

Research Article

One-Point and Multiline Calibration Fiber-Optic Laser-Ablation Spark-Induced Breakdown Spectroscopy for Quantitative Analysis of Elements in Aluminum Alloys

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Rapid and accurate analysis of element concentrations in aluminum alloys is crucial due to their widespread use in modern industry. This paper proposes a one-point and multiline calibration fiber-optic laser-ablation spark-induced breakdown spectroscopy (OP-MLC FO-LA-SIBS) for the quantitative analysis of elements in aluminum alloys. The experimental system utilizes a compact fiber laser as the laser-ablation source and spark discharge to enhance the atomic emission. A portable multichannel fiber spectrometer is used to quickly collect spectra in the nongated mode. The concentrations of four elements (Mg, Cr, Cu, and Mn) in four aluminum alloy samples were calculated using the simple and efficient OP-MLC method, which involves taking another sample with a similar matrix as the standard sample. The average relative errors (AREs) for Mg, Cr, Cu, and Mn were 6.38%, 28.09%, 21.92%, and 18.97%, respectively. When the certified concentrations are greater than 0.02 wt.%, the ARE is only 13.04%. The OP-MLC FO-LA-SIBS system is compact, features simple spectra processing, and offers effective measurement, providing a convenient method for rapid and efficient quantitative analysis of elements in aluminum alloys in industrial production.

1. Introduction

Aluminum alloy, an important composite metal material, is widely used in aerospace, shipbuilding, chemical engineering, construction, and other industries. The contents of micro- or trace elements in aluminum alloys are closely related to their properties. Therefore, monitoring the concentrations of micro- or trace elements in aluminum alloys is essential for quality control of aluminum alloys production or industrial products produced with them. Traditional concentration measurement methods for elements in aluminum alloys include chemical analysis [1–3] and inductively coupled plasma atomic emission spectrometry (ICP-AES) [4]. Although these methods show low detection limits and high measurement accuracy, they require complex chemical treatment for samples, which is timeconsuming and not convenient or efficient for on-site practical applications.

Laser-induced breakdown spectroscopy (LIBS) has numerous advantages, such as rapid multielement analysis, real-time and in situ detection, remote sensing capability, and direct analysis of almost any type of material [5]. Currently, LIBS has been successfully applied in agricultural production [6], biological and medical detection [7, 8], alloy element analysis [9–11], ocean exploration [12], cultural relic identification [13], and more. This method is a good candidate for rapid on-site analysis of micro- or trace elements in aluminum alloys. Generally, LIBS uses a laser with a low repetition frequency as the light source to excite plasma [14, 15]. In order to achieve high sensitivity and faster analysis for alloy elements, researchers have adopted a high repetition rate laser as the light source for more than ten years [16-18]. In our previous works, we developed the high repetition rate laser ablation-spark-induced breakdown spectroscopy (HRR LA-SIBS) technique, which enabled the quantitative analysis of micro- and trace elements in aluminum and copper alloys using a diode-pumped acoustooptically (AO) Q-switched Nd: YAG or a femtosecond laser as the laser-ablation sources [19-21]. These lasers are typically large in size and have poor resistance to harsh environments such as dust, vibration, humidity, and temperature fluctuations, making them more suitable for laboratories and specialized testing environments. To overcome the shortcomings induced by the laser source, we further developed a fiber-optic laser-ablation spark-induced breakdown spectroscopy (FO-LA-SIBS) system using a compact pulsed fiber laser light source. The FO-LA-SIBS system is compact and environmentally suitable, and the detection capacity of elements in aluminum alloys was also demonstrated [22]. However, the complexity of establishing a calibration curve with multiple samples with the same matrix limits its practical application, indicating that a simple and efficient calibration method is further needed.

In terms of calibration methods, many researchers have devoted their efforts to developing them, and numerous calibration methods have been proposed. The relation of light intensity to element concentration is the most commonly used calibration method. However, as we mentioned, this method requires many samples with the same matrix as a reference, which is time-consuming. Another kind of method is the calibration-free (CF) method and its variations [23]. Although the CF method has been widely used in the quantitative analysis of elements in alloys [24], coral skeletons [25], and other samples [26], it is more suitable for analyzing the main elements of samples because it is based on several simplified assumptions of plasma conditions. As for the variations of the CF method, such as the calibration-free inverse method (CF-IM) [27, 28], one-point calibration (OPC) [29], and CSigma method ($C\sigma$) [30, 31], although the results of quantitative analysis can be improved, their algorithms are complicated and time-consuming, which greatly limits their on-site practical applications. In contrast, the one-point and multiline calibration (OP-MLC) method is simpler and more efficient [32, 33]. The OP-MLC does not need to use plasma temperature, electron density, and other experimental parameters, and it only uses a standard sample with a similar matrix to the analytes to implement quantitative analysis for each element. Therefore, using OP-MLC is expected to build an efficient quantitative analysis system for elements in aluminum alloys.

Considering the features of FO-LA-SIBS and OP-MLC, OP-MLC FO-LA-SIBS was proposed for the first time for the quantitative analysis of elements in aluminum alloys, and the feasibility of this strategy was experimentally verified. In this study, five aluminum alloy samples were used, one of which was used as the standard sample, and the others were used as analytes. The concentration of each element was measured. The internal reference line intensity ratio and multiline fitting were used to improve the accuracy. The measured concentrations were compared with the certified concentrations to evaluate and discuss the ability of this method to quantitatively analyze micro- and trace elements in aluminum alloys.

2. Experimental

2.1. Setup. The schematic diagram of the experimental system is shown in Figure 1, which mainly consisted of a fiber laser, a spark discharge unit, and a spectrum recording and analysis unit. The fiber laser used in this study was a compact AO Q-switched Nd: YAG fiber laser (Shenzhen Chuangxin Laser Co., Ltd., model: MFP-30) pumped by a diode. The laser was used as the laser-ablation source to ablate the target sample and generate plasma on the sample surface. The laser had a central wavelength of 1064 nm and could be operated in an adjustable repetition rate range of 30-60 kHz, with a maximum single pulse energy of 0.67 mJ and a pulse width of 50-350 ns. The diameter of the laser beam was approximately 7.5 mm, and the M2 factor of the beam was 1.3. The laser beam was focused on the sample surface using a 10x UV microscope objective lens with a focal length of 15 mm and a numerical aperture of 0.25 (Thorlabs Inc., LMU-10X-266).

In our experiment, the samples were mounted on a selfmade programmable X-Y moving platform that moved at a constant speed of 2 mm/s to allow the laser pulse and spark discharge to act on different positions of the sample. To ensure electrical insulation, a ceramic plate was used to separate the sample from the platform.

The spark discharge unit comprised a direct current (DC) high-voltage power supply (3 kV, 200 mA), two current-limiting resistors $(R1 = R2 = 12.5 \text{ k}\Omega)$, a high-voltage capacitor (5 nF), and a tungsten needle with a 2 mm diameter. The high-voltage power supply charged the capacitor through the current-limiting resistors. The tip of the tungsten needle, which was ground into a cone shape and used as an anode in spark discharge, was installed at a tilted angle of about 45° to the sample surface. The samples themselves served as the cathodes for spark discharge. Once plasma was generated on a sample's surface, the gap resistance between the anode and cathode would decrease dramatically, and the energy stored in the capacitor would immediately ignite by spark discharge, which would further decompose the ablated sample and enhance the plasma.

The spectrum recording and analysis unit consisted of a portable multichannel fiber spectrometer (Avantes, models: 1202156U3, 1202157U3, and 1202158U3) and two quartz lenses: L2 (f= 100 mm) and L3 (f= 150 mm). The light radiation of the generated plasma was collected by L2 and collimated via L3 to the entrance of the fiber spectrometer. The spectrometer recorded the spectrum in the wavelength range of 200–500 nm with three channels (200–317 nm, 317–415 nm, and 415–500 nm). Since the CCD detector of each channel had 2048 pixels, the spectral resolution was better than 0.1 nm. The CCD of the spectrometer was operated in the nongated signal recording mode, and synchronization was not required. The spectral integration time was 1 ms.

2.2. Sample Preparation. Five certified aluminum alloys (Institute of Standard Materials in Fushun Factory of Aluminum, GBW02215, 02216, 02217, 02218, and 02219)



FIGURE 1: Schematic diagram of the OP-MLC FO-LA-SIBS experimental setup.

were selected as the experimental samples in this study. These aluminum alloys contain Al, Mg, Cr, Cu, and Mn as their main elements, and the certified concentration of each element is shown in Table 1. To validate the accuracy of OP-MLC FO-LA-SIBS for quantitative analysis of elements in aluminum alloys, sample No. 3 was selected as the standard calibration sample, while the other four samples were considered as "unknown" analyte samples.

2.3. One-Point and Multiline Calibration Method and Spectra Processing. Assuming that the experiment meets the criterion of stoichiometric ablation, the plasma is in a local thermodynamic equilibrium (LTE) state, and the plasma is uniform in space and time and optically thin, the plasma can be regarded as an ideal state. The spectral line intensity corresponding to the transition of particles between two energy levels can be deduced from the Boltzmann equation [34]:

$$I_{\lambda} = FC_{s} \frac{A_{ki}g_{k}}{U_{s}(T)} e^{-\left(E_{k}/k_{B}T\right)},$$
(1)

where λ is the transition wavelength, I_{λ} is the integral intensity of the spectral line, C_s is the concentration of the particle, A_{ki} is the transition probability, and g_k and E_k are the statistical weight and the energy of quantum state k with respect to the ground state of the emitting species, respectively, F is the experimental parameters, which are related to the instrument system, plasma temperature, and volume, etc., k_B is the Boltzmann's constant, T is the plasma temperature, and $U_s(T)$ is the partition function of the particle when the plasma temperature is T.

According to (1), for two emission lines λ_1 and λ_2 from the same plasma and the same element, their intensity ratio can be expressed as

$$\frac{I_{\lambda_1}}{I_{\lambda_2}} = \frac{A_{k_1 i_1} g_{k_1}}{A_{k_2 i_2} g_{k_2}} e^{-\left(E_{k_1 - E_{k_2}/k_B T}\right)}.$$
(2)

The spectral parameters A_{ki} , g_k , and E_k can be obtained from the National Institute of Standards and Technology (NIST) database according to the wavelength of characteristic spectral lines. Under a certain experimental condition, *T* is approximately constant, and the intensity ratio of two characteristic lines emitted from the same element and the same matrix but different samples can be described as

TABLE 1: List of the concentrations (wt.%) of Al, Mg, Cr, Cu, and Mn in five experimental samples.

Sample no.	Product no.	Al	Mg	Cr	Cu	Mn
1	GBW02215	98.639	1.00	0.15	0.19	0.010
2	GBW02216	98.843	0.81	0.10	0.15	0.051
3	GBW02217	99.062	0.60	0.050	0.10	0.099
4	GBW02218	99.247	0.39	0.010	0.053	0.15
5	GBW02219	99.359	0.21	0.0047	0.016	0.21

TABLE 2: Analytical lines of Mg, Cr, Cu, and Mn and reference line of Al used for multiline calibration (nm).

Elements	Wavelength of the	Reference lines	
	analytical lines (nm)	(nm)	
Mg	277.98, 279.08, 280.98, 291.55, 292.86	Al I 266.04	
Cr	299.51, 303.42, 363.53, 427.48	Al I 308.22	
Cu	222.47, 226.32, 230.95, 287.77, 324.75	Al I 226.92	
Mn	255.86, 259.33, 261.89, 268.74, 274.25	Al I 257.51	

$$\frac{I_{\lambda_1}^a}{I_{\lambda_2}^b} = \frac{C_s^a}{C_s^b} \frac{A_{k_1 i_1} g_{k_1}}{A_{k_2 i_2} g_{k_2}} e^{-\left(E_{k_1 - E_{k_2}/k_B T}\right)},$$
(3)

where the upper subscripts *a* and *b* indicate two different samples. In the case of $\lambda_1 = \lambda_2 = \lambda_x$, A_{k1i1} , g_{k1} , and E_{k1} can be considered equal to A_{k2i2} , g_{k2} , and E_{k2} , respectively. Then, (3) can be rewritten as

$$\frac{I_{\lambda_x}^a}{I_{\lambda_y}^b} = \frac{C_s^a}{C_s^b}.$$
(4)

According to (4), when the concentration of an element in the standard sample is certified, since the value $I^a{}_{\lambda x}/I^b{}_{\lambda x}$ can be obtained by measuring the intensity of the characteristic lines of the standard sample and the analyte sample, the concentration of the same element in the analyte sample can be estimated.

To reduce the error induced by a continuous background and single characteristic line, the intensities of multiple lines emitted by each element in two samples were linearly fitted, and the slope of the fitted line was taken as the concentration ratio of the analyte sample to the standard sample. As the OP-MLC method is based on the assumption of optical thinness, to ensure the accuracy of measurement results, the spectral lines which were not easy to self-absorb and did not suffer overlapping spectral interference were selected. Besides, the internal standardization method based on the intensity ratios of spectral lines of analytical elements and reference elements were adopted, in which the weak lines of the matrix element Al were used as the reference line, which would be beneficial to reduce the influence of the laser power change of FO-LA-SIBS system and the error in spectra acquisition on the measurement results. The content of the main element Al in the five samples is approximately equal, and thus under the same experimental conditions, the spectral line intensities of Al for all samples approximately remain constant. For the above reasons, the analytical lines of Mg, Cr, Cu, and Mn and the reference line of Al used for multiline calibration were selected, as listed in Table 2.



FIGURE 2: Functional relationship of normalized intensity of elements between four analyte samples and the standard sample: (a) Mg, (b) Cr, (c) Cu, and (d) Mn.

3. Results and Discussion

The multiline normalized intensities of the selected spectral lines in Table 2 are fitted, as depicted in Figure 2. Since sample No. 3 was selected as the standard calibration sample, the linear fitting functions of the elements in sample No. 3 are y = x. Figure 2 illustrates the excellent linear relationship between the normalized intensities of multilines of the four elements Mg, Cr, Cu, and Mn in the four analyte samples No. 1, 2, 4, and 5 and the standard sample, with *r*-squares higher than 0.96.

The slopes of the fitting lines in Figure 2 were taken as the concentration ratios of the analyte samples to the standard sample, as per the analysis in Section 2.3. Hence, the concentration of each element in the four analyte samples was estimated. Table 3 lists the estimated concentrations and relative errors (REs) of the four elements in the four analyte samples. Three or four decimal places are reserved for the

values of the estimated concentrations, and two decimal places are reserved for the values of REs. The results demonstrate that the average relative error (ARE) of the element Mg is 6.38%, which is the smallest among the four analytical elements. The AREs of Cr, Cu, and Mn elements are 28.09%, 21.92%, and 18.97%, respectively. Most REs are less than 20%, indicating the feasibility of OP-MLC FO-LA-SIBS in the quantitative analysis of elements in aluminum alloys.

Figure 3 intuitively depicts the correlation diagram of the measured concentrations and the certified concentrations for all elements, and most data points are near the line y = x, indicating that the measured results agree well with the certified concentrations.

To assess the capability of OP-MLC FO-LA-SIBS for quantitative analysis of micro- and trace elements in aluminum alloys, the REs corresponding to the certified concentrations of all analytical elements are plotted in Figure 4.

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Sample	Element	Measured concentration (wt.%)	Certified concentration (wt.%)	Relative errors (%)
1	Mg	0.927	1	7.32
	Cr	0.103	0.15	31.26
	Cu	0.154	0.19	18.83
	Mn	0.013	0.01	32.25
2	Mg	0.788	0.81	2.68
	Cr	0.091	0.1	9.23
	Cu	0.137	0.15	8.99
	Mn	0.043	0.051	16.36
4	Mg	0.419	0.39	7.40
	Cr	0.012	0.01	20.24
	Cu	0.043	0.053	19.00
	Mn	0.138	0.15	7.97
5	Mg	0.227	0.21	8.12
	Cr	0.0071	0.0047	51.62
	Cu	0.023	0.016	40.85
	Mn	0.169	0.21	19.30







FIGURE 3: Comparison of element concentrations measured by OP-MLC FO-LA-SIBS with the certified concentrations in aluminum alloy samples.

The results show a clear negative correlation between the RE and the concentration of elements. When the concentration of elements is below 0.02 wt.%, the ARE is 36.24%, but when it is higher than 0.02 wt.%, the ARE drops significantly to 13.04%. This suggests that OP-MLC FO-LA-SIBS is more accurate for measuring microelements in aluminum alloys. However, for trace elements, weak plasma emission, continuous background interference, and system noise may lead to greater interference to the spectral line intensities and hence larger REs.

Furthermore, a comparison of the REs under different concentration differences of the main element Al between the analyte samples and the standard sample is performed, as shown in Figure 5. It is obvious that the ARE increases with the increase of the Al concentration difference. This can be

FIGURE 4: The correlation between the REs and the certified concentrations of the analytical elements.

explained as follows: In the ideal OP-MLC, the spectral line intensities of the internal standard element Al of all samples are equal. However, in reality, the content of Al in analyte samples and the standard sample is slightly different, leading to a difference in the spectral line intensity of the internal standard element Al. The larger the concentration difference, the larger the difference in spectral line intensity, resulting in a positive correlation between the ARE and Al concentration differences. In addition, under a certain Al concentration difference (absolute value), there are two situations: The sample with an Al concentration higher than that of the standard sample and the sample with an Al concentration lower than that of the standard sample. Comparing these two situations, when the concentration of internal standard element Al in the analyte sample is higher than that in the standard sample, the average concentration of other elements is lower, and thus the ARE will be higher due to the



FIGURE 5: Comparison of the REs under different concentration differences of Al between the analyte samples and the standard sample.

negative correlation between the RE and the concentration of elements mentioned above. Therefore, it can be observed that the analyte samples on the right side of Figure 5 show larger AREs than those on the left.

Therefore, it can be expected that OP-MLC FO-LA-SIBS-based quantitative analysis of elements in aluminum alloys is suitable for rapid detection and quality monitoring of industrial batch aluminum alloys before production or use because they usually have standard samples, and the samples to be measured have similar concentrations of Al element to the standard samples.

4. Conclusions

In conclusion, an OP-MLC FO-LA-SIBS for quantitative analysis of elements in aluminum alloys was developed in this study. The system used a compact fiber laser as the laserablation source and a spark discharge unit to enhance the plasma emission and collected spectra with a portable multichannel fiber spectrometer. By taking one of the samples as the standard sample and the spectral lines of the main element Al as the reference lines of internal standardization, the concentrations of four elements in four analyte samples were estimated. The AREs of Mg, Cr, Cu, and Mn were 6.38%, 28.09%, 21.92%, and 18.97%, respectively. The compact and robust experimental devices, as well as the simple and efficient calibration method, indicate that OP-MLC FO-LA-SIBS has great potential for quantitative analysis of elements in aluminum alloys. However, it should be noted that despite performing OP-MLC, there are many interference factors that cannot be avoided, such as continuous background interference, which can lead to measurement deviation, especially in the quantitative analysis of trace elements where plasma emission is weak. Moreover, the ideal OP-MLC assumes equal spectral line intensities of the internal standard element Al in all samples, whereas in reality, there are slight differences in the content of Al in analyte and standard samples, which can affect the measurement accuracy. Therefore, OP-MLC FO-LA-SIBS is suitable for rapid analysis and quality monitoring of industrial aluminum alloy materials during mass production or use, where the samples to be measured have similar concentrations of Al element to the standard samples.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest.

Authors' Contributions

Y. Liao conceptualized the study, provided software, performed formal analysis, contributed to visualization, wrote the original draft, and provided funding acquisition. X. He performed supervision, contributed to methodology, performed investigation, wrote, reviewed, and edited the article, and provided funding acquisition. X. Wu performed investigation and provided funding acquisition.

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