Spectrochimica Acta Part B 112 (2015) 40–48

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

journal homepage: www.elsevier.com/locate/sab

In situ analysis of steel melt by double-pulse laser-induced breakdown spectroscopy with a Cassegrain telescope

Lanxiang Sun [a,b,*], Haibin Yu [a,b], Zhibo Cong [a,b], Yong Xin [a,b], Yang Li [a,b], Lifeng Qi [a,b]

[a] *Shenyang Institute of Automation, Chinese Academy of Sciences, Shenyang 110016, China*
[b] *CAS Key Laboratory of Networked Control Systems, Shenyang 110016, China*

A R T I C L E I N F O

Article history:
Received 28 April 2015
Accepted 20 August 2015
Available online 28 August 2015

Keywords:
Laser-induced breakdown spectroscopy
Double-pulse
In situ analysis
Cassegrain telescope
Liquid steel

A B S T R A C T

A laser-induced breakdown spectroscopy (LIBS) system combining a Cassegrain telescope and a double-pulse laser mode was developed for the in situ analysis of steel melt. Optical- and electrical-related devices were sealed in an enclosed box away from the high-temperature steel melt surface. Connected to the box by a flange, a long hollow steel tube was used for the laser and plasma emission transmission path. At the tip of the steel tube, a refractory lance that can withstand high temperatures was immersed into the molten steel surface to pass through the surface slag layer. The designed optical structure successfully keeps the photoelectric-associated system components away from the high-temperature environment, thus reducing the complexity of system protection and maintenance. The signals obtained from single-pulse and double-pulse LIBS were comprehensively compared; the effect of argon blowing on spectral stability was analyzed; and the quantitative analysis of Si, Mn, Cr, Ni and V in molten steel samples was evaluated using both a univariate model and a partial least squares (PLS) model. The relative root mean square error of prediction (RMSEP) values and average relative standard deviations (RSDs) of the PLS model were approximately 5% and 2%–3%, respectively, both of which are less than those of the univariate calibration model. The sealed LIBS setup was also transferred to a steel plant for application testing, and the obtained accuracy approached the plant's accuracy requirements. Furthermore, quantitative analysis of carbon was also achieved on the basis of the PLS models. These results demonstrate that the developed system is promising for the in situ analysis of melt steel in the steelmaking industry.

1. Introduction

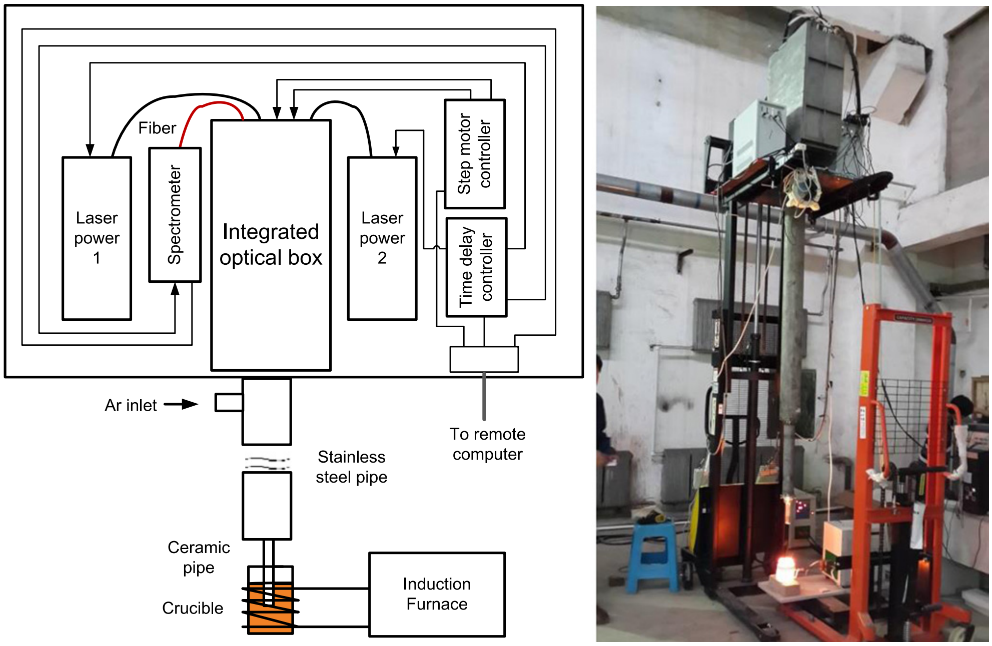
In the metallurgical industry, in situ analysis of the chemical elemental components in the metal smelting process is a significant requirement for process control and quality assurance. At present, the conventional techniques used for elemental analysis in steelmaking plants are still off-line methods that require solidified samples to be transported to an adjacent laboratory for analysis. Common measurement methods such as spark source optical emission spectrometry (Spark-OES), X-ray fluorescence (XRF) spectrometry and inductively coupled plasma optical emission spectrometry (ICP-OES) are not easily applied to real-time and in situ analysis because of the need for sample pre-treatment [1]. Under optimum conditions, the total time required for analysis, including the sample pre-treatment time, is still greater than 3 min.

Laser-induced breakdown spectroscopy (LIBS) is a versatile elemental analysis technique for many types of materials [2–6]. In LIBS, light emitted from plasma induced by focusing high-power laser pulses onto the sample surface is collected for spectral analysis. Because no sample pre-treatment is required and because of its versatile analysis of solids, liquids and gases, LIBS is most suitable for in situ and stand-off measurements [7]. In the metallurgical industry, LIBS can be used to perform in situ monitoring of melt composition during production, which is one of the most interesting and promising areas of LIBS research [8–17].

Carlhoff and Kirchhoff [18] were the first to apply LIBS for the in situ analysis of molten steel in a converter. Aragón et al. [19] also reported a melt-steel analysis method involving LIBS, in which the laser beam was focused onto a free melt surface from above, resulting in a precision of 10% for carbon content analysis in the concentration range 150–1100 ppm. Noll et al. [13,20] developed a LIBS system for the on-line measurement of molten steel composition by using a model lance consisting of a vacuum optical probe, a permanent lance and a lance tip immersed into the liquid steel melt; using this system, light elements including C, P and S were successfully quantified directly in a molten steel bath. Gruber et al. [21] studied changes in the LIBS signal induced by adding admixtures containing elemental Cr, Cu, Mn, and Ni in a laboratory induction furnace. In this setup, the LIBS signal was carried by a 12-m fiber-optic bundle to the spectrometer. These authors later developed a portable LIBS system for the rapid on-line analysis of

* Corresponding author at: Shenyang Institute of Automation, Chinese Academy of Sciences, Shenyang 110016, China.
E-mail address: sunlanxiang@sia.cn (L. Sun).

http://dx.doi.org/10.1016/j.sab.2015.08.008
0584-8547/



(a) (b)

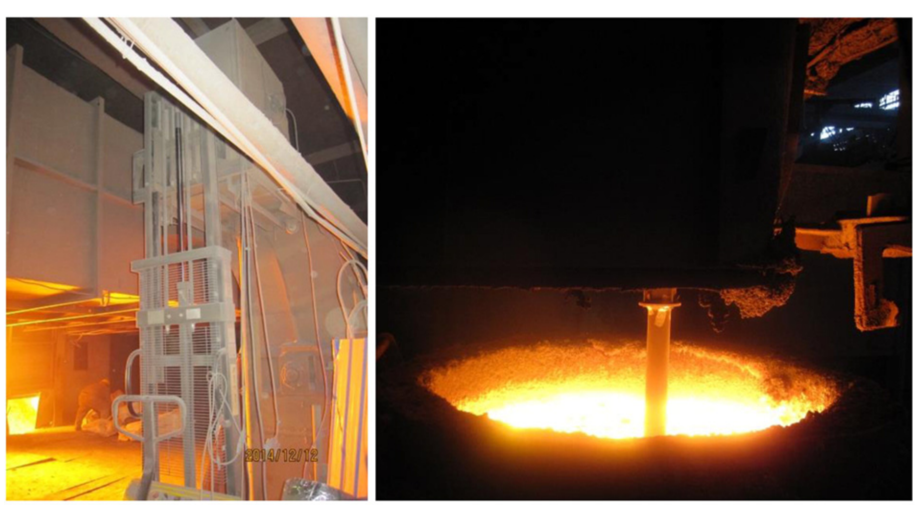
Fig. 1. (a) Schematic of the LIBS system for the in situ analysis of molten metal. (b) Experimental photo in the laboratory.

liquid steel in two different vacuum furnaces [22]. Hubmer et al. [10] proposed a method for analyzing liquid high-alloy steel using a fiber-optic cable to carry the signal over a distance of approximately 10 m. The analyzed elements included Cr, Ni, Mo, Cu, and Co, and the obtained errors were less than 0.2 wt.% in the concentration range below 24.4 wt.%.

Palanco et al. [11] described an open-path and remote LIBS system with a 7.5-m beam path. A laboratory-scale induction furnace with a 1 kg capacity was used for the tests, and the changes in content of Cr and Ni were successfully monitored. Victor et al. [23] successfully adopted a Newton telescope to continuously monitor changes in Si and Mn in blast-furnace runners. Sun et al. [24–26] developed an open-path LIBS system for monitoring compositional changes in Cr, Mn, Si and Ni in a 30 kg capacity induction furnace and demonstrated that the detection capability of minor elements in molten steel is greater than in solid normal steel.

Although the literature contains numerous such studies on melt metal measurements using LIBS, applying LIBS in an active steelmaking process remains a challenge. The probes used in LIBS setups for melt measurements can broadly be divided into two styles: those in which the probe is immersed in the melt surface and those in which a telescope structure is adopted to execute open-path measurements. In the case of the immersion-style probes, long-term protection and maintenance of the probes is one of the greatest challenges to their widespread adoption. In the case of the open-path style, the serious influence of surface slag on measurements is unavoidable.

The Fraunhofer-Institut für Lasertechnik (ILT) designed an automatic liquid slag LIBS analyzer that consists of an optical module connected by



(a) (b)

Fig. 2. Application test photos in a steel plant. (a) Sealed LIBS setup installed along the ladle path. (b) The refractory lance tip immersed into the liquid steel in the ladle during measurements.