Comparative study of laser induced plasma spectroscopy and spark-optical emission spectroscopy for quantitative analysis of aluminium alloys†

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Electrical spark-optical emission spectroscopy (OES) has been used for over 50 years for the direct analysis of alloys in the aluminium industry. This method has undergone continual improvement over time, but conventional OES can barely reach the new specification limits required for some critical aluminium alloys. As part of a continuous improvement process, instrument manufacturers, academic and industrial researchers are now showing a particular interest for laser induced plasma spectroscopy (LIPS) as an alternate and/or complementary approach for the analysis of aluminium alloys. In this work, by using the same optical mounting (i.e. same spectrometer model with the same spectral lines), we have directly compared the analytical performances of these two sources. By comparing the calculated concentrations obtained with these two sources using the same samples and the same standards, we show that in general the two sources give comparable quantitative results for major, minor and trace elements. The precision obtained with LIPS is improved by a factor of two when compared to traditional spark-OES. The results obtained in this work establish LIPS as a potential method for the quantitative analysis of aluminium alloys in industry.

Introduction

Many investigations have studied LIPS for the analysis of aluminium alloys.1–15 However, they are often fundamental investigations,10–15 or they do not meet the aluminium industry’s requirements for quantitative analysis of alloying elements in aluminium.1–10 Most of the published LIPS work uses a conventional Czerny-Turner spectrometer coupled with a photomultiplier tube (PMT), intensified photodiode array or charge transfer device (including intensified charge coupled device or interline charge coupled device). An Echelle spectrometer coupled with an intensified charge coupled device has also been used for quantitative analysis of aluminium.9 However, one of the drawbacks of using these types of spectrometer is the limited dynamic range of the detector; gain control is necessary to avoid blooming on major alloying elements. Limiting the gain of the detector reduces the sensitivity for trace elements. The problem can be avoided by selecting different analytical conditions for major and trace elements (for example limiting the spectral window). This situation is hardly compatible with industry requirements for rapid quantitative analysis of more than 25 elements. Furthermore, the industry requires a simple apparatus with a robust methodology for routine quality control analyses.

Paschen-Runge spectrometers can cover broad spectral ranges with high resolution and have individual detectors for each element that can be independently adjusted for sensitivity. Multiple detectors for a single element covering different concentration ranges are common. This type of spectrometer has long been the standard for routine analysis in the industry as it enables single or dual condition analysis for major, minor and trace elements in aluminium. The drawback of these spectrometers is that the optical configuration must be fixed at fabrication and only the raw intensity of emission lines are measured; measurement of the underlying background is difficult.

In this work we compare the analytical performance of two optically equivalent commercially available Paschen-Runge spectrometers; one using a laser-excitation source (LIPS) and one using a traditional spark-excitation source (spark-OES).

Experimental

Instrumentation

All LIPS measurements were performed with a Thermo ARL (Ecublens, Vaud, Switzerland) Laser-Spark 7011 spectrometer. All spark-OES measurements were performed with a Thermo ARL 4460 optical emission spectrometer. Both systems possess a Paschen-Runge 1-meter vacuum spectrometer with a 1080 grooves mm−1 grating optimized at 600 nm and are configured with the same emission lines (Table 1). The Laser-Spark 7011 has a Quantel Brillant ARL type Nd:YAG laser as the excitation source. This laser can supply 5 ns (FWHM) 250 mJ pulses at 20 Hz at the fundamental wavelength (1064 nm). All samples were prepared on a Herzog (Osnabruck, Germany) HN-2F milling machine as normally done prior to spark-OES analysis.

Metallographic studies used a Zeiss (Thornwood, NY, USA) Axioskop optical microscope coupled to a Sony (Lake Forest, CA, USA) Power HAD CCD camera. Image analysis was accomplished with Clemex Vision (Longueuil, QC, Canada) software for dark field metallographic analysis. A JEOL (Peabody, MA, USA) model 840A Scanning Electron Microscope with an acceleration potential of 15 kV was used for SEM analysis. The SEM is equipped with a Kevex (Scotts Valley,
CA, USA) Model EDX-3600 energy dispersive X-ray spectrometer for localized semi-quantitative analysis.

Procedure
Results for the optimisation of conditions and instrument parameters allowing analytical signals to approach the requirements of the aluminium industry were presented elsewhere.\textsuperscript{16,17} The 250 mJ laser beam at the fundamental wavelength is focussed 13 mm behind the sample surface and the diameter of the spot produced is 0.8 mm. These conditions correspond to a laser fluence of around 40 J cm\textsuperscript{2}. During the analysis, an argon (ICP grade 99.999\%) flow of 5 L min\textsuperscript{-1} is maintained in the ablation chamber of both the Laser-Spark 7011 and spark-OES instruments. Also during analysis, the Laser-Spark table rotates the sample table to produce a 5 mm diameter analysis region. The analysis region of the spark-OES is approximately 7 mm in diameter. The analysis conditions on the Laser-Spark 7011 are 8 s argon purge, 10 s surface preparation (200 laser shots) and 15 s integration (300 laser shots). The analysis conditions on the spark-OES are 10 s argon purge, 10 s surface preparation (400 Hz) and 5 s integration (400 Hz). The relative standard deviation (RSD) values were calculated on 3 measurements of 300 laser shots on the sample for the LaserSpark and 5 sparks series on the spark-OES. Furthermore, no measurements were rejected to calculate the RSD.

Results and discussion
In order to compare the laser source with the electrical source systematically, both spectrometers were calibrated with the same set of binary aluminium standards (approximately 250 standards) and used the same analysis algorithm\textsuperscript{18} (a matrix matching technique known as the Alcan master curve method) with two-point standardisation using matrix-matched alloy standards.

LIPS vs. Spark-OES
To evaluate the potential application of LIPS for the quantitative analysis of alloying elements in aluminium under industrial quality control requirements, we have chosen a series of production samples from four different major alloys (approximately 100 samples of 356.2, 3104, 5182 and 6063 alloys).

Fig. 1 displays the comparative analysis of the calculated concentrations by LIPS and OES for Mg and Si as major alloying element (concentrations between 0.1 and 1\% (w/w)). For these three alloying elements, the two methods show excellent agreement for the four alloys investigated.

The comparison of results for Ni, Zn and Ti as trace elements is presented in Fig. 3. The Ni concentration are in good agreement between the two techniques. The LIPS calculated concentration for Zn show a significant spread, primarily because the values are close to the detection limit (0.001\% (w/w)) for the selected excitation conditions.

Table 1 Partial configuration of the two Paschen-Runge spectrometers

<table>
<thead>
<tr>
<th>Element name</th>
<th>Emission line/nm</th>
<th>Diffraction order</th>
<th>Delay/μs</th>
<th>Gate/μs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-H\textsuperscript{a}</td>
<td>382.93</td>
<td>1</td>
<td>8</td>
<td>49 992\textsuperscript{d}</td>
</tr>
<tr>
<td>Mg-L\textsuperscript{b}</td>
<td>285.21</td>
<td>2</td>
<td>8</td>
<td>49 992</td>
</tr>
<tr>
<td>Si</td>
<td>390.55</td>
<td>2</td>
<td>8</td>
<td>49 992</td>
</tr>
<tr>
<td>Fe</td>
<td>371.99</td>
<td>2</td>
<td>27</td>
<td>50</td>
</tr>
<tr>
<td>Mn</td>
<td>343.45</td>
<td>2</td>
<td>27</td>
<td>50</td>
</tr>
<tr>
<td>Ni</td>
<td>341.48</td>
<td>2</td>
<td>8</td>
<td>49 992</td>
</tr>
<tr>
<td>Zn</td>
<td>213.86</td>
<td>2</td>
<td>8</td>
<td>49 992</td>
</tr>
<tr>
<td>Ti</td>
<td>337.28</td>
<td>2</td>
<td>8</td>
<td>49 992</td>
</tr>
</tbody>
</table>

\textsuperscript{a} - H indicates line used for major concentration. \textsuperscript{b} - L indicates the line used for trace and minor concentration. \textsuperscript{c} Time resolved condition only for LIPS spectrometer. \textsuperscript{d} Typical gate time with the use of switch board on PMTs.

Fig. 1 Comparison of concentrations determined by LIPS and OES for two major alloying elements: Mg and Si.

Fig. 2 Comparison of concentrations determined by LIPS and OES for three minor alloying elements: Fe, Mg and Mn.

Fig. 3 Comparison of concentrations determined by LIPS and OES for trace alloying elements.
The calculated concentration for Ti by LIPS is systematically lower than the concentration calculated by OES by a few ppm (see Fig. 3). The reasons for this bias are also under investigation. The Ti in aluminium alloys is usually present as TiB2 particles so several samples were examined metallographically to see if differences in microstructure could explain the bias.

Results obtained for other elements are similar, but the space limitation prohibited their inclusion here.17

Metallographic studies

Optical microscopy of the ablation craters in both LIPS and spark-OES (see Fig. 4) shows a homogeneous phase created at the surface from the rapid solidification of liquid aluminium after the ablation process. Localized EDX analysis with a SEM on the new phase shows that the phase created by the laser source (see Fig. 4b) is extremely uniform. A similar phase is observed under the spark-OES ablation crater (see Fig. 4a) though unlike LIPS craters, there are still traces of intermetallic constituents. The increased homogeneity of the phase in the LIPS crater is due to the higher energy delivered by the laser pulse. It also can account for the better RSDs observed with laser excitation (Table 2).

One can see that LIPS’s average RSD in our optimized conditions16,17 on the Laser-Spark 7011 is about a factor of two better than the OES’s average RSD. Attempts to use smaller sampling regions with laser excitation by decreasing the amplitude of the table rotation leads to increased RSDs compared to the optimized conditions.

Results show that LIPS quantitative analysis of alloying elements in aluminium is comparable to Spark-OES for major, minor and trace concentrations. Metallographic studies of the aluminium constituents under ablation craters show the presence of a new highly homogeneous phase. The metallurgical structure suggests that this new phase is the result of the rapid solidification of the liquid film formed after the laser–matter interaction process.

In a production environment, stability of the measurement system is necessary. The results clearly demonstrate the potential of LIPS as an excitation source for the routine analysis of aluminium alloys in industry. The source of the minor systematic biases observed is being investigated. The extra energy delivered by laser excitation produces a more homogeneous residual phase that can explain the increased precision of the measurements. Evaluation of the technique must continue to consider the benefits obtained versus the increased complexity and potential problems of using a laser as an excitation source in a production laboratory.

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References