Online Compositional Analysis of Molten Steel by Laser-Induced Breakdown Spectroscopy

Lanxiang Sun¹, a, Yong Xin¹, Zhibo Cong¹, Yang Li¹, Lifeng Qi¹

¹Key Laboratory of Industrial Informatics, Shenyang Institute of Automation, Chinese Academy of Sciences, Liaoning, Shenyang 110016, China

aemail: sunlanxiang@sia.cn

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Abstract. Quick analysis of chemical composition is very important for process control and quality assessment in metallurgical industry, especially in steelmaking process. A prototype equipment for online analysis of molten steel composition was developed based on laser-induced breakdown spectroscopy. The effect of steel temperature on different spectral line intensities was studied, and calibration curves of Cr, Ni, Si and Mn were built. Results show that most line intensities are greatly enhanced when steel temperature is higher than 1200°C, and the detection capability of minor elements in molten steel is higher than in normal solid steel. Line intensity, however, is easier saturated in molten steel, leading to narrow linear ranges of calibration curves for molten steel. Furthermore, for online analysis, by using a median filter the abnormal points were inhibited and the changing compositional concentrations were successfully monitored.

Introduction

The measurement of chemical composition of raw materials and in-process products is very important in industry, especially in metallurgical industry. General measurement methods, such as the spark emission spectrometry, x-ray fluorescence spectrometry and atomic absorption spectrometry, are not easy to be applied to real-time and on-line analysis because of need of sample preprocessing. For the steel making process using converters, complicated sample preparation processes delay the production cycles, and cause unstable product quality and high cost [1].

Laser-induced breakdown spectroscopy (LIBS) is a very useful atomic emission spectral analysis method for quick online analysis. In LIBS, emission light of plasma induced by focusing high power laser pulses onto the sample surface is collected for spectral analysis. Because of unnecessary sample preparation and versatile analysis of solids, liquids and gases, LIBS is most suitable for on-line and stand-off measurement [2-4].

The application for quality monitoring of industrial products is one of the most interesting study fields of LIBS. In metallurgical industry, taking advantage of LIBS to perform on-line monitor of melt compositions during producing processes is very promising [4-13]. By on-line monitor, production cost and energy consumption will be greatly reduced and technology innovation will be promoted.

We developed a prototype equipment based on LIBS for online analysis of molten steel composition. Using this equipment, we studied the effect of temperature on different spectral line intensity, built calibration curves of Cr, Ni, Si and Mn, and successfully monitored the changing compositional concentration. Detailed experimental and result description is following.

Experimental

Setups. An experimental equipment named SIA-LIBS-02 was produced for online compositional analysis of molten steel. The schematic setups of the equipment is shown in Fig. 1. The equipment includes two parts, one of which is the front probe and the other of which is the control platform. The laser head, optical lens and high-temperature shield constitute the front probe which performs the convergence of laser pulses and the collection of plasma emission. The front probe can be rotated in an angle less than 45 degree, and can be moved back and forth, up and down. Computer and
spectrometer integrated in the control platform complete the detection and spectral analysis. A medium-frequency induction furnace is used to smelt steel. The rated power of the furnace is 50 kilowatts and the rated capacity is 30 kilograms. Detailed setup description can be found in reference [14].

Samples. Some cylindrical steel samples with about 35mm diameter and 300mm length were prepared as the basic materials. The weight of the steel samples is about 20 kilograms. The mass concentration of the element Si is less than 0.07%, Mn is less than 0.6%, Cr and Ni are about 0.04%. Furthermore, some raw Mn-Fe alloys (the content of Mn is between 75% and 85%), Si-Fe alloys (the content of Si is between 72% and 80%), Cr-Fe alloys (the content of Cr is about 59.9% and the content of Fe is about 39%), and pure Ni materials (the content of Ni is more than 99.9%) were prepared for adjusting the concentration of some elements during smelting. These raw materials were divided into six parts which were gradually added into the furnace during smelting. The every additive quantity of the raw materials are shown in Table 1. At a proper angle, 300 shots were continually fired at an 150ms time interval between two shots. The pulse energy of the laser is 100mJ, the delay time between the beginning of the fired laser and the detection is 0.42µs and the integration time is 1ms. The 300 shot data were saved, some steel liquid was sampled by using a quartz tube of 11mm diameter for further analysis.

| Materials | 1  | 2  | 3  | 4  | 5  | 6  | Sum (g) |
|-----------|----|----|----|----|----|----|---------|
| Cr-Fe     | 154| 166| 100| 100| 100| 100| 720     |
| Ni        | 92 | 100| 100| 100| 100| 100| 592     |
| Si-Fe     | 48 | 40 | 40 | 40 | 40 | 40 | 248     |
| Mn-Fe     | 100| 75 | 50 | 50 | 50 | 50 | 375     |
| Sum       | 394| 381| 290| 290| 290| 290| 1935    |

Results and Discussion

Selection of analytical lines. A classical spectrum of liquid steel is shown in Fig. 2. The spectra of liquid steel are very complicated because of a great amount of lines and serious overlap between lines. Analytical lines must be chosen carefully. The principle of line selection is that the overlap lines and self-absorption lines should be avoided, but the absolutely isolated analytical lines are difficult to find because of serious interference caused by many characteristic lines of element Fe. By preliminarily screening, for analytical element Cr, Ni, Si and Mn, two lines were selected for each element, and for matrix element Fe three lines were selected as reference lines. Lines selected are shown in Table 2.
Temperature effect. During smelting steel, the ambient temperature was about 10°C and the temperature of molten steel in the furnace was controlled between 1630°C and 1680°C. After the on-line measurement of molten steel in the furnace, some molten steel was dumped into a crucible to cool off. A hand-hold electronic infrared thermometer was used to continuously monitor the temperature of the surface of the steel in the crucible every 2 seconds. The relationship between temperature and elapsed time is shown in Fig. 3.

The infrared thermometer was held by hands at the beginning of the temperature measurement. Since the temperature of sample surface were greatly inhomogeneous and every measurement was done on different points of sample surface because of hand shaking, there was a large fluctuation of the measured temperature. After about 400 seconds, the infrared thermometer was fixed on a frame, and then the temperature fluctuation almost disappeared. Two exponential function were used to fit the real measured temperature before and after 100 seconds.

Because the liquid steel was cooling during the dumping process and there were a few seconds delay to start the temperature measurement, the temperature of the steel had dropped near to 1500°C at the beginning of the temperature measurement. The temperature dropped down quickly using less than one minute from 1500°C to 1100°C. The surface of the steel had solidified in less than half a minute. After the temperature dropped below 1100°C, the falling speed of the temperature gradually slowed down.

The relationship of line intensity and steel temperature can be derived and shown in Fig. 4 that indicates the effect of the sample temperature to the intensity of different lines is different. From Fig.4 (a), we can see that the intensity of line Fe 297.31nm and line Fe 432.58nm do not have a consistent relationship with the steel temperature. The line Fe 297.31nm is flat and not sensitive to temperature, but the line Fe 432.58nm is chaotic. Because of different excitation energy of different lines, the sensitivity of the line intensity to plasma temperature in a range is different. The different relationships with the steel temperature of the two lines, therefore, might be caused by different plasma temperature.

The relationships of line Si 288.158nm and Cr 428.97nm to the sample temperature are similar and both approximate to exponential functions indicated by the fitted lines. The intensity of the two lines are both sensitive to sample temperature when sample temperature is higher than 1200°C, and are both flat when sample temperature is lower than 1200°C. The intensity of line Si 288.158nm at 1500°C is about four times higher than at 1200°C, and the intensity of line Cr 428.97nm at 1500°C is about twice higher than at 1200°C.

The points of line Mn 293.3nm and line Ni 331.56nm are more scattered than Si 288.158nm and Cr 428.97nm, which might be caused by the inconsistency of the two elements in samples. Since the temperature decreases rapidly along with the intense physical and chemical reaction of the sample, the inconsistency of some elements is produced in the sample.
In principle, if the sample is heated, the thermal activity of atoms and electrons will be enhanced, especially when the temperature is approximated to melting point, because more materials will be ablated than in normal temperature. For that reason, enhancing the sample temperature is helpful for the detection of trace elements, but there will be greater fluctuation in the line intensity because of their sensitivity at high temperature. The insensitivity of some lines of Fe element to steel temperature might be caused by the self-absorption due to high concentration. Because of the insensitivity, the fluctuation of line intensity caused by the fluctuation of temperature cannot be reduced by selecting lines of Fe element as reference lines.

Calibration. During smelting process, because the additive materials were added into the furnace six times the concentration of some elements were adjusted six times. we just made the semi-quantitative analysis according to the elemental concentration estimated by using the possible contents of the additive materials and the initial steel materials. During experimental processes, 300 shots were made for the initial molten steel and the mixed molten steel after adding the additives. The each first 200 shots were used for calibration, and the latter 100 shots were used for verification. Average value of 20 shots was adopted as one time measurement, so 200 shots is corresponding to 10 times measurement.

Calibration curves of some characteristic lines are shown in Fig. 5, where error bars are the standard deviation of 10 times measurement. From the calibration curves, only the former three points were used, because all the line intensity were saturated and did not increase with the concentration after second adding the additive materials. This indicates that the line intensity is very easily saturated when temperature up to a certain value, so linear ranges are narrower in high temperature. Parameters of calibration curves and some other quantitative characters including the limit of detection (LOD), average relative standard deviation (RSD) and root mean square error (RMSE) are listed in Table 2.

From the performance of calibration curves, intercepts were still high though the continuous background had been deducted from the intensity because of the serious overlaps of adjacent lines for liquid steel of high temperature and the nonlinearity caused by self-absorption effects. If the overlaps are produced by the lines of element Fe, the quality of the calibration curves can still be good, because the concentration of element Fe is nearly constant. But if the overlaps are produced by the lines of other elements, the quality of the calibration curves will be greatly affected.
In principle, the sensitivity of the line Ni 336.956nm and line Mn 294.92nm should be higher than the sensitivity of the line Ni 331.56nm and line Mn 293.3nm respectively, but the real results were opposite. Especially the intensity of the resonance line Ni 336.956nm was lower than the intensity of the line Ni 331.56nm. The phenomena that the intensity of weaker lines is higher than the intensity of stronger lines might be due to the self-absorption effects, that is, photons are partly absorbed by self-species in transmission path in plasma.

The slope of the line Si 288.158 is highest and the detection limit is the lowest in all calibration curves. Compared with other three elements, element Si is most difficult to excite according to the atomic structure. However, the intensity of line Si 288.158nm is most sensitive to concentration in these characteristic lines, might because the thermal activity of atom Si is greatly increased under high temperature.

**Online measurement.** Based on the calibration curves of Cr 359.35 /Fe 346.58, Ni 331.56 /Fe I 346.58, Si 288.158 /Fe 297.31 and Mn 293.3 /Fe 297.31, elemental concentration can be derived from the on-line measurement. The other 100 shots of the 300 shots were used to calculate the concentration based on the calibration curves, the average value of 10 shots was adopted as one time measurement, so 10 times measurement were performed for each sample. The curves of predicted...
concentration are shown in Fig. 6. In order to reduce noise effect and increase measurement repeatability, a median filter with 5-point wide window was used. In Figures, blue lines with points are the initial measured concentration, red lines with circles are the filtered concentration, and numbers above lines are the average values of 10 times measurement.

Results shown that the median filter effectively reduced the fluctuations and abnormal points, the concentration values and the changing times of concentration values were accurately identified for the first three levels, but the identification was unsuccessful for the concentration of higher levels because of saturation. In practice, if more accurate calibration can be made by completely mixing the material, more accurate quantitative results will be obtained, but linear ranges of calibration will be still narrow.

![Fig. 6 Concentration monitoring of element (a)Cr, (b)Ni, (c)Si and (d)Mn](image)

**Conclusions**

For the compositional analysis of high temperature liquid steel, the effect of steel temperature to the intensity of spectral lines is very strong, especially when the temperature is higher than 1200°C. The effect is different for different lines. The intensity of lines of element Cr, Si and Mn is approximated to an exponent function of the sample temperature when sample temperature is higher than a value, but the function is different for element Fe and Ni. Increasing the sample temperature can increase the limit detection of some elements, but because the effect of temperature to the intensity of some lines of element Fe is weak and not proportional to other elements, taking advantages of lines of Fe as reference lines cannot reduce the effect of fluctuated temperature. In order to obtain more precise quantitative results, therefore, the stable high temperature of samples should be kept during measurement. Furthermore, semi-quantitative online analysis was performed for some element composition. The elemental concentration can be correctly estimated, but the linear ranges are narrow because the intensity of lines are easily saturated in high temperature.
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