Plant-Floor Chemical Composition Analysis of Liquid Aluminum

Kristján Leósson
Chief Scientific Officer, DTE ehf., Reykjavik, Iceland
Corresponding author: kristjan.leosson@dte.ai

Abstract

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Recent progress in chemical composition analysis of primary aluminum and aluminum alloys in the liquid state using laser-induced breakdown spectroscopy (LIBS) will be discussed. The company DTE has developed first-in-industry elemental analyzers for plant-floor operation in aluminum smelters. This includes semi-automatic portable analyzers for use in primary aluminum production, and fully automatic stationary analyzers applicable to secondary production and aluminum recycling. Here, the use of portable liquid-metal elemental analyzers for monitoring reduction cells in primary aluminum smelters will be described. Instantly available chemical composition information on the plant floor allows for faster decision making and improved process control. Furthermore, the transfer of data from the portable analyzers to a machine-learning driven data platform has been demonstrated, providing predictive insights, e.g., for reduction of tap-out risk. In addition to process monitoring applications, direct chemical analysis of liquid metal analysis also offers new opportunities in fundamental research into melt dynamics.

Keywords: Aluminum electrolysis, LIBS, Chemical composition analysis of liquid aluminum.

1.   Introduction

The aluminum industry relies on chemical analysis throughout the entire production chain, from the electrolysis process through alloying, modification, refining, and recycling. Since the 1970s, spark optical emission spectroscopy (spark-OES) has been the dominant chemical analysis technique in the industry, allowing rapid analysis of multiple trace and alloying elements simultaneously. In spark-OES analyzers, a plasma is induced by electrical breakdown across a small gap between the electrically conductive sample and an electrode. Spark-OES (like other atomic emission spectroscopy techniques) offers only *comparative* analysis and must therefore be standardized against known reference samples, unlike the much more time-consuming *definitive* analysis methods, based mainly on wet chemistry [1].

Another atomic emission spectroscopy technique, developed soon after the invention of the laser in the 1960s, involves inducing a plasma using laser light. It is nowadays typically referred to as laser-induced breakdown spectroscopy (LIBS) [2]. In LIBS analysis, high-energy laser pulses are focused on the surface of a sample, which does not have to be electrically conductive. Laser ablation and laser-induced plasma formation generates atomic (and, in some cases, molecular) optical emission containing chemical information about the sample.

The potential of generating laser-induced plasma for chemical analysis on the surface of liquid metal was realized early on [3], and many pilot projects across different metals industries using LIBS technology have since been conducted [4], including measurements directly on reduction cells [5]. In recent years, DTE has performed extensive validation of LIBS analysis in primary aluminum smelters, using both fully automatic stationary analyzers [6] and semi-automatic portable analyzers [7], confirming that LIBS offers a possibility to transfer chemical analysis for process control out of the laboratory and onto the plant floor, even in the challenging environmental conditions of primary aluminum smelters.

2. Experimental

2.1 Measurement Principle

Chemical analysis of liquid aluminum sampled directly from reduction cells in different smelters was carried out on mobile, battery-powered, and wirelessly connected devices (model number EA-1000), typically mounted on a transport vehicle as shown in Figure 1. The device contains the pulsed laser, high-resolution spectrometer, intensified photodetector, timing electronics, and on-board computer for spectral analysis. Furthermore, the system has built-in sensors for monitoring vibration, magnetic field vector, and internal and external temperatures. Stable system operation has been verified at ambient temperatures up to 45°C and magnetic field strengths exceeding 200 Gauss (20 mT).
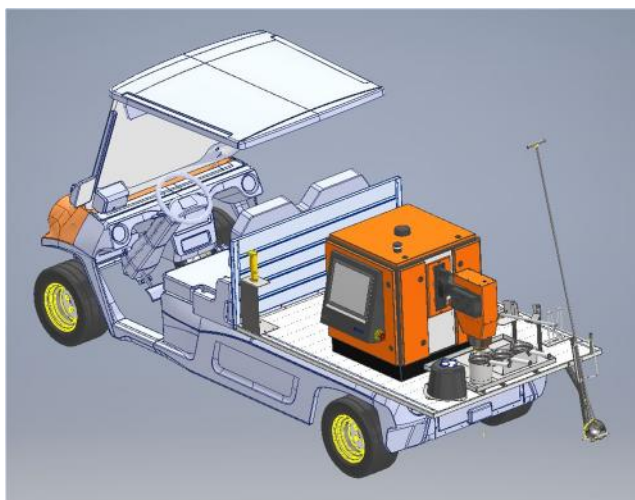

Figure 1. Portable LIBS analyzer mounted on a transport vehicle.

The swivel-mounted measurement head contains a Nd:YAG Q-switched laser module and focusing optics. Before measuring, the head closely approaches the liquid metal surface. In DTE's EA-1000 model portable LIBS analyzer, a measurement is performed by 70 laser pulses of ≈100 mJ pulse energy impinging on the liquid metal surface at a 20 Hz repetition rate (measurement time 3.5 seconds). The resulting plasma emission is collected and transmitted via optical fiber to the high-resolution spectrometer, where it is dispersed and accumulated using an intensified CCD detector. The combination of high spectral resolution and high detector sensitivity ensures that emission signals from individual elements are efficiently separated and detected even at ppm-level concentrations.

Figure 2 illustrates a section of a LIBS spectrum collected by an EA-1000 analyzer, measuring aluminum collected directly from a reduction cell. Although the section shown in the figure covers only a small part of the UVC wavelength range (less than 1% of the full spectrum collected by the device), it contains many emission peaks that can be used for quantification of Si and Fe in the liquid metal sample. Other sections of the spectrum will contain information about additional elements of interest. The recorded spectrum matches well a calculated spectrum based on tabulated properties of the respective atomic energy levels and transitions [8], using typical values of plasma temperature of 8000 K and an electron density of 5×10^{16} cm^{-3} for the calculation [9], and the expected spectral resolution of the detection system Following standard spectroscopic notation, the calculated emission peaks of neutral atoms are labeled I, while emission peaks from singly ionized atoms are labeled II.

Figure 5. Example screen from DTE's IREAS platform for a hypothetical smelter.

The platform also provides tools for verification of the stability of the LIBS analyzers, including historical data of solid control samples measured with the analyzers, as well as correlation with comparison samples measured using other analysis methods. Furthermore, the environmental and operating parameters tracked by individual LIBS analyzers being used by the plant can be monitored remotely in the platform.

An analysis of potential profitability of implementing real-time chemical analysis and the data processing platform has been presented elsewhere, indicating a potential 1.5-4 % increase in profitability in primary aluminum smelter, mainly due to reduced operational costs [14].

4.   Conclusion

Chemical analysis of molten metal performed in situ promises to radically change process control in the aluminum industry. Analytical performance of LIBS-based molten metal analyzers matching that of current industry practices has been demonstrated for elements of interest. This includes portable LIBS analyzers for monitoring the chemistry of aluminum from reduction cells. Moving the responsibility of chemical analysis from the laboratory to the plant floor and making use of real-time data collection and dynamic data analysis presents new opportunities but also requires organizational changes to extract maximum operational value for the smelter.

5.   References

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