ISIJ International, Vol. 56 (2016), No. 5, pp. 723–735

Review

Application of Laser-Induced Breakdown Spectroscopy to Real-Time Elemental Monitoring of Iron and Steel Making Processes

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(*Received on September 22, 2015; accepted on January 19, 2016; J-STAGE Advance published date: March 31, 2016*)

Steel industry is the irreplaceable foundation in heavy industries, which have been developed and improved. The advanced monitoring methods including detection and control technology contribute to its development of iron and steel manufacturing processes. With the development of the measurement techniques, laser-induced breakdown spectroscopy (LIBS) has been developed and applied for many industrial fields of elemental monitoring due to the non-contact, fast response, high sensitivity, real-time and multi-dimensional features. The elemental measurement methods in steel industry were summarized and compared in this paper. LIBS measurements of raw material, smelting processes, products, slag, *etc.* have been reviewed in detail. Challenges for the future of LIBS application in iron and steel making processes have also been discussed. LIBS has a high potential to improve the detection ability of elemental analyses and to promote the on-line monitoring characteristics in iron and steel making plants.

KEY WORDS: laser-induced breakdown spectroscopy; elemental monitoring; iron and steel making processes; real-time.

1. Introduction

The iron and steel are the important raw materials of industrial production. The steel industry as a foundation in heavy industries has been regarded as a significant indicator of the comprehensive national strength and the industry level. The development of steel industry is of many dimensions, ranging from material resources and power resources to transport facilities and various related conditions. The level of the steel industry can be evaluated by yield, quality, economic benefits, labor productivity, and so on. There are various types of iron and steel products concerning the applications of ship, automobile, boiler, nuclear power plants and others.[1,2)]

Steel industry is the resource and energy intensive industries. The pollutant discharge from the steel industry also provides the share of environmental pollution. Reasonable production process and equipment parameters are beneficial to the energy saving and environmental protection. Even more important, the efficiency of the entire production processes and the quality of the products can be improved. Accordingly, the monitoring and control methods are very significant during iron and steel making processes, as well as the metallurgical techniques.[3,4)] The procedure of iron and steel making processes is descripted in brief, such as sintering, iron making, steel making, continuous casting and rolling. Some of the species monitoring and control in each stage of iron and steel production processes consist of material and product, process control, environment and safety, *etc.*

There are various measurement techniques, which include biological methods, chemical methods, optical methods, *etc.* The rapid and precise measurements of content, temperature, inspection, and so on are imperative according to different applications. The measurement methods, such as X-ray fluorescence (XRF), inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS), have been applied for species monitoring in iron and steel making processes.[5–7)] On the other hand, laser diagnostics, recently, has attracted a great attention in various industries because of the non-contact, fast response and multi-dimensional features as the qualitative and quantitative analytical detection technique.[8,9)] Laser-induced breakdown spectroscopy (LIBS) is an analytical detection technique based on atomic emission spectroscopy to measure the elemental composition, which has been widely applied in the metallurgy field.[10)]

In this paper, the measurement methods of elements during iron and steel making processes will be summarized and discussed. The applications and challenges of LIBS technique in iron and steel making processes will be discussed

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DOI: http://dx.doi.org/10.2355/isijinternational.ISIJINT-2015-542

exhaustively. The focus of a laser beam of LIBS is one of the most important factors to be concerned by applying LIBS for iron and steel making processes with the change of a target profile. 3D profile measurement techniques[11–17] have also been discussed as one of the challenges of LIBS practical applications.

2. Measurement Methods of Elements in Iron and Steel Making Processes

2.1. Conventional Methods

In the steel industry, there have been a number of measurement methods for analyzing the components and controlling the procedures during iron and steel making processes. The sampling and preparing procedures are very necessary for the conventional methods. In the traditional steel metallurgical industry, different samples should be prepared in the whole processes including the pretreatment of molten iron, converter steelmaking, secondary steelmaking processes, continuous casting, and so on. The analytical samples should be pretreated before the measurement due to the strict requirements for some conventional methods.

Conventional analytical methods such as XRF,[18–23) prompt gamma neutron activation analyses (PGNAA),[24,25] spark discharge atomic emission spectrometry (SD-AES),[26,27] ICP-AES[28–30] and ICP-MS[31] have been applied for the measurement of iron ore, steels, slags, *etc.* in the steel industry. However, these analytical methods sometimes cannot meet the demands of on-line measurement due to the time consumption of sample preparation and the limitation of each specific method. For example, XRF is sometimes difficult for the analyses of light elements. It is not selective enough in many cases, because many elements with the characteristic emissions present the similarity to those of the valuable components. The principal advantage of PGNAA method is the volume measurement. These bulky devices of PGNAA, however, represent the potential health-hazard and strict regulatory demands.[32] The liquid phase samples are usually measured using ICP-AES and ICP-MS. Therefore, sample preparation is necessary before the measurement.

The monitoring and control of elemental compositions are very important in iron and steel making processes. The conventional measurement methods cannot obtain satisfactory results in some specific applications due to its restrictions, resulting in the unstable product quality and high energy cost. The detection techniques should be developed in these processes. The demands of iron and steel production drive the detection and control technology. On the contrary, the advancement of detection and control technology also contributes to the development of steel industry. These two aspects would illuminate each other. LIBS is recognized as the most likely technique to achieve the real-time and on-line analyses of elemental compositions during iron and steel making processes. LIBS technique has been already demonstrated as the most promising candidate in metallurgical industry.

2.2. Laser-induced Breakdown Spectroscopy

LIBS is also called LIPS (laser-induced plasma spectroscopy) and other related names,[33] which is an analytical detection technique based on atomic emission spectroscopy to measure the elemental composition.

2.2.1. Theory

The principle of LIBS was clarified as follows. In the LIBS process, a laser beam is focused into a small area, producing the hot plasma. The material contained in the plasma is atomized and the light corresponding to a unique wavelength of each element is emitted from the excited atoms in the plasma, as shown in **Fig. 1**.

A calibration of the LIBS signal is necessary for quantitative analysis. Despite the fact that the LIBS processes involved are complex, the emission intensity from the atomized species can be described by the following equation with the assumption of uniform plasma temperature[34]

$$I_i = n_i K_{i,j} g_{i,j} \exp\left(-\frac{E_{i,j}}{kT}\right) \quad (1)$$

In the above expression, I_i is the emission intensity of species i, n_i is the concentration of species i, $K_{i,j}$ is a variable that includes the Einstein A coefficient from the upper energy level j, $g_{i,j}$ is the statistical weight of species i at the upper energy level j, $E_{i,j}$ is the upper level energy of species i, k is the Boltzmann constant and T is the plasma temperature. Equation (1) is applicable under the conditions of local thermodynamic equilibrium (LTE). In Eq. (1), there are several factors that affect the emission intensity I_i, including plasma temperature, plasma non-uniformity, and matrix effects, *etc.* The appropriate correction factors must be contained in $K_{i,j}$ to obtain the quantitative results.

2.2.2. System

A typical geometric arrangement of LIBS is shown in **Fig. 2**. The apparatus fundamentally consist of laser, measured material, lens, spectrometer, ICCD camera, and so on. Lasers such as a pulsed Nd: YAG laser are used as the light source. The output laser beam is focused into the measurement area using the focal lens to make plasma. The plasma emission is focused onto the optical fiber. Emission signals are finally detected by the combination of a spectrometer, an ICCD camera and auxiliary equipment. According to the measured materials of solid, liquid and gas phases, different measurement chambers or platforms can be employed. It

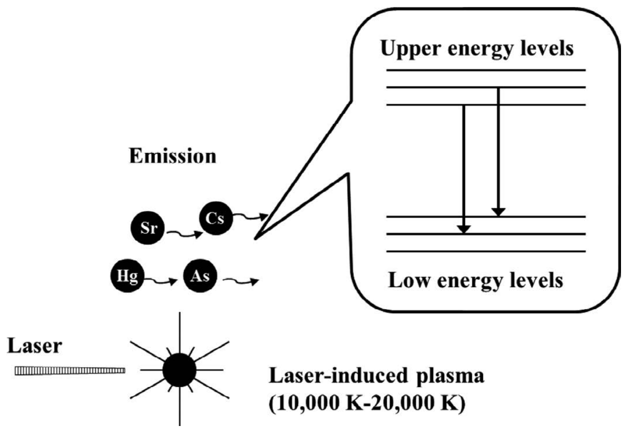


Fig. 1. LIBS plasma process.

is worth noting that the reflection of a laser light from the windows must be considered carefully. Its reflection often results in the damages of optics due to the high energy laser light. The reflection from plasma is sometimes tricky and malicious for LIBS systems. Plasma absorbs the light and also reflects it. Damages of optics by the reflection from plasma cause troubles in some cases, especially in the analyses of liquids.

2.2.3. Detection Abilities

The versatility and multi-elemental capability of LIBS have been demonstrated for the analyses of heterogeneous materials such as coal and mineral ores. Various elements included in samples can be detected simultaneously within a very short time.[35–38] The solid sample features higher homogeneity than powdered counterparts. The feasibility of binder for elemental composition measurement in coal samples has been investigated.[39–41] In these studies, all samples should be prepared before measurement. LIBS has also been applied for detection of unburned carbon in fly ash, char and pulverized coal under high-pressure and high-temperature conditions without any sample preparation. The calibration difficulty of aerosol sample was surpassed by the correction factors for quantitative measurement. This automated LIBS apparatus was applied in a boiler-control system of a power plant with the objective of achieving optimal and stable combustion,[42,43] which enabled real-time measurement of unburned carbon in fly ash without time consumption, as shown in **Fig. 3**. The plasma temperature correction method was also introduced to the size-segregated fly ash and pulverized coal measurements to detect their quantitative contents depending on particle diameter.[44]

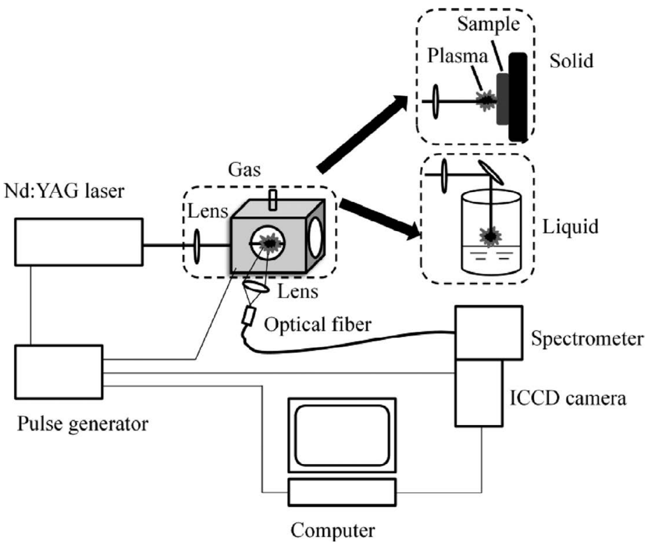
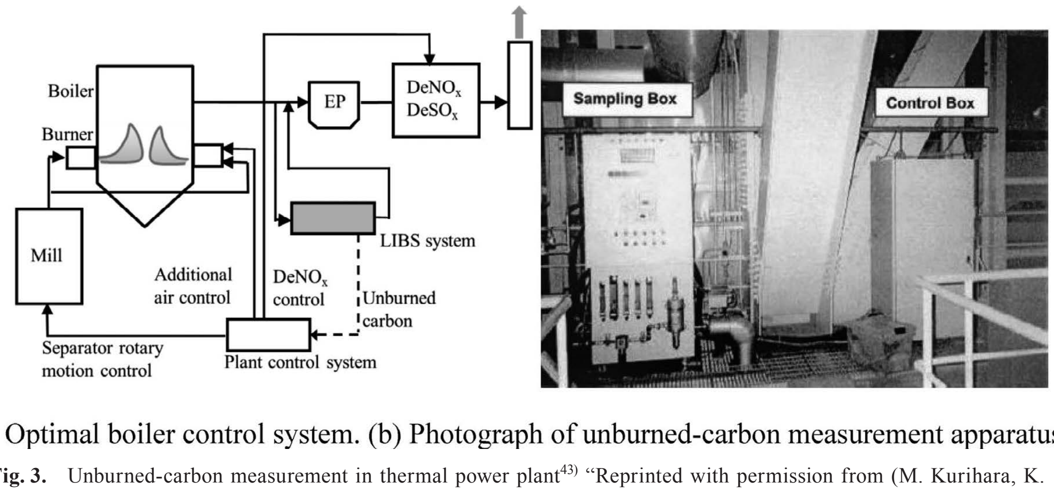


Fig. 2. Typical geometric arrangement of LIBS.

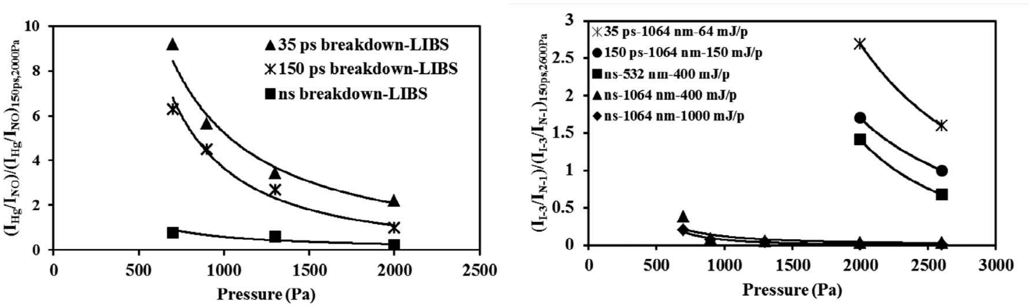
The detection ability of trace species using LIBS has been improved due to the development of laser technology, such as short pulse width lasers. As a result of the short duration, the laser pulse has terminated before the interactions of laser and material, plasma and buffer gas concerning the complicated procedure. The utilization of short pulse laser for plasma generation has been extensively studied.[45,46] Short pulse irradiation allowed for a specificity of excitation that could yield LIBS signals more tightly correlated to particular chemical species and showed significantly lower background emission. LIBS plasma generation process in gas phase is different from that in solid phase with ablation process. One of the challenging targets of LIBS is the enhancement of detection limit of gas phase materials. Though the experiments have been mainly applied to direct observation of post-breakdown processes, a new method to control the LIBS plasma generation process is necessary for the enhancement of detection limit, *i.e.* low pressure and short pulse LIBS. The trace species of Hg and iodine were measured using low pressure and short pulse LIBS under various conditions.[47–50] **Figure 4** shows partial measurement results of Hg and iodine. According to the experimental results, the detection limits of Hg and iodine in N_2 were 3.5 ppb and 60 ppb. The detection limit of gas phase LIBS analysis has been improved using low pressure LIBS.

Because of the pressure, volatility and quenching effects of liquid, the plasma lifetime of liquid sample is shorter compared with that of solid and gas phases. Meanwhile, sputtering of liquid water by a LIBS plasma often raises the problem of the measurement windows. The sensitivity,



(a) Optimal boiler control system. (b) Photograph of unburned-carbon measurement apparatus.

Fig. 3. Unburned-carbon measurement in thermal power plant[43] "Reprinted with permission from (M. Kurihara, K. Ikeda, Y. Izawa, Y. Deguchi and Tarui H: Optimal boiler control through real-time monitoring of unburned carbon in fly ash by laser-induced breakdown spectroscopy. Applied Optics. 2003; 42(30), 6159–6165. DOI: 10.1364/AO.42.006159. Copyright (2003) Optical Society of America".



(a) Pressure dependence of I_{Hg}/I_{NO} [47] (b) Pressure dependence of I_{I-3}/I_{N-1} [50]

Fig. 4. Pressure dependence of the intensity ratios of I_{Hg}/I_{NO} and I_{I-3}/I_{N-1} under different conditions using LIBS.

Table 1. Applications of LIBS to typical iron and steel making processes.

Application	Measurement target	Concentration range	References
Measurements of raw materials (Direct measurement)	Ag, Mo, Pb, Cu, Cr, Ca, Mg, Zn, Ti, Si, Fe and Al	0.3–14 ppm	61,62,65)
Measurements of smelting processes (Direct measurement)	C, (Cr, Cu, Mn, Ni), P	(25 ppm), (Cr: 0.11%–13.8%; Cu: 0.044%–0.54%; Mn: 1.38%–2.5%; Ni: 0.049%–5.92%), (12 ppm and 9 ppm)	82,83,86)
Measurements of products and slags (Direct measurement)	(P, B, V, Cr, Fe, Cu), (Al, Ti, Mn, Co, As, Nb, Mo, Sn), (C, Si, Ni, W), S	(1–50 ppm), (50–200 ppm), (200–1 000 ppm), (0.008 to 0.22%, 70 ppm)	88,89,93)
Measurements of heavy metals in flue gas (preconcentration)	V, Cr, Mn, Co, Ni, Cu, As, Cd, Sn, Sb, Tl and Pb	0.01–0.39 ppb	117,118)

stability and repeatability of LIBS signal are much lower, leading to the increasing difficulty of its analyses. Numerous papers have reported LIBS measurement of different forms of liquid phase materials including the solidification, liquid bulk, liquid surface and others,[51–56] which show different detection features and detection limit. The detection limit of trace traces in liquid jet can be enhanced compared with that in bulk liquid.[57–59]

3. Applications of Laser-induced Breakdown Spectroscopy

LIBS has actively applied to the commercial plants such as iron-making plants, thermal power plants, waste disposal plants, and so on, which have successfully demonstrated to monitor plant control factors using LIBS. Elemental analyses of metals are one of the most suitable applications of LIBS. There have been lots of applications to measure elemental compositions in iron and steel making processes. LIBS with the features of excellent temporal and spatial resolutions appears to be a very promising analysis method in steel industry where element distribution measurements of materials at all stages of production provide the information of material quality and production process. LIBS applications to steel industry are shown in **Fig. 5** according to the iron and steel making processes. **Table 1** lists the brief summary of LIBS applications including the measurements of raw materials, smelting processes, products and slags, heavy metals in flue gas in steel industry.

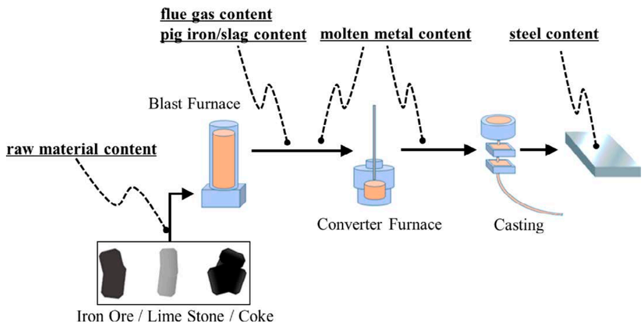


Fig. 5. Technical flow chart for the typical iron and steel making processes. (Online version in color.)

3.1. Measurements of Raw Materials

By the continuous monitoring of element distributions, the raw materials with narrow composition tolerances can be available ahead of further processing. Qiao *et al.*[60] reviewed the recent development of LIBS instrumentation in the field of geology, such as the qualitative and quantitative analyses of geological materials, the LIBS applications in some specific fields to the analyses of ores, extraterrestrial materials, speleothems, marine sediments, fluid inclusion, *etc.* Lorenzen *et al.*[61] described the basis and some details of the different industrial LIBS applications at Krupp. LIBS measurement of geological materials on the conveyor belts was studied and discussed preliminarily. The intensity ratio of Si(I) line at 288.2 nm to Ca(II) line at 317.9 nm showed the good linearity of the concentration ratio of SiO_2 to CaO, which demonstrated the very good measurement precision.

Popov *et al.*[62] reported an analytical assessment of Ag, Mo, Cu and Pb in certified and natural soils, and ores by LIBS for the purposes of geochemical exploration. The detection limits of Ag, Mo, Cu and Pb were 0.3, 0.3, 0.6 and 8 ppm, respectively. It is sufficient to determine these species at the level of their crustal abundance.

Álvarez *et al.*[63] investigated a fast and robust method of LIBS to determine the fluorite (CaF_2) mass-content of powdered ore samples. The emission from CaF molecular bands was measured to determine the fluorite concentration in powdered ore samples in air. Wan *et al.*[64] built a remote LIBS system with a compact custom of 15 m focus optical component, combining a six times beam expander using a telescope to measure the elemental compositions of minerals. A multi-spectral line calibration method was proposed for the quantitative analysis of elemental compositions. Its feasibility and superiority over a single-wavelength determination have been confirmed by the comparison with the traditional chemical analysis of the copper content in the ore. Hussain *et al.*[65] discussed the LIBS ability as a rapid tool for the material analysis. The open pit ore sample was tested. The various trace elements of Cu, Cr, Ca, Mg, Zn, Ti, Si, Fe and Al presented in the ore sample were measured to study the capabilities of LIBS measurement. The estimated concentrations of trace metals using the LIBS setup agreed with the well-established standard method of ICP-AES. This work is useful for the development of a portable system to analyze the solid waste from open pits, mineral processing units and geological rock on line. Laville *et al.*[66] applied LIBS for the multi-elemental analyses of solidified mineral melt samples containing several oxides present in various concentrations. The LIBS technique presents a great potential for mineral melt. However it is necessary to combine with a multivariate model for the improvement of the accurate measurements. The proposed calibration approach also provides a new field of LIBS applications for the analysis of complex matrices.

Death *et al.*[67] set two iron ore samples to complete the mineralogical classification using a combination of LIBS and principal components analysis (PCA) or principal components regression (PCR), which offered the potential for both broad mineralogical and elemental analyses in the minerals industry for exploration, as well as in the mine production for on-line monitoring of ore quality. The combined method of LIBS and PCR was applied to determine the elemental compositions of a series of run-of-mine iron ore samples.[68] The background stripping, normalization and spectral cleaning were employed to minimize the relative standard deviations of the LIBS data. PCR analysis was valid to produce the calibration models for Fe, Al, Si, Mn, K and P using independent LIBS measurements. The combination of LIBS and PCR exhibited the potential for in-situ determination of ore composition. Sheng *et al.*[69] developed and applied LIBS integrated with random forest to identify and discriminate the iron ore grades. The classification and recognition of the iron ore grade were completed using their chemical properties and compositions. The study demonstrated that LIBS integrated with random forest showed better predictions of classification compared with that of support vector machine (SVM). LIBS integrated with random forest is a useful technique for the identification and discrimination of iron ore samples. It is promising for automatic real-time, fast, reliable and robust measurements.

Pedarnig *et al.*[70] detected Cl in industrial iron oxide in air by single pulse and dual pulse LIBS in the near infrared range. In compacted powder measured by single pulse excitation, Cl was detected with the detection limit of 440 ppm and quantitation limit of 720 ppm. Enhanced Cl emission and substantially higher signal to background ratio at much shorter delay time were observed in orthogonal dual pulse LIBS measurements, which is feasible for some technical applications of the elemental detection in the case of the direct access to the samples under investigation. Grant *et al.*[71,72] presented the measured results of the elemental analyses of iron ore using LIBS. The optimum period in the plasma lifetime for spectrochemical analysis of Ca, Si, Mg, Al and Ti was determined using the excimer laser. The calibration curves for Ca, Si, Mg, Al and Ti were produced with the precision ranges from 2 to 25%. The detection limits of different elements were the order of 0.01%. The extension of LIBS technique from the laboratory to a field-based analytical technique was also discussed. Michaud *et al.*[73] applied LIBS for the analyses of iron ore to determine the influence of particle size and mineral phase on the LIBS signals. A linear and systematic decrease in iron intensities as a function of magnetite content could be modeled into an empirical correction equation, as well as an equation of the observed increase in intensity with particle fineness. Applying these simple linear corrections, an on-line trial was planned to validate the feasibility of the approach. **Table 2** summarized the partial measured elements and the specific wavelengths using LIBS in these studies.

The calibration models of LIBS have also been studied and discussed in the measurement of ores. Yaroshchyk *et al.*[74] applied LIBS and partial least squares regression

Table 2. The partial measured elements and the specific wavelengths.

Element	Wavelength (nm)	Upper energy (cm^{-1})
Fe(I)	389.56	26 550.479[72]
Fe(I)	404.582	36 686.176[62]
Fe(I)	537.14	26 339.696[65]
	832.71	29 732.736[70]
	833.19	47 377.955[70]
	833.94	47 755.537[70]
Fe(I)	836.08	48 036.673[70]
	836.56	38 175.355[70]
	838.78	29 469.024[70]
	842.41	51 837.238[70]
Al(I)	396.15	25 347.756[71]
Mg(I)	518.36	41 197.403[72]
Ca(I)	431.86	38 464.808[71,72]
Ti(II)	337.280	29 734.6206[62]
Ti(I)	498.17	26 910.709[71,72]
Si(I)	390.55	40 991.884[71]
Cl(I)	837.59	83 894.037[70]

(PLSR) to perform the quantitative measurements of a multiple-species parameter. Global calibration models based on 65 samples and their duplicates from all the deposits were successful for the prediction of loss on ignition content in pressed pellets, as well as the bulk ore samples. Spectra normalization options, automatic outlier removal and automatic continuum background correction were employed to improve the performance of the PLSR method. The different data-driven multivariate statistical predictive algorithms, such as PCR, PLSR, multi-block PLSR (MB-PLSR), and serial PLSR (S-PLSR), were compared for the quantitative analysis of Fe content in iron ore measured using LIBS.[75] There were notably less latent variables in the case of PLSR. PLSR and PCR models, however, produced similar prediction accuracy. MB-PLSR and S-PLSR algorithms treated available UV and VIS data blocks separately demonstrated the inferior performance compared with PCR and PLSR models.

The on-line measurement system of LIBS has been discussed for the real applications. Barrette *et al.*[76] developed an analytical instrument based on LIBS technique that can be operated on line in the iron-ore pelletizing plants. The detection system was successful for the measurements of Si, Ca, Mg, Al and graphitic C contents in different iron ore slurries prior to filtration and pelletizing. Either graphitic carbon (coke breeze) or total carbon (coke breeze, flux and natural carbonate) can be directly measured when employing the detection system with specific settings. A multivariable calibration was utilized to correct the matrix effects and to evaluate a confidence level based on expertise for each measurement. Rosenwasser *et al.*[77] developed a method for automated quantitative analysis of ores using a commercial LIBS instrument fitted with a developed computer controlled auto-sampler, which was capable for analysis of the required elements in the phosphate ore samples supplied with 2–4% relative standard deviations for most elements. The calibrations were achieved for P, Ca, Mg, Al and Si with the linear regression coefficients of 0.985, 0.980, 0.993, 0.987 and 0.985, respectively. The preparation and analysis time for each sample was less than 5 min. The similar method was suitable for a range of ores and minerals. Gaft *et al.*[32] proved the LIBS ability to provide on-line analyses for raw ores in field conditions. An industrial LIBS machine was successfully developed and tested for on-line evaluation of phosphate and coal on the moving belt conveyers, as shown in **Fig. 6**. The comparison of LIBS on-line data with control analyses revealed the good correlation corresponding to the required detection limits and accuracy.

3.2. Measurements of Smelting Processes

Analysis and control of the continuous casting of molten steel are significant for the quality of products. For on-line monitoring in metallurgical industry, the metals sometimes have to be analyzed in molten state. Realization of on-line analysis of molten steel composition has been considered one of the great difficulties in metallurgical industry. Noll *et al.*[78] gave an overview of R&D activities and first routine industrial applications of LIBS for quality monitoring or production controlling in the steel making and processing industry. Analyzed substances range from top gas of the blast furnace, via liquid steel up to finished products. Carlhoff *et al.*[79,80] investigated the fundamental scientific study and instrument development of LIBS technique applied to the solid and liquid steel samples. A LIBS system was employed in a production steel plant to monitor the molten metal in a steel converter.

Figure 7 shows the process control concept of target component concentration using a conventional method and LIBS technique. The rapid and precise control of the iron process can be realized using the real-time measurement technology. Concept of LIBS application to a decarburization converter is shown in **Fig. 8**. Hubmer *et al.*[81] developed a process optimization and control system using LIBS to quasi-continuously chemically analyze the liquid high-alloy steel under different pressure conditions. Performing the LIBS analysis together with parallel measurements of the temperature using a pyrometer resulted in the improved process control for both the decarburization (refining) phase and the reduction phase. The mean residual deviations obtained from 12 references of different high alloyed samples were close to those reported for other comparable high-alloy samples that were investigated under room temperature and normal atmospheric pressure condition.

Aragón *et al.*[82] applied LIBS to determine the carbon

Fig. 6. On-line monitoring in iron making processes[32] "Reprinted with permission from (M. Gaft, I. Sapir-Sofer, H. Modiano and R. Stana: Laser induced breakdown spectroscopy for bulk minerals online analyses. Spectrochimica Acta Part B: Atomic Spectroscopy. 2007; 62, 1496–1503. DOI:10.1016/j.sab.2007.10.041). Copyright (2007) Elsevier".

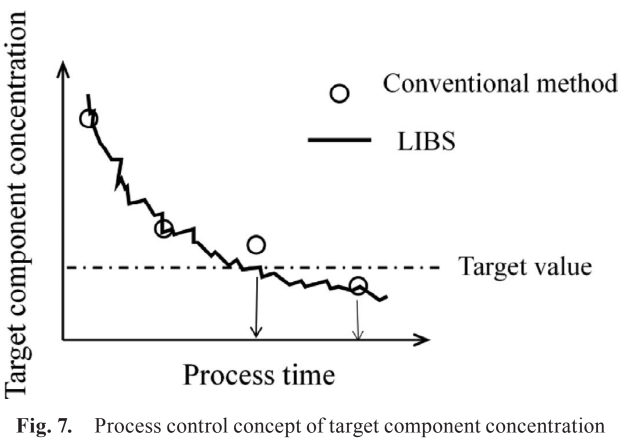


Fig. 7. Process control concept of target component concentration using a conventional method and LIBS technique.

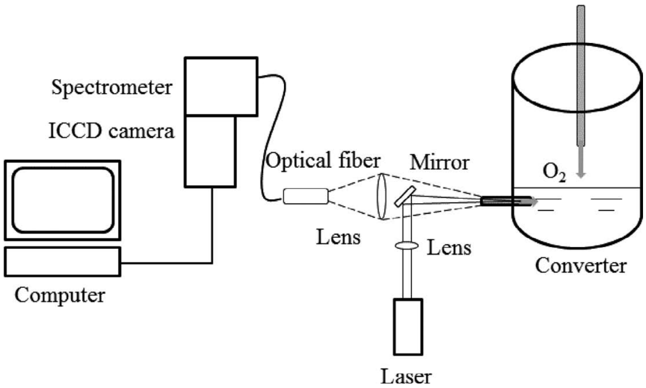


Fig. 8. Concept of LIBS application to a decarburization converter.

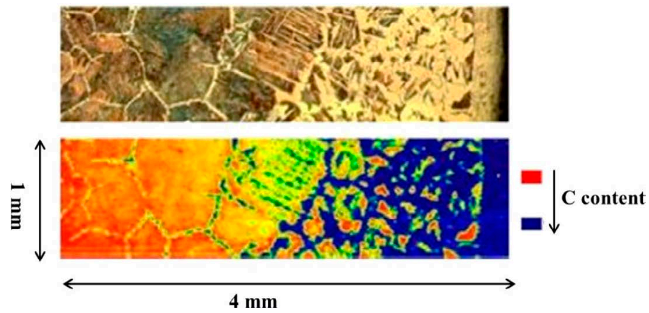


Fig. 9. Comparison between the photographs of the crystal structure revealed by sample polishing and etching (top) and the C map generated by LIBS measurement on the same sample surface (bottom)[94] "Reprinted with permission from (F. Boué-Bigne: Laser-induced breakdown spectroscopy applications in the steel industry: Rapid analysis of segregation and decarburization. Spectrochimica Acta Part B: Atomic Spectroscopy, 2008; 63, 1122–1129. DOI:10.1016/j.sab.2008.08.014). Copyright (2008) Elsevier". (Online version in color.)

content in molten steels using an induction furnace in the laboratory. The plasma was produced and generated on the liquid surface in argon atmosphere. The measured results with precision of 10% and detection limit of 250 ppm show that the LIBS technique can be applied for direct composition determination in molten metals. Gruber *et al.*[83] designed a LIBS setup for process control in a laboratory induction furnace. The concentration of an element was analyzed within 7 s. The measured results demonstrated that the temporally variable Cr, Cu, Mn and Ni contents can be monitored in real-time within certain concentration ranges in liquid steel, such as Cr from 0.11% to 13.8%, Cu from 0.044% to 0.54%, Mn from 1.38% to 2.5%, Ni from 0.049% to 5.92%. Panne *et al.*[84] tested a customized mobile LIBS system for on-line process analysis of major constituents in a mineral melt of 1 600°C. The elements of Ti, Fe, Mn, Mg, Ca, Si, Na and Al were identified from the melt in such industrial environment. LIBS revealed a superior temporal resolution compared with the methods of manual sampling and XRF. Rai *et al.*[85] evaluated the performance of a fiber-optic LIBS (FO-LIBS) sensor by analyzing the elemental spectra of different solid Al alloys, the molten Al alloy in the laboratory furnace and a large pilot furnace. The measured results definitely demonstrated that the FO-LIBS sensor is useful for on-line monitoring of the minor metal concentration in an industrial furnace, which makes LIBS applicable to the process control in metallurgy.

3.3. Measurements of Products and Slags

As the most important part in the steel industry, it is very necessary to detect the elemental compositions of the products, as well as the slags. Li *et al.*[86] showed a simple LIBS setup that can be used for the accurate quantitative analysis of P in iron and low alloy steel in air. The interference from the iron and copper lines on the P emission line at 214.91 nm using different delay time was studied to reduce the matrix effect. The detection limits of P were 12 ppm and 9 ppm for pig-iron and low-alloy steel samples, respectively. Zeng *et al.*[87] developed and employed a portable FO-LIBS system to quantitatively analyze the elements of Mn and Ti in pig iron. The time-resolved images of plasma plumes were obtained with lower temperature and electron density, which means a lower self-absorption. The leave-one-out cross-validation method was used to evaluate the detection accuracy. The ablated craters and the detection accuracy were better than those obtained by the conventional LIBS. Furthermore, the FO-LIBS system was more promising for industrial applications because of the cost effective, more compact and suitable features.

Zhang *et al.*[88] investigated the steel measurement using LIBS under various experimental conditions, such as lens-to-sample distances, delay time, atmospheric condition, laser pulse energy, *etc.* Under the optimum parameter condition, the detection limits were dozens of ppm for C, Si, Mn, P, S, Ni and Cr in the pure steel. González *et al.*[89] determined the S content in steel by LIBS without the noticeable matrix effects. The calibration curves were linear for the concentration range from 0.008 to 0.22%. The detection limit of S was 70 ppm with the measured precision of 7%. Leis *et al.*[90] measured Si and Cr in homogeneous and low-alloyed standard steel samples in the noble gas to find the optimum conditions for laser ablation and atomization. Cr at 425.2 nm, Si at 288.2 nm and 251.4 nm were detected as the analytical lines with the standard deviation of 6%. The detection limits of these measured spectral lines were 24 ppm, 30 ppm and 200 ppm respectively.

Grant *et al.*[91] examined the plasma induced by the excimer laser irradiation of mild steel in various ambient of air, argon, nitrogen and helium, at pressures from 66.5 Pa to 101 kPa. The maximum spectral intensity and signal-to-background ratio occur in argon at pressure of 6 650 Pa, which were important for quantitative elemental analyses. Thiem *et al.*[92] employed LIBS for the multi-elemental analyses of transition metals in solid and granular alloy samples. The background signal reduced in an ultra-high vacuum. Detection limits from 0.0001% for Ni in a simple copper alloy to 0.16% for Al in a complex granular sample, varied with sample composition. Noll *et al.*[93] investigated the influence of the laser pulse structure on the emission of the LIBS plasma to improve the detection limits for multi-elemental analyses. 16 elements in an iron matrix were distinguished and analyzed under atmospheric conditions. The detection limits were enhanced using dual pulse LIBS. Boué-Bigne[94] considered the analyses of segregation and decarburization in steel samples using LIBS to control and improve the quality of the final steel product. **Figure 9** shows the 2D distribution of carbon content on a metal surface measured by LIBS. The parameters that influence the detailed mapping of large sample areas were determined and optimized. Vrenegor *et al.*[95] studied the matrix effects in LIBS plasma of high-alloy steel for matrix and minor elements including Ni, Cr, Cu, Mo, Si, Ti, Mn, Al and C. The single pulse and dual pulse LIBS and two different laser pulse energies were employed to discuss the mean residual deviation for the quantitative determination of concentrations. The inter-element corrections were studied to reduce the influence of matrix effects on the calibration curves.

Sun *et al.*[96] applied calibration-free LIBS (CF-LIBS) method combined with self-absorption correction for quantitative analysis of different alloys including aluminum-based alloy, iron-chromium alloy and iron-chromium-nickel alloy. **Figure 10** shows the Boltzmann plot corrected by internal reference for self-absorption correction (IRSAC) for the iron-chromium-nickel alloy sample. When employing the IRSAC method, the quantitative results of all elements except Mn acquire a notably improvement compared with that of the basic CF-LIBS, as listed in **Table 3**. Palanco *et al.*[97] built and evaluated an instrument to reduce the quality assessment time in stainless steel-factories based on LIBS. Stainless-steel samples of different grades were employed to assess the full automation of the instrument with sample handling, surface preparation and quantitative analysis capabilities. The element compositions of various steels and alloys have been detected using LIBS extensively under different experimental conditions to discuss the detection features and to improve the detection ability. The analytical instrument and the calibration methods have been studied and developed extensively.[98–104]

In iron and steel making processes, the slags are as important as the products. Sturm *et al.*[105] analyzed the solidified samples taken from the liquid slag layer in a vacuum degasser station of a steel plant using LIBS. LIBS has also been applied for the on-line analysis of liquid slag at a steel plant,[106] as shown in **Fig. 11**. The slag in the ladle of a slag transporter was measured automatically at a distance of several meters during a short stop of the transporter within 2 min. The major components, such as CaO, Fe, SiO_2, MgO, Mn and Al_2O_3, were analyzed and compared with reference values from the laboratory for solid pressed slag samples as well as for samples from the liquid slag. Stable 24/7 operation during the first three-month test run has been demonstrated successfully under these conditions.

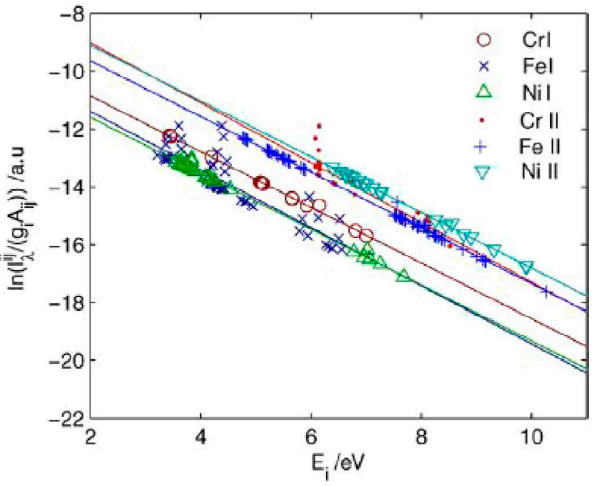
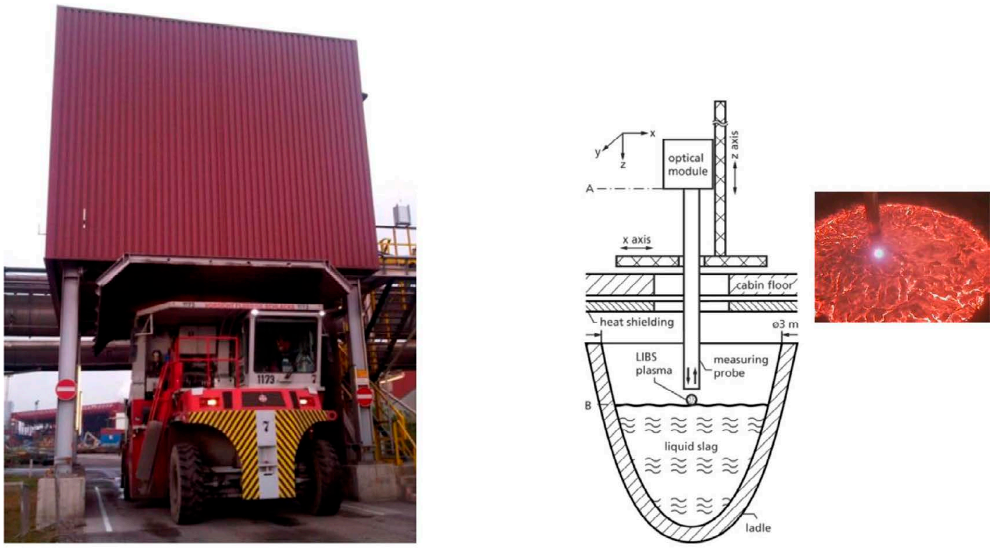


Fig. 10. Boltzmann plot corrected by the IRSAC for the iron-chromium-nickel alloy sample[96] "Reprinted with permission from (L. X. Sun and H. B. Yu: Correction of self-absorption effect in calibration-free laser-induced breakdown spectroscopy by an internal reference method. Talanta. 2009; 79, 388–395. DOI:10.1016/j.talanta.2009.03.066). Copyright (2009) Elsevier". (Online version in color.)

Table 3. Quantitative results for the aluminum-based alloy, iron-chromium alloy and iron-chromium-nickel alloy[96] "Reprinted with permission from (L. X. Sun and H. B. Yu: Correction of self-absorption effect in calibration-free laser-induced breakdown spectroscopy by an internal reference method. Talanta. 2009; 79, 388–395. DOI:10.1016/j.talanta.2009.03.066). Copyright (2009) Elsevier".

Element	Concentration (wt%)			Relative standard deviation (%) IRSAC
	Certified value	Basic CF-LIBS	IRSAC	
Aluminum alloy				
Cu	3.99	89.54	4.79	20.05
Mn	0.81	0.45	0.47	41.98
Al	83.89	4.40	83.46	0.51
Other elements	11.31	–	–	
Iron-chromium alloy				
Cr	14.26	28.07	13.32	6.59
Fe	84.54	71.93	86.68	2.53
Other elements	1.2	–	–	
Iron-chromium-nickel alloy				
Cr	28.24	68.92	29.90	5.88
Fe	40.57	21.25	41.61	2.56
Ni	24.28	2.91	21.59	11.08
Other elements	6.91	–	–	



(a) Slag transporter with ladle during analysis underneath the measuring cabin.
(b) Schematic diagram of the LIBS analyzer setup.

Fig. 11. Application of LIBS in liquid slag analysis[106] "Reprinted with permission from (V. Sturm, R. Fleige, M. de Kanter, R. Leitner, K. Pilz, D. Fischer, G. Hubmer, and R. Noll: Laser-Induced Breakdown Spectroscopy for 24/7 Automatic Liquid Slag Analysis at a Steel Works. Analytical Chemistry. 2014; 86, 9687–9692. DOI: 10.1021/ac5022425). Copyright (2014) American Chemical Society". (Online version in color.)

Hussain *et al.*[65] presented the developed LIBS system applied for qualitative and quantitative measurement of elemental concentration in iron slag and open pit ore samples. Various elements of Cd, Ca, Mg, Cr, Mn, Ti, Ba, P, Cu, Fe, Zn, *etc.* in these samples were determined. The concentrations of trace metals estimated with the LIBS setup were in close agreement with the results achieved with ICP-AES. The LIBS detection limits were estimated for these mentioned elements under the optimal experimental conditions. Ni *et al.*[107] proposed a normalization method using the integral intensity of plasma image to reduce the influence of experimental parameter fluctuations on quantitative analysis of slag components. A series of experiments with slag samples were performed by increasing set threshold for edge extraction of plasma image. The relativity between spectral line intensity and mass fraction can be enhanced efficiently compared with the results without normalization and normalized by whole spectrum area. Zhang *et al.*[108] applied the LIBS technique coupled with SVM and PLSR methods to perform the quantitative and classified analysis of 20 slag samples. It has been confirmed that the LIBS technique coupled with SVM and PLSR methods is a promising approach to achieve the on-line analysis and process control of slag in the metallurgy field.

Besides the analyses of elemental compositions, LIBS has also been used for the surface diagnostics. Yao *et al.*[109] proposed a non-destructive diagnostics technology of LIBS to detect the failure trend for heat transfer surfaces of steel. The employed method based on the matrix effects that were caused by the changes of microstructure and mechanical properties. The PCA method was employed to distinguish the samples with different microstructures of the pearlite and martensite. The discrimination of microstructures was determined by the selection of rigorous wavelength range and statistical modeling approaches. These investigations indicated that LIBS can be utilized as a new way to determine the microstructure changes of steel samples with little sample preparation in the field. Kim *et al.*[110] described a sensitive optical technique for compositional mapping of solid surfaces using LIBS. A standard aluminum alloy was used to select and characterize the compositional distribution and an image of the surface display. The surface contamination of a copper stain around the conductor area has been clearly characterized in the scanning LIBS map. LIBS technique displays the high sensitivity, selectivity, wide dynamic range and versatility compared with other on-line analytical techniques, which is significant for the performance of the products and the metallurgical processes. Labutin *et al.*[111] investigated the correlation between the mechanical properties of aluminum-lithium alloys, lithium ferrites and the LIBS plasma parameters. The relationship between the hardness of metal and nonmetallic samples and the parameters of ablated mass and excitation temperature was useful to develop the fast LIBS techniques for the identification of ceramics and powder ferrites during the annealing procedure, as well as the monitoring mechanical strength of aviation aluminum alloys.

Anderson *et al.*[112] examined the depth profile measurement of coatings on steel using LIBS. Under the preferred operating conditions, linear calibrations against coating thickness for Zn/Ni from 2.7 to 7.2 μm, Sn from 0.38 to 1.48 μm and Cr of 20 nm on steel were achieved with the relative standard deviation of 3.5%. This depth profile performance coupled with the rapid analysis time, typically less than 60 s, indicated that the technique may be useful in industrial applications. St-Onge *et al.*[113] examined how LIBS depth profiles can be fully calibrated by the measurement of the representative case of galvannealed coatings on steel. The method of the second derivative of Zn intensity profile was proposed to determine the coating and substrate interface position. The intensity ratio of Fe to Zn showed the non-linear dependence on the concentration ratio of Fe to Zn. Quantitative depth profiles of three elements of Al, Fe and Zn were obtained for two galvannealed samples.

The products of steel industry are applied to various fields, such as the pressure vessels in nuclear power stations, high-temperature steel pipes in industrial environment, *etc.* LIBS has also been applied for the material analyses and diagnostics of steel products in the actual applications.[114–116)]

3.4. Measurements of Heavy Metals in Flue Gas

Various heavy metal pollutions in flue gas have resulted in serious influences on environment and human health. Much more attention should be paid to this issue. LIBS can be applied to measure the solid and liquid materials, as well as the gas phase samples. Smelting dusts contain appreciable metal values and a large amount of poisonous heavy metals due to its volatilization. In order to recover the metal values and eliminate the pollution from smelting dusts, it is necessarily important to measure the heavy metal contents in the smelting dusts.

Neuhauser *et al.*[117,118)] developed a mobile LIBS system for a direct analysis of automatically acquired aerosol filter samples to provide quasi-on-line information on the elemental composition of the deposited aerosols. The elements of V, Cr, Mn, Co, Ni, Cu, As, Cd, Sn, Sb, Tl and Pb have been measured by collecting the aerosol particles on filters, resulting in lower detection limits from 0.01 to 0.39 ppb. The system was demonstrated to be suitable for waste incineration facilities or other industrial combustion processes. However, the preconcentration process is pivotal before LIBS measurement to enhance the detection limit in this range. According to the literature review, LIBS has been employed in flue gas measurement that can be applied in thermal power plants. With the development of the metallurgical industry and the improvement of environmental requirements, the measurements of heavy metals in flue gas using LIBS should be extensively and further studied in iron and steel making processes.

3.5. Challenges for the Future

It is important to control the smelting and rolling processes in the steel industry, which need the continuous and direct on-line measurement. The measurement accuracy and control speed are also the considerable factors for the efficiency and product quality. On the other hand, the accurate measurement of the released gas, solid and liquid allows no negligence concerning the environment and human health. The detection method should be developed due to the increasingly stringent criteria.

3.5.1. Accuracy

In iron and steel making processes, the measurement samples in all the stages consist of bulk, solid, liquid and gas phase samples. The LIBS plasma processes are different from the different phase samples. The measurement methods and parameters should be determined according to the specific conditions. There are several important factors to get quantitative information using LIBS. It is very difficult to solve the LIBS process theoretically because it contains laser-material interactions, rapid temperature changes over 10 000 K in a nano- or pico-second time scale and plasma cooling phenomena which include the recombination process of ions, electrons and neutrals. Therefore, choosing appropriate experimental parameters is important to make the theoretical treatment applicable for quantitative measurements. On the other hand, data processing and modeling play the important roles to LIBS for the analytical results of the measured spectra. An ideal data processing method should be based on a deep understanding to the plasma physics and capable of minimizing the noise effects, compensating for the signal fluctuations, and reducing the matrix effects. There have been several calibration methods such as the Boltzmann plot method using many emission lines to increase the correction precision. The calibration methods should be developed to realize the quantitative analysis with the precision and accuracy of a measurement. As for the on-line application in the industry, the system simplicity and real-time measurement capability are also the significant factors considered. The methods for quantitative analyses should be workable and satisfactory for practical applications.

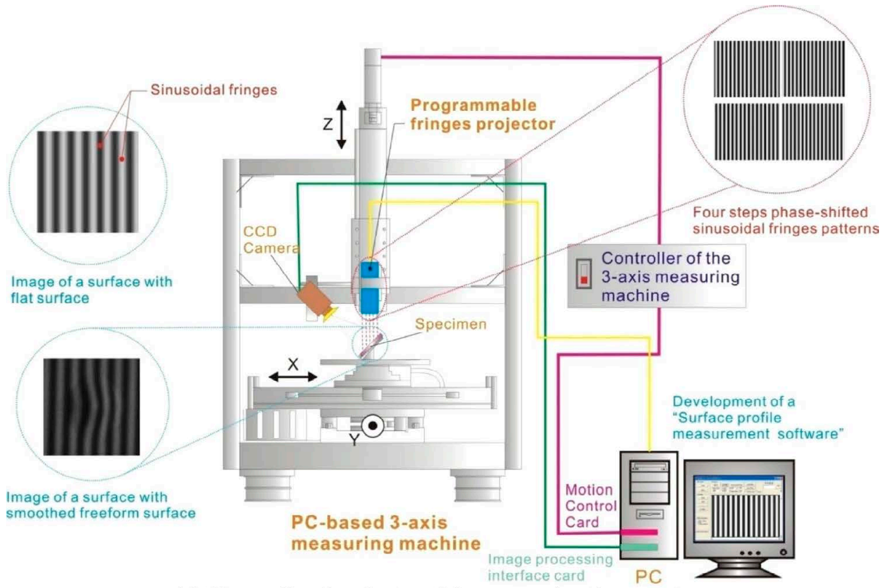
3.5.2. Durability

The real advantage of LIBS technique is that the results are delivered continuously and in real time compared with periodic sampling and standard analytical methods with the time consumption. Consequently, LIBS gives a more representative reading of the state of the process, particularly when rapid perturbations occur, and allows process optimization and quality improvement. Current research aims to develop the commercial equipment for continuous industrial applications. In these applications, however, the long term stability and durability of LIBS devices, especially lasers, is one of the challenges. The vulnerability of lasers is the primary drawback to the industrial applications. LIBS employs pulsed lasers and their lifetime often limits the plant applications, especially the long-term continuous use for plant monitoring and control. Actually, in iron and steel making plants, all the devices should be paid attention, as well as lasers.

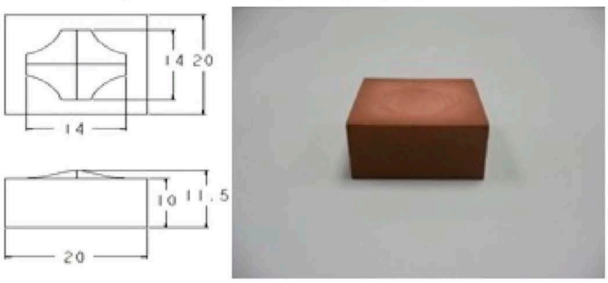
It has become increasingly important to monitor factors in plant conditions in order to improve the operation of industrial plants. As a consequence, improved on-line monitoring techniques for plant control factors are necessary to enhance the capability of maintaining the overall plant operation under control. Elemental measurement, such as carbon content, is an important factor in iron and steel making plants. The associated monitoring and control techniques are needed for continued operational improvement. Emphasis is placed mainly on instrument development for the applications, as well as the fundamental scientific investigations.

3.5.3. Combination with 3D Measurement

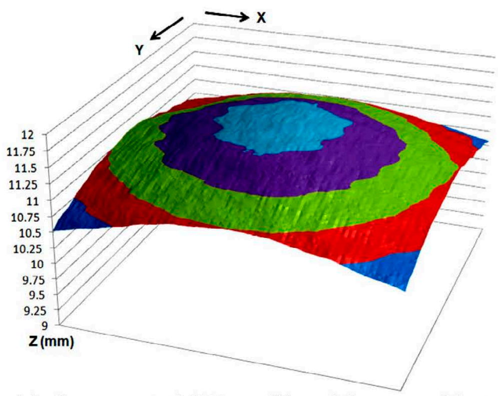
The focus of a laser beam of LIBS is one of the most important factors to be concerned by applying LIBS to the industrial processes with the change of a target profile. 3D Profile information of the object is required for the positioning of a focused laser beam. The non-contact laser assisted measurement system equipment, due to its high measuring speed, lack of contact force and no probe radius compensation calculation, *etc.* is nowadays the dominant tool used for engineering measurement applications. According to the literature review, the non-contact type profile measurement systems, in general, can be divided into three categories: first, a measurement machine integrated with a triangulation laser probe;[11] second, a measuring machine integrated with a laser line projector and one/two CCD cameras;[12–14] third, a measurement machine integrated with a structured fringes projector and two CCD cameras.[15] To digitize small complex objects with dimensions smaller than about 30 mm, a measurement machine integrated with a triangulation laser probe is a good strategy due to its small spot size. The standard triangulation laser probes and the circular triangulation laser probes are commercially available. However, the scanning speed using a triangulation laser probe is limited concerning the single point data acquisition. A laser scanning measurement system integrated with a CCD camera is appropriate for high speed measurement of material instantaneous flow on belt conveyors.[16] Phase shifting algorithm is, in general, applied to calculate the phase map and the 3D profile of an object using the structured fringes projection system.[17] The structured fringes can either be generated by the Michelson interferometric method or be designed by a PC and be projected onto a workpiece surface via a projector. **Figure 12**(a) shows the fringes projection system using the 4-step phase shifting method to measure the 3D profile of a test object. The black and white structured fringes with sinusoidal intensity distribution can be generated by a PC and be projected sequentially onto a 3D object. A CCD camera is used to capture the deformed fringes. The 3D profile of a workpiece can be determined based on the calculated



(a) Setup for the 4-step fringes projection system



(b) Photo of the test object



(c) Constructed 3D profile of the test object

Fig. 12. Schematic illustration of a fringes projection system for 3D profile measurement. (Online version in color.)

phase map of the captured images. The 3D profile deviation of the test object (Fig. 12(b)) with a convex in the middle was about 65 microns by using the 4-step phase shifting method, as shown in Fig. 12(c). If a 3D profile measurement system can be integrated with a LIBS, the measured 3D profile information of the object can be used for the real-time positioning of a focused laser beam in a LIBS system.

4. Conclusions

At present LIBS has been developed and applied for different industrial fields due to the non-contact, fast response, high sensitivity, real-time and multi-dimensional features. The measurement methods of elements in steel industry have been summarized and discussed, especially the LIBS applications of real-time elemental monitoring in iron and steel making processes including the measurement of raw material, smelting processes, products and slag, *etc.* In order to develop the on-line detection method and system, the detection accuracy and the durability of LIBS should be improved to meet the need of industrial demand in real time.

Acknowledgments

The present work was supported by Collaboration Program between Tokushima University and National Taiwan University of Science and Technology.

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