Spectrochimica Acta Part B 142 (2018) 14–22

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

journal homepage: www.elsevier.com/locate/sab

Enhancement and stabilization of plasma using collinear long-short double-pulse laser-induced breakdown spectroscopy☆

Minchao Cui [a,b], Yoshihiro Deguchi [b,*], Zhenzhen Wang [b,c], Yuki Fujita [b], Renwei Liu [b,c], Fang-Jung Shiou [d], Shengdun Zhao [a]

[a] School of Mechanical Engineering, Xi'an Jiaotong University, Xi'an 710049, China
[b] Graduate School of Advanced Technology and Science, Tokushima University, Tokushima 770-8501, Japan
[c] State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Xi'an 710049, China
[d] Department of Mechanical Engineering, National Taiwan University of Science and Technology, Taipei 10607, Taiwan

ARTICLE INFO

Article history:
Received 27 February 2017
Received in revised form 1 February 2018
Accepted 1 February 2018
Available online 02 February 2018

Keywords:
Collinear long-short DP-LIBS
Long-pulse-width laser
Steel sample
Signal enhancement
Stabilized plasma

ABSTRACT

A collinear long-short dual-pulse laser-induced breakdown spectroscopy (DP-LIBS) method was employed to enhance and stabilize the laser-induced plasma from steel sample. The long-pulse-width laser beam with the pulse width of 60 μs was generated by a Nd: YAG laser which was operated at FR (free running) mode. The comparative experiments were carried out between single pulse LIBS (SP-LIBS) and long-short DP-LIBS. The recorded results showed that the emission intensities and the temperature of plasma were enhanced by long-short DP-LIBS. The plasma images showed that the plasma was bigger and had a longer lifetime in long-short DP-LIBS situation. Through the calculation of time-resolved plasma temperature and intensity ratio, it can be concluded that the plasma was stabilized by the long-pulse-width laser beam. The long-short DP-LIBS method also generated the stable plasma condition from the samples with different initial temperatures, which overcame the difficulties of LIBS in the online measurement for steel production line.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) as a rapid and convenient analytical method has been successfully applied in the industrial applications [1,2]. LIBS is a kind of atomic emission spectroscopy (AES) method which uses the laser-induced plasma as the emission source. The laser-induced plasma is formed by focusing the pulsed laser beam. The emitted spectra from the plasma are detected by the combination of spectrometer and detection device [3]. The qualitative and quantitative analysis of materials can be achieved by measuring the emission intensities of the characteristic lines. LIBS is an all-optical measurement system which has the considerable features, such as no sample preparation required, remote detection, online analysis, simultaneous multi-element analysis and relatively cheap price [4]. However, compared with other traditional analytical methods, LIBS suffers the drawbacks of low sensitivity and poor repeatability of measurement, which limit the development of LIBS application. There are many reasons for these drawbacks due to the complexity of LIBS process. The major reasons for these drawbacks include the pulse energy fluctuation, temporal and spatial non-uniformity of laser-induced plasma, uneven sample surface, matrix effects and influence of environment. Because of these difficulties, many studies of LIBS are still based on the polished samples. Some of the features of LIBS can't be reflected, such as no sample preparation, remote detection and online analysis.

Therefore, how to enhance and stabilize the laser-induced plasma is an important issue for the development of LIBS technique, especially for the industrial applications. Several methods have been reported to enhance the signal intensity or control the laser-induced plasma by employing an external energy source, such as spatial or magnetic confinement [5,6], spark discharge LIBS [7,8], microwave-assisted [9–11] and dual-pulse [12–14]. Usually, the additional devices for the energy supply should be installed nearby the measurement target, which is difficult in the industrial application. In dual-pulse LIBS (DP-LIBS), the additional energy is supplied by the laser beam, which is possible to be applied in online measurement. DP-LIBS configuration is realized with two independent lasers in some studies, while other researchers use a single laser to fire the dual-pulse [15,16]. A lot of experimental results have proved that DP-LIBS is an effective method to enhance the signal intensity. The configurations of collinear, cross beam, orthogonal pre-ablation and orthogonal re-heating have been studied and reviewed with different laser power, wavelength and pulse width [17]. With the use of UV fs-ns DP-LIBS, the 360-fold signal enhancement has been

☆ Selected paper from the 9th International Conference on Laser-Induced Breakdown Spectroscopy (LIBS), Chamonix-Mont-Blanc, France, September 12 – September 16 2016.

* Corresponding author at: Graduate School of Advanced Technology and Science, Tokushima University, 2-1, Minamijyosanjima, Tokushima 770-8506, Japan.
E-mail address: ydeguchi@tokushima-u.ac.jp (Y. Deguchi).

https://doi.org/10.1016/j.sab.2018.02.002
0584-8547/

obtained on a single-crystalline Si sample [18]. Using collinear DP-LIBS, the signal from the aluminum sheet sample has been enhanced near 300 times compared with that of tradition single pulse LIBS (SP-LIBS) [19].

The mechanisms of signal enhancement for DP-LIBS have been widely discussed. Freeman et al. [20] have suggested that the signal enhancement can be attributed to the re-heating of plasma plume. The experiments were carried out using crossed-beam DP-LIBS. The signal enhancement was also observed when the second pulse didn't ablate any of the brass samples. It means that the signal enhancement was attributed to the re-heating of plasma plume. However, Noll et al. [21] have concluded that the second pulse of the collinear DP-LIBS mainly transmitted through the plasma and generated the new plasma from the pre-ablated sample surface based on the plasma observation and the calculation of plasma transmission factor. In traditional DP-LIBS, the second laser pulse is also a Q-switched Nd:YAG laser pulse, which may not only re-heat the plasma but also generate new plasma from the sample surface. Therefore, the plasma generation process and cooling process become complicated in the cases of traditional DP-LIBS.

In previous studies, the 10.6 μm CO_2 laser pulse, which can be considered as long pulse laser beam, has been applied to DP-LIBS. The enhancement of emission signal and plasma temperature has been confirmed based on the setup of Nd:YAG-CO_2 DP-LIBS [22,23]. This dual-pulse technique was also applied to the measurement of organic films. The molecular emission signals from C_2 and CN were enhanced through the energy supply of CO_2 laser [24]. However, the CO_2 laser beam is unsuitable for the transmission with optical fiber and the CO_2 laser itself is also difficult to couple with Nd:YAG laser compactly, which may suffer the limitations in industrial application. For our research interest, we are focusing on the industrial application of LIBS, especially the non-contact and real-time measurement of industrial production lines. In this work, a long-pulse-width Nd:YAG laser was applied to the laser-induced plasma process in order to enhance and stabilize the plasma. The long-pulse-width laser means that the duration time of laser pulse is long but the peak power of laser pulse is low. More specifically, a Nd:YAG laser, which was operated at free running (FR) mode, was employed in current study to generate the long-pulse-width laser beam with 1064 nm wavelength and 60 μs pulse width.

2. Method

Fig. 1 shows an explanation of the collinear long-short DP-LIBS method, meanwhile the diagrams of traditional LIBS methods are presented. For SP-LIBS, as shown in Fig. 1(a), the plasma is generated by the short-pulse-width laser within a few nanoseconds or dozens of nanoseconds. Once the laser pulse ends, the plasma temperature continues to decrease temporally. It is obvious that the plasma is spatially and temporally non-uniform during the signal recording. For the traditional collinear DP-LIBS method, two short-pulse-width laser beams are used to generate the plasma, as shown in Fig. 1(b). Using traditional DP-LIBS, the temperature and lifetime of plasma have been enhanced. It is reported that the plasma is formed apart from the target surface and expanded to a globe shape [25]. However, the plasma condition is still non-uniform and unstable because that the energy supply from the nanosecond laser pulses is very short. Moreover, the second laser pulse makes the LIBS process more complex since the energy of second pulse can be absorbed by the plasma plume and also can generate new plasma from the target [21]. Therefore, the plasma conditions are still unstable in traditional DP-LIBS. In this study, a collinear long-short DP-LIBS method was employed to enhance and stabilize the plasma, as shown in Fig. 1(c). A long-pulse-width laser beam is focused on the surface before the short-pulse-width laser beam. The peak power of long pulse is lower than the breakdown threshold power which can generate a noticeable plasma. The long-pulse-width laser beam is expected to have the pre-heating effect of samples and re-heating effect of plasma in the LIBS process. In the duration time of long pulse, the plasma is generated from the sample surface by the short pulse. Once the plasma is generated, the long-pulse-width laser continuously irradiates the plasma plume and provides a continuous energy supply during the plasma cooling process. Thus the plasma is stabilized by controlling the cooling process of plasma.

3. Experimental setup

The experimental setup for long-short DP-LIBS configuration is illustrated in Fig. 2. As shown in Fig. 2a, the measurement system was composed of two lasers, a digital delay generator, optical fiber, a spectrometer, an ICCD (Intensified Charge Coupled Device) camera and other auxiliary devices. The nanosecond laser 1 (LOTIS TII, LS-2137U, 6–8 ns, 10 Hz, beam diameter: 8 mm) was operated at 1064 nm and FR mode. The FR mode, which has been rarely used in LIBS, means the Q value of optical resonant cavity does not change during laser pulse formation. Thus the laser pulse can be sustained for dozens of microseconds with low peak power density. In this work, the pulse energy of long-pulse-width laser was set to 200 mJ with the pulse width of 60 μs. The pulse width was determined by an oscilloscope (Tektronix, MDO3014) with a Si photodiode sensor (Hamamatsu, S1336-18BQ). The nanosecond laser 2 (LOTIS TII, LS-2134UTF, 5–8 ns, 10 Hz, beam diameter: 6 mm) was operated at 1064 nm (Q-Switch, pulse width 5.4 ns) with the pulse energy of 20.5 mJ. The inter-pulse delay between the two pulses was adjusted by a digital delay generator (Stanford Research Systems, Model DG645) and was also verified by the oscilloscope. These two laser beams were combined using a polarization prism. The combination of the two laser beams is important for the collinear long-short DP-LIBS. In this study, the polarization prism was used to combine the two beams. The orthogonal components in short pulse and long pulse were reflected and transmitted by the prism respectively. The beam combination was realized by matching the reflection position and transmission position of the two beams. Then the combined laser beam was focused on the sample using a lens (focal length 800 mm). Moreover, the short-pulse-width laser, long-pulse-width laser and related optics can also be combined in one package for the industrial application, which has been done in our research group. The emission signals from the plasma were collected in the reverse direction and focused on the fiber entrance using a lens (focal length 100 mm). After delivered 10 m by the optical fiber, the emission signals were detected by the combination of a spectrometer (SOL, NP-250-2M), an ICCD camera (Andor, iStar DH334T-18U-03). The delay time of ICCD was triggered by the short pulse. The detailed explanation of signal timing and the measured intensity shape of laser pulses were presented in Fig. 2 of Ref. [26].

The manganese with the matrix of iron was the measurement target in current study. Specifically, a standard steel sample with the composition of C (0.454%), S (0.044%), Si (0.444%), Mn (0.752%), P (0.041%), Cr (0.141%), Ni (0.122%), Mo (0.113%), Cu (0.017%), V (0.005%), Al (0.137%), As (0.010%) and Fe (Others) was used in all experiments. Several reports suggest that the neutral lines of Mn and Fe in the range of 400–410 nm can be used for the quantitative analysis of Mn in steel matrix [27–29]. Therefore, the emission was detected in this range employing a grating with 3600 grooves/mm to obtain a relatively high resolution (0.0097 nm). In addition, the plasma morphology was studied in this work. ICCD coupled with a camera lens (Nikon, 602,095, focus length 35 mm) and a band pass filter (Asahi Spectra, 405 nm, FWHM 10 nm) was employed to record the images of plasma, as shown in Fig. 2b. Through the band pass filter, the emission images of plasma in the wavelength range of 400–410 nm were recorded. Accordingly, the recorded plasma images can be discussed with the spectra results in the wavelength range of 400–410 nm.

For the experiments at room temperature, the sample was fixed on a rotational stage. For the experiments at high temperature, a muffle furnace with a hole on the upper surface was employed to carry out the