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Quantitative analysis of C, Si, Mn, Ni, Cr and Cu in low-alloy steel under ambient conditions via laser-induced breakdown spectroscopy

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Abstract

A diode-pumped solid-state laser (DPSSL) with a high energetic stability and long service life is applied to ablate the steel samples instead of traditional Nd:YAG laser pumped by a xenon lamp, and several factors, such as laser pulse energy, repetition rate and argon flow rate, that influence laser-induced breakdown spectroscopy (LIBS) analytical performance are investigated in detail. Under the optimal experiment conditions, the relative standard deviations for C, Si, Mn, Ni, Cr and Cu are 3.3%–8.9%, 0.9%–2.8%, 1.2%–4.1%, 1.7%–3.0%, 1.1%–3.4% and 2.5%–8.5%, respectively, with the corresponding relative errors of 1.1%–7.9%, 1.0%–6.3%, 0.4%–3.9%, 1.5%–6.3%, 1.2%–4.0% and 1.2%–6.4%. Compared with the results of the traditional spark discharge optical emission spectrometry technique, the analytical performance of LIBS is just a little inferior due to the less stable laser-induced plasma and smaller amount of ablated sample by the laser. However, the precision, detection limits and accuracy of LIBS obtained in our present work were sufficient to meet the requirements for process analysis. These technical performances of higher stability of output energy and longer service life for DPSSL, in comparison to the Q-switch laser pumped by xenon lamp, qualify it well for the real time online analysis for different industrial applications.

Keywords: laser-induced breakdown spectroscopy (LIBS), diode-pumped solid-state laser (DPSSL), optical emission spectrometry, laser-induced plasma

(Some figures may appear in colour only in the online journal)

1. Introduction

Elements such as C, Si, Mn, Ni, Cr and Cu have a significant influence on the quality of steel. Traditional analytical techniques, such as atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES), and spark discharge optical emission spectrometry (SD-OES) are widely used to analyze steel samples and perform quality control. AAS and ICP-OES are types of wet chemistry analytical techniques which require a complicated sample pretreatment and have a low speed of analysis. For the SD-OES analysis, the sample preparations include cutting, milling, grinding, or drilling, which are always time consuming and require high maintenance efforts, even in automated container laboratories. In addition, non-conducting samples cannot be analyzed using the SD-OES technique.

Laser-induced breakdown spectroscopy (LIBS) has increasingly received the attention of the scientific and industrial communities as a laser-based analytical technique for rapid, multi-elemental detection in solid, liquid and gas
samples due to its versatility, minimal sample preparation and simplicity of configurations [1–4]. It has become a widely adopted tool for qualitative and quantitative analysis of samples both in the laboratory and in the field. LIBS analysis can even be performed at a long distance in hostile environments with the help of optical fibers. Owing to these technical advantages of LIBS, it was described as ‘a future super star’ in a review article written by Winefordner, who is a world-renowned analytical spectroscopist [5]. There are many studies on quantitative elemental analysis of steel using LIBS [6–9]. Gonzalez and his group executed the sulfur LIBS analysis in steel with the reported calibrations within the concentration range of 0.008%–0.28%, and a detection limit of 70 ppm was obtained [10]. Aragon et al performed LIBS analysis for C, Si, Cr, and Ni in steel with calibration curves in the range of 0.005%–1.5%, and for C and Si, the detection limits were 80 ppm [11]. The precision obtained for the carbon was 10% in the range of 150–1100 ppm and the detection limit was 250 ppm as reported in Aguilera’s research [12]. These results showed that LIBS can be directly applied for composition determination in molten alloys. Analytical performances of LIBS and SD-OES were compared in Hemmerlin’s work [13], and detection limits as low as 5 ppm were obtained by LIBS for C, P, and S. Multi-pulse bursts of a Nd:YAG laser at 1064 nm were used to locally ablate the scale layer of low-alloy steel samples in the first step, and the bulk material was analyzed via LIBS in the second step. Detection limits below 10 μg/g were obtained for elements C, P, S, Al, Cr, Cu, Mn and Mo, and the values of correlation coefficient were greater than 0.99 averaged over the observed elements. LIBS analysis of light elements, such as P, S, and C, using emission wavelengths in the range of 178.28–193.09 nm were investigated in detail by Sturm, and detection limits below 10 μg/g were achieved for these light elements [14]. A quantitative analysis of high-alloy steel samples was carried out for Ni, Cr, Cu, Mo, Si, Ti, Mn, Al and C, and the influence of single and double pulse excitation for two different laser burst energies were systematically investigated [15]. The results indicated that matrix effect caused mean residual deviations for the calibration curves depending on the analyte, single or double pulse excitation and laser burst energy.

In this paper, a different experimental setup consisting of an Ar-flushed sample stand and a Paschen–Runge spectrometer with a high spectral resolution in a greater spectral range was constructed, and C, Si, Mn, Ni, Cr and Cu in low-alloy steel were quantitatively analyzed under atmosphere conditions. Instead of the Q-switch laser pumped by xenon lamp is usually used to ablate samples for LIBS, diode-pumped solid-state laser (DPSSL) was employed in this experimental setup as a light source to ablate samples. Compared Q-switch laser pumped by xenon lamp, the DPSSL can give higher energetic stability and longer service life. Hence, it is more suitable to perform real time, online analysis for different industrial applications. In the case of the optical path configuration of spectrometer, Czerny–Turner or crossed Czerny–Turner light path are widely used in LIBS experiments. While in this study, we chose a spectrometer with a Paschen–Runge light path as a dispersed system and photomultiplier tubes (PMTs) to detect the optical signal. The aim of this work is to investigate the factors of influencing DPSSL LIBS analytical performance, and to provide guide for improving LIBS performance. Additionally, analytical performance of DPSSL LIBS and SD-OES was compared as well.

In order to decrease the matrix effect, calibration is provided using the ratio of the element signal to the signal produced by the reference element. In this paper, Fe(I) 273.098 nm was selected as the internal standard line, and spectral lines of C(I) 193.090 nm, Si(I) 288.157 nm, Mn(II) 293.306 nm, Ni(I) 231.604 nm, Cr(II) 267.716 nm and Cu(II) 224.262 nm were chosen for the quantitative analysis. In the atmospheric environment, the effects of laser pulse energy, repetition rate and argon flow rate upon the sample surface on analytical results were systematically studied, and then a comparison of DPSSL LIBS with the traditional SD-OES method was performed. The calibration curves of C, Si, Mn, Ni, Cr, Cu and other elements in low-alloy steel samples were eventually established with their evaluation of the precision and accuracy.

2. Experimental

2.1. Instrumentation and experimental conditions

DPSSL was used for the ablation of low-alloy samples. Compound light was dispersed using a Paschen–Runge spectrometer, and optical signal was detected by PMTs. The LIBS instrumental setup is shown in figure 1.

The output wavelength of DPSSL was 1064 nm with maximum output energy of 200 mJ, pulse width of 7 ns, highest repetition rate of 20 Hz, and pulse-to-pulse stability of 2%. The focal length of the Paschen–Runge spectrometer was 750 mm, and the resolution was better than 0.02 nm. There were 30 channels installed in the spectrometer including O, N and P channels. The focal length of the laser focusing lens was 150 mm, and the flow rate of argon was controlled by using a flow meter.

The low-alloy steel sample was ablated by 30 consecutive laser pulses at the same site with the pulse energy of 70 mJ. Figure 2 shows the surface morphology of the laser ablation crater observed by a scanning electron microscope (JEOL ZSM-6510).
From figure 2, we can see that the morphology of the laser ablation crater is nearly round, and its diameter is approximately 0.9 mm. A small central crater is surrounded by a ring-shaped structure that originates from residues of the melt being pushed out of the interaction region by the pressure of the laser-induced plasma and the accompanied shock wave. The crater center is relatively deep, while the surrounding area is shallower because the laser pulse energy in the center is higher than that at the edge. The morphology of the crater edge is mainly caused by the thermal effect of the instantaneous heat, which is caused by the interaction between the laser and the sample.

The spectral signal was detected in a synchronous mode in this experiment. After 50 pre-ablation pulses used to clean the sample surface, 100 integral pulses were used to ablate the sample and spectra collected with the gate width of 1 μs after the laser pulse. The factors that influence the LIBS analytical performance, such as laser pulse energy, repetition rate, and argon flow rate on the sample surface were investigated in detail, and then, a comparison of the LIBS and SD-OES analytical performance was performed.

2.2. Factors that affect the LIBS analysis

There are many factors that influence the LIBS analytical performance, such as the distance from lens to the sample surface, laser wavelength, the roughness of sample surface, as well as the type and pressure of the environmental gas, etc [16, 17]. In this paper, the laser pulse energy, repetition rate and environmental gas, which affect the LIBS analytical performance, were investigated in detail. Under ambient conditions, the low-alloy steel sample numbered BHG1606-4 was used to study the effects of factors mentioned above on LIBS performance under different experimental conditions.

2.2.1. Laser pulse energy effect on the LIBS analysis

Experiments were conducted in a gaseous atmosphere. The laser pulse repetition rate was 20 Hz, and spectral signals were collected in synchronous mode. By adjusting the laser power supply current to control the pulse energy, the BHG1606-4 sample was ablated using pulse energies of 30, 50, 70, 90 and 100 mJ sequentially. The spectral line intensities and analytical precision for elements C, Si, Mn, Ni, Cr and Cu changed with the pulse energy are displayed in figure 3.

It can be seen in figure 3(a) that when the pulse energy was in the range of 30–100 mJ, the spectral line intensities for C, Si, Mn, Ni, Cr and Cu became stronger when the pulse energy increased at the beginning, and then, the intensities got close or even slightly weakened with the increase of pulse energy. This may well due to the plasma shielding effect from the interaction between the laser and plasma. Specifically, part of the energy is absorbed by the plasma and the energy that reaches the sample surface decreases. This makes the spectral line intensity weaker.

As illustrated in figure 3(b), when the pulse energy is too low or too high, the relative standard deviation (RSD) values for the analyzed elements are larger. In contrast, when the energy is close to 70 mJ, the RSD value decreases and the analytical precision becomes much better. Lower pulse energy ablates fewer samples, and the sample inhomogeneity is easily manifest, which leads to poor analytical precision. Similarly, pulse energy at higher level also results in poor precision when analyzing C in steel because CO2 in the air is dissociated by high-temperature plasma. In addition, higher...
pulse energy is not so stable compared with a medium-energy pulse. Considering the stability and the service lifetime of the laser, the pulse energy of 70 mJ was used to ablate the sample in this experiment.

2.2.2. Repetition rate effect on the LIBS analysis. Experiments were conducted under atmospheric environment and the pulse energy was set as 70 mJ. Spectral signals were collected in synchronous mode. The BHG1606-4 sample was ablated with a laser repetition rate of 5, 10, 15 and 20 Hz sequentially. The RSDs for target elements of C, Si, Mn, Ni, Cr and Cu, which changed with the repetition rate, are shown in figure 4.

As seen from figure 4, the RSD values for C, Si, Mn, Ni, Cr and Cu decrease with the increased repetition rate as a whole, which significantly improves the LIBS analysis precision. When the repetition rate increased, quasi-continuous plasma was produced, yielding much more stable of the spectral line intensities. In addition, a high repetition rate leads to an increase in the ablation efficiency owing to heat accumulation at the same site. Consequently, an efficient removal of material on the target surface can be achieved at very low fluency which is much lower than the ablation threshold with a low repetition rate. Accordingly, the amount of aerosol produced by the interaction between the laser and material per unit time increases, and the precision of the analytical data is hence improved. Therefore, an optimized repetition rate of 20 Hz was used for the steel sample ablations in this experiment.

2.2.3. Argon flow rate on the sample surface effect on the LIBS analysis. Experiments were conducted under ambient conditions, the laser pulse energy was set to 70 mJ, and the repetition rate was 20 Hz. Spectral signals were collected in synchronous mode. Sample numbered BHG1606-4 was ablated with argon blowing on its surface, and the argon flow rate was 0, 2.5, 4, 4.5, 6, 8 and 10 l min$^{-1}$. The spectral line intensity and RSDs for C, Si, Mn, Ni, Cr and Cu changing with the argon flow rate on the sample surface are shown in figure 5.

As shown in figure 5(a), the spectral line intensity of each element is clearly enhanced in the presence of argon blowing on the sample surface. The spectral line intensity of each element increased gradually with the increase in the argon flow rate until 4.5 l min$^{-1}$. As seen from figure 5(b), the RSD values for the analysis of these elements first decreased and then increased when the argon flow rate increased. When the argon flow rate was 4.5 l min$^{-1}$, the smallest RSD values were obtained for these elements. Therefore, the argon gas flow rate of 4.5 l min$^{-1}$ was an optimum parameter.

The spectral line intensity is clearly improved in the presence of argon gas blowing onto the sample surface. Being an inert gas, compared with oxygen in the air, argon in high-temperature plasma is hard to combine with the elements to be analyzed, which leads to the enhancement of spectral line intensity. On the other hand, argon has a meta-stable state and a longer lifetime. Accordingly, the atom density in the higher-energy state increases. Hence, the spectral line intensity is enhanced, and the sensitivity and precision of LIBS analysis were greatly improved. However, the analytical precision worsens at a low flow rate, which may be related to the presence of air on the sample surface. When the argon flow
Figure 6. Calibration curves of C (a), Si (b), Mn (c), Ni (d), Cr (e) and Cu (f).

Table 1. Percent compositions of low-alloy steel samples used.

<table>
<thead>
<tr>
<th>Sample numbers</th>
<th>C (%)</th>
<th>Si (%)</th>
<th>Mn (%)</th>
<th>Ni (%)</th>
<th>Cr (%)</th>
<th>Cu (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BHG1601-1</td>
<td>0.0518</td>
<td>0.523</td>
<td>1.915</td>
<td>0.071</td>
<td>2.51</td>
<td>0.0518</td>
</tr>
<tr>
<td>BHG1601-2</td>
<td>0.296</td>
<td>0.339</td>
<td>0.941</td>
<td>0.271</td>
<td>1.47</td>
<td>0.301</td>
</tr>
<tr>
<td>BHG1601-3</td>
<td>0.164</td>
<td>0.0975</td>
<td>0.160</td>
<td>0.197</td>
<td>1.942</td>
<td>0.179</td>
</tr>
<tr>
<td>BHG1601-4</td>
<td>0.429</td>
<td>0.312</td>
<td>0.649</td>
<td>0.394</td>
<td>0.932</td>
<td>0.419</td>
</tr>
<tr>
<td>BHG1601-5</td>
<td>0.572</td>
<td>0.262</td>
<td>1.58</td>
<td>0.599</td>
<td>0.383</td>
<td>0.580</td>
</tr>
<tr>
<td>YSBS18201-94</td>
<td>0.076</td>
<td>1.64</td>
<td>1.10</td>
<td>0.025</td>
<td>0.013</td>
<td>0.034</td>
</tr>
<tr>
<td>YSBS18203-94</td>
<td>0.316</td>
<td>0.568</td>
<td>0.613</td>
<td>0.782</td>
<td>1.460</td>
<td>0.239</td>
</tr>
<tr>
<td>YSBS18205-94</td>
<td>0.425</td>
<td>0.127</td>
<td>1.39</td>
<td>1.50</td>
<td>0.465</td>
<td>0.135</td>
</tr>
<tr>
<td>YSBS18206-94</td>
<td>0.347</td>
<td>0.752</td>
<td>0.290</td>
<td>0.441</td>
<td>0.753</td>
<td>0.233</td>
</tr>
</tbody>
</table>
rate increases higher than 4.51 min\(^{-1}\), the plasma become unstable and the precision becomes poor again.

3. Results and discussion

3.1. Established calibration curves

Calibration curves were generated in this experiment by analyzing nine low-alloy steel samples named BHG1606-1, BHG1606-2, BHG1606-3, BHG1606-4, BHG1606-5, YSBS18201, YSBS18203, YSBS18205, and YSBS18206. Percent compositions of C, Si, Mn, Ni, and Cr in these certified samples are shown in table 1.

These nine samples were ablated using laser pulse energy of 70 mJ and a repetition rate of 20 Hz, with argon blowing on the sample surface at 4.51 min\(^{-1}\). The same samples were used to construct a calibration curve via SD-OES. The calibration curves of C, Si, Mn, Ni, Cr, and Cu, which were established using LIBS, are shown in figure 6.

3.2. Comparison of analytical performance between LIBS and spark-SD-OES

Based on the above mentioned calibration curves for C, Si, Mn, Ni, Cr, and Cu, eight low-alloy steel samples, named 94-1 to 94-6, 11298 and Q235, were also analyzed using SD-OES. The analytical results of LIBS and SD-OES are listed in table 2.

For C, Ni, Mn, Cu, Cr, and Si, the RSD values of LIBS analysis (calculated from six independent measurements) are 3.3%–8.9%, 0.9%–2.8%, 1.2%–4.1%, 1.7%–3.0%, 1.1%–3.4% and 2.5%–8.5% respectively, while the RSD values of SD-OES analysis are 0.6%–4.4%, 0.4%–2.7%, 0.4%–3.0%, 0.9%–1.9%, 0.2%–1.5% and 0.5%–2.5% respectively. The relative errors of LIBS are 1.1%–7.9%, 1.0%–6.3%, 0.4%–3.9%, 1.5%–6.3%, 1.2%–4.0%, and 1.2%–6.4% respectively, while those of SD-OES are 0.3%–4.3%, 0.2%–3.2%, 0.1%–2.1%, 0.4%–2.1%, 0.1%–3.7% and 0.8%–3.4% respectively. The experimental data show that the LIBS analytical performance is slightly worse than that of SD-OES. One reason is that the transient plasma induced by laser is less stable than the plasma induced by spark, and the poor repetition is a significant drawback of LIBS [18]. The other reason is that the amount of ablated samples using laser-induced plasma is always smaller. Therefore, the analytical results are easily affected by sample inhomogeneity [19]. In contrast, the amount of ablated sample using spark discharge is much larger than that of LIBS, thus the precision of SD-OES is slightly better than LIBS. However, in view of the precision, detection limits and accuracy of LIBS obtained in our present work, LIBS analysis based on our experimental configurations is sufficient to meet the requirements of ladle analysis.

4. Conclusions

In this paper, low-alloy steel samples were ablated using DPSSL. The factors influencing quantitative analysis, such as laser pulse energy, repetition rate and argon flow rate on the sample surface were studied. Under the optimum experimental conditions, the calibration curves of a set of low-alloy steel standard samples were established. The samples of unknown low-alloy steel were analyzed quantitatively, and element C in steel samples were analyzed in atmosphere and with an argon flow upon the sample surface as well, which provided a method to measure C much more expeditiously and rapidly. The analytical results were compared with those of the conventional analytical SD-OES method. The results showed that the analytical performance of LIBS was slightly worse than that of SD-OES, which was due to the small size of the focused laser beam and the small sample mass that was vaporized by the laser, making the accuracy closely depended

<table>
<thead>
<tr>
<th>Sample numbers</th>
<th>Method</th>
<th>C (%)</th>
<th>Ni (%)</th>
<th>Mn (%)</th>
<th>Cu (%)</th>
<th>Cr (%)</th>
<th>Si (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>94-1</td>
<td>LIBS</td>
<td>0.396</td>
<td>0.227</td>
<td>0.634</td>
<td>0.033</td>
<td>0.958</td>
<td>0.201</td>
</tr>
<tr>
<td>94-2</td>
<td>SD-OES</td>
<td>0.416</td>
<td>0.224</td>
<td>0.639</td>
<td>0.049</td>
<td>0.991</td>
<td>0.191</td>
</tr>
<tr>
<td>94-3</td>
<td>LIBS</td>
<td>0.337</td>
<td>0.801</td>
<td>1.235</td>
<td>0.198</td>
<td>1.239</td>
<td>0.409</td>
</tr>
<tr>
<td>94-4</td>
<td>SD-OES</td>
<td>0.400</td>
<td>0.801</td>
<td>1.212</td>
<td>0.205</td>
<td>1.254</td>
<td>0.422</td>
</tr>
<tr>
<td>94-5</td>
<td>LIBS</td>
<td>0.234</td>
<td>1.210</td>
<td>0.923</td>
<td>0.248</td>
<td>0.656</td>
<td>0.325</td>
</tr>
<tr>
<td>94-6</td>
<td>SD-OES</td>
<td>0.220</td>
<td>1.205</td>
<td>0.915</td>
<td>0.254</td>
<td>0.650</td>
<td>0.364</td>
</tr>
<tr>
<td>11298</td>
<td>LIBS</td>
<td>0.064</td>
<td>0.388</td>
<td>1.518</td>
<td>0.075</td>
<td>1.521</td>
<td>0.599</td>
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<tr>
<td></td>
<td>SD-OES</td>
<td>0.070</td>
<td>0.401</td>
<td>1.466</td>
<td>0.091</td>
<td>1.536</td>
<td>0.618</td>
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<tr>
<td>Q235</td>
<td>LIBS</td>
<td>0.594</td>
<td>1.751</td>
<td>0.137</td>
<td>0.352</td>
<td>0.149</td>
<td>0.255</td>
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<tr>
<td></td>
<td>SD-OES</td>
<td>0.680</td>
<td>1.713</td>
<td>0.144</td>
<td>0.352</td>
<td>0.127</td>
<td>0.309</td>
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<td></td>
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<td>0.140</td>
<td>1.477</td>
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<td>0.100</td>
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<td>0.034</td>
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<td></td>
<td></td>
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<td>0.044</td>
<td>1.355</td>
<td>0.091</td>
<td>0.046</td>
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<td></td>
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<td>0.056</td>
<td>1.376</td>
<td>0.131</td>
<td>0.063</td>
<td>0.217</td>
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<tr>
<td></td>
<td></td>
<td>0.195</td>
<td>0.048</td>
<td>0.463</td>
<td>0.029</td>
<td>0.028</td>
<td>0.139</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.228</td>
<td>0.068</td>
<td>0.466</td>
<td>0.095</td>
<td>0.061</td>
<td>0.188</td>
</tr>
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</table>
on the sample homogeneity. On the other hand, the transient plasma induced by the laser is less stable than that of spark discharge. However, the analytical precision of LIBS can meet the needs of rapid furnace analysis, and the technique of LIBS has a great potential on online, rapid and remote material analysis. Thus it is essential to study more and further on LIBS quantitative analysis method. Compared with a traditional Q-switched laser, which is pumped by xenon lamp, DPSSL employed in this experiment has advantages of higher energetic stability and longer service life with no necessary to replace the lamp, which makes LIBS technique suitable for the industrial online analysis.

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