Applications of laser-induced breakdown spectroscopy in the aluminum electrolysis industry

Lanxiang Sun [a,b,c,]*, Haibin Yu [a,b], Zhibo Cong [a,b], Hui Lu [d], Bin Cao [d], Peng Zeng [a,b], Wei Dong [a], Yang Li [a]

[a] *Shenyang Institute of Automation, Chinese Academy of Sciences, Shenyang 110016, China*
[b] *CAS Key Laboratory of Networked Control Systems, Shenyang 110016, China*
[c] *University of Chinese Academy of Sciences, Beijing 100049, China*
[d] *National Engineering and Technology Research Center of Aluminum and Magnesium Electrolysis Equipment, Guiyang 550081, China*

ARTICLE INFO

ABSTRACT

The industrial aluminum reduction cell is an electrochemistry reactor that operates under high temperatures and corrosive conditions. Monitoring the molten aluminum and electrolyte components is very important for controlling the chemical reaction process. Due to the lack of fast methods to monitor the components, controlling aluminum reduction cells is difficult. In this work, laser-induced breakdown spectroscopy (LIBS) was applied to aluminum electrolysis. A new method for calculating the molecular ratio, which is an important control parameter that represents the acidity of the electrolyte, was proposed. Experiments were first performed on solid electrolyte samples to test the performance of the proposed method. Using this method, the average relative standard deviation (RSD) of the molecular ratio measurement was 0.39%, and the average root mean square error (RMSE) was 0.0236. These results prove that LIBS can accurately measure the molecular ratio. Then, in situ measurements of the molten aluminum and electrolyte were performed in industrial aluminum induction cells using the developed LIBS equipment. The spectra of the molten electrolyte were successfully obtained and were consistent with the spectra of the solid electrolyte.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

The aluminum electrolysis industry is a typically energy-intensive industry in China. The electricity consumption of the aluminum electrolysis industry accounts for more than 3% of the total electricity consumption in China [1]. The annual power consumption of a medium-scale aluminum manufacturer in China is approximately 3 billion kW·h [2]. The potential for energy conservation and emissions reductions in the aluminum electrolysis industry is large.

The industrial aluminum induction cell, which is the most important piece of equipment in the aluminum electrolysis industry, is an electrochemistry reactor that operates under high temperatures and highly corrosive conditions [3,4]. The cell parameter measurements and control operations are restricted by the high temperature, highly corrosive fluoride melt, and electromagnetic field in the running cell. As a result, the pot-line amperage and cell voltage are the only parameters that can be measured in real time, causing cell control to be a difficult problem in the aluminum electrolysis industry [3].

The cell contains two substances, aluminum and the electrolyte, and the substances are in lower and upper layers depending on their densities. Usually, the concentrations of impurities in aluminum are analyzed by spark source optical emission spectrometry (Spark-OES), and the compositional concentrations in the electrolyte are analyzed by X-ray fluorescence (XRF) spectrometry. Because hundreds of cells are analyzed every day in a plant and the current process includes time-consuming manual sampling and a sample preparation process, only one measurement is obtained for a cell each day. In situ and fast measurement instruments to determine the aluminum and electrolyte compositions are highly desirable for industrial aluminum induction cells.

Laser-induced breakdown spectroscopy (LIBS) is a versatile elemental analysis technique with applications in many fields, and LIBS can be used on solids, liquids and gases [5–7]. In LIBS, high-power laser pulses are focused on the sample surface to produce a plasma, and the resultant atomic emission light is detected and analyzed. The lack of sample preparation makes this technology ideal for in situ analyses.

In the metallurgical industry, LIBS can be used for in situ monitoring of melt compositions during production, which is one of the most interesting and promising areas in LIBS research [8,9]. The first reported experiment using LIBS on molten metal was performed by Runge et al. in 1966 [10]. As lasers and other optoelectronic devices have become more advanced, LIBS attracted further interest as a tool for melt measurements in the late 1980s [11–14]. Carlhoff and Kirchhoff [15] first reported the application of LIBS on molten steel in a converter. Aragón et al. [16] reported using LIBS on molten-steel surface and obtained a precision of 10% for the carbon content analysis in a concentration

range of 150 to 1100 ppm. Single digit ppm detection limits for C, P and S were achieved by Noll et al. by combining a Paschen-Runge VUV spectrometer, photomultiplier detectors, and a vacuum optical probe that was immersed in a 100 kg steel melt [17,18]. Sun et al. [19] developed a double-pulse LIBS system for in situ analyses of molten steel from a distance of more than 4 m.

In addition to ferrous metals, LIBS has also been used for in situ measurements of elements in non-ferrous metals. Rai et al. [20,21] first developed a fiber-optic LIBS probe to measure the composition of an aluminum melt, and the minor elements, Cr, Cu, Mg, Mn, Si, and Zn, were determined. The Energy Research Company (ERCo) demonstrated this LIBS immersion probe at the Commonwealth Aluminum's foundry [22]. Sabsabi et al. [23,24] developed another LIBS immersion probe to analyze molten zinc. In this probe, the laser head is mounted directly on the LIBS probe without an optical fiber.

The feasibility of applying LIBS to in situ measurements of steel, aluminum and zinc melts has already been confirmed. However, to our knowledge, using LIBS for electrolyte compositional analyses has not been studied. Testing the potential of the LIBS technique to quantify electrolyte compositions is important for promoting LIBS applications in the aluminum electrolysis industry. In this work, we first tested and verified the ability of LIBS to measure the molecular ratio of a solid electrolyte. We proposed a new method for calculating the molecular ratio. Using this method, the average RSD of the molecular ratio measurement was 0.39%, and the average RMSE was 0.0236. These results proved that LIBS can accurately measure the molecular ratio. Then, we used our developed LIBS equipment for in situ measurements of the electrolyte and aluminum melt in industrial aluminum induction cells. The electrolyte melt spectra were successfully obtained and were consistent with those of the solid electrolyte.

2. Method

The main components of the aluminum electrolyte are Al_2O_3, NaF, MgF, CaF, and AlF_3, and other minor components, such as LiF, KF, Fe_2O_3 and SiO_2, may also exist. The molecular ratio, which is defined as the ratio of the number of molecules of NaF to AlF_3, is an important control parameter that represents the acidity of the electrolyte [25]. The molecular ratio is often denoted CR. The molecular ratio can also be expressed as the ratio of the mass fractions, denoted BR. CR can be converted to BR using the following relationship, CR = 2BR. For an

alkaline electrolyte, the BR value is greater than 1.5, and for an acidic electrolyte, the BR value is less than 1.5. The BR value is typically controlled in the range from 1 to 1.5 for acidic electrolytes in industrial aluminum induction cells [26,27]. Currently, the aluminum electrolysis industry generally uses X-ray fluorescence to measure the concentrations of Al, Na, Mg, Ca, F and O and to calculate the molecular ratio [28].

Two forms of elemental Al exist in the electrolyte, i.e., AlF_3 and Al_2O_3. Two methods are typically used to calculate the BR, i.e., deduction from the F content or deduction from the O content. For the former method, the contents of Al, Na, Mg, Ca and F are measured, and the AlF_3 content can be calculated by omitting the other fluorides. For the latter method, the contents of Al, Na, Mg, Ca and O are measured, and the Al_2O_3 content can be calculated by omitting the other oxides. In the latter method, the AlF_3 content can be determined using the Al and Al_2O_3 contents.

We used the following derivation process to prove that the molecular ratio can be directly modeled to minimize the cumulative error introduced by indirect calculations.

The mass fractions of AlF_3, Al_2O_3, NaF and Al are indicated by m_1, m_2, m_3 and m_4, respectively, in the following expression

$$m_4 = m_1\lambda_1 + m_2\lambda_2 \tag{1}$$

where $\lambda_1 = \frac{27}{27+193}$ and $\lambda_2 = 272/(272+163)$. Then, the reciprocal of BR can be expressed as

$$\frac{1}{BR} = \frac{m_1}{m_3} = \frac{m_4 - m_2\lambda_2}{\lambda_1 m_3} = \frac{m_4}{\lambda_1 m_3} - \frac{\lambda_2 m_2}{\lambda_1 m_3} \tag{2}$$

For spectral analyses, the mass ratio of the two components is related to the ratio of their characteristic line intensities. The relationship can be linear or nonlinear. Assuming the relationship is linear, the matrix effect is ignored, and Al_2O_3 is the only oxide, Eq. (2) becomes

$$\frac{1}{BR} = k_1 \cdot \frac{I_{Al}}{I_{Na}} + k_2 \cdot \frac{I_O}{I_{Na}} + k_3 \tag{3}$$

where I_{Na}, I_{Al} and I_O represent the characteristic line intensities of Na, Al and O, respectively, and k_1, k_2 and k_3 represent the linear regression coefficients.
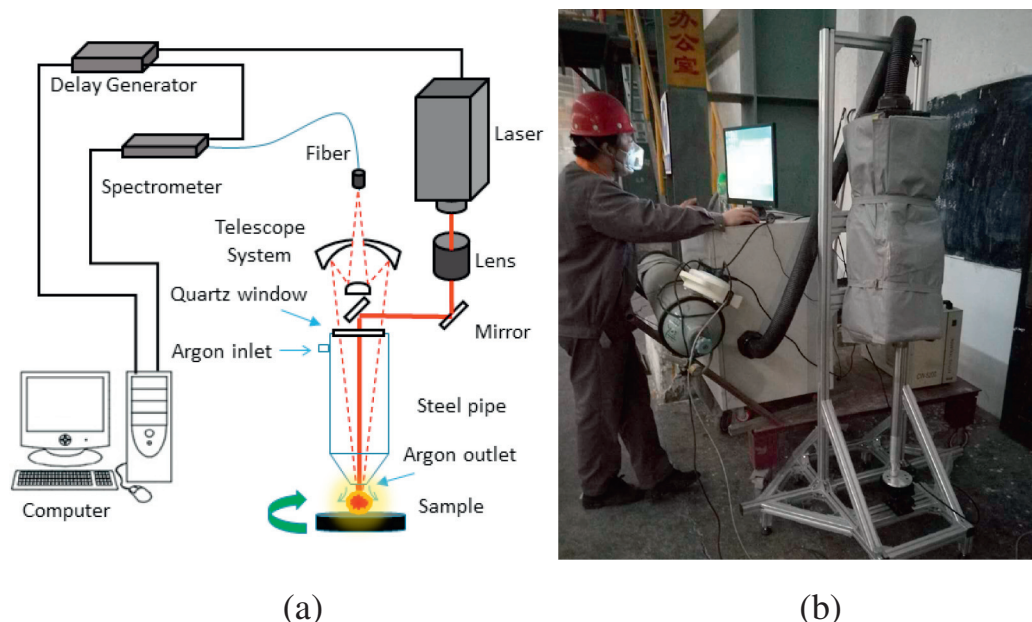

Fig. 1. Schematic diagram of the SIA-LIBS melt analyzer (a), and the setup used in an aluminum electrolysis plant (b).