Instant Monitoring of Aluminum Chemistry in Cells Using a Portable Liquid-metal Analyzer

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Abstract

A portable analyzer for monitoring the aluminum chemistry in production cells is presented. With the portable battery-powered device, trace element concentration analysis can be obtained within 45 seconds of manually extracting a liquid metal sample from the cell. The device uses laser-induced breakdown spectroscopy (LIBS) to directly analyze the composition of the liquid metal, down to concentrations of approx. 10 ppm for a range of elements. We compare the performance of the portable analyzer with conventional off-line laboratory analysis of cast process samples. In addition to the significant time savings and reduced chance of human error, we show that direct analysis in the liquid metal is particularly advantageous in the case of trace elements that display significant segregation upon solidification, such as silicon.

Keywords: LIBS, aluminum, process technology, chemical analysis

Introduction

Real-time monitoring of the status of reduction cells is receiving increased attention, including analysis of cell temperature and bath chemistry [1], individual anode current signals [2], cell voltage noise [3] and the multiple additional parameters affecting the current efficiency, energy consumption and operational lifetime of the cell [4]. Differential thermal analysis has been successfully applied to determine bath chemistry, i.e. bath ratio and Al_2O_3 content within a few minutes using, e.g., the commercially available STARprobe[TM] [1], replacing the alternative time-consuming sample preparation and X-ray analysis in a central laboratory. Chemical analysis of solid samples of bath material using laser-induced breakdown spectroscopy (LIBS) has recently been reported, where a direct measurement of the molten electrolyte was also attempted [5]. In this case, the bath ratio is inferred (assuming the absence of significant matrix effects) from the intensities of atomic emission lines of Na, Al and O. LIBS is an atomic emission spectroscopy technique, applicable to the measurement of liquids and solids, both conductive and non-conductive [6]. It has previously been applied to measure the impurity content of liquid aluminum [7-10]. Sun et al. [5] mounted a LIBS probe directly onto a reduction cell, thereby measuring bath chemistry and aluminum chemistry with a single instrument, but the device could not be calibrated due to the influence of the external magnetic field on the properties of the excitation laser. While compact hand-held LIBS analyzers for, e.g. metal sorting applications, are available from several vendors, they are not suitable for analyzing liquid metal and do not provide the detection limits or accuracy required for monitoring aluminum from reduction cells. Here, we present the first fully portable LIBS-based analyzer that provides in-situ concentration measurements directly on liquid aluminum in less than one minute, providing the missing link in enabling complete real-time characterization of reduction cell chemistry.

Potroom implementation

The portable liquid metal analyzer (EA-1000, DT-Equipment), shown in Figure 1, was tested in Century Aluminum's potroom (Grundartangi, Iceland). In the current configuration, the battery life of the analyzer for regular operation was up to 6 hours. The analyzer is non-immersive and has no consumables, except for argon gas. Thousands of measurements can be performed using the 5L Ar cylinder shown in the figure. During the testing, the analyzer was transported between cells on a pushcart, as shown, but the unit can also be readily mounted on a motorized vehicle.

Figure 1. Portable liquid metal analyzer.

During the testing period, extending over three days, aluminum samples were extracted from a number of different reduction cells, for a total of 56 unique samples. Reference samples were separately extracted and cast into standard molds for laboratory (spark-OES) analysis. The sampling sequence for the portable analyzer is illustrated in Figure 2. A sample is extracted using a standard ladle and poured into a second ladle clamped to the analyzer platform. The measurement head automatically approaches the liquid metal surface. The time interval for the actual concentration measurement was around 15 seconds in the present configuration. The head retracts automatically, measurement results are displayed on-screen and filed to a database. After analysis, the sample can be discarded or stored for reference.
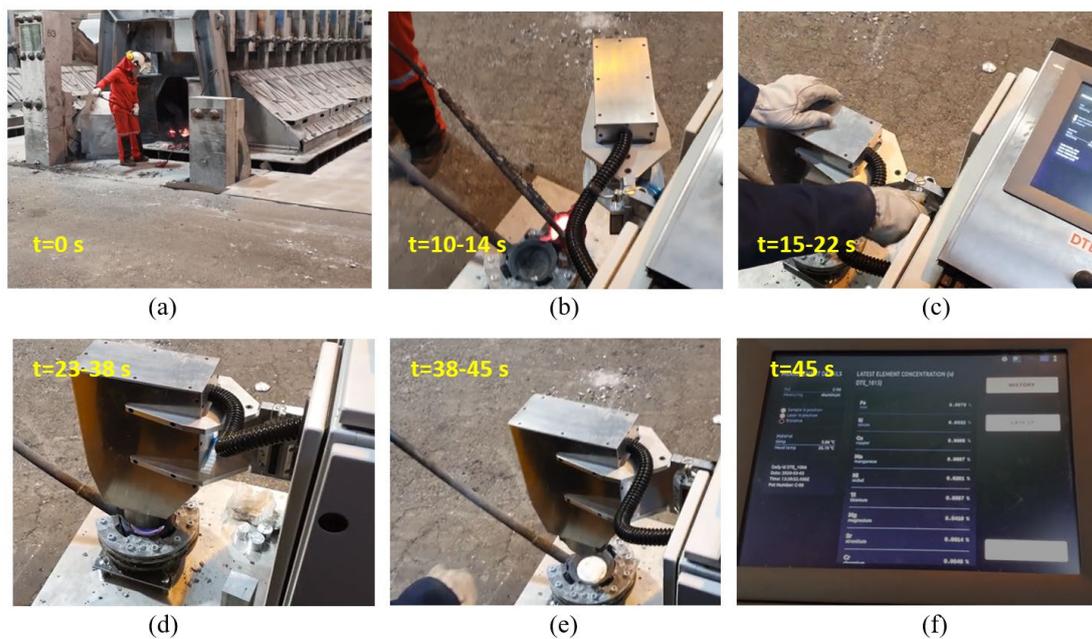

Figure 2. Timing the operation of the portable LIBS analyzer: (a) Liquid metal sample extracted from reduction cell. (b) Metal transferred to the portable analyzer. (c) Measurement head moved into position. (d) Laser excitation. (e) Measurement head retracting. (f) Chemical analysis completed.

Results

Portable analyzer measurements on Fe in the liquid aluminum samples are shown in Figure 3 and compared with laboratory measurements on the reference samples. The observed correlation coefficient between the analysis in the liquid metal and the reference measurements was R=0.985 in the case of Fe. The error bar in Fig. 3 indicates the level of agreement ($\pm 1\sigma_\Delta$, $\sigma_{\Delta,Fe}$=86 ppm) between the in-situ analysis and the reference laboratory analysis. For a more detailed discussion on this parameter, see Ref. [12].

It should be noted that measurements on multiple samples extracted in sequence from the same pot (not shown here) revealed a variation between samples that was larger than the variation in measurement results within each sample. Comparing results from the portable analyzer with separately collected reference samples therefore introduces an additional random error that will affect the correlation between in-situ measurements and the corresponding reference measurements. This is supported by the fact that previous LIBS measurements on molten aluminum have been shown to give correlations with reference samples exceeding R=0.997 for Fe, Si, Mn, Ti and Cr, when the reference samples were cast from the exact same melt sample [11].
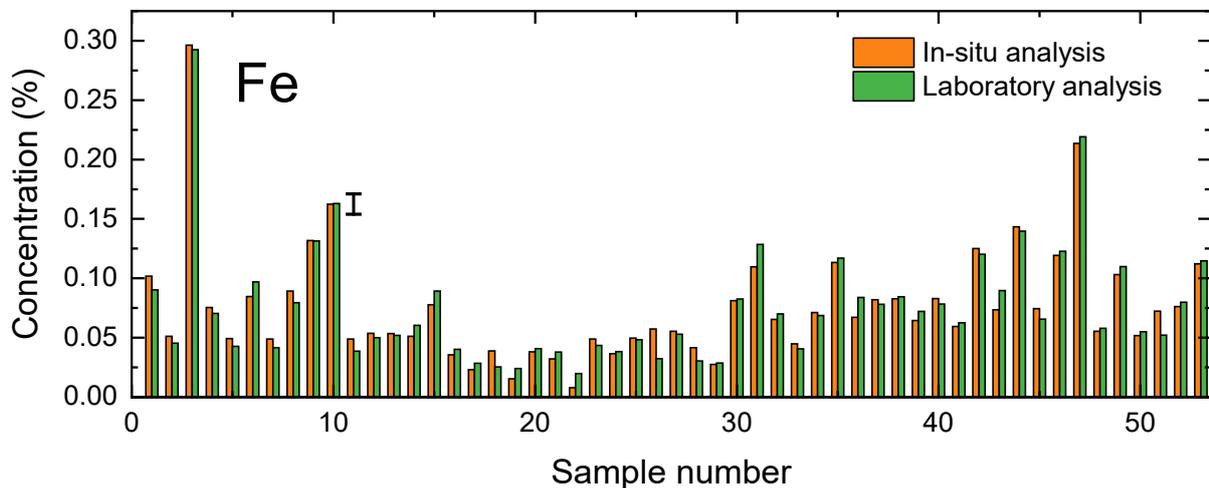

Figure 3. Comparison of Fe concentration measurements carried out with the portable liquid metal analyzer and reference concentration measurements performed with spark-OES. The error bar indicates the level of agreement between the two measurements.

A similar analysis was carried out for the Si concentration of aluminum in the reduction cells, as shown in Figure 4. The measured concentration of silicon was typically around 300 ppm. The correlation between in-situ and laboratory analysis was found to be lower than in the case of iron (R=0.895), which can be attributed to the narrower concentration range and higher uncertainty in the reference measurements (average %RSD in the spark-OES measurements was ≈7% for Si but ≈2% for Fe). The level of agreement between the in-situ analysis and the laboratory measurements, indicated by the error bar in Fig. 4, was $\sigma_{\Delta,Si}$=30 ppm (where the observed internal uncertainty on the spark-OES measurements, %RSD≈20 ppm clearly plays a significant role).
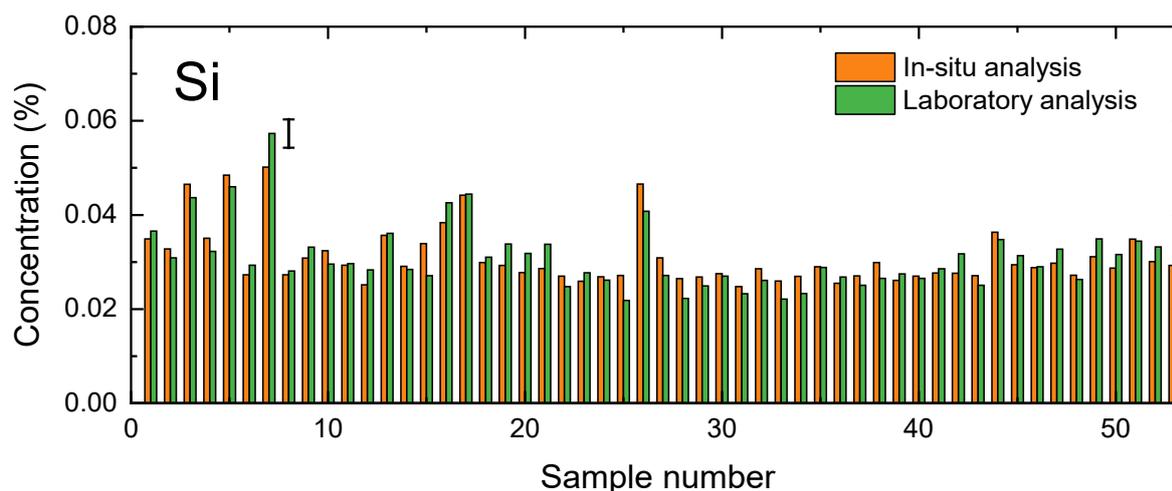
Figure 4. Comparison of Si concentration measurements carried out with the portable liquid metal analyzer and reference concentration measurements performed with spark-OES. The error bar indicates the level of agreement between the two measurements.

Several other elements in the pot samples were measured with the portable analyzer, as listed in Table I. These elements are present in considerably lower concentrations than Fe or Si, as expected. LIBS analysis on liquid aluminum using comparable (stationary) equipment has previously shown that accurate measurements of trace elements in molten aluminum can be performed down to single ppm levels [9-11]. When performing in-situ measurements using the portable analyzer, we find that the level of agreement with reference measurements is typically in the 4-13 ppm range for the presently investigated trace elements. In a sense, this can be taken as an indication of the limit of quantification (LoQ) for the present configuration of the portable analyzer, for each particular element. Additional data is required, including measurements of samples with intentionally added impurities, in order to establish wider calibration ranges and conclusively determine detection and quantification limits as well as confidence limits for prediction for the portable analyzer. This work is underway and the results will be published elsewhere.

Table I. Concentration range and difference between in-situ LIBS analysis and spark-OES reference measurements for the investigated elements.

Element	Approx. conc. range (ppm)	LoQ estimate (ppm)
Fe	200-3000	90
Si	200-600	30
Ga	30-100	13
Zn	70-100	5
Mg	10-60	13
Ni	10-60	10
Cu	10-30	3
Ti	5-40	7
Mn	5-25	6
Cr	1-15	4

Conclusions

We have demonstrated the first, to our knowledge, systematic quantitative in-situ chemical analysis of iron and silicon in aluminum directly from reduction cells using a portable element analyzer. The presence of other minor elements in the potroom samples has also been identified and their approximate quantification limits established. A number of changes can be made to the present device and measurement configuration in order to increase sensitivity and accuracy in the detection of the minor elements, paving the way towards complete characterization of real-time melt chemistry during aluminum production.

Acknowledgements

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