Quantitative Analysis of Multi-elements in Steel Samples by Laser-Induced Breakdown Spectroscopy

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ABSTRACT

Through a Nd:YAG pulse laser of 1064nm wavelength, a multichannel grating spectrometer, and seven CCD detectors, the plasma emission spectrum of the 200 – 980nm wavelength range were simultaneously observed. First, we studied the influences of some factors like laser energy and measurement time delays on emission intensity of plasma. By experiments, we found that the unusual phenomenon that the emission intensity of plasma is possibly stronger when laser energy is smaller for steel samples. However, this stronger intensity obtained under smaller laser energy is not suitable to quantitative analysis because of poorer repetition. Second, we determined the optimal experimental parameters and quantitatively analyzed the concentrations of the element Mn, Ni, Cr, V, Ti and Cu in some steel samples under the optimal experimental parameters. The calibration curves of these elements were built, and good linearity was obtained. The average relative errors of the quantitative results of these elements are between 13.31% and 4.54%. Consequently, LIBS can be used for quantitative analysis for steel samples; however, the accuracy of the quantitative results still needs to be improved.

Keywords: Laser-induced breakdown spectroscopy; Laser energy; Time delay; Quantitative analysis; Steel samples

1. INTRODUCTION

The chemical analysis of steel is necessary for process control and quality assessment in steel making. X-ray fluorescence (XRF), spark discharge-optical emission spectrometry (SD-OES), and absorption spectroscopy are major analytical tools used nowadays. These techniques require sample preparation including steps such as cutting, milling, grinding, or drilling, which are time consuming and block the practice of the on-line analysis [1].

Laser-induced breakdown spectroscopy (LIBS) is a powerful and attractive analytical technique of material compositions [2-7]. In LIBS, plasma is generated by focusing a laser beam with high power onto a sample surface, and the emission from the plasma is collected with optics for the analysis of the elemental composition of the sample. Compared with other analytical techniques, LIBS has many benefits, such as the capability of multi-element simultaneous analysis, needless of sample preparation, quickness of data acquisition, and applicability to all sample types like solids, liquids, and gases. Hence, LIBS is the preferred technique for executing on-line analysis, shortening producing period, and increasing the quality of products [8-11].

As a quantitative analysis technique, however, LIBS is unstable because of many factors that affect the precision and accuracy of measurement, such as the laser pulse energy, measurement time delays, ambient air pressure, sampling geometry, and inhomogeneity of the physical and chemical properties of samples [12-16].

The main purpose of this paper is to study the influences of some factors on plasma emission, and the capability of the LIBS technique for multi-element quantitative analysis of steel samples. Generally, the plasma emission intensity is direct ratio to the laser energy [12, 13, 17]. However, a particular experimental phenomenon was found that for steel samples the plasma emission intensity at low laser energy was possibly stronger than the plasma emission intensity at high laser energy. However, this stronger intensity obtained under smaller laser energy is not suitable to quantitative analysis because of poorer repetition. After studying the influence of some factors on plasma emission, the optimal experimental...
parameters were determined, and the calibration study of some constituent elements, Mn, Ni, Cr, V, Ti and Cu in steel samples was made.

2. EXPERIMENTAL

Figure 1 gives a schematic LIBS experimental set-up used. The laser source is a Q-switched Nd:YAG laser (CFR200 Nd:YAG from Big Sky Laser) with pulse energy up to 200 mJ, pulse width about 10 ns, wavelength of 1064nm, and repetition rate of 1-15Hz. Samples are placed on an x-y manually controlled stage in the air ambient, and the laser beam is focused on the sample surface by a convergent lens of 75mm focal length. The emission of plasma is collected by a 7-fiber bundle and sent to the LIBS2500-7 spectrometers (from Ocean Optics, Inc.) for analysis. With seven 2048-pixel linear CCD array detectors, the LIBS2500-7, which has a wide spectral range (200-980nm) corresponding to seven high-resolution (~0.1nm at FWHM) spectrometers, is connected to a PC that is used for storage and analysis of spectral signal.

Samples analyzed are 5 certified standard high-alloy steel samples, and the reference concentrations of some components are listed in Table 1. These samples are certified reference material of high-alloy steel from Chinese National Technique Monitoring Bureau. We only gave the concentration of the elements, Fe, Mn, Ni, Cr, V, Ti and Cu, and other elements including C, Si, S, P, Mo, Co, and W were not depicted, because we could not find proper analytical lines for these elements by using our experimental conditions. Indeed, this is due to the low concentration of these elements in the samples and the low sensitivity of the spectrograph and CCD detectors in the spectral regions where these elements emit the most intensively.

Table 1 Composition of the reference samples analyzed in wt. %

<table>
<thead>
<tr>
<th>Reference sample</th>
<th>Fe</th>
<th>Cr</th>
<th>Cu</th>
<th>Mn</th>
<th>Ti</th>
<th>V</th>
<th>Ni</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>GBW 01605</td>
<td>84.544</td>
<td>14.26</td>
<td>0.056</td>
<td>0.130</td>
<td>0.041</td>
<td>0.059</td>
<td>0.500</td>
<td>0.410</td>
</tr>
<tr>
<td>GBW 01606</td>
<td>86.342</td>
<td>11.03</td>
<td>0.284</td>
<td>0.337</td>
<td>0.079</td>
<td>0.151</td>
<td>0.393</td>
<td>1.384</td>
</tr>
<tr>
<td>GBW 01607</td>
<td>85.284</td>
<td>12.52</td>
<td>0.171</td>
<td>0.496</td>
<td>0.091</td>
<td>0.089</td>
<td>0.207</td>
<td>1.143</td>
</tr>
<tr>
<td>GBW 01608</td>
<td>86.637</td>
<td>9.37</td>
<td>0.374</td>
<td>0.740</td>
<td>0.371</td>
<td>0.201</td>
<td>0.461</td>
<td>1.846</td>
</tr>
<tr>
<td>GBW 01609</td>
<td>87.264</td>
<td>7.84</td>
<td>0.522</td>
<td>0.983</td>
<td>0.187</td>
<td>0.287</td>
<td>0.771</td>
<td>2.146</td>
</tr>
</tbody>
</table>

The selected spectral lines used for the calibration of elements of interest are listed in Table 2. These lines were chosen in order to minimize spectral interferences and self-absorption. Calibrations were based on the internal reference method, which can reduce the influence of the fluctuation of some experimental conditions. Considering that the analytical lines and the reference lines should have similar upper energy levels, we selected the Fe (II) 271.441 nm as the reference line of Cr (II) 286.257 nm, and the Fe (I) 371.993 nm as the reference line of other analytical lines of interest.

Table 2 Spectral lines used for the calibration

<table>
<thead>
<tr>
<th>Elements</th>
<th>Spectral lines (nm)</th>
<th>upper energy levels (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>Mn (I) 403.076</td>
<td>3.0753</td>
</tr>
<tr>
<td>Ni</td>
<td>Ni (I) 341.476</td>
<td>3.6554</td>
</tr>
<tr>
<td>Cr</td>
<td>Cr (II) 286.257</td>
<td>5.8558</td>
</tr>
<tr>
<td>V</td>
<td>V (I) 437.923</td>
<td>3.1312</td>
</tr>
<tr>
<td>Ti</td>
<td>Ti (II) 337.28</td>
<td>3.6869</td>
</tr>
<tr>
<td>Cu</td>
<td>Cu (I) 324.754</td>
<td>3.8169</td>
</tr>
<tr>
<td>Fe</td>
<td>Fe (I) 371.993</td>
<td>3.3322</td>
</tr>
<tr>
<td>Fe</td>
<td>Fe (II) 271.441</td>
<td>5.5530</td>
</tr>
</tbody>
</table>
We first studied the influences of some factors on plasma emission intensity. The factors include the laser energy, measuring time delays, and number of pulses for sample preparation. Since the five samples include the same matrix element, Fe, the matrix effects can be neglected. On the process for investigating the influencing factors, only the sample GBW 01605 was used to be tested, because there are same characteristics for the five samples. Limited by our detectors, the integration gate width was fixed at 1 millisecond, which is the minimal value of the detectors.

3. RESULTS AND DISCUSSION

3.1 Influence of laser energy on plasma emission

Many authors have studied the laser ablation in various materials and its relation with the laser energy or laser power. The formation of plasma needs the laser intensity exceed a threshold value. Generally, there is an initial linear correlation between the line emission intensity and the laser intensity before the emission signal reaching a saturation regime\(^\text{[13]}\). We also studied the correlation between the line emission intensity and the laser energy, while we found an exceptional phenomenon for high-alloy steel samples. The laser energy was turned from 10mJ to 200mJ at a step of 10mJ, surface positions of the sample GBW 01605 were changed for each value of laser energy, and each position was shot by 100 laser pulses. The former 20 pulses were used for cleaning, and the average emission intensity and the RSD of the emission intensity of the later 80 excitations were recorded. The time delay between the beginning of the laser pulse and the CCD acquisition was set at 2.5 \(\mu\)s. Figure 2 and Figure 3 show the relations of the line emission intensity and the RSD of the line emission intensity with the laser energy. From these pictures, both for matrix elements and minor elements we can find the tendency that the line emission intensity at low laser energy can exceed the line emission intensity at high laser energy. Before the threshold of the laser intensity, there was a maximum of the line emission intensity. When the laser energy exceeded the value at the maximum, the line intensity started to fall until the laser energy reaching the threshold of the formation of plasma. After the laser energy exceeding the threshold energy, the line emission intensity is linearly versus the laser energy until reaching saturation, which is consistent to other reports.

Figure 4 shows the phenomenon of plasma excited by a laser pulse with 130mJ energy (left picture), and 50mJ energy (right picture). We can see homogeneous plasma was produced by 130mJ pulse energy, while flame with spark splashing was produced by 50mJ pulse energy. We guessed the main reason of this phenomenon was that more gaseous oxides like \(\text{CO}_2\) were produced at 50mJ pulse energy, and the gaseous oxides made the volume of the material vaporized immediately expand and brought other constituents in solid or melt status out of the sample surface. More oxidation reaction happened before the formation of homogeneous plasma, and thus more material may be heated to vaporize. Furthermore, laser energy can be fully absorbed by the material of the sample surface before the formation of plasma, because the shield of the plasma has not been built.

Although the emission intensity may be higher at low laser energy than at high laser energy, we cannot use the low pulse energy as the experimental condition for quantitative analysis, because the RSD of emission intensity is extremely high before the formation of homogeneous plasma, as shown in Figure 2b and Figure 3b. Considering the line emission intensity and the RSD of emission intensity, we chose 130mJ as the optimal laser energy.

![Fig. 2 The average emission intensity (a) and the RSD of the emission intensity (b) of Fe (II) 271.441 nm versus the energy of the laser pulses.](image-url)
3.2 Optimization of the measuring time delays

At the initiation of the laser-induced plasma, continuum background is very intense and unfavorable for quantitative analysis. In order to obtain a maximum signal-to-noise ratio (SNR), the measuring time delays between the beginning of the laser pulse and signal acquisition should be set at proper values.

Since the functions of the line emission intensity versus time delays are different for different emission lines, the SNRs of all emission lines cannot reach the maximums at a same time delay. Considering the performance of multi-element analysis, the optimal time delay is about at 0.83 $\mu$s.

3.3 Depth profile

An advantage of the LIBS technique is that the work of cleaning the sample surface before analysis can be finished by several laser shots, that is to say exceptional sample preparation is unnecessary. In order to determine how many laser shots are needed to clean the impurity on the sample surface, we studied the relation of the emission intensity and the laser shots. The laser energy selected was 130mJ, the time delay was 0.83 $\mu$s, and 2000 laser pulses were sequentially shot at the same position on the sample surface. Figure 5 gives the intensity of Fe II 271.441nm versus the number of the laser pulses, where each point respects the average line intensity of 20 excitations. From the figure, we did not find the obvious impure level on the sample surface. Hence, it is unnecessary to clean the sample surface by laser shots. However, we still used 20 laser shots for preparation of sample surface with the intention of avoiding some uncertain situations on sample surfaces.
3.4 Calibrations

Based on the above analysis of some experimental conditions, we selected the optimal experimental parameters for calibration studies (laser energy of 130mJ, time delay of 0.83μs, 20 laser shots for surface preparation). Furthermore, we selected 5 different surface positions for each sample in order to reduce the influence might produced by inhomogeneous sample surfaces. For each position, we shot 40 laser pulses, of which the former 20 pulses were used for cleanliness, and the latter 20 pulses were recorded. Hence, 100 spectra were recorded for each sample, and their averages were used for calibrations. Figure 6 gives the calibration curves of the 6 elements, and the error bars indicate the standard deviations of the line intensity ratios. From Figure 6, we can see good linearity was obtained for most elements.

In order to judge the accuracy of the qualitative analysis, we defined the average relative errors of the quantitative results as:

$$ R(i) = \sqrt{\frac{1}{N_s} \sum_{s=1}^{N_s} \left( \frac{c_{i,\text{reference},s} - c_{i,\text{measure},s}}{c_{i,\text{reference},s}} \right)^2} $$  

(1)

where $i$ denotes the elements, $s$ denotes the samples, $N_s$ is the total number of samples, $c_{i,\text{reference},s}$ and $c_{i,\text{measure},s}$ are the reference concentration and the measured concentration of element $i$ in the sample $s$, respectively.

<table>
<thead>
<tr>
<th>Element</th>
<th>Average relative errors %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>10.17</td>
</tr>
<tr>
<td>Ni</td>
<td>12.53</td>
</tr>
<tr>
<td>Cr</td>
<td>4.54</td>
</tr>
<tr>
<td>V</td>
<td>8.56</td>
</tr>
<tr>
<td>Ti</td>
<td>11.93</td>
</tr>
<tr>
<td>Cu</td>
<td>13.31</td>
</tr>
</tbody>
</table>

As shown in Table 3, the average relative errors of the quantitative results are between 13.31% and 4.54%. The relative error of Cr is lowest and the relative error of Cu is highest. From the quantitative results, we can see LIBS technique is suitable to quantitative analysis for steel samples; however, the accuracy of the quantitative results still needs to be improved.
4. CONCLUSION

The goal of this work was to evaluate the potential of the Laser-induced breakdown spectroscopy technique for multi-element analysis of high-steel samples. The chemical analysis of steel is operated nowadays by some techniques requiring sample preparation, which are time consuming. LIBS technique is the first preferred technique for executing
We studied some factors that affect the emission intensity of plasma for high-alloy steel samples, and a particular experimental phenomenon was found that the plasma emission intensity at low laser power was possibly stronger than the plasma emission intensity at high laser power. We guessed the reason was that more oxidation reactions were produced in low laser energy before the formation of plasma. This stronger intensity obtained under smaller laser energy, however, is not suitable to quantitative analysis because of poorer repetition. Optimal experimental parameters were determined for the quantitative analysis of the constituent elements, Mn, Ni, Cr, V, Ti and Cu. Although good linearity of the calibration curves was obtained, the accuracy of quantitative results was not enough.

For further investigations, more measuring parameters must be considered to optimize the experimental conditions. Additional, for further improvements, spectrographs and detectors with higher resolution must be provided for quantitative analysis of steel samples, because of the extremely intricate spectral lines.

ACKNOWLEDGEMENTS
This work has been supported by the Chinese Academy of Sciences for Key Topics in Innovation Engineering (Grant No. KGCX2-YW-126) and the National High-Tech Research and Development Program of China (Grant No. 2009AA04Z160). The authors would like to thank Zhi-jia Yang, Qian-jin Guo, Zhi-bo Cong and Yong Xin (Shenyang Institute of Automation, Chinese Academy of Sciences) for helpful discussions while realizing the experimental setup and developing the analyzing device.

REFERENCES