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On-line measurement of the hot metal temperature and composition in the blast furnace runners by LIBS

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ABSTRACT

This paper presents an application of LIBS to the chemical analysis of the molten hot metal at the blast furnace by direct measurement in the runner. The new measuring system developed by CRMGroup with the support of ArcelorMittal and Tata Steel, allows real time, on-line determination of the silicon, carbon and manganese concentrations with accuracy compatible with the production process requirements.
This development is aimed at dealing with potential difficulties in controlling the blast furnace arising from recent changes in the buying policy of most steelmakers. Indeed, due to economical factors, the characteristics and composition of the ores and other minerals entering the blast furnace largely vary. As a result, it becomes more difficult to ensure a constant silicon content of the hot metal. However, a better control of this element could result in large savings for the whole blast furnace process but also at the steelmaking stage.
In this paper, a description is given of the successive steps leading to the industrial prototype, the results obtained at different cast floors and the advantages and drawbacks of the method. The current development stage is also presented as well as the industrialisation phase carried out with the expertise of TMT, a company specialised in the instrumentation of cast floors.

1. INTRODUCTION

Decreasing the cost of raw materials generally results in a larger variability of the characteristics and composition of the ores and other minerals entering the blast furnace. As a consequence, it becomes more difficult to get a stable process. Notably, the silicon content of the hot metal, which is linked to the temperature inside the furnace, can vary much largely even during the same heat [1, 2]. To avoid dramatic situations like frozen hearth, the mean level of silicon concentration has to be kept high enough. However, a better control of this element could result in a lower mean concentration and hence lower temperatures with large cost savings for the blast furnace process but also at the steelmaking stage. Recent studies have shown that a decrease by 0.1% of the mean silicon concentration could result, in some cases, to a saving of 2 € per ton hot metal.
For that reason, CRMGroup has developed a new measuring system with the support of ArcelorMittal and Tata Steel. The equipment allows real time, on-line determination of the hot metal silicon concentration directly in the blast furnace runner and is based on Laser Induced Breakdown Spectroscopy (LIBS). This method has already been applied for characterising molten metals but, to the knowledge of the authors, it has never been tested industrially during long periods of time at temperatures around 1500°C [3, 4, 5, 6].
In the current application, the slag composition can also be assessed and the optics needed for LIBS can be used to measure the hot metal temperature, the variations of which could give information about the origin of the hot metal inside the furnace [7].
This paper explains the procedure followed to assess the feasibility of the measurements in harsh industrial conditions, starting from preliminary laboratory experiments. Pilot scale tests as well as "dummy" industrial trials aimed at identifying the main threats are also described. The industrial campaigns are commented and the analytical

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results obtained are highlighted. The current stage of the developments towards a commercially available system is finally presented.

2. Principle of The Method

The principle of LIBS (Laser Induced Breakdown Spectroscopy), as a stand-off analytical method, is illustrated in Figure 1.
A short pulse from a high energy laser is focused on the surface to be analysed. The target can be located at distances varying from a few millimetres to more than 100 metres. In the current application, this distance is in the range of a few metres.
Due to the high energy density at the focal point, plasma is created which emits light at wavelengths specific to the elements composing the material of the target. This light is collected, usually by a telescope, and analysed by a spectrometer. By a suitable calibration, it is possible to quantitatively determine the composition of the material from the intensity of the spectral lines.

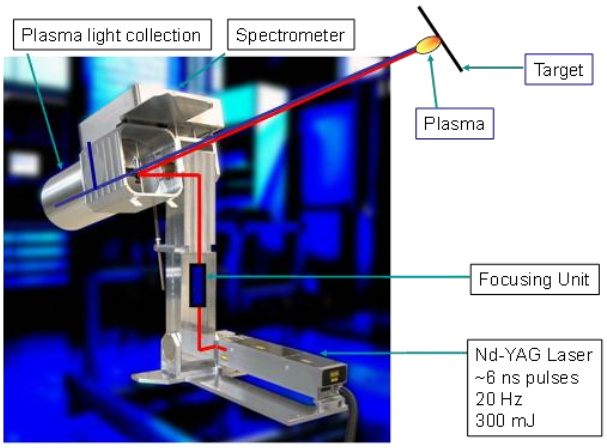

Figure 1: LIBS principle for chemical analysis at stand-off.

3. Laboratory Tests

3.1 Conditions of the measurements

In a first step, in order to assess the sensitivity of the method, preliminary laboratory tests were carried out. The measurements were performed on solid samples of hot metal supplied by ArcelorMittal Ghent. These ones were in fact "Lollipop" samples generally used to control the production. A large range of concentrations in silicon and manganese was made available by a suitable selection amongst the samples analysed in the Ghent's laboratory during several months.
Since the final aim is to measure the silicon concentration directly at the blast furnace runner, it is necessary to assess the feasibility of the analysis at 1 to 4 metre stand-off, taking into account the low concentration of silicon in the hot metal, usually between 0.1 and 0.8%, and a needed accuracy of 10% relative, for process control reasons. Moreover, further difficulties are due to the presence of very close Fe lines around the most sensitive Si line (Figure 2) and to the black body radiation emitted by the molten metal at 1500°C, practically limiting the useful wavelength range to below 500nm.

3.2 Experimental setup

The setup used for the laboratory tests is based on a commercial, multi-purpose LIBS device. The system, called TeleLis is manufactured by LSA in Germany [8,9]. It consists in a carriage containing a 300 mJ, 20 Hz, 6 ns, double pulse laser and a foldable mast supporting a focusing unit, a 300 mm Newton telescope for collecting the plasma light and a 12-CCD spectrometer covering the wavelengths between 170 and 520 nm with a resolution of about 0.025 nm.
The focus can be adjusted between 2.5 and 12 metres, based on the data of a range finder, and the laser beam path can be rotated 180° around the vertical axis and 90° around the horizontal axis. This gives a substantial flexibility in the relative position between the laser and the target.
The experimental conditions were defined to maximise the sensitivity of the measurements while working at a distance longer than the longest one expected in the plant. Hence, double pulse laser shots were fired with the maximum total available energy, i.e. 300 mJ. The distance between the TeleLis and the target was 4 metres.
To compute the intensity of the spectral lines, background removal and outlier rejection procedures, developed in-house, were applied to the spectra. For each measurement, 200 laser pulses were fired at the same location and the mean value of 3 measurements is calculated.

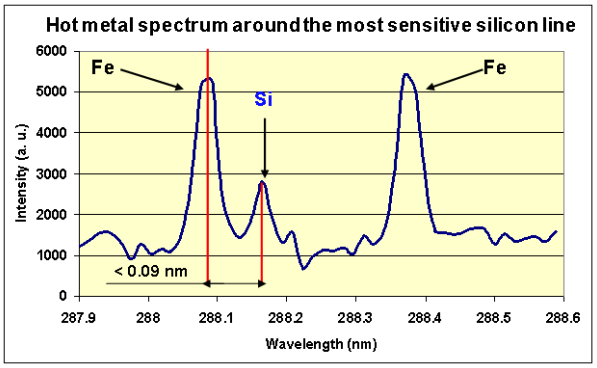

Figure 2: Fe lines closely surrounding the most intense Si lines.

3.3 Results

The LIBS concentrations are compared to laboratory XRF measurements, used as reference. The results are plotted in Figure 3.

As it can be observed, the LIBS data fit within +/- 10% of the nominal concentrations, which is the required target. Similar results are also obtained for manganese and for carbon.

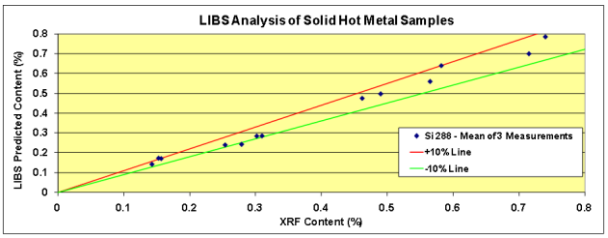

Figure 3: Comparison between LIBS measurements and XRF silicon concentrations for solid hot metal samples.

4. Pilot Tests on Molten Metal

4.1 Conditions of the measurements

Since the feasibility of the measurements was demonstrated in the lab on solid samples, the next step was to carry out measurements on molten metal. The testing conditions are however more difficult to realise due to the high temperatures involved and to the need for an adaptation of the laser beam path to cope with the liquid state of the target.
These tests were hence performed using the pilot facilities of the CRMGroup. A 10-kg induction furnace was filled with cast iron, the composition of which is similar to the blast furnace hot metal. The silicon content was kept to a low value and progressive additions were done during the course of the measurements.

4.2 Experimental setup

The TeleLis was fitted with a 3-metre tube surrounding the beam path to protect the personnel from accidentally crossing the laser beam and to allow argon flushing in order to avoid that fumes from the molten material enter in contact with the optics.
The same laser settings and measurement conditions were used as for the laboratory tests, except that each measurement was made of 400 laser pulses instead of 200. The results are given in Figure 4.
The experimental points correspond to successive additions of silicon in the same base metal. After each addition, the bath was stirred to homogenise the composition and the oxidised slag formed on top of the molten metal was removed before each LIBS measurement.
As demonstrated by these results, the LIBS analysis at 1500°C on molten metal is indeed feasible with the required accuracy.

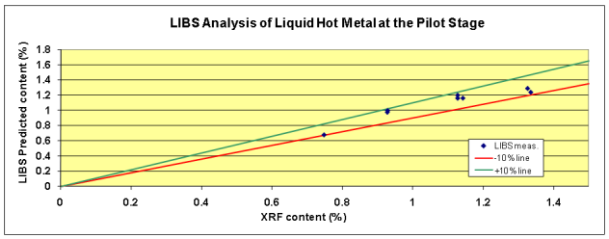

Figure 4: Results of the LIBS tests on molten metal at pilot stage.

5. Industrial Tests

5.1 Dummy tests

In order to get a real time, on-line analysis of the silicon of the hot metal in the plant, LIBS equipment is implemented in a cabinet located at 1.5 metre from the molten metal and able to directly measure in the runner through the use of a nozzle slightly dipping inside the hot liquid. The design of this system takes into account variations in the liquid level as well as the presence of fumes and dust in the environment. Also, an important part of the design work was to ensure that the operation of a “class 4” laser remains compatible with the industrial safety rules in use at the casting floor.
Because of the proximity of costly and sensitive optical equipment with molten metal at 1500°C, it was necessary to verify in real industrial conditions whether the cooling system was efficient enough to guarantee a safe working of all the components. To this aim, a dummy test was carried out, during which no sensitive device was placed inside the cabinet. Instead, thermocouples were installed at critical points and a cheap webcam was aimed at taking images of the inside of the nozzle to verify the presence of dust or other potential problems.
During these trials, temperatures inside the cabinet were continuously recorded. In the same way, the temperature increase of the cooling water was monitored as well as the total flow rate. From these data, the amount of heat to remove was computed and therefrom, a suitable closed circuit cooling unit was defined for the real LIBS tests.
These measurements proved that the temperature inside the cabinet remains compatible with the use of optical elements and electronic devices. Moreover, this trial also confirms the good behaviour of the mechanical parts among which the nozzle as well as the efficiency of the dust removal system.

5.2 Preliminary industrial measurements at ArcelorMittal Ghent

For the first measurement campaign, an implementation minimising the cost and development time has been adopted. Notably, the

TeleLis spectrometer was used and connected to the measuring cabinet by a 10-metre optical fibre. In-house software was developed to start and stop the acquisition, to monitor the remote head temperature, to compute in real time the corrected spectral line intensities (background removal and outlier rejection), to display the spectra and to back-up the collected data. The auto-focus system to take into account variations of the molten metal level in the runner was controlled manually.
During these tests, LIBS measurements were carried out on two casts for a total duration of 9 hours non-stop on the runner. Silicon, manganese, carbon and iron were measured. Each measurement corresponds to 100 laser pulses. For comparison purposes, "Lollipop" samples were taken during the casts.
An example of results obtained during the second cast is given in Figure 5 where the evolution of silicon, manganese and carbon is reported. Compared to the "Lollipop" values, the LIBS measurements are always within the +/-10% margin.

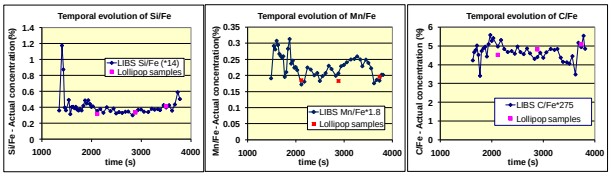

Figure 5: Results of industrial LIBS measurements (1st campaign ArcelorMittal Ghent – 2nd cast).

It is worth noting that the sensitivity of the measurement, even in the UV range, allows quantitative analysis, despite the use of a long optical fibre.
Moreover, beside the good accuracy of the results, it is proved that the measuring system was designed in a way able to withstand the heat and hot metal radiation during long periods of time. Notably, the nozzle resists to extreme temperatures and thermal shocks.

5.3 Industrial campaign at ArcelorMittal Ghent with stand-alone LIBS device

After the good results obtained during the first campaign, a more compact and stand-alone measuring system was designed. Its main features include a more compact but more powerful laser as well as the replacement of the expensive spectrometer by a combination of 3 low cost and compact ones. Finally, hot metal temperature measurement is added by use of the LIBS optics coupled to a near infrared spectrometer and a suitable data processing.
The main aim of this campaign was to check the long term behaviour of the new prototype in conditions where the silicon content varies more largely than during the preceding tests. It was also planned to check the temperature measurement accuracy as well as carrying out some tests on the slag runner.
The LIBS analyses took place during a week for a total time of more than 41 hours on the hot metal runner among which 23 hours without interruption. In this period of time, 8 casts and the cooling down during one intercast were continuously monitored. The tests on the slag runner lasted more than 4 hours.
Since enough silicon concentration variations were observed during these tests, it is possible to calibrate the LIBS measurements with the XRF analyses on "Lollipop" samples taken at the same time. Figure 6 shows the correlation between the LIBS results on molten hot metal and the XRF analyses on the corresponding solid "Lollipop". For comparison purposes, the calibration curve obtained by LIBS measurements at room temperature is plotted in red.
It is worth noting that, compared to measurements on solid samples, the LIBS intensities determined on the liquid phase show a more linear and more sensitive relationship with the actual silicon concentration.
Such a difference in calibration curves at room and elevated temperature has already been reported [10].

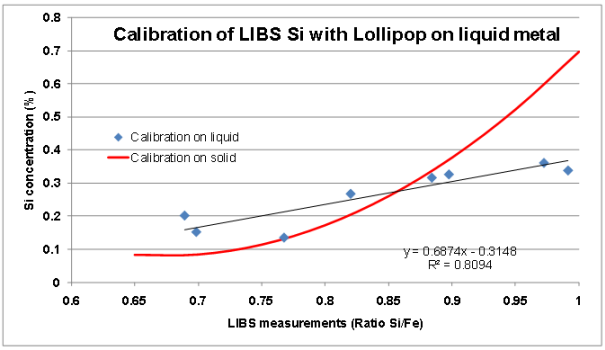

Figure 6: Comparison of calibration curves on liquid and solid phases for LIBS measurements of silicon in the hot metal.

For illustration purpose, Figure 7 shows the comparison of the LIBS analyses of silicon and manganese with the classical measurements (Lollipop and torpedo measurements). As exemplified by the Figure, one interest of the continuous LIBS analysis is that short term variations of the silicon or manganese content can be highlighted while they can be missed by the classical way of analysing, based on one or two samples per heat.
During this trial, limited tests were also carried out on the slag runner. In this case, the important elements for the process are Fe, Si, Ca Al, Mg and Mn. As shown in Figure 8, the sensitivity of the measurements is high enough to allow identifying all main elements with a sufficient signal to noise ratio. If a quantitative analysis is requested, a

calibration procedure should be defined and further tests would probably be needed to this aim.
At the right hand side of the Figure, representing the data from the VIS spectrometer, the large increase of the background emission observed for wavelengths above 500 nm is due to the black body radiation of the slag at the high temperature of the material in the runner. As a consequence, spectral lines in this range are potentially more difficult to process and saturation of the signal can occur more readily.

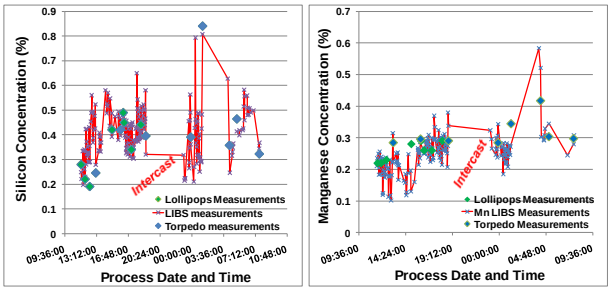

Figure 7: Comparison between LIBS Si and Mn continuous analysis and classical "Lollipop" samples.

Since, for the control of the blast furnace, it is very important to know the temperature of the hot metal, it could be interesting to use the LIBS measuring head and the associated optics to carry out on-line optical temperature measurements directly in the runner. To this aim, the telescope was used to focus an image of the molten metal surface onto a near infrared spectrometer. By an optimised choice of the wavelength, a fairly good relationship between the intensity measured with the spectrometer and the temperature could be obtained. A first result is presented in Figure 9. Except for two outliers, +/- 15°C accuracy could be achieved. Work is currently in progress to improve this result by a suitable calibration of the spectrometer response as a function of the wavelength and data processing involving the whole recorded spectrum.

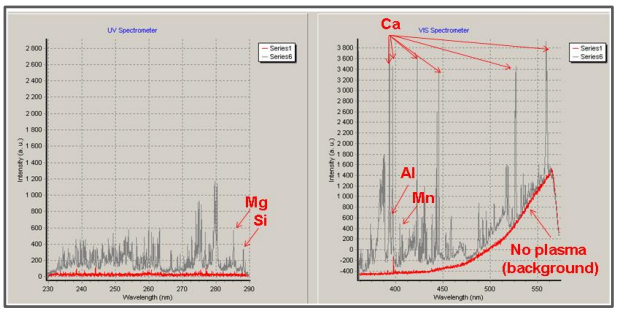

Figure 8: LIBS spectrum obtained on the slag runner. The elements important for the process are clearly identified.

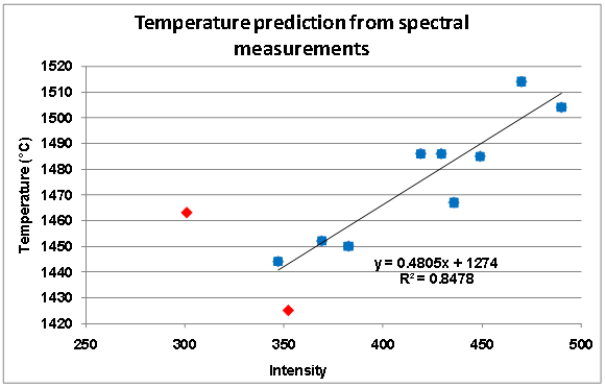

Figure 9: Use of the LIBS light collecting optics to assess the temperature of the hot metal in the runner.

5.4 Testing in harsh conditions at Tata Steel Port Talbot

The blast furnace BF4 at Tata Steel Port Talbot (U.K.) was rebuilt in 2013. The restarting period after a long stop is always rather critical and the conditions are usually extreme in terms of hot metal composition and amount of fumes, solid matters in the runner...
The LIBS prototype was tested in such harsh environment to ensure that the method can withstand nearly all possible conditions being encountered at a cast floor.
During these tests, a new system for cleaning the exit window was in operation and proved to be very efficient to maintain the cleanliness of the optics, despite the sometimes unusual amount of dust.
The measurements confirmed the possibility of LIBS analysis in the runner. However, the main interest of the tests in such exceptional conditions was to give hints for further improvements to the method, among which a new design of the nozzle tip to avoid clogging by solid matters and a better auto-focus system to take into account larger variations of the liquid metal level. A patented method has been developed for this purpose allowing an accuracy of a few millimetres at a distance of 1.5 metre.

CONCLUSIONS

This paper reports the development and results of a LIBS-based measuring system to assess the composition and temperature of the hot metal and slag in the blast furnace runners. The procedure followed for the design of an industrial prototype is described.
The research work started by experiments in the laboratory on solid samples, in order to determine the sensitivity of the measurement in conditions similar to what is expected at the blast furnace cast floor. A second step consisted in proving the feasibility on molten metal at 1500°C thanks to the availability of the pilot facilities of the CRMGroup.

Finally, several test campaigns were carried out at industrial sites. The results have proved the possibilities of the LIBS method to allow accurate measurements in harsh environment. The assessment of the silicon, manganese and carbon content of the hot metal could be done for long periods of time with accuracy compatible with the requirements of the blast furnace process control. Moreover, elements important for the process, like Ca, Si, Al, Mg, Fe, could be identified on-line in the slag runner.
Finally, the collecting light optics of the LIBS system can also be used, coupled with an NIR spectrometer, to continuously measure the temperature of the hot metal in the runner.
It is worth noting that the company TMT, industrial member of the CRMGroup, has been licensed to commercialize the LIBS technology applicable to the blast furnace and is currently developing the industrial version of this equipment.

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