Determination of Molybdenum, Nickel, and Chromium in Low-alloy Steels Using Laser-induced Breakdown Spectroscopy Assisted with Laser-induced Fluorescence and Discrete Wavelet Transform

Nan Zhao, a,b Zeren Luo, a Jiaming Li, b,* Qiongxiong Ma, b Liang Guo, b Chun Shan, a and Qingmao Zhang b

a School of Electronics and Information, Guangdong Polytechnic Normal University, Guangzhou 510665, P. R. China
b Guangdong Provincial Key Laboratory of Nanophotonic Functional Materials and Devices, South China Normal University, Guangzhou 510006, P. R. China

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ABSTRACT: Molybdenum, nickel, and chromium play important roles in steel property. Laser-induced breakdown spectroscopy (LIBS) assisted with laser-induced fluorescence (LIF) is a promising technique with high sensitivity to elemental analyses. However, the spectra suffered from strong and unstable background from laser scattering when determining these three elements in steel matrix, which would deteriorate the accuracy. In this work, a self-adaptive method based on discrete wavelet transform (DWT) was introduced to solve this problem. No manual or subjective intervention is needed even if changing spectral ranges and elemental species. The LIBS-LIF spectral data were decomposed by Daubechies wavelet with the wavelet function db7 and the decomposition level 7. Then the spectra were reconstituted with background removal. In quantitative analyses, R squares in calibration curves of chromium, nickel, and molybdenum were greatly increased from 0.976, 0.965, and 0.981 to 0.995, 0.993, and 0.997, respectively; and the root-mean-square errors of cross-validation (RMSECVs) were significantly decreased from 0.0153, 0.0290, and 0.0152 wt.% to 0.00649, 0.00832, and 0.00793 wt.%, respectively. The results demonstrated both calibration model accuracy and analytical accuracy were greatly improved. This work provides an effective and convenient approach for modifying LIBS-LIF analyses in determination of molybdenum, nickel, and chromium in steels.

INTRODUCTION

Chromium, nickel, and molybdenum are indispensable doping elements in modern steel metallurgy, which can improve strength and abrasive resistance of steel. In the meantime, these three elements would make some interaction in steels and co-influence the steel performance. For example, high content molybdenum provides high heat resistance and hardenability, but weakens the abilities of anti-oxidation and anti-corrosion, where moderate chromium and nickel can provide symbiotic structures and eliminate these side-effects. Therefore, it is of great importance to accurately control concentrations and proportions of these doping elements during steel manufacturing. Conventionally, elemental determination and quality evaluation are based on ICP-AES, spectrophotometry, spark-induced plasma spectrometry, and so on. However, these methods are so lengthy, contact-needed, and time-material consuming, which are only operated in laboratories for bulk and offline analyses. A rapid, in-situ, remote, and non-contact technique for online monitoring is urgently needed in intelligent industrial systems to realize real-time evaluation.

Laser-induced breakdown spectroscopy (LIBS) is an atomic spectrometry based on laser-induced plasma. A laser pulse is used...
to ablate a sample in interest, and then generates a tiny plasma. The elemental information can be deduced by analyzing the plasma spectra. LIBS has many attractive advantages, such as fast response, in situ analysis, remote detection, minimal sample preparation, multi-elemental detections. Therefore, it shows great potential in fields of geology, agriculture, food safety, mineral analysis, space exploration, marine science, metallurgy, etc. However, higher analytical accuracy is required with the development of industry, poor sensitivity in LIBS hinders its further application.

Several spectral enhancement methods were proposed by researchers around the world to improve LIBS accuracy. They can be fallen into two categories. (I) plasma intensification: the temperature and electronic density of the plasma are increased by some energy sources, including dual-pulse re-heating, microwave enhancement, surface enhancement, and micro torch heating; (II) decay postponement: the temporal and spatial decay of the temperature and electronic number density are postponed by some fields, including spatial confinement, magnetic confinement, and noble gas protection. These methods can enhance LIBS spectra of all elements simultaneously by about one order of magnitude. However, sensitivity is hardly improved in these methods when it is limited by spectral interference in complex matrix (such as steel material), where signal and interference will be enhanced simultaneously. Moreover, non-contact and remote sensing cannot be realized in most of these methods.

LIBS assisted with laser-induced fluorescence (LIBS-LIF) is a promising method for spectral enhancement using stimulated fluorescence. Target atoms in the plasma are stimulated by a wavelength-tunable laser, and then emit fluorescence, while other atoms in the plasma are almost unchanged. The resonant excitation in laser stimulation process provides LIBS-LIF high excitation efficiency and selectivity. Enhancement of about two orders of magnitude can be obtained, while spectral interference is effectively eliminated. F. Hilbk-Kortenbruck et al., R. Yi et al., R. Zhou et al., and P. Gao et al. reported sensitive detection of trace heavy metal thallium, lead, cobalt, and antimony in soil, respectively. R. Zhou et al. also provided sensitive determination of micronutrient elements in soil using LIBS-LIF. C. Zhu et al. improved LIBS sensitivity with LIF for lead detection in rhododendron leaves. Ore analyses with high sensitivity also benefited from LIBS-LIF. Water pollution analysis using LIBS-LIF was also investigated by M. Nakane, H. Loudyi, de Lima Filho, and Y. Godwal. Diatomic molecules were also selected to be resonantly excited in LIBS-LIF for sensitive isotopic analysis. Continuous wave diode laser was utilized by G. Nicolodelli et al. as LIBS-LIF excitation source for cost reduction and reliability improvement. LIBS-LIF was also used to provide high sensitivity in microanalysis in LIBS. In steel manufacturing, detection of trace boron, carbon, cobalt, and phosphorus, silicon were reported, which demonstrated feasibility of LIBS-LIF in steel analysis, especially significant sensitivity improvement under spectral interference condition.

However, only sensitivity was focused in above works. In steel plasma with high density and fluctuant morphology, the radiation laser is scattered by plasma and sample surface in the laser stimulation process. The homogeneity of plasma density and sample surface roughness in a series of steel samples cannot be guaranteed in steel industry, which makes the laser scattering light unstable. The wing of the scattering light in the spectrum would cover the observation window, raising up the background value and destabilizing the spectral signal. Solving the problem of scattering background is critical to improve analytical accuracy in LIBS-LIF. Generally, the background value is deduced by blank range near the signal line. In steel matrix, spectral lines were too plentiful to find a blank range. Moreover, subjective operation was hardly to avoid in this conventional method. Wavelet transform is a powerful signal decomposition method, firstly proposed by D. G. Childers et al. Discrete wavelet transform (DWT) was demonstrated to remove plasma bremsstrahlung background in LIBS. Without subjective operation and blank range need, DWT is probably effective in removing laser scattering background in steel plasma with self-adaptive ability.

In this work, determination of LIBS-LIF for molybdenum, nickel, and chromium determination in low-alloy steels was investigated. The accuracy influenced by radiation laser scattering in plasma was also discussed. A self-adaptive background removal method based on DWT was introduced. The mechanisms of laser stimulation and fluorescence in molybdenum, nickel, and chromium atoms were described. Besides, we investigated the selection of wavelet function and decomposition level in DWT. The spectral profiles and analytical performances were used to make comparison. The aim of this work is to realize sensitive and accurate determination of molybdenum, nickel, and chromium determination in steel manufacturing.

**INSTRUMENTATION**

**Samples.** Ten steel samples with certified Cr contents, eighteen steel samples with certified Ni contents, and nine steel samples with certified Mo contents were used to build calibration models in this work, listed in Table 1.

**Experimental setup and process.** A schematic of the setup used in this work is shown in Fig. 1. A Q-switched Nd:YAG laser (Quantel, pulse duration of 6 ns, flattened Gaussian beam) operating at 532 nm and 10 Hz was used. The laser beam was reflected by a dichroic mirror and then focused on a steatite
Table 1. Steel samples and certified concentrations used in this work

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cr content (wt%)</th>
<th>Sample</th>
<th>Ni content (wt%)</th>
<th>Sample</th>
<th>Ni content (wt%)</th>
<th>Sample</th>
<th>Mo content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr-1</td>
<td>0.08</td>
<td>Ni-1</td>
<td>0.409</td>
<td>Ni-10</td>
<td>0.513</td>
<td>Mo-1</td>
<td>0.005</td>
</tr>
<tr>
<td>Cr-2</td>
<td>0.03</td>
<td>Ni-2</td>
<td>0.086</td>
<td>Ni-11</td>
<td>0.021</td>
<td>Mo-2</td>
<td>0.334</td>
</tr>
<tr>
<td>Cr-3</td>
<td>0.117</td>
<td>Ni-3</td>
<td>0.218</td>
<td>Ni-12</td>
<td>0.002</td>
<td>Mo-3</td>
<td>0.103</td>
</tr>
<tr>
<td>Cr-4</td>
<td>0.171</td>
<td>Ni-4</td>
<td>0.133</td>
<td>Ni-13</td>
<td>0.183</td>
<td>Mo-4</td>
<td>0.353</td>
</tr>
<tr>
<td>Cr-5</td>
<td>0.387</td>
<td>Ni-5</td>
<td>0.03</td>
<td>Ni-14</td>
<td>0.194</td>
<td>Mo-5</td>
<td>0.2007</td>
</tr>
<tr>
<td>Cr-6</td>
<td>0.157</td>
<td>Ni-6</td>
<td>0.175</td>
<td>Ni-15</td>
<td>0.046</td>
<td>Mo-6</td>
<td>0.005</td>
</tr>
<tr>
<td>Cr-7</td>
<td>0.322</td>
<td>Ni-7</td>
<td>0.142</td>
<td>Ni-16</td>
<td>0.032</td>
<td>Mo-7</td>
<td>0.0035</td>
</tr>
<tr>
<td>Cr-8</td>
<td>0.092</td>
<td>Ni-8</td>
<td>0.041</td>
<td>Ni-17</td>
<td>0.094</td>
<td>Mo-8</td>
<td>0.02</td>
</tr>
<tr>
<td>Cr-9</td>
<td>0.062</td>
<td>Ni-9</td>
<td>0.174</td>
<td>Ni-18</td>
<td>0.026</td>
<td>Mo-9</td>
<td>0.164</td>
</tr>
<tr>
<td>Cr-10</td>
<td>0.036</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Fig. 1 Schematic diagram of the experimental setup.

Fig. 2 Mother wavelet $\psi_{j,k}(t)$ function db7 (red line) and scaling function $\phi_{j,k}(t)$ (blue line).

ceramics sample surface by a lens (f = 75 mm). An optical parametric oscillator (OPO) wavelength-tunable laser (OPOTEK Inc., Vibrant HE 355 LD, wavelength range of 225–2400 nm, pulse duration of 10 ns, flattened Gaussian beam) operating at 10 Hz was focused by a lens (f = 150 mm) and radiated the plasma. The plasma light emission was collected into a multicore fiber, then coupled to a Czeny-Turner spectrometer (Princeton Instruments, SCT320, grating of 1200 lines/mm). An intensified charge-coupled device (ICCD) (Andor Technology, iStar 334T, 1024×1024 pixels) was equipped with the spectrometer to record the spectra. Both lasers and the ICCD were synchronized by a digital delay generator (Stanford Research Systems, DG535). The OPO laser and the ICCD gate were simultaneously triggered. Each spectrum was accumulated by 100 shots. Each sample was measured repeatedly 10 times.

Data processing algorithm. DWT is an algorithm for signal processing based on frequency decomposition. Compared with conventional Fourier transform, DWT has attractive characteristics of time-frequency localization and multiresolution analyses. In DWT, mother wavelet $\psi_{j,k}(t)$ and scaling function $\phi_{j,k}(t)$ are dilated and translated as following:

$$\psi_{j,k}(t) = 2^{-j/2}\psi(2^{-j}t - k)$$  \hspace{1cm} (1)

$$\phi_{j,k}(t) = 2^{-j/2}\phi(2^{-j}t - k)$$  \hspace{1cm} (2)

$j$ represents the scale and frequency; $k$ represents the translation (wavelength in spectral data). It is assumed that spectra are consisted of noise (high frequency), spectral lines (medium frequency), and background (low frequency). $\psi_{j,k}(t)$ and $\phi_{j,k}(t)$ are respectively considered as a high and low pass filter for LIBS spectral data. In this work, the Daubechies wavelet family was adopted with the wavelet function db7 and the decomposition level 7 according to spectral characteristics in LIBS-LIF. The $\psi_{j,k}(t)$ and $\phi_{j,k}(t)$ function graphs were
shown in Fig. 2. Any spectrum can be decomposed as:

\[ f(t) = \sum_{j \leq J} \sum_{k \in Z(j)} d_{j,k} \psi_{j,k}(t) + \sum_{k \in Z} c_{j,k} \phi_{j,k}(t) \]  

\[ \sum_{j \leq J} \sum_{k \in Z(j)} d_{j,k} \psi_{j,k}(t) \] and \[ \sum_{k \in Z} c_{j,k} \phi_{j,k}(t) \] represent components of high frequency and low frequency in the spectral data, respectively; \( d_{j,k} \) and \( c_{j,k} \) correspond to detail and approximation coefficient. Background in spectra in low frequency can be extracted, and its coefficient \( c_{j,k} \) is set to zero. Then the spectral data are reconstituted with background removal.

The algorithm was programmed using Matlab 2019b.

**LASER-INDUCED FLUORESCENCE THEORY**

The fluorescent intensity is mathematically expressed as:

\[ I_f = Q \cdot P_{ki}^\lambda \]  

where \( Q \) and \( P_{ki}^\lambda \) are

\[ Q = \frac{1}{4\pi^2 \Delta \nu_c} \cdot \phi I_{Exc} LN \]  

Higher \( P_{ki}^\lambda \) value represents higher fluorescence intensity. The strong transitions of \( 3d^4(3S)4s \rightarrow 3d^4(3D)4s4p(3P^o) \), \( 3d^4(3P)4s^2 \rightarrow 3d^4(3D)4s4p(3P^o) \), and \( 4d^5(4S)5s \rightarrow 4d^5(4D)5p \) in chromium, nickel, and molybdenum were chosen, respectively.

Under same experimental conditions, \( Q \) is a constant value. The \( P_{ki}^\lambda \) values of chromium, nickel, and molybdenum under different wavelengths of the radiation laser and different plasma temperatures were shown in Fig. 3. The temperatures of laser-induced plasma were generally in the range of 5000–15000K. 357.87, 234.56, and 313.26 nm showed higher \( P_{ki}^\lambda \) values in chromium, nickel, and molybdenum atoms, respectively. Therefore, these three lines were used for stimulation in this work.

For example, chromium atoms in the plasma were stimulated by the laser beam with wavelength of 357.87 nm, and then transited up from the level \( 3d^4(3S)4s \) to the level \( 3d^4(3D)4s4p(3P^o) \). After the collision transition, chromium atoms continued transited down back to the ground level \( 3d^4(3S)4s \) and emitted 425.43 nm Stokes fluorescence simultaneously.
RESULTS AND DISCUSSION

Under the optimized conditions, LIBS and LIBS-LIF spectra of molybdenum, nickel, and chromium in the low-alloy steel samples were shown in Fig. 4. The Mo, Ni, and Cr atomic lines were enhanced by 37, 120, and 38 times, respectively. However, the spectral backgrounds were also enhanced by the OPO laser scattering. Moreover, the enhanced background curves in the spectra were random and unstable, as shown in Fig. 5a. The spectra fluctuated with the unstable background and deteriorated the quantitative analysis. In contrast, the spectral repeatability was obviously improved after background removal by DWT in Fig. 5b. The standard deviation (SD) and relative standard deviation (RSD) of Cr I 425.43 nm were decreased from 921.95 and 5.22% (Fig. 5a) to 201.59 and 3.06% (Fig. 5b), respectively.

The original LIBS-LIF spectra of chromium in the 10 low-alloy samples were shown in Fig. 6a. With unstable background, the signal intensities depended on not only the element concentration, but also the fluctuant background. Conventionally, the background value can be obtained in a blank range near the signal line. However, iron element has thousands of atomic and ionic lines as the steel matrix, which leaves few spectra blank for background measurement. Moreover, subjectivity in searching a suitable blank is ineluctable.

With fixed algorithm and basic parameters, DWT is self-adaptive after spectral data input, without any subjective intervention. The spectra after background removal by DWT were shown in Fig. 6b. Obviously, the background curves were effectively removed, and spectral baselines were almost constant. Except the chromium lines changing with its contents, other matrix lines were stable among different low-alloy samples. The self-adaptive universality of DWT was demonstrated by nickel and molybdenum in low-alloy steels, shown in Figs. 7 and 8.
Fig. 7 Steel spectra in the observation window of nickel lines before (a) and after (b) DWT background removal.

Fig. 8 Steel spectra in the observation window of molybdenum lines before (a) and after (b) DWT background removal.

Fig. 9 Calibration curves of chromium (a), nickel (b), and molybdenum (c) in low-alloy steels with original spectra (black scatters and lines) and DWT background removal spectra (red scatters and lines).

Similar with chromium, nickel, and molybdenum spectra (Figs. 7a and 8a) suffered from fluctuant background originally, with the optimized interpulse delay of 5 μs. In contrast, the backgrounds were effectively removed without any manual intervention in Figs. 7b and 8b.

To build a quantitative analysis model, linear calibration curves of spectral intensities and element contents were established in Fig. 9. Observation lines of Cr I 425.43 nm, Ni I 305.08 nm, and Mo I 379.83 nm were used. As the well-known advantage of LIBS-LIF, sensitivity in LIBS-LIF was greatly improved compared to that in LIBS. LoDs of chromium, nickel, and molybdenum elements were decreased from 24.1, 502, and 127 μg·g⁻¹ to 2.53, 10.2, and 34.4 μg·g⁻¹. The background removal has little no influence on LoDs in LIBS-LIF, because the calibration curve slope and spectral noise were almost unchanged. Calibration model accuracy was evaluated by determination coefficient R² values. Comparing the blue lines (original data without background removal) and the red lines (pre-processed data with background removal), R² values were greatly improved from
0.976, 0.965, and 0.981 to 0.995, 0.993, and 0.997 in chromium, nickel, and molybdenum, respectively. Analytical accuracy was evaluated by calculating root-mean-square error of cross-validation (RMSECV) in the leave-one-out cross-validation (LOOCV). The RMSECV values were significantly decreased from 0.0153, 0.0290, and 0.0152 wt.% to 0.00649, 0.00832, and 0.00793 wt.% in chromium, nickel, and molybdenum, respectively, showing effective accuracy improvement. $R^2$ and RMSECVs in conventional LIBS method were also shown in Fig. 9 for comparison. The results demonstrated that the proposed method was an effective modification for LIBS-LIF in accurate determination of chromium, nickel, and molybdenum in steels.

CONCLUSION

In summary, this work introduced an effective approach for accurate determination of chromium, nickel, and molybdenum in low-alloy steels. In experiment and data processing, LIBS-LIF and DWT were combined. The unstable spectral background from laser scatter was self-adaptively removed by DWT without any manual and subjective intervention. The $R^2$ square and RMSECV were utilized to quantitatively demonstrate the calibration model accuracy and analytical accuracy. The results show that $R^2$ squares in calibration curves of chromium, nickel, and molybdenum were greatly improved from 0.976, 0.965, and 0.981 to 0.995, 0.993, and 0.997, respectively; and the RMSECVs was significantly decreased from 0.0153, 0.0290, and 0.0152 wt.% to 0.00649, 0.00832, and 0.00793 wt.% respectively. The results demonstrated effective improvement of the calibration model accuracy and analytical accuracy, showing feasibility of the proposed method. This work realized accurate determination of chromium, nickel, and molybdenum in low-alloy steels based on LIBS-LIF method, promoting its great potential in steel manufacturing field.

AUTHOR INFORMATION

Jiaming Li received his BSc in 2013 and PhD in 2018, both from Huazhong University of Science and Technology. He is associate professor in South China Normal University. His major research interests are laser spectroscopy and laser manufacturing. Jiaming Li is author or co-author of over 70 articles published in peer-reviewed scientific journals, with an h-index of 23 (ResearchGate). He is a member of Laser Processing Committee of Chinese Optical Society.

Corresponding Author

* J. M. Li

Email address: jmli@mscnu.edu.cn

Notes

The authors declare no competing financial interest.

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