Laser-Induced Breakdown Spectroscopy of Molten Metals: Influence of Sample Temperature

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The aim of this work was to determine the influence of sample temperature on the laser-induced microplasma (LIP) emission intensity and to ascertain the possibility of laser-induced breakdown spectroscopy (LIBS) utilization for the monitoring of impurities in molten metals. Pure low-melting metals (bismuth, gallium, indium, lead, tin, and zinc) were used for all experiments. It was found out that the LIP emission increases linearly with increasing temperature within the range 25 °C to 70 °C above the melting point of the metal. The slope of this change in LIP intensity is related to the transition probability of a given emission line. If the LIP intensity of given solid and molten metals are compared, then their relative change is related to the coefficient of thermal conductivity. The LIBS shows possibilities for the identification of impurities in molten metals. Amounts of impurities in the order of tens mg/kg can be identified.

Key words: Laser-Induced Breakdown Spectroscopy; Molten Metals; Sample Temperature.

1. Introduction

Nowadays, laser-induced breakdown spectroscopy (LIBS) represents a new type of atomic emission spectroscopy enabling elemental analysis of any type of the sample. LIBS exploits a focused laser beam for sampling of any material (gaseous [1, 2], liquid [3 – 5], solid [6, 7]). The basic principle consists of the interaction of a focused laser beam with a sample surface which results in laser-induced microplasma (LIP) creation. The LIP emits radiation which includes analytical information about analyzed sample. A great advantage when compared with well established analytical methods, such as inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma with optical emission spectrometry (ICP-OES), and atomic absorption spectrometry (AAS), lies in the fact that the sample does not have to be dissolved, which is often the most time consuming step of the analytical process. In addition, a lot of sources of contamination are possible during this step [8]. LIBS enables analysis of solid samples with minimal or no sample preparation. For example, in the case of a powdered material, the sample is placed on a double-side carbon tape and is analyzed in a few seconds [9]. In addition, LIBS is applicable for the online monitoring control processes of molten metals, steels, and alloys [10].

In this paper, the influence of sample temperature and phase of the metal (solid or molten) on LIP intensity is studied. The working range was chosen as 25 °C to 500 °C. An earlier, temperature study was performed by Rauschenbach et al. [11]. However, they only explored this influence at low temperatures. Their working range was from −60 °C to 25 °C, and they simulated a Martian atmosphere. Finally, the possibility of LIBS utilization for the monitoring of impurities in molten metals is also presented.

2. Description

The experimental setup used in this work consists of a Q-switched Nd:YAG laser (Quantel, France), Goldsmith furnace (0412G, Clasic, Czech Republic) with a programmable temperature regulator (Clare 4.0, Clasic, Czech Republic), focusing system, fiber optic system, monochromator TRIAX 320 (Jobin Yvon, France) and intensified CCD (Jobin Yvon, France). A Q-switched Nd:YAG laser operating at 1064 nm

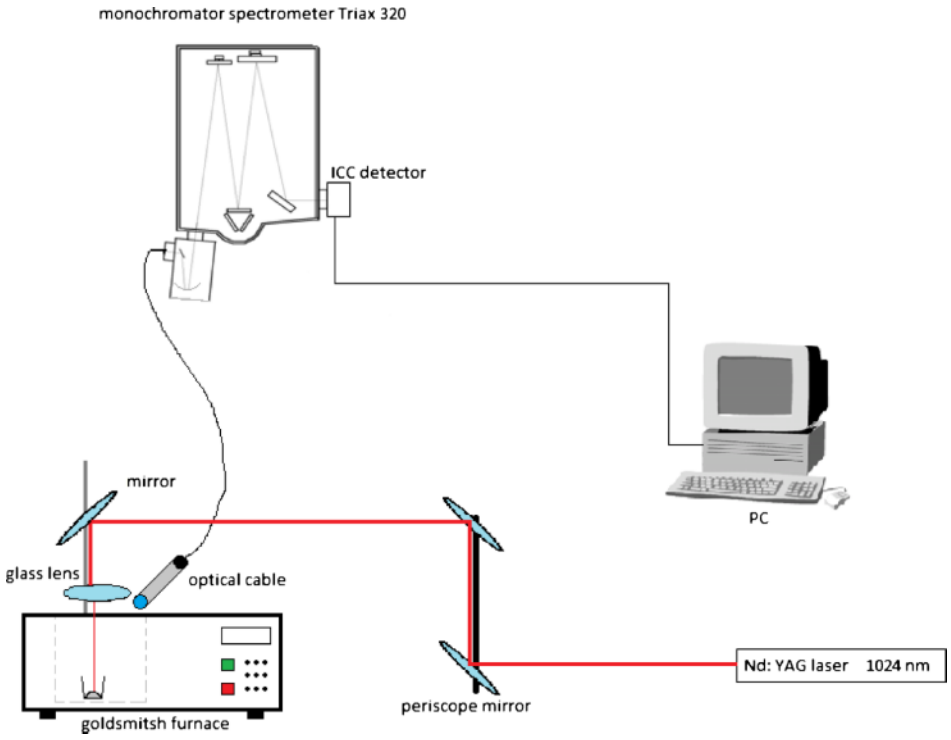

Fig. 1 (colour online). Experimental setup for the analysis of molten metal consists of a Nd:YAG laser (1064 nm), Goldsmith furnace, and detection system (monochromator and ICCD).

was used for the plasma formation. A metal sample was placed into the Goldsmith furnace which can be heated up to 1200 °C. Two apertures were incorporated into the furnace cover. The first one is used for the quartz lens of the laser instrument. The second one serves as a quartz window to collect the spectra. The laser beam was focused perpendicular to the molten metal surface by a plano-convex lens with a focal distance of 125 mm. Its laser power density was set to 2.8 GW cm^{-2} with a repetition rate of 1 Hz. The low repetition rate was chosen due to avoid splashing of the liquid sample. The plasma radiation was collected by the objective and transported into a spectrometer by means of an optic fiber where it was dispersed by a 2400 grooves mm^{-1} grating. Dispersed radiation was detected by an intensified CCD camera. The LIP emission signal was acquired by averaging 50 laser shots so as to suppress any laser beam energy fluctuations.

The plasma emission was acquired 2.5 µs after the laser pulse and the integration time of the emission signal was 10 µs. Both parameters were optimized in relation to the best signal/noise ratio.

The influence of sample temperature on the LIP emission signal and the detection of impurities in pure molten metals were studied. Pure low-melting metals, such as bismuth, gallium, indium, lead, tin, and zinc were used for these experiments. Each metal was inserted into the Goldsmith furnace which was gradually heated to temperatures of 50, 100, 150, 200, 250, 300, 350, 400, 450, and 500 °C. At each temperature the LIP spectra were obtained (one spectral window with a range of 15 nm for each metal). Heating was finished when the furnace temperature achieved 70 °C above melting point of the metal. Thereby melting of the sample was ensured.

For the detection of impurities in molten metals the sample was placed into the furnace which was heated. 15 minutes after reaching 50 °C above the melting point of the metal the LIP emission spectra in the range from 220 to 600 nm were obtained.

Dissolution of the samples was necessary to obtain a content of impurities in pure samples. The metals were dissolved in a mixture of hydrochloric and nitric acid. The obtained solutions were diluted by deionized water and their analysis was performed by means of an inductively coupled plasma mass spectrometer (ICP-MS) Agilent 7500CE (Agilent, Japan) equipped with an octopole reaction cell for removing isobaric

interferences. The content of chromium, copper, manganese, lead, zinc, tin, magnesium, iron, and nickel were determined.

3. Results and Discussion

3.1. Influence of Temperature on LIP Intensity

The first experiments performed with the new setup described above were devoted to the study of the influence of the sample temperature on the LIP emission intensity. First, the LIP spectra of pure bismuth, gallium, lead, indium, zinc, and tin were obtained at different temperatures. The temperature was chosen in the range of laboratory temperature to a temperature 70 °C above melting point of the selected metal, approximately (Table 1). The line intensities of all elements were background corrected. Figure 2 shows the dependence of intensity of five tin emission lines on sample temperature. Linear increase of emission line intensities with increasing temperature in the range from laboratory temperature to 300 °C is clearly visible. However, the slope of this dependence is not same for each tin emission line. Their values differ from 19.0 °C^{-1} to 35.0 °C^{-1}. The different slopes mean that each emission line has a different sensitivity to temperature treatment. Similar course of the temperature dependence is observed for metals such as gallium, lead, indium, and zinc. The LIP intensities of emission lines of these elements linearly increase with increasing temperature. Contrary to this observation, the LIP intensities of bismuth emission lines decrease with increasing temperature (Fig. 3). Similarly to above mentioned elements, the change of LIP intensity is linearly dependent on the temperature. The slopes of these de-

Table 1. Melting point of measured metals and maximal working temperature of the furnace.

	melting point [°C]	furnace temperature [°C]
Bi	271	350
Ga	30	100
In	157	250
Pb	328	400
Sn	232	300
Zn	420	500

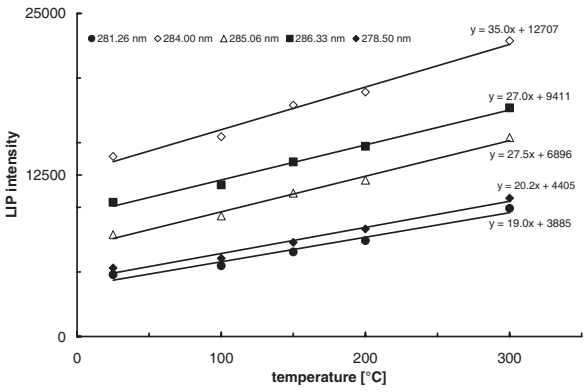

Fig. 2. Influence of temperature on LIP intensity of Sn emission lines (278.50 nm, 281.26 nm, 284.00 nm, 285.06 nm, and 286.33 nm).

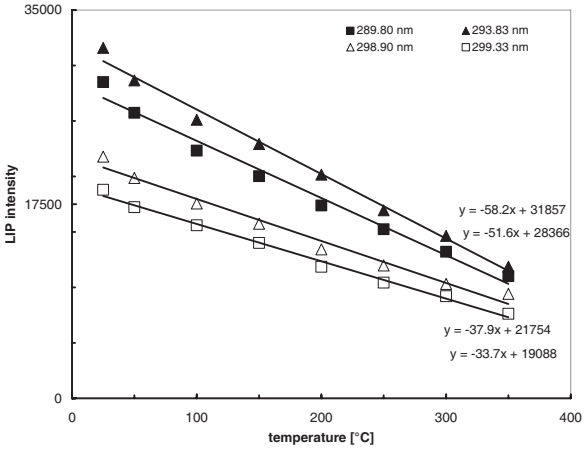

Fig. 3. Influence of temperature on LIP intensity of Bi emission lines (289.80 nm, 293.83 nm, 298.90 nm, and 299.33 nm).

Table 2. Slope of the dependence of LIP intensity on sample temperature and transition probability of selected Sn, Bi, Pb, and Zn emission lines.

emission line [nm]	slope [°C^{-1}]	transition probability [s^{-1}]
Sn 278.50	20.2	1.80E+07
Sn 281.26	19.0	1.20E+07
Sn 284.00	35.0	1.70E+08
Sn 285.06	27.5	3.30E+07
Sn 286.33	27.0	5.40E+07
Bi 289.80	−54.1	1.53E+08
Bi 293.83	−48.6	1.23E+08
Bi 298.90	−36.1	5.50E+07
Bi 299.33	−30.2	1.60E+07
Bi 302.46	−40.3	8.80E+07
Pb 373.99	16.1	7.30E+07
Pb 367.15	11.7	4.40E+07
Pb 368.35	21.8	1.50E+08
Zn 328.33	45.1	9.00E+07
Zn 330.30	54.7	1.20E+08
Zn 334.50	61.4	1.70E+08

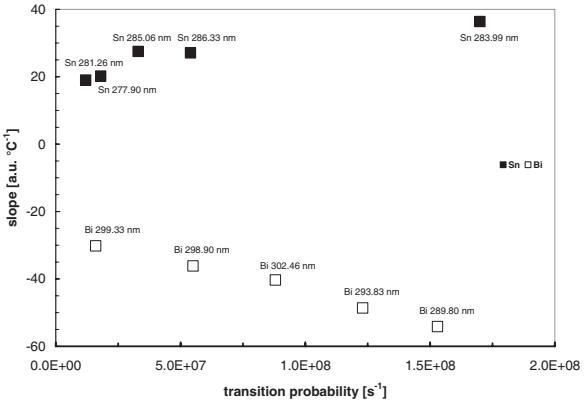

Fig. 4. Dependence of slope of temperature dependence on transition probability of Sn emission lines (278.50 nm, 281.26 nm, 284.00 nm, and 286.33 nm) and Bi emission lines (289.80 nm, 293.83 nm, 298.90 nm, 299.33 nm, and 302.46 nm).

pendences are different not only between various elements, however, it also differs for various emission lines of the same element (Table 2). Hence, some possible correlations with parameters of emission lines (upper and lower energy level, relative intensity, transition probability [12]) were sought. It was found that there is a close correlation between the transition probabilities of the emission lines of the given elements and the slope of dependence of the LIP intensity on temperature. This correlation is shown in Figure 4 for bismuth and tin. It therefore follows that the sensitivity of the emission line to temperature increases with increasing transition probability. The transition probability A_{ul} (s^{-1}) for the transition from the excited level u to a lower level l is given by

$$A_{ul} = \frac{\mathrm{BF}_{ul}}{\tau_u}, \tag{1}$$

where τ_u is the radiative lifetime and BF_{ul} is the emission branching fraction for the transition [13]. The value of BF_{ul} depends on the intensity of the emission line and is given by

$$\mathrm{BF}_{ul} = \frac{I_{ul}}{\sum_l I_{ul}}, \tag{2}$$

where I_{ul} means the intensity of the emission line, and the sum is taken over all lower levels to which the upper level transits. A combination of (1) and (2) gives the relationship between transition probability and the intensity of the emission line. This relationship is given by

$$A_{ul} = \frac{I_{ul}}{\tau_u \sum_l I_{ul}}. \tag{3}$$

No other correlation with parameters of emission line was found. Thus, the transition probability can explain differences in different sensitivity of emission lines of the same element. For each measured element holds: the higher the transition probability of emission lines, the more sensitive the given emission line to the influence of the sample temperature. However, this does not explain the different course for bismuth (the decrease of LIP intensity with increasing temperature).

Hence, the change of LIP intensity for solid and liquid metals was studied. LIP intensity was measured for a given metal in a solid state. Then, the metal was heated to a temperature 70 °C above its melting point and the LIP intensity was measured for the liquid metal. The relative change of LIP intensity I_{rel} is given by

$$I_{\mathrm{rel}}\,(\%) = \frac{I_{\mathrm{l}}}{I_{\mathrm{s}}}\,100, \tag{4}$$

where I_{s} is the LIP intensity for the solid metal measured at 25 °C and I_{l} the LIP intensity for the liquid metal measured at a temperature 70 °C above melting point of the given metal. Values of relative change of LIP intensity for each measured emission line are summarized in Table 3. It follows from this table that the relative change of LIP intensities for a given metal are very close, but the change varies between various

sample	emission line [nm] (relative change of LIP intensity in %)
Bi	289.80 (51); 293.83 (47); 298.90 (46); 299.33 (45); 302.46 (47)
Ga	417.20 (127)
In	294.11 (215); 303.94 (236)
Pb	367.15 (126); 368.35 (142); 373.99 (136)
Sn	278.50 (199); 281.26 (195); 284.00 (208); 285.06 (202)
Zn	328.23 (310); 330.30 (315); 334.50 (330)

Table 3. Relative change of LIP intensities for various emission lines of Bi, Ga, In, Pb, Sn, and Zn.

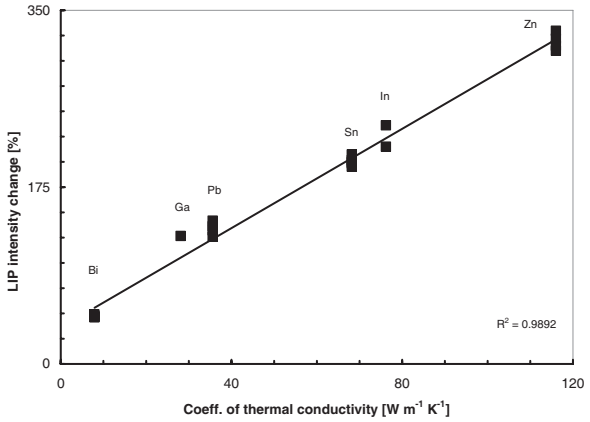

Fig. 5. Dependence of increasing LIP intensity of various elements on coefficient of thermal conductivity.

metals. Hence, some correlation between the relative change of LIP intensity and the thermal properties (coefficient of thermal conductivity, thermal capacity, latent heat, melting and boiling point) of the metals was sought. It was found that the correlation between the relative changes of LIP intensity of various elements in solid and liquid state (Bi, Ga, In, Pb, Sn, Zn) is related to the coefficient of thermal conductivity (Fig. 5).

3.2. Identification of Impurities in Molten Metals

The system described above was used for the identification of impurities in pure molten metals. First, the metals were dissolved in a mixture of hydrochloric and nitric acid. The dissolved sample was diluted and the content of impurities was measured by means of ICP-MS. The content of impurities in the examined metals is summarized in Table 4.

For this purpose optimization of parameters was performed to obtain the best signal-to-noise ratio. Optimization was performed using a zinc sample placed in the furnace. The laser beam energy, focusing distance, and placement of the objective with respect to the LIP were optimized. A best signal-to-noise ratio was reached at 2.8 GW cm^{-2}, and the focus was set to 15 mm below the sample surface.

Table 4. Content of impurities in pure metals determined by means of ICP-MS. Impurities identified using LIBS are marked in bold.

	impurities (content in mg/kg)
Bi	**Cu (35)**, **Fe (58)**, **Pb (76)**, Ag (25)
Ga	**Cu (20), Fe (32)**, Ca (9), Sc (9)
In	Ca (25), **Pb (61)**, **Ni (94)**
Pb	**Sn (221)**, **Zn (178)**, **Sb (122)**
Sn	As (102), **Pb (206)**, **Cu (95)**, **Fe (103)**, **Zn (58)**, Cd (11)
Zn	**Fe (42)**, **Pb (52)**

In this experiment, the LIP emission spectra of pure molten metals were collected in the range from 220 to 600 nm. All experiments were performed at a furnace temperature of 70 °C above melting point of the metal (Table 1). Pure bismuth, gallium, lead, indium, zinc, and tin were used for these experiments. Emission lines of the elements which were determined by ICP-MS in dissolved samples were sought.

In the spectrum of liquid gallium, iron, and copper emission lines were identified. Content of the remaining elements was lower than the limit of the detection (LOD) of LIBS for these elements. In the case of the molten bismuth, emission lines of copper, iron, and lead were detected. Silver was not detected due to its low content in the sample. Similarly, analysis of the impurities in molten indium, lead, tin, and zinc was performed. All detected impurities in molten metals are marked in bold in Table 4. Impurities with the content larger than 25 mg/kg were determined, except for arsenic in tin. In this case, its content in tin was 102 mg/kg, which means the LOD is higher than 102 mg/kg. This is caused by the fact that the most intensive arsenic emission lines lie below 200 nm [12]. In this spectral region, UV radiation is absorbed by air (primarily by molecular oxygen in the optical path). Hence a higher LOD is observed.

One of the main characteristics of the analytical method is the lowest detectable amount of the element – limit of the detection (LOD). According to the IUPAC definition, the LIBS LOD is concentrations producing background corrected intensity equal to three times the standard deviation of the background $3\sigma_B$,

$$\mathrm{LOD} = \frac{3\sigma_B}{S},$$

where S is the sensitivity for the given emission line.

The LODs were calculated for all identified impurities in molten metals. Their values are summarized here: Cu (12 mg kg^{-1}), Fe (25 mg kg^{-1}), Ni (40 mg kg^{-1}), Pb (40 mg kg^{-1}), Sb (35 mg kg^{-1}), Sn (30 mg kg^{-1}), and Zn (35 mg kg^{-1}).

4. Conclusion

In this paper a new experimental set-up for in situ monitoring molten metals by means of laser-induced breakdown spectroscopy was shown. Firstly, this new set-up was used for the study of sample temperature on LIP intensity. The temperature was changed through the range 25 °C to 70 °C above the melting point of a given metal. It was found that the LIP intensity of a given emission line changes linearly with increasing temperature. The slope of this linear dependence is related to the transition probability of the given emission line. When the LIP intensity of the metal in the solid and the liquid state was compared, it was found that the relative change of the LIP intensity is related to the coefficient of thermal conductivity of the given metal.

In the second part of this paper, utilization of LIBS for the in-situ monitoring of impurities in molten metals was demonstrated. In the spectra of molten bismuth, gallium, indium, lead, tin, and zinc impurities were identified. The amount of these impurities can be identified down to an order of ten mg/kg.

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