On-line Chemical Analysis in an Aluminium Recycling Plant using LIBS Technology and Automation

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Abstract

We report on the implementation of fully automated chemical composition analysis in an aluminium recycling plant. The system is based on robotic extraction of liquid alloy from a furnace sidewell, followed by automated chemical analysis using laser-induced breakdown spectroscopy (LIBS). We will discuss the system configuration, analytical capabilities, cycle times, long-term drift, laser safety, and other practical considerations for industrial implementation of LIBS technology. On-line chemical analysis improves plant safety and offers new opportunities for casthouse process control by providing immediate feedback and frequent data points.

Keywords: LIBS, Chemical composition analysis of liquid aluminium, Casthouse process control, Industry 4.0, Process automation.

1. Introduction

Recycling of aluminium plays an increasingly important part in global aluminium industry. Even as production increased from 20 Mt in 1980 to 100 Mt in 2020, the share of recycled aluminium grew from 20 % to 30 % and is projected to reach 50 % of an approximately 170 Mt global production in 2050. Initially, most of the recycled aluminium using in production was pre-consumer scrap. Since 1990, however, the share of post-consumer scrap has exceeded that of pre-consumer scrap [1]. With an increasing share of recycled input into the production process comes an increased uncertainty of the chemical composition, especially in the case of post-consumer scrap. Although high-throughput sensor technologies are increasingly being applied for improved sorting of solid scrap before melting [2] there will still be impacts from incomplete sorting, foreign objects, coatings, etc., into the production process. Once introduced into the melt, most impurities are difficult to remove and may therefore make it impossible to meet the desired targets in alloy production without dilution with primary metal or known alloys. Tight control on melt chemistry during melting is therefore essential when maximizing the use of mixed scrap in production.

In the aluminium industry, melt chemistry has traditionally been monitored by manually extracting samples of the liquid metal and casting them into moulds for laboratory analysis. In some cases, smelters have container labs close to the sampling points with built-in automation for sample preparation and handling. The chemical analysis itself is most often performed using the method of spark optical emission spectroscopy (spark-OES), also referred to as spark atomic emission spectroscopy (spark-AES). The measurement instrument itself is sometimes referred to as a quantometer or simply a spark-OES. The manual handling of molten metal puts plant operators at risk and while high-end quantometers can be highly accurate, it has been shown that the main sources of measurement uncertainty in an industrial situation arise from the sample collection, preparation, and handling, rather than the measuring instrument itself [3].

In recent years, automated laser-induced breakdown spectroscopy (LIBS) has emerged as an alternative to more conventional methods of chemical analysis. LIBS is suitable for analysis of materials in the solid, liquid, or gas phase [4]. Furthermore, it is suited for deployment in harsh environments [5] and its potential for production control in the metals industry has long been recognized [6]. We have previously reported on the industrial applications of LIBS analysers for primary aluminium from reduction cells [7] and transport crucibles [8], as well as laboratory tests on various aluminium alloys [9]. In the present paper, we describe automated sampling and analysis of liquid alloys from an aluminium recycling furnace.

2. System Description

DTE's sampling and analysis system consists of a foundry-grade robot that collects liquid metal from an open side pocket of a recycling furnace and a non-immersive LIBS analyser that measures the chemical composition of the extracted molten metal sample, as illustrated in Figure 1. After analysis, the sample is returned to the furnace. The full cycle time (collecting a sample, bringing it to the analyser, performing the chemical analysis, returning and discarding the sample) is under 5 minutes. The actual measurement time is 45 seconds.

Figure 1. Automated sampling and chemical analysis system. Left: schematic illustration of a typical setup. Right: a system installed in a recycling plant.

In the LIBS analyser, the laser head approaches the surface of the molten metal. A sequence of focused laser pulses is directed onto the surface, generating a plasma that emits specific wavelengths of light for the different elements present in the sample. Using a high-resolution spectrometer, the spectral fingerprints of each element can be identified and separated from the signal of the host metal. Basic principles of LIBS analysis and device calibration have been described in more detail in a previous paper [8]. The analyser is certified as a Class 1 laser device, meaning that no harmful laser light or emitted plasma radiation escapes the device enclosure.

Figure 2 shows examples of simulated emission spectra for plasma conditions similar to those realized in the LIBS analyser. The calculated emission spectra are derived from the respective energy level configurations and transition probabilities [10], under the assumptions of local thermodynamic equilibrium and an optically thin plasma. For the elements shown here, the atomic emission mostly originates from neutral and singly ionized atoms and primarily occurs in the ultraviolet part of the optical spectrum. When using LIBS to analyse molten aluminium alloys, however, it is important to realize that the above assumptions do not hold for all alloying or trace elements. In the case of magnesium, for example, its electronic structure, activity, volatility, and oxygen affinity all play a role in shaping the observed LIBS spectrum [11, 12]. DTE has developed proprietary patent-pending measurement techniques to eliminate the resulting dependencies on melt temperature and melt chemistry to enable accurate Mg analysis. Additionally, numerous studies have been performed showing that the upper concentration limit of LIBS analysis in the molten metal is limited only by the solubility of a given element in the melt at a given melt temperature [13–15], as opposed to spark-OES analysis of cast samples where phase segregation may prevent accurate analysis at high concentrations.

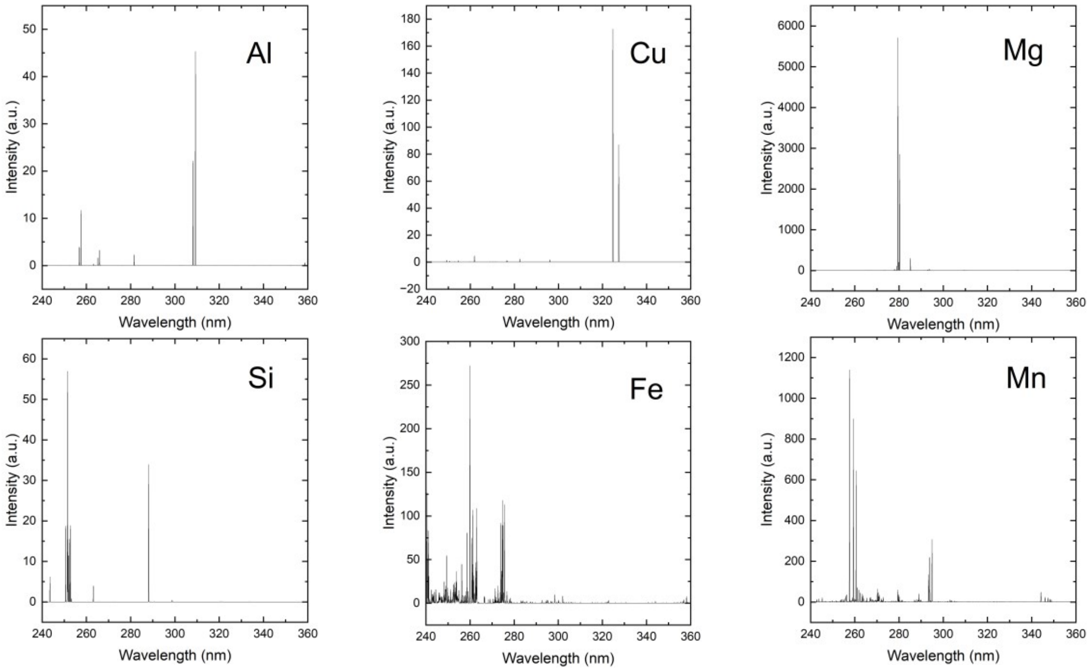

Figure 2. Calculated emission spectra of aluminium and common alloying elements.

3. Stability of Analysis

The analytical stability of the LIBS analyser was tested for a 3-month period in the factory before implementing the automated sample retrieval system. Throughout this period, 100 molten-metal samples corresponding to the chemistry of a 6000-series wrought alloy were measured in the LIBS analyser. After each analysis, a solid sample was cast from the same melt and analysed using the smelter's standard spark-OES laboratory equipment. As shown in Figure 3, agreement between the two methods was maintained throughout the test period. The relative standard deviation of differences between the LIBS and OES results shown in Figure 3 was close to 3 % of the measured concentration for Si, Ti, and Cr, 4 % for Fe and Cu, and 5 % for Mn. These values are related to measurement variance in both the OES analysis and the LIBS analysis.

During the 3-month test period, the spark-OES was regularly standardized using certified reference materials. Conversely, no recalibration or standardization of the LIBS analyser was required during the same period. This can be understood when the different methods of plasma generation are considered. In the former case, the plasma is generated using a spark electrode that erodes slightly on each measurement, changing the subsequent conditions for plasma generation. In the latter case, however, the plasma is generated by the laser pulses alone and no physical change is induced with each laser pulse. Furthermore, the liquid sample is not permanently modified by the laser ablation, unlike LIBS analysis of solid samples [16]. Of course, other factors can influence the stability of both LIBS and spark-OES analysis in the long term and periodic drift monitoring of any analytical device is always recommended.

With the automatic sampling equipment shown in Figure 1, the sampled metal starts cooling down as soon as it is extracted from the furnace. Furthermore, the melt temperature in the furnace can vary. Consequently, it is of importance to know how stable the LIBS analysis is with respect to changes in the sample temperature. A separate test was conducted on an identical LIBS analyser equipped with induction heating (see device description in Ref. [17]). This confirmed that the LIBS analysis was stable for melt temperatures in the range 680–750 °C, i.e. that in this temperature range the variation in the measurement results obtained at different melt temperatures was within the degree of measurement uncertainty. This was found to be true both for tests made at a stable sample temperature and tests made where samples were allowed to cool down during the measurement cycle from different starting temperatures.

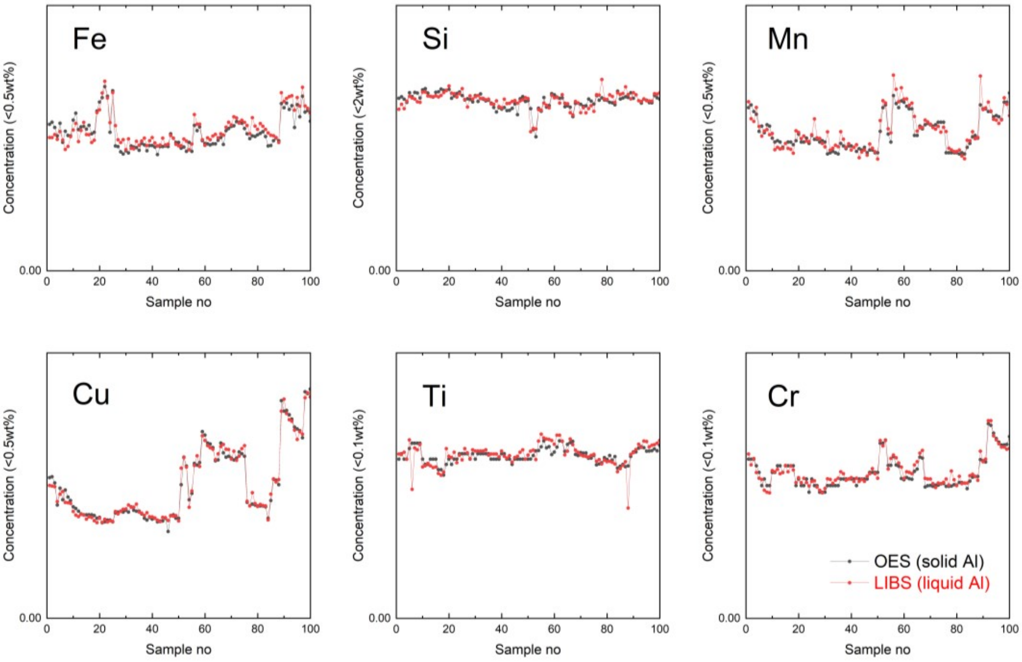

Figure 3. Comparison between molten-metal LIBS analysis and OES laboratory analysis for several of the analysed elements. Absolute concentration values have been removed at the customer's request.

For a non-immersive LIBS measurement system such as the one used here, it is also important to confirm that the chemical analysis is not affected by the sample handling time, due to the formation of oxide layers on the molten metal surface. The speed of oxide layer formation and its chemical composition is dependent on the composition of the alloy, in particular its magnesium concentration [18]. Tests were performed with a 5000-series alloy using the abovementioned system maintaining a stable sample temperature. It was shown that waiting times of up to 15 minutes from sampling to measurement did not adversely affect the measurement results (no significant change in average value or measurement variance), confirming that the action of the laser ablation is sufficient to immediately remove any oxide layer formed in the time span from the extraction of the sample from the furnace side-well to the delivery to the analyser by the sampling robot.

4. Continuous Operation

After installation, the automated sampling and analysis system (Figure 1) was operated on four consecutive day shifts, monitoring the melt chemistry in the recycling furnace every 10–15 minutes. A total of 200 samples were collected for comparison with laboratory data, obtained from spark-OES samples that were collected separately at 1–2-hour intervals, using conventional methods. During the test period, the melt composition in the furnace corresponded approximately to that of a 5000-series alloy. The composition was relatively stable, with concentrations of the measured elements varying no more than 30 %.

During the test period, the agreement between the automated LIBS analysis and the offline laboratory analysis was maintained (no standardization of the LIBS analyser performed during the test period). For the non-volatile elements, the coefficient of variation (CV) of the difference between the two sets of results (LIBS vs. OES) was approximately 2–4 % of the measured concentration, as shown in Table I (higher CV was observed for lower elemental concentrations, as expected). The analysis of Mg in the 5000-series alloy showed a higher CV of ≈6 %, larger than was observed in low-Mg alloys. The observed relative error is about two times larger than typical OES coefficient of variance for process samples. A moving average of 2-3 data points would make the CV of LIBS analysis comparable to the laboratory analysis, at the cost of reduced time resolution, assuming normally distributed results.

Table I shows the relative standard deviation of differences between LIBS and OES analysis during automated analysis. These values are only representative, in each case the relative standard deviation depends on several factors, including the concentration of the element, the alloy type, the intensity of LIBS signals, the measurement time, and properties of the detection system. Zr concentration in the melt was too low to accurately determine the Relative Standard Deviation (RSD).

Table 1. Relative standard deviation of differences between LIBS and OES

Element	**RSD Δ(LIBS-OES)**	**RSD, 3-point moving average**
Mn	2.6 %	1.5 %
Fe	1.8 %	1.0 %
Si	4.3 %	2.5 %
Cu	4.5 %	2.6 %
Cr	2.4 %	1.4 %
Ti	4.0 %	2.3 %
Ni	3.9 %	2.3 %
Zr	n/a	n/a
Mg	6.3 %	3.6 %

The deviation between OES and LIBS analysis of magnesium concentration did not show a significant correlation with furnace temperature (±30 °C temperature variation), which is consistent with the previously mentioned tests of melt temperature dependence on the LIBS analysis.

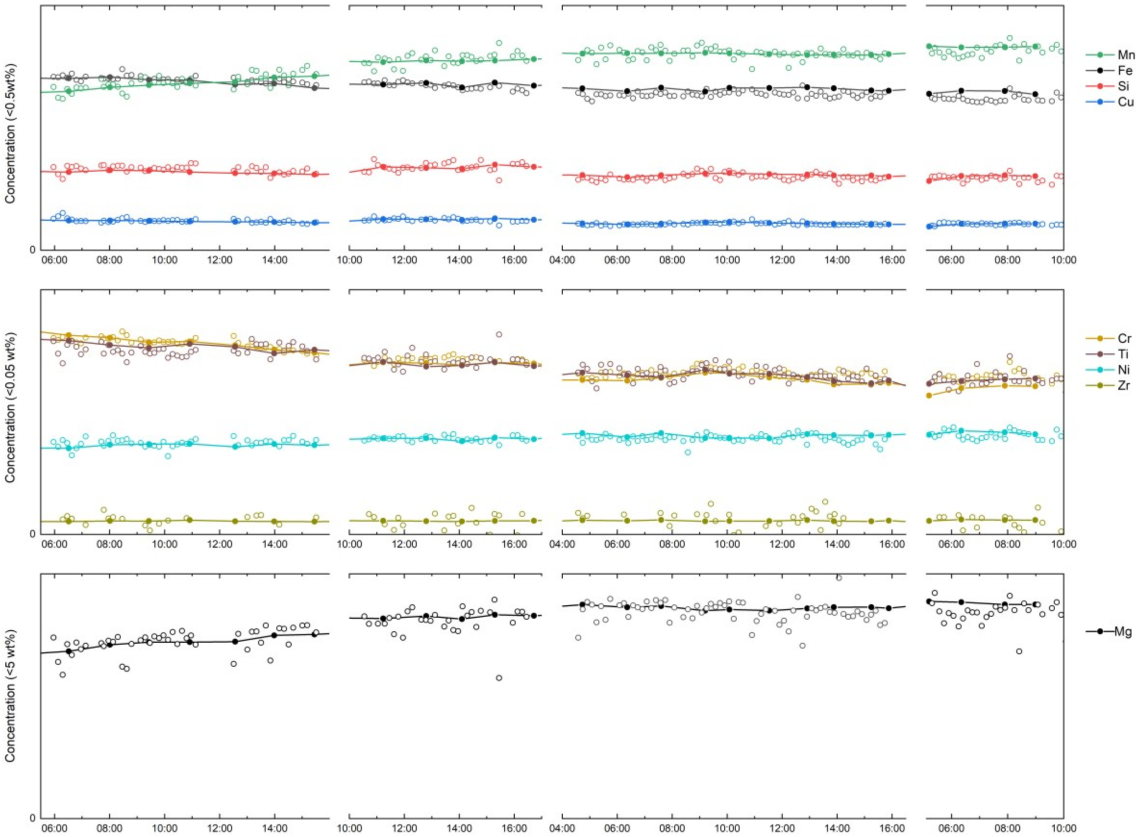

Figure 4. Results from fully automated chemical composition analysis of a recycling furnace (open symbols) compared with laboratory analysis of spark-OES (closed symbols). Absolute concentration values have been removed at the customer's request.

5. Conclusions and Future Work

We have demonstrated the applicability of automated molten metal sample retrieval from a side-well furnace, coupled with real-time LIBS analysis of chemical composition. The concentration of alloying and trace elements was monitored at 10–15-minute intervals, but more frequent analysis is also possible. In separate tests, the LIBS analysis was shown to be stable for several months without standardization, as well as being shown to be independent of melt temperature and insensitive to surface oxidation. For non-volatile elements, the coefficient of variance in the LIBS analysis was 2–4 %, which is about two times higher than typical values for spark-OES analysis for the same elemental concentrations, which can be compensated for by using a 3-point moving average of data points. Future work will focus on further reducing the measurement variance, particularly for magnesium in high-Mg alloys. In summary, the automated LIBS analysis yields rapid immediate analysis results (within 5 minutes from sampling), requires minimal standardization, and eliminates the personnel risks associated with manual sampling of molten metal from furnace.

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