Calibration-free analysis of steel slag by laser-induced breakdown spectroscopy with combined UV and VIS spectra

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ABSTRACT

Slag from secondary metallurgy in industrial steel production is analyzed by calibration-free laser-induced breakdown spectroscopy (CF-LIBS). The slag pieces are homogenized by ball milling and sintering. LIBS spectra are measured under ambient conditions using nanosecond Nd:YAG laser pulses (1064 nm) for ablation. A fiber-coupled Echelle spectrometer with two separate detection arms in the UV range (190 to 360 nm) and in the VIS range (298 to 864 nm) and one ICCD camera is used for detection. The UV and VIS spectra are measured sequentially and combined to one spectrum to increase the number of highly resolved emission lines for the calculation of oxide concentrations in slags. The combination of spectra requires an adaption procedure including independent radiometric calibration, the de-convolution of spectrometer functions, baseline corrections, and intensity scaling. More than 60 emission lines of elements Ca, Al, Mg, Si, Fe, Mn, and Ti are evaluated. The electron density is derived from Stark broadening of a Mg line, and the plasma temperature is determined from Saha–Boltzmann plots of Ca, Mn, or Ti lines. With the combined LIBS spectra, the CF-LIBS calculated concentrations C_{CF} are closer to the nominal concentrations C_N determined by x-ray fluorescence spectrometry. Significantly reduced relative errors of concentration $e_r = |C_{CF} - C_N| / C_N$ are observed for the oxides CaO, Al$_2$O$_3$, MgO, SiO$_2$, and MnO, and no reduction was found for FeO and the minor phase TiO$_2$. The improved accuracy of concentrations is attributed to a better detection of the major elements Ca, Al, and Si in the combined LIBS spectra.

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1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a versatile technique for fast multi-element compositional analysis of gaseous, liquid, and solid materials [1–3]. This method is employed in various fields including materials identification, environmental monitoring, detection of hazardous materials, and for different on-site and in-line industrial applications [4–6]. For quantitative analysis of material composition, univariate or multivariate regression models are commonly employed. Matrix-matched reference materials and sample materials are measured under similar experimental conditions in order to calibrate the employed LIBS measurement system. Calibration-free LIBS (CF-LIBS) methods, on the other hand, determine the composition of materials directly from measured spectra by modeling the laser-induced plasma and the optical plasma emission [7,8]. This approach is of interest as calibration samples are not required and constraints regarding the control of experimental parameters are less stringent. The CF-LIBS method has been applied to a wide range of materials [9–12]. It is especially suited

for the analysis of materials that vary strongly in composition. An example is slag from industrial steel production, where the concentration of major components varies over wide ranges for different steel grades and production steps [13,14].

For CF-LIBS analysis, emission spectra covering a broad spectral range and having high spectral resolution are required. All major elements contained in the sample material have to be detected with at least one and preferably several emission lines (broad spectral range). The correction of self-absorption of plasma radiation, the determination of plasma parameters electron temperature T_e and electron number density N_e, and the discrimination of closely neighboring lines require spectra of high resolution. Typically, a spectrometer has either a high resolution or a broad spectral range but not both features together. A compromise is the use of two high-resolution spectrometers to cover a broader range. Some Echelle-type spectrometers have two separate optical paths (arms) for the UV and the VIS spectral range in one device that share the same time-resolved detector. We measured LIBS spectra using the UV and VIS arms of such a spectrometer. As the spectrometer characteristics (e.g., resolution, spectral sensitivity, diffraction order, polarization dependence, stray light) are different for both arms, these spectra are not directly comparable. In this contribution, we show that it is possible to combine the UV and VIS spectra to one broad-range

high-resolution spectrum applying a mathematical adaption procedure. The combined spectra enable to obtain improved CF-LIBS results for the steel slag samples.

2. Experimental

2.1. Experimental setup

Fig. 1 shows the experimental setup that was employed for LIBS measurements. The pulsed radiation of a Nd:YAG laser (Continuum Surelite I-20, wavelength $\lambda = 1064$ nm, pulse duration $\tau_L \approx 6$ ns, laser pulse energy around 180 mJ, repetition frequency 20 Hz) was employed for ablation and excitation of sample materials. The samples were placed on a rotation stage and all measurements were performed in ambient air. Nitrogen gas was flushed onto the sample surface and along the optical beam paths to remove ablation residues. The sample surface was located 2 mm in front of the focal plane to avoid breakdown in air. The collection of plasma emission was achieved by direct coupling into two quartz fibers without lenses to avoid effects from chromatic lens aberration. The fibers were placed at a distance of approx. 5 cm to the sample and an angle of approx. 45 ° to the optical axis. LIBS spectra were measured with an Echelle spectrometer having two detection paths and one gated intensified CCD (ICCD) camera (LTB, model Aryelle). The first path (VIS arm) covered the spectral range from 298 to 864 nm with a spectral resolution $\lambda/\Delta\lambda \geq 9400$, and the second path (UV arm) covered 190 to 360 nm with resolution $\lambda/\Delta\lambda \geq 11000$. The UV and VIS spectra were acquired for an ICCD delay time and gate width of $t_d = 2.5$ μs and $t_g = 4$ μs, respectively. All components required for LIBS measurements and the computer for measurement control and data evaluation were integrated in a rugged mobile housing with a temperature regulation unit. The whole setup is transportable and can be operated out of the laboratory, for instance, on-site in a steel production plant.

2.2. Sample materials

The multi-component oxide materials under investigation were slag samples from industrial steel production (secondary metallurgy) at voestalpine Stahl GmbH Austria. A liquid slag sample was taken manually from the steel ladle during production by means of a slag spoon. After solidification, the material was divided. One part of the slag material was sent to an analysis laboratory of voestalpine Stahl GmbH for x-ray fluorescence spectrometry (XRF) measurements. For the LIBS measurement, the second part of the slag material was ball milled, and the resulting powder was hydraulically pressed into a disc-shaped
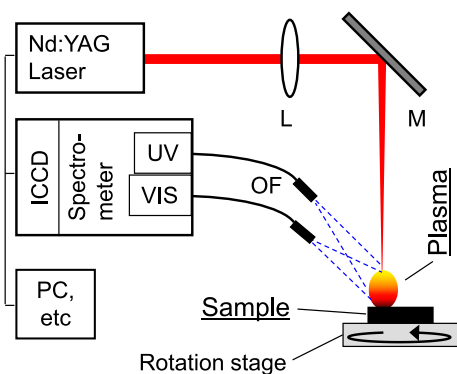

Fig. 2. Photographs of two homogenized slag samples of different chemical composition (diameter 30 mm).

pellet. Subsequently, the pellet was sintered at 1200 °C for 12 h in air to produce a compact and robust sample (typ. parameters: diameter 30 mm, thickness 3 mm, weight 5 g). This procedure was applied to produce samples of homogeneous composition and structure. Fig. 2 shows exemplarily two sintered slag pellets, which appear homogenous and with smooth surfaces. The different color originates from their different chemical composition. After LIBS measurements, the homogenized slag samples were also XRF analyzed at voestalpine Stahl GmbH. These XRF results served as reference data and were denoted as nominal chemical concentration of oxides C_N. With this procedure, the same set of slag samples was measured with LIBS and XRF. In the present work, 12 different slag samples were investigated. The samples contained CaO, Al_2O_3, MgO, SiO_2, FeO, MnO, and TiO_2 with concentration values in the range 0.07–50.8 wt% (Table 1).

2.3. Measurement and combination of spectra

The Echelle spectrometer was wavelength calibrated by means of a built-in Hg calibration lamp. The spectral response function of the spectrometer was determined by measuring the emission of a certified calibration lamp for the entire optical path of the experiment and for both spectrometer arms (UV and VIS) separately. Wavelength calibration was performed before each measurement series in order to avoid large spectrometer drifts, e.g., due to variation of ambient temperature. For one LIBS spectrum (UV or VIS), the plasma emission was accumulated over typically 60 laser pulses on the ICCD detector before read-out. Typically, at least 4 spectra were measured per sample and spectrometer arm. These spectra were evaluated by calculating the linear correlation coefficients r_{ij} (correlation matrix). The indices i and j refer to the different spectra measured per sample and spectrometer arm. Single spectra with low correlation ($r_{ij} < 0.95$, i ≠ j) were dropped. The highly correlated spectra were averaged. As next step, the averaged spectrum was subjected to a radiometric correction followed by the de-

Fig. 1. Schematic setup for optical emission spectroscopy of laser-induced plasma on industrial slag samples. Nd:YAG laser pulses are focused on sample surface with lens (L) and mirror (M). The plasma emission is collected by direct coupling into two optical fibers (OF) at oblique angle. Fibers are connected to two ports of an Echelle spectrometer for UV and VIS detection.
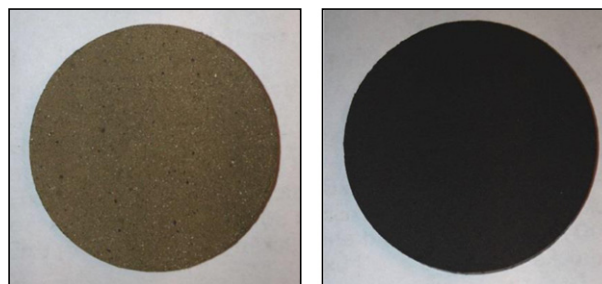
Table 1
Nominal concentration of oxides C_N in 12 homogenized slag samples measured by X-ray fluorescence spectroscopy.

No.	Unit	CaO	Al_2O_3	MgO	SiO_2	FeO	MnO	TiO_2
1	[wt%]	28.03	21.56	12.12	9.01	17.57	11.02	0.40
2	[wt%]	45.04	31.83	9.71	5.32	3.77	4.16	0.12
3	[wt%]	45.82	25.06	13.31	9.24	2.13	4.11	0.18
4	[wt%]	48.45	23.44	10.45	14.36	1.51	1.54	0.22
5	[wt%]	50.19	29.07	10.71	8.35	1.00	0.48	0.09
6	[wt%]	31.30	16.56	10.43	9.52	18.85	10.82	0.63
7	[wt%]	48.66	28.02	8.75	12.16	0.60	1.58	0.14
8	[wt%]	50.76	24.78	8.61	13.59	0.78	1.26	0.13
9	[wt%]	47.93	29.22	11.11	5.12	3.46	2.86	0.09
10	[wt%]	40.23	28.95	12.70	5.40	10.26	2.14	0.10
11	[wt%]	39.32	33.08	12.29	3.25	9.59	2.11	0.07
12	[wt%]	40.10	35.9	11.18	4.82	6.03	1.65	0.11