser (Quantel, CFR200,  $\lambda_L = 532$  nm,  $\tau_L \approx 8$  ns,  $E_L \leq 140$  mJ,  $f_r \leq 15$  Hz) was focused perpendicular onto the sample to ablate target material. The 1064 nm laser beam spot had an elliptical shape (1.5 mm  $\times$  2 mm) and the 532 nm laser spot was circular in shape (diameter 1.2 mm). The focal plane was 1–2 mm below the target surface to avoid breakdown in air. For most experiments the fundamental radiation of the Nd:YAG laser was used and the laser pulse energy was set to  $E_L = 230$  mJ (experiments using the 532 nm laser radiation are stated otherwise). The samples were placed on a rotating sample holder. Two cylindrically shaped copper electrode rods (Umicore, 99.99%, diameter 3 mm, length 5 cm) were placed parallel to the sample surface for the pulsed electric discharge (PED). The distance of electrodes to the sample was 1 mm and the separation between electrode end faces was between 1.5 and 3.5 mm. The laser spot was positioned in between the electrode end faces. The electrodes were connected to a discharging unit which consisted of a DC power supply (Philips PE 1647) and a load capacitor (capacitance  $C = 9.4$  mF, maximum operating voltage 63 V) in parallel connection to the electrodes. The capacitor was charged by applying a loading voltage in the range  $U_L = 0$ –60 V. The applied electric field ( $\leq 40$  V/mm) was much below the electrical breakdown field strength in air (typ.,  $E_B \approx 3$  kV/mm [36]). The plasma was induced by an ablating laser pulse (LP) which triggered the discharge. Without laser ablation and the laser-induced plasma the PED was not observed. The transient discharge voltage at the electrodes  $U(t)$  was measured by means of an oscilloscope (Hameg, HMO 722). The discharge current  $I(t)$  was determined by measuring the voltage drop along the cable connecting capacitor and electrodes (measured resistance of cable 8 m $\Omega$ ). Stable electric load and discharge cycles limited the laser pulse repetition rate due to the current limitation of the power supply ( $f_r \leq 10$  Hz). In order to avoid strong heating of the metal electrodes all experiments using the pulsed electric discharge were performed at  $f_r = 1$  Hz.

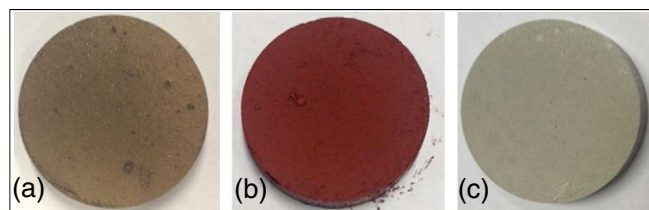


**Fig. 1.** Schematic setup for time-resolved plasma photography and optical emission spectroscopy. The plasma is induced by laser ablation and boosted by low-voltage high-current pulsed electric discharge. Time-resolved photography is performed by an ICCD camera. Plasma emission is collected by fiber optics (FO), dichroic mirror (DM), and off-axis parabolic mirror (OAP) in backward direction.

For time-resolved plasma imaging a fast intensified CCD camera (Photometrics, ICCD S300:7895, 512  $\times$  512 pixel, 14 bit) and a 105 mm objective lens were employed. The ICCD camera was mounted with its optical axis oriented parallel to the sample surface. Optical broadband and spectrally filtered emission of the plasma were recorded by the camera and one photo per laser pulse was taken with an integration time  $t_{\text{int}}$  of 10 or 50 ns. For the study of temporal plasma evolution the delay time between laser pulse and ICCD camera was varied ( $t_d = 0.1 \mu\text{s}$ –3 ms). The recorded ICCD photos were read-out electronically and cropped. The plasma size was derived from image data  $I(x,y)$ . For each photo the maximum intensity  $I_{\text{max}}$  and minimum intensity  $I_{\text{min}}$  were determined and a plume boundary was defined by the intensity  $I_b = (I_{\text{max}} - I_{\text{min}}) / e + I_{\text{min}}$  (Euler's constant  $e$ ). The width and height of plumes were determined from line sections across intensity maps applying  $I_b$  as threshold for cut-off. For emission spectroscopy the plasma radiation was detected in the direction backwards to the incident laser beam. A dichroic mirror (DM), an off-axis parabolic mirror (OAP), and fiber optics were used to collect the emission. An Echelle spectrometer was used to cover the UV-VIS-NIR range (LTB Berlin, Aryelle 400, ranges 190–360 nm and 297–850 nm, spectral resolution  $\lambda / \Delta\lambda \geq 10,000$ ). Measured emission intensities were accumulated at the detector over 1 to 40 laser pulses ( $E_L = 230$  mJ,  $f_r = 1$  Hz). The gate width of the spectrometer  $t_g$  was varied from 500 ns to 0.5 ms for different samples. Emission lines were identified using available atomic spectra databases [37,38]. For the calculation of plasma temperature  $T_e$ , electron number density  $N_e$ , and oxide concentrations by calibration-free analysis the measured spectra were de-convolved from instrumental functions and normalized for radiometric calibration [39]. The instrumental functions were determined by measuring the radiation of mercury/argon halogen lamps. The measured FWHM depended on wavelength and was in good agreement with the device specifications [40]. The radiation of a calibrated broadband deuterium/tungsten lamp was used for radiometric calibration.

### 2.2. Sample materials

Three different types of bulk materials were investigated in this study (Fig. 2). The first material was slag from secondary metallurgy that was powdered, pressed, and sintered (Fig. 2a). The slag consisted of seven major and minor oxides CaO,  $\text{Al}_2\text{O}_3$ , MgO,  $\text{SiO}_2$ , FeO, MnO, and  $\text{TiO}_2$ . The nominal oxide concentration  $C_N$  of two slag samples was analyzed by X-ray fluorescence spectroscopy XRF (Table 1). Trace oxides were not considered. The second material was pressed pellets of  $\text{Fe}_2\text{O}_3$  powder that contained various trace elements (Fig. 2b). The first and second types of material were provided by the industrial steel producing company voestalpine Stahl GmbH (Austria). The third type of samples was pressed pellets of  $\text{CaSO}_4$  with a polytetrafluoroethylene (PTFE) cover layer (Fig. 2c). Commercially available gypsum powder with main component  $\text{CaSO}_4$  was mixed with water and dried. A thin layer of PTFE was sprayed on the surface of the hardened  $\text{CaSO}_4$  bulk (Tygaflo PTFE dry lubricant). The samples were investigated as prepared without any pre-treatment.



**Fig. 2.** Photographs of disc shaped sample materials (diameter 30 mm). Sintered slag ceramics (a), pressed  $\text{Fe}_2\text{O}_3$  powder (b), gypsum ( $\text{CaSO}_4$ ) with PTFE polymer surface layer (c).

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