

Sample Temperature Effect on Steel Measurement Using SP-LIBS and Collinear Long-short DP-LIBS

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Laser induced breakdown spectroscopy (LIBS) has been investigated as a potential multi-element quantitative analysis tool for the quality control of on-line steel production. This research investigated influence of sample temperature on steel sample measurement using collinear long-short dual-pulse LIBS (long-short DP-LIBS) and single-pulse LIBS (SP-LIBS). The standard steel sample has been uniformly heated in a muffle furnace from 20°C to 700°C. The experimental results show that sample temperature has significantly effect on measurement result using SP-LIBS. However, long-short DP-LIBS can effectively reduce the sample temperature effect on measurement result. The detection characteristics of long-short DP-LIBS and SP-LIBS were compared using the intensity ratio of $I_{\text{Mn } 404.136 \text{ nm}}/I_{\text{Fe } 400.524 \text{ nm}}$ and $I_{\text{Fe } 402.187 \text{ nm}}/I_{\text{Fe } 400.524 \text{ nm}}$ under different delay time and different sample temperature conditions. The signal intensity and plasma temperature can be maintained higher and more stable for a period of time and at different sample temperature by long-short DP-LIBS with smaller error bar compared with that of SP-LIBS, which indicated long-short DP-LIBS has better measurement repeatability than SP-LIBS. The plasma temperature correction method was applied to compare the detection features of long-short DP-LIBS and SP-LIBS. The signal stability of long-short DP-LIBS measurement was improved significantly at different sample temperature with plasma temperature correction. These results demonstrated that the effect of sample temperature can be reduced using long-short DP-LIBS method to improve the on-line detection capability for steel measurement in complex environment.

KEY WORDS: steel elemental analysis; sample temperature effect; SP-LIBS; collinear long-short DP-LIBS.

1. Introduction

Steel is one of the most widely used metals in industrial fields. The rapid on-line analysis of steel components is important to control the quality of steel-making process. Therefore, advanced control and measurement technologies are required in the steel production line. Some analysis methods of steel have been put forward with more or less success, such as X-ray fluorescence spectroscopy, spark discharge-optical emission spectrometry, absorption spectroscopy and spark optical emission spectroscopy. However, due to the need of sample preparation, cost and other aspects, these methods are difficult to be applied for on-line real-time analysis of element compositions of iron and steel products, which limits the production efficiency

of high-quality steel.^{1–4)} Laser induced breakdown spectroscopy (LIBS) is an alternative method to develop on-line qualitative and quantitative multi-element analytical instruments for iron and steel production, which can be used for a variety of materials, such as solids, gas and liquids.^{5–8)} LIBS is an element analysis method based on atomic emission spectrometry. Pulse laser is focused on surface of the material to generate plasma, and the emission of plasma is collected by spectrometer and detector. The qualitative and quantitative measurement of sample can be realized by calculating wavelength and emission intensities of the characteristic lines. There are various advantages of LIBS technique, such as no sample preparation, low sample consumption, multi-element simultaneous monitoring, fast detection, real-time analysis, *etc.*^{9–11)}

LIBS technique shows the potential for fast detection and real-time analysis, which has attracted many scholars to study the application in the steel-making process. Aragón

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*et al.*¹²⁾ used LIBS method to detect the carbon content of molten steel samples in a laboratory induction furnace and proved that this method can be used for the direct determination of alloy melt composition. Palanco *et al.*¹³⁾ designed an open-path laser-induced plasma spectrometer (OP-LIPS) and proved it is a reliable technology to identify the composition changes of hot-solid and liquid stainless steel. Sun *et al.*¹⁴⁾ used LIBS method to carry out multi-element quantitative analysis of steel sample and obtained good measurement results. Li *et al.*¹⁵⁾ also applied LIBS to quantitative analysis of phosphorus both in pig iron and low alloy steel in air atmosphere. In recent years, in order to improve the industrial application of LIBS, many researchers developed LIBS technique to enhance and stabilize laser-induced plasma, in which the use of external energy is an effective method and has been widely studied.^{16–18)}

The process of steel production is extremely complicated. The changes of sample temperature and morphology are involved in this process, which will greatly affect the real-time measurement accuracy of LIBS. Some researchers have studied the influence of steel sample temperature on LIBS measurement results. Palanco *et al.*¹⁹⁾ analyzed the influence of steel temperature on LIBS measurements for high alloy steel samples heated up to 1 200°C. The results shown that the signal emission intensity was obviously affected by sample temperature. When the temperature was above 600°C, the surface composition changes due to the formation of variable thickness slag layer, which will have an impact on the measurement results. Zhigilei *et al.*²⁰⁾ found that the increased sample temperature can decrease the ablation threshold and increase the intensity of the spectral line according to simulation calculations. Eschlböck-Fuchs *et al.*²¹⁾ studied the effect of sample temperature on the laser-induced plasma dynamics and emission intensity for different solid sample. The results shown that spectral intensity of all samples increased with the increase of sample temperature. The above study shows that sample temperature affects the signal intensity and plasma stability, which will affect the application of LIBS on-line measurement of steel. Therefore, a method is necessary to stabilize the plasma and improve the LIBS ability to measure steel on-line. Double-pulse LIBS is a promising way to enhance the analytical performance in practical application. The experimental results have proved that double-pulse LIBS is an effective method to enhance the signal intensity and improve the plasma stability.^{22–24)} The collinear long-short dual-pulse laser-induced breakdown spectroscopy (long-short DP-LIBS) method has been studied to measure steel sample. It demonstrated the feasibility and enhanced detection ability of long-short DP-LIBS method due to pre-heating and re-heating effects of long pulse.^{25–27)}

In this paper, the collinear long-short DP-LIBS was employed to discuss the sample temperature effect on steel measurement for the improvement of LIBS technique. The standard steel sample with different sample temperature was measured by single pulse LIBS (SP-LIBS) and collinear long-short DP-LIBS respectively to systematically study the sample temperature effects for steel measurement. Furthermore, the comparative analysis has been carried out from several aspects between SP-LIBS and long-short DP-LIBS to evaluate the detection ability of collinear long-short

DP-LIBS at different sample temperature.

2. Experimental Setup

The main purpose of this work was to study the influence of sample temperature on steel measurement using SP-LIBS and long-short DP-LIBS. The schematic diagram of SP-LIBS and long-short DP-LIBS system is shown in **Fig. 1**. The system includes two lasers, a digital delay generator, a spectrometer, an ICCD camera, optical fiber, computer and other auxiliary optical devices. A long pulse laser with wavelength of 1 064 nm, pulse width of 60 μ s, pulse energy of 200 mJ and frequency of 10 Hz is generated by the Laser (LOTIS TII, LS-2137U) in the FR mode. The laser oscillation is free to output in a relatively long duration. Thus FR laser pulse has lower energy density which is not enough to produce an observable plasma emission.^{25–27)} A short pulse laser with wavelength of 1 064 nm, pulse width of 5–8 ns, pulse energy of 24.5 mJ and frequency of 10 Hz is generated by the Laser (LOTIS TII, LS-2134U). The reflected short pulse laser beam combined with the long pulse laser beam by polarization prism to realize the collinear long-short DP-LIBS. The inter-pulse delay time between long pulse and short pulse was adjusted by a digital delay generator and was set to 30 μ s in this study. When the long pulse laser did not work and only short pulse laser passed through polarization prism, it can realize the SP-LIBS. The combined laser beams or short pulse laser beam was reflected by the mirror and then focused on the steel sample by the lens with focal length of 800 mm to generate plasma. The plasma emission was collected and focused on entrance of the optical fiber by a lens with focal length of 100 mm. The emission signals were delivered by optical fiber and detected by spectrometer (SOL, NP-250-2M) and ICCD camera (Andor, iStar DH334T-18U-03), and then data were transmitted to computer for analysis. The delay time was the record start time after the short pulse was triggered, which can be adjusted by ICCD camera.

In this study, the standard block steel sample was used to analyze the influence of sample temperature on LIBS measurement. **Table 1** lists the elemental compositions of standard steel sample and the iron content was obtained by

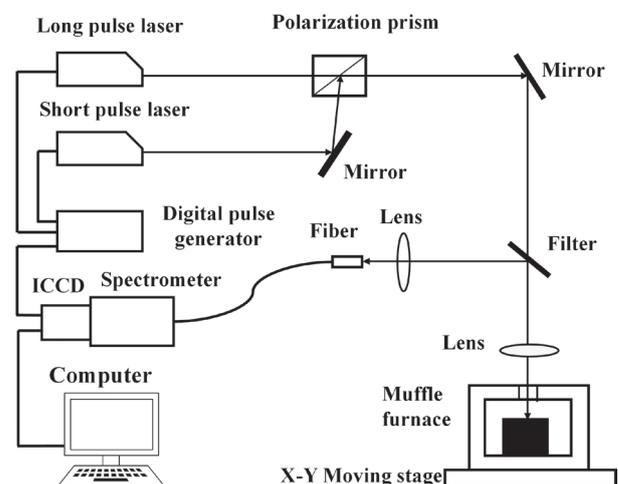


Fig. 1. Experimental setup for steel sample measurement using collinear long-short DP-LIBS and SP-LIBS.

Table 1. Elemental compositions of standard steel sample.

Sample	Content (%)							
	C	Si	Fe	Mn	P	S	Ni	Cr
YSBS37223-15	0.192	0.363	97.519	1.12	0.031	0.026	0.246	0.201

subtracting the other major elements.²⁷⁾ The sample were heated to the specified temperature in the muffle furnace, and the muffle furnace was operated at the atmosphere environment. The sample temperature varied as 20°C, 300°C, 500°C and 700°C. Because the melting point of steel usually reaches about 1 500°C, the standard steel sample can keep in solid phase during the experiment. Before LIBS measurement, the sample was heated for 30 minutes to guarantee thermal balance, and then the laser beam was irradiated to the sample through a hole with the diameter of 10 mm on the furnace cover. For each experimental condition, five times measurements were repeated for the average signal. The steel sample in the muffle furnace was kept moving on the X-Y moving stage during the measurement to reduce the surface effects.

3. Results and Discussion

The standard steel sample of YSBS37223-15 was measured at different sample temperature of 20°C, 300°C, 500°C and 700°C by SP-LIBS and long-short DP-LIBS in different delay time. The detection characteristics was investigated under different conditions to analysis the effect of steel sample temperature on LIBS signals. In order to reduce the influence of sample temperature on the measurement results, the plasma temperature correction method was applied to analyze the ability to reduce the influence of sample temperature using SP-LIBS and long-short DP-LIBS.

3.1 Sample Temperature Effect Using SP-LIBS

Figure 2 shows the measurement results at different sample temperature of 20°C, 300°C, 500°C and 700°C using SP-LIBS. Measured spectra were the average of five measurements and normalized by maximum signal from SP-LIBS measurement, as shows in Figs. 2(a)–2(d). The measured spectral wavelength range was 400–410 nm, from which many manganese and iron emission lines can be identified. The specifications of these emission lines were checked using NIST database and has been shown in previous work.²⁶⁾ By observing the spectra, it can be found that the spectra at each sample temperature can be clearly distinguished and the signal intensity of each spectra line was obviously different with sample temperature variation, which means that sample temperature would have a significant impact on the spectra measured by SP-LIBS. **Figure 2(e)** shows the sample temperature dependence of Fe I 400.524 nm, Mn I 404.136 nm and Fe I 402.187 nm signal intensity. As the sample temperature increased from 20°C to 700°C, the emission intensity of Fe I 400.524 nm, Mn I 404.136 nm and Fe I 402.187 nm increased and reached maximum value around 700°C. In addition, signal intensity variation of this three spectral lines had similar trend with increasing sample temperature. It indicates that the sample temperature has significantly effect on signal intensity mea-

sured by SP-LIBS and the influence mechanism on each spectral line is similar.

In the sample temperature increased from 20°C to 700°C stages, the measured signal intensity increased with the increase of sample temperature, and the change of ablation mass had an important contribution for this phenomenon. The intensity of spectral line has obvious relationship with the total ablation mass of the sample, which depends on many factors, such as specific heat, partial reflectance of the sample surface, sample temperature, *etc.* High sample temperature is an effective way to improve total ablation mass.²⁸⁾ The maximum ablated amount of sample M was calculated by following equation:¹⁹⁾

$$M = \frac{E_c}{C_p(T_b - T_0) + l} \dots\dots\dots (1)$$

Where, E_c is the laser energy coupled to the sample, C_p is the specific heat, T_b is the boiling temperature, T_0 is initial sample temperature and l is latent heat. It can be seen from the Eq. (1) that increasing the initial sample temperature T_0 under the same conditions can effectively increase the amount of laser energy used for ablation of the sample. Therefore, less laser energy is required to heat the sample under high sample temperature condition and high sample temperature can enhance the ablation amount of the sample. More energy in the laser pulse is also used for the plasma evolution process, including electron impact ionization process and inverse bremsstrahlung absorption process.²⁹⁾ Therefore, signal intensity will increase with sample temperature.

3.2 Comparison of SP-LIBS and Long-short DP-LIBS

The variation of sample temperature shows an effect on signal intensity using SP-LIBS, which will affect the quantitative analysis accuracy. Long-short DP-LIBS method is an effective way to improve the plasma stability and signal intensity. Therefore, collinear long-short DP-LIBS was used to measure the standard steel sample to further analyze the influence of the sample temperature. **Figure 3** shows the measurement results at different sample temperature using long-short DP-LIBS. Measured spectra were the average of five measurements and normalized by maximum signal from long-short DP-LIBS measurement, as shown in Figs. 3(a)–3(d). By observing the spectra, it can be clearly seen that the emission spectra at different sample temperature almost overlapped together and didn't change as sharply as SP-LIBS. This result shows that long-short DP-LIBS can get more stable measurement results with different sample temperature. **Figure 3(e)** shows the variation trend of emission spectral intensity with sample temperature. Compared with SP-LIBS, the signal intensity of Fe I 400.524 nm, Mn I 404.136 nm and Fe I 402.187 nm measured by long-short DP-LIBS tended to be more stable at different sample temperature. It indicates that long-short DP-LIBS method can reduce the influence of sample temperature on the signal intensity, which was mainly due to the heating effect of long pulse in long-short DP-LIBS. In long-short DP-LIBS process, the long pulse first irradiates the sample. Due to the low peak power of long pulse, the sample absorbs the energy of long pulse to raise the temperature without plasma generation. After the short pulse radiation, the sample

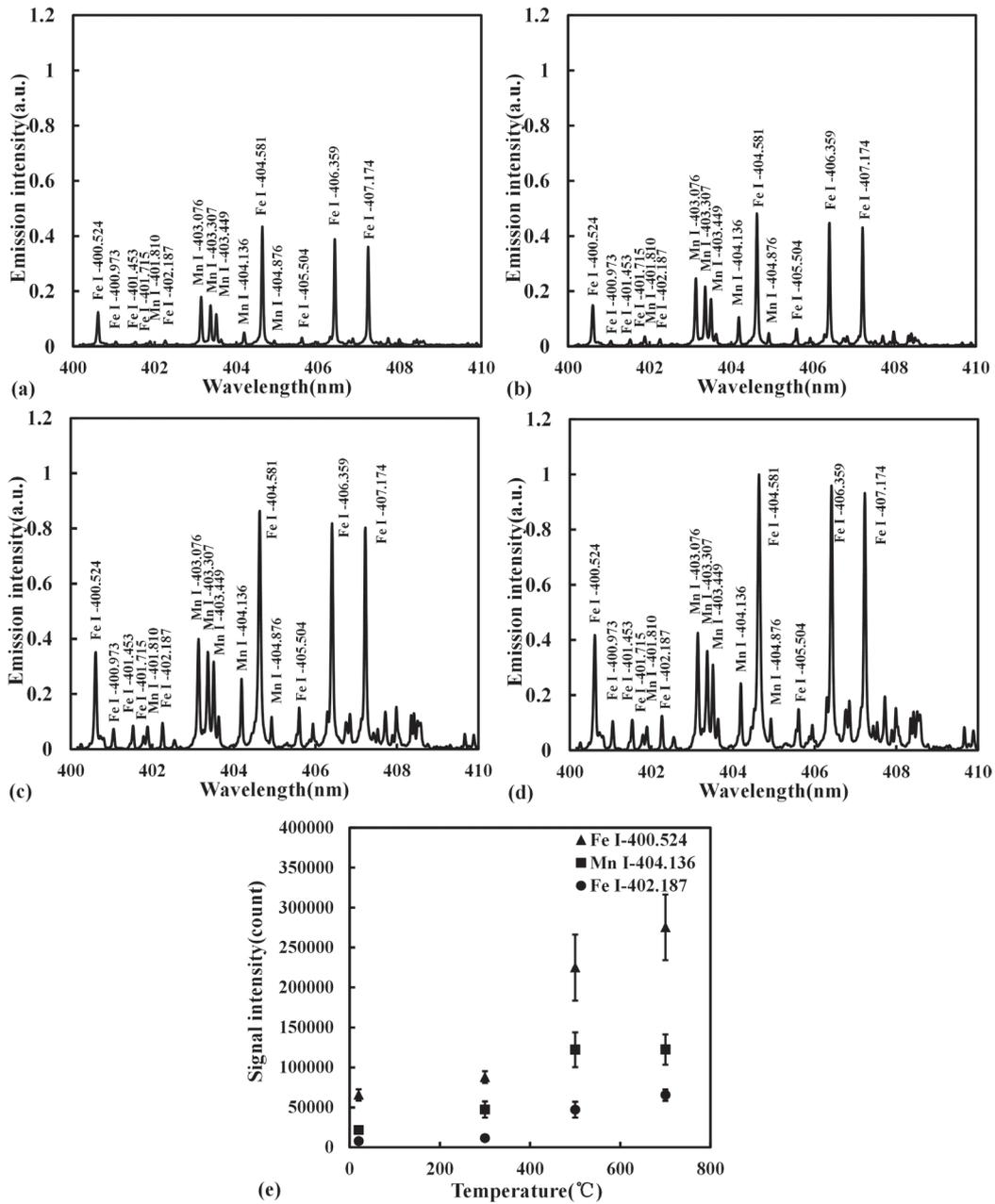


Fig. 2. Measured results at different sample temperature by SP-LIBS. Experimental conditions: short pulse energy: 24.5 mJ, delay time: 3 000 ns, gate width: 1 000 ns. (a) Measured spectra at sample temperature 20°C. (b) Measured spectra at sample temperature 300°C. (c) Measured spectra at sample temperature 500°C. (d) Measured spectra at sample temperature 700°C. (e) Signal intensity of Fe I 400.524 nm, Mn I 404.136 nm, Fe I 402.187 nm at different sample temperature.

heated by the long pulse will be atomized and vaporized to generate plasma. Therefore, the short pulse will irradiate the sample under a relatively stable condition.

3.2.1 Delay Time Effect

In order to clarify the sample temperature effect using long-short DP-LIBS, the intensity ratio of $I_{\text{Mn } 404.136 \text{ nm}}/I_{\text{Fe } 400.524 \text{ nm}}$ and $I_{\text{Fe } 402.187 \text{ nm}}/I_{\text{Fe } 400.524 \text{ nm}}$ were discussed in detail under different delay time conditions. The main reason for using ratio of $I_{\text{Mn } 404.136 \text{ nm}}/I_{\text{Fe } 400.524 \text{ nm}}$ is to eliminate the variations caused by the fluctuations of the laser energy between each shot and the ratio with an internal standard also is a common method for normalizing calibration spectra.³⁰⁾ For the same atom with different upper level energy, the emission intensity from upper level with higher energy

is more sensitive to plasma temperature compared with that from lower energy.³¹⁾ Therefore, $I_{\text{Fe } 402.187 \text{ nm}}/I_{\text{Fe } 400.524 \text{ nm}}$ was employed as the plasma temperature indicator to discuss the detection features. **Figure 4** shows the effect of the delay time on $I_{\text{Mn } 404.136 \text{ nm}}/I_{\text{Fe } 400.524 \text{ nm}}$ at sample temperature of 300°C. It can be seen that $I_{\text{Mn } 404.136 \text{ nm}}/I_{\text{Fe } 400.524 \text{ nm}}$ of SP-LIBS fluctuated sharply with the delay time and had large error bar. So the signal measured by SP-LIBS showed poor signal stability with delay time, which will lead to low repeatability and accuracy. Compared with SP-LIBS, $I_{\text{Mn } 404.136 \text{ nm}}/I_{\text{Fe } 400.524 \text{ nm}}$ of long-short DP-LIBS was higher and more stable with delay time and had smaller error bar. This phenomenon indicates that the signal intensity measured by long-short DP-LIBS can be stabilized for a period of time, which can effectively improve measurement

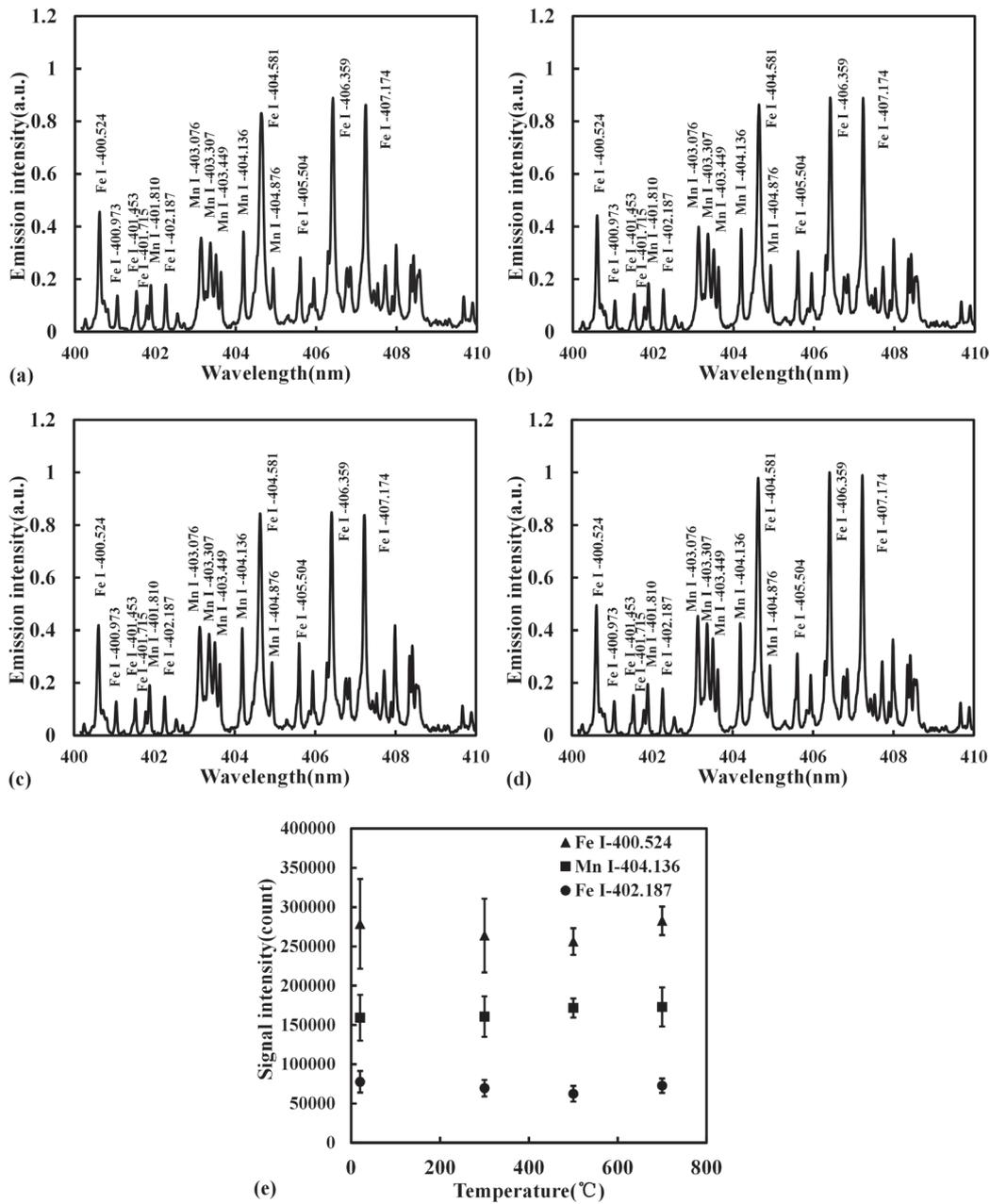


Fig. 3. Measured results at different sample temperature by long-short DP-LIBS. Experimental conditions: short pulse energy: 24.5 mJ, long pulse energy: 200 mJ, inter-pulse delay time: 30 μ s, delay time: 3 000 ns, gate width: 1 000 ns. (a) Measured spectra at sample temperature 20°C. (b) Measured spectra at sample temperature 300°C. (c) Measured spectra at sample temperature 500°C. (d) Measured spectra at sample temperature 700°C. (e) Signal intensity of Fe I 400.524 nm, Mn I 404.136 nm, Fe I 402.187 nm at different sample temperature.

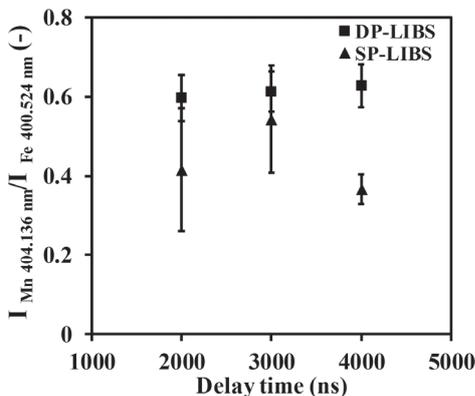


Fig. 4. Variation of intensity ratio of Mn I 404.136 nm/Fe I 400.524 nm with delay time for long-short DP-LIBS and SP-LIBS at sample temperature of 300°C.

repeatability and accuracy. **Figure 5** shows the variation of intensity ratio of $I_{\text{Fe 402.187 nm}} / I_{\text{Fe 400.524 nm}}$ with delay time for long-short DP-LIBS and SP-LIBS at sample temperature of 300°C. $I_{\text{Fe 402.187 nm}} / I_{\text{Fe 400.524 nm}}$ of SP-LIBS also fluctuated when increasing the delay time due to the unstable plasma. Theoretically $I_{\text{Fe 402.187 nm}} / I_{\text{Fe 400.524 nm}}$ has a tendency to decrease as the delay time increases in SP-LIBS, but the results didn't show this tendency because of the unstable plasma. However, long-short DP-LIBS can get higher and more stable value of $I_{\text{Fe 402.187 nm}} / I_{\text{Fe 400.524 nm}}$ than that using SP-LIBS when increasing the delay time, which means the plasma temperature was maintained at a higher level using long-short DP-LIBS. As the delay time increased, the $I_{\text{Fe 402.187 nm}} / I_{\text{Fe 400.524 nm}}$ of long-short DP-LIBS displayed remarkable stabilization compared with that using

SP-LIBS. The long-short DP-LIBS can maintain plasma stability and the plasma decay was deferred to extend the plasma lifetime. The main reason is the long pulse width laser of long-short DP-LIBS can control cooling process of plasma and plasma can maintain higher temperature and more stable state.

3.2.2. Sample Temperature Effect

According to the above comparison of measured spectra using SP-LIBS and long-short DP-LIBS, the signal was enhanced and became stable using long-short DP-LIBS. The detection features at different sample temperature were

discussed here. **Figure 6** shows the variation of intensity ratio of $I_{\text{Mn } 404.136 \text{ nm}}/I_{\text{Fe } 400.524 \text{ nm}}$ with sample temperature for long-short DP-LIBS and SP-LIBS in delay time of 3 000 ns. Due to the variation of sample ablation mass, $I_{\text{Mn } 404.136 \text{ nm}}/I_{\text{Fe } 400.524 \text{ nm}}$ of SP-LIBS fluctuated sharply with the sample temperature. Compared with SP-LIBS, long-short DP-LIBS can also obtain higher and more stable ratio under different sample temperature conditions. This phenomenon indicates that long-short DP-LIBS can enhance the signal intensity and keep signal intensity stable at different sample temperature. Long pulse width laser heats and softens the sample before the short pulse irradiation, and short pulse laser will generate a relatively stable ablation mass. Therefore, the signal intensity can be maintained in a stable situation. Plasma temperature indicator $I_{\text{Fe } 402.187 \text{ nm}}/I_{\text{Fe } 400.524 \text{ nm}}$ was employed to compare the plasma temperature at different sample temperature using SP-LIBS and long-short DP-LIBS in delay time of 3 000 ns, as shows in **Fig. 7**. Fe I 402.1 868 nm has a higher upper energy than that of Fe I 400.524 nm. With the increased sample temperature, $I_{\text{Fe } 402.187 \text{ nm}}/I_{\text{Fe } 400.524 \text{ nm}}$ of SP-LIBS had a trend of continuous increased. Therefore, plasma temperature had continuously changes with the sample temperature, which means plasma of SP-LIBS can be effect by sample temperature. However, there was quite different phenomenon for long-short DP-LIBS, as shows in **Fig. 7(b)**. $I_{\text{Fe } 402.187 \text{ nm}}/I_{\text{Fe } 400.524 \text{ nm}}$ of long-short DP-LIBS was higher and more stable than that of SP-LIBS at different sample temperature, which means plasma with higher and

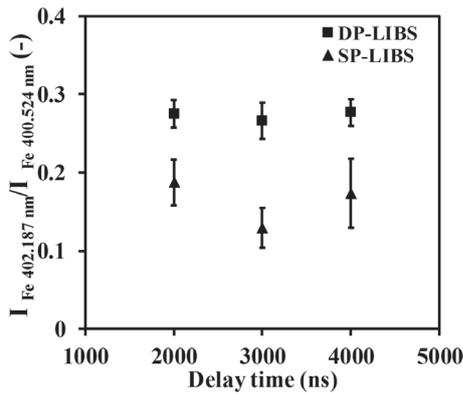


Fig. 5. Variation of intensity ratio of Fe I 402.187 nm/Fe I 400.524 nm with delay time for long-short DP-LIBS and SP-LIBS at sample temperature of 300°C.

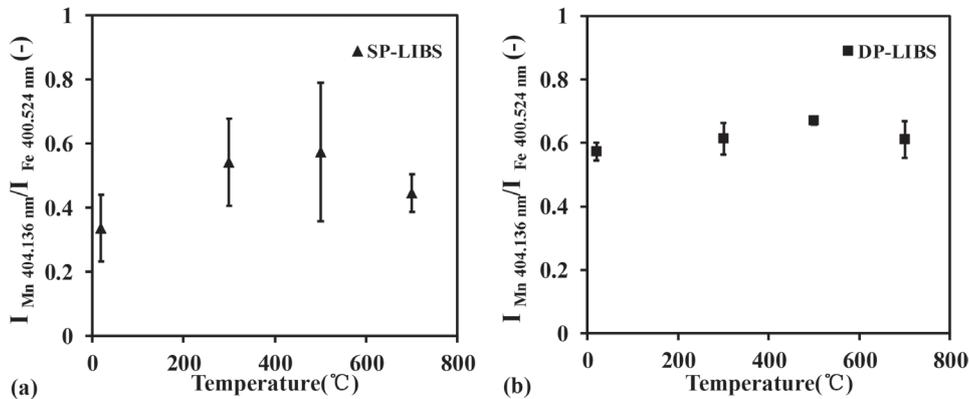


Fig. 6. Variation of intensity ratio of Mn I 404.136 nm/Fe I 400.524 nm with sample temperature for long-short DP-LIBS and SP-LIBS in delay time of 3 000 ns. (a) SP-LIBS. (b) Long-short DP-LIBS.

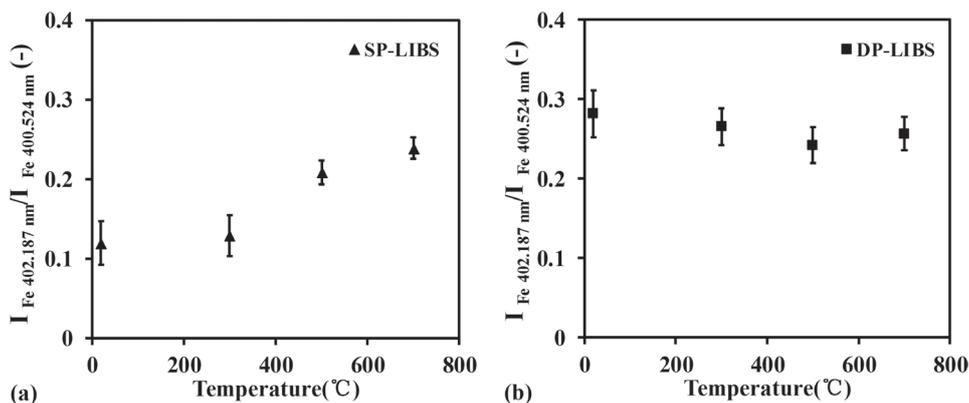


Fig. 7. Variation of intensity ratio of Fe I 402.187 nm/Fe I 400.524 nm with sample temperature for long-short DP-LIBS and SP-LIBS in delay time of 3 000 ns. (a) SP-LIBS. (b) Long-short DP-LIBS.

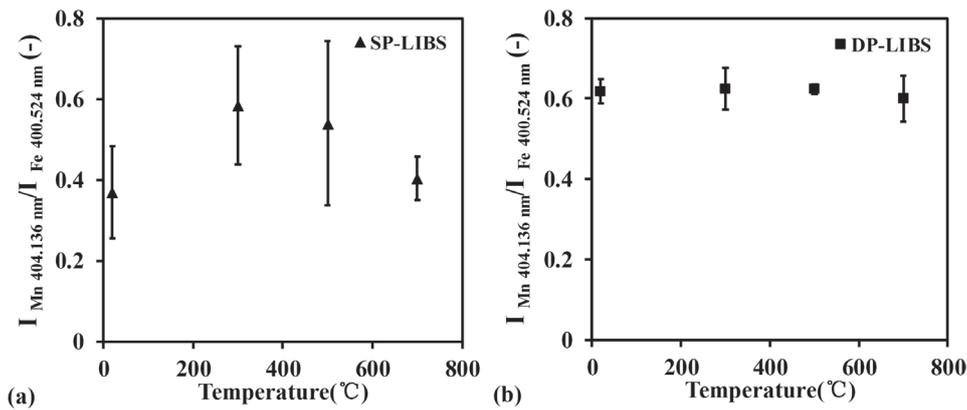


Fig. 8. Plasma temperature correction result for long-short DP-LIBS and SP-LIBS in delay time of 3 000 ns. (a) SP-LIBS. (b) Long-short DP-LIBS.

more stable temperature can also be obtained by long-short DP-LIBS under different sample temperature conditions. In LIBS process, a part of pulse laser energy was used to heat the material before the material was evaporated and vaporized to produce plasma, so the laser energy involved in the plasma generation process was affected by the initial temperature of sample.³²⁾ For long-short DP-LIBS, because of the pre-heat process of the long pulse, the short pulse produces the plasma at relatively stable surface temperature. Thus, for long-short DP-LIBS, the laser energy involved in the plasma generation process was basically same in different sample temperature conditions. So long-short DP-LIBS technique can reduce the effect of initial sample temperature and improve the detection capability for steel in complex environment. In addition, when comparing Figs. 6(a) and 6(b), Figs. 7(a) and 7(b), ratios at same sample temperature also presented the smaller error bar in long-short DP-LIBS condition, which means that long-short DP-LIBS can achieve a better measurement repeatability than SP-LIBS and further proves that long-short DP-LIBS can achieve more stable plasma state.

3.2.3. Plasma Temperature Correction

In order to reduce the influence of sample temperature on the measurement results, the plasma temperature correction method was applied to analyze the detection characteristics of long-short DP-LIBS and SP-LIBS at different sample temperature. In LIBS process, the emission intensity is a function of concentration of species and plasma temperature.³³⁾ Due to the plasma and plasma temperature are not stable and uniform, the emission intensity for each element will fluctuates with plasma temperature, which will affect the accuracy of quantitative analysis. Therefore, a plasma temperature correction method was proposed to improve the quantitative analysis capability of LIBS signal by our group, which was described in the previous work.³⁴⁻³⁷⁾ Theoretical analysis shows that the dependence of emission intensity on plasma temperature can be corrected using the plasma temperature correction factor according to the temperature indicator which is the intensity ratio of different spectral lines from the same element. In the actual process, the plasma from LIBS process is inhomogeneous and complex. The plasma temperature correction factor depends on the experimental conditions include the experimental system, environment

temperature and so on, which should be determined under actual experimental conditions. In this study, the emission intensity ratio of $I_{\text{Fe } 402.187 \text{ nm}}/I_{\text{Fe } 400.524 \text{ nm}}$ was used as temperature indicator for the determination of the plasma temperature correction factor. After plasma temperature correction, the variation trend of $I_{\text{Mn } 404.136 \text{ nm}}/I_{\text{Fe } 400.524 \text{ nm}}$ for long-short DP-LIBS and SP-LIBS with sample temperature in delay time of 3 000 ns as shows in Fig. 8. It can be seen from Figs. 6(a) and 8(a), after the plasma temperature correction, the $I_{\text{Mn } 404.136 \text{ nm}}/I_{\text{Fe } 400.524 \text{ nm}}$ ratio for SP-LIBS still fluctuates sharply with the sample temperature. The relative standard deviations of $I_{\text{Mn } 404.136 \text{ nm}}/I_{\text{Fe } 400.524 \text{ nm}}$ for SP-LIBS before the plasma temperature correction in Fig. 6(a) and after the plasma temperature correction in Fig. 8(a) were 22.56% and 21.86% respectively, which was not obviously optimized. It indicates that the temperature correction method could not significantly reduce the effect of sample temperature on measurement results of SP-LIBS. However, it can be seen from Figs. 6(b) and 8(b) that there was different result for long-short DP-LIBS. After the plasma temperature correction, $I_{\text{Mn } 404.136 \text{ nm}}/I_{\text{Fe } 400.524 \text{ nm}}$ of long-short DP-LIBS was significantly more stable with the different sample temperature than that before the plasma temperature correction. The relative standard deviations of $I_{\text{Mn } 404.136 \text{ nm}}/I_{\text{Fe } 400.524 \text{ nm}}$ for long-short DP-LIBS before the plasma temperature correction in Fig. 6(b) and after the plasma temperature correction in Fig. 8(b) were 6.46% and 1.78% respectively, which was significantly reduced by plasma temperature correction. Therefore, when employing the plasma temperature correction method, the change of plasma temperature caused by different sample temperature was corrected and the signal of long-short DP-LIBS becomes quite stable with the sample temperature compared to the measurement without plasma temperature correction. Therefore, the accuracy of the element content reflected by the spectral intensity can be significantly improved.

4. Conclusion

Sample temperature effect on steel measurement using SP-LIBS and collinear long-short DP-LIBS was experimentally investigated to improve the application ability of LIBS technique for steel on-line inspection in this study. Standard steel sample was measured by SP-LIBS and long-short

DP-LIBS at different sample temperature of 20°C, 300°C, 500°C, and 700°C. Main conclusions are shown as follows:

(1) Through observing the measurement results of SP-LIBS and collinear long-short DP-LIBS at different sample temperature, the results show that the sample temperature has significantly effect on signal intensity measured by SP-LIBS. For long-short DP-LIBS, measured spectra at each sample temperature did not change obviously and the signal intensity tend to be more stable at different sample temperature. Long-short DP-LIBS can reduce the influence of sample temperature on the measurement results.

(2) The changes of $I_{\text{Mn } 404.136 \text{ nm}}/I_{\text{Fe } 400.524 \text{ nm}}$ and $I_{\text{Fe } 402.187 \text{ nm}}/I_{\text{Fe } 400.524 \text{ nm}}$ with delay time indicate that the signal intensity and plasma temperature fluctuated drastically under SP-LIBS with delay time, but it can be kept high and stable for a period of time by long-short DP-LIBS. The variations of $I_{\text{Mn } 404.136 \text{ nm}}/I_{\text{Fe } 400.524 \text{ nm}}$ and $I_{\text{Fe } 402.187 \text{ nm}}/I_{\text{Fe } 400.524 \text{ nm}}$ with sample temperature show that sample temperature will affect the signal intensity and plasma temperature measured by SP-LIBS. However, long-short DP-LIBS maintains high and stable plasma temperature and signal intensity at different sample temperature. In addition, smaller error bar of long-short DP-LIBS shows it can achieve a better measurement repeatability than SP-LIBS.

(3) Through plasma temperature correction, the relative standard deviations of SP-LIBS changes from 22.56% to 21.86% and the fluctuation of signal intensity did not improve with sample temperature. For long-short DP-LIBS, the relative standard deviations changes from 6.46% and 1.78% and the fluctuation of signal intensity with sample temperature was improved. The plasma temperature correction method can improve the stability of long-short DP-LIBS measurement signals at different sample temperature.

These results presented here demonstrated that long-short DP-LIBS method can reduce the effect of sample temperature and improve the on-line detection capability for steel in complex environment.

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