A method of laser focusing control in micro-
laser-induced breakdown spectroscopy

Wei WANG (汪为)1,2,3,4, Lanxiang SUN (孙兰香)1,2,4, Peng ZHANG (张鹏)1,2,3,4, Liming ZHENG (郑黎明)1,2,4, Lifeng QI (齐立峰)1,2,4 and Wei DONG (董伟)1,2,4

1 Shenyang Institute of Automation, Chinese Academy of Sciences, Shenyang 110016, People’s Republic of China
2 Institutes for Robotics and Intelligent Manufacturing, Chinese Academy of Sciences, Shenyang 110016, People’s Republic of China
3 University of Chinese Academy of Sciences, Beijing 100049, People’s Republic of China
4 Key Laboratory of Networked Control System, Chinese Academy of Sciences, Shenyang 110016, People’s Republic of China

E-mail: sunlanxiang@sia.cn

Received 31 July 2018, revised 18 September 2018
Accepted for publication 20 September 2018
Published 23 November 2018

Abstract
This paper presents a method for the automatic adjustment of the laser defocusing amount in micro-laser-induced breakdown spectroscopy. A microscopic optical imaging system consisting of a CCD camera and a 20× objective lens was adopted to realize the method. The real-time auto-focusing of the system was achieved by detecting the effective pixels of the light spot generated by the laser pointer. The focusing accuracy of the method could achieve 3 μm. The element concentrations of Mn and Ni in low-alloy steels were analyzed at a crater diameter of about 35 μm using the presented method. After using the presented method, the determination coefficients of Mn and Ni both exceeded 0.997, with the root-mean-square errors being 0.0133 and 0.0395, respectively. Scanning analysis was performed on the inclined plane and the curved surface by means of focusing control and non-focusing control. Ten characteristic spectral lines of Fe were selected as the analysis lines. With the focusing control, the average relative standard deviations obtained on the inclined plane and curved surface were both less than 5%, and much less than the values without focusing control, 14.6% and 40.39%.

Keywords: LIBS, microanalysis, ablation crater, focusing control

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

1. Introduction

Micro-laser-induced breakdown spectroscopy (μLIBS) is a powerful tool to investigate structure, chemical or mineral components on the micro-scale. It can not only provide a convenient approach to conduct elemental analysis in metals [1–7], fluids [8], ceramics [9] and so on, but be used as an elemental surface mapping tool. Bette et al. [10] gathered 250 000 spectra on a 1 × 1 cm² steel sample within 11 min. The distribution of oxides and nitrides in steel was determined by plotting the intensity distributions of O, N, Al and Mn, and comparing the correlations between them. Wessel et al. [11] used a femtosecond laser-induced breakdown spectroscopy to scan the microcrack zone in AlTi alloy. The obtained crater has a spatial resolution of 2 μm. Liu et al. [12] applied μLIBS to herbal minerals research. The mineral content distribution of Juncus effusus L. in 12 different regions was studied by plotting the spectral intensity distributions of elements such as Mg, Ca, Ba and Na. The difference in the distribution of Ca and Ba is particularly prominent. Vadillo et al. [13] analyzed the 3D distribution of carbon impurities on the surface of solar panels using a nitrogen laser with wavelengths of 3.65 J cm⁻² and 337.1 nm. The resulting crater had a lateral resolution of 30 μm. Fabre et al. [14] analyzed the longitudinal profile of coral skeletons. This study shows that the ratio of chemical composition of Mg/Ca and Sr/Ca has a
significant time dependence during coral growth. The lateral resolution of the crater obtained in this experiment was 5 μm. In addition, Yang et al [15] characterized the delamination defects of marine steel by plotting the distribution of elements such as Al, Ca, Mn and Si. Compared with other elemental analysis techniques, such as laser ablation inductively coupled plasma mass spectrometry, electron microprobe, secondary ion mass spectroscopy or synchrotron radiation x-ray microprobe, the μLIBS mapping allows us to realize fast spatial scanning without complicated sample preparation. Although μLIBS technology has such outstanding advantages, it is restricted by other factors. In microanalysis, laser-excited plasma radiation is relatively weak, greatly increasing the difficulty of spectral signal acquisition. The roughness and flatness of the sample surface directly lead to changes in the plasma topography excited at the surface of the sample during the scanning analysis. This fluctuation in the plasma topography makes the intensity of the line acquired by the detector unstable [16–18]. In order to achieve spectral stability at high crater resolution, silicon wafers [19, 20] or metal films [21, 22] are commonly used for research. However, in practical applications, the laser beam defocus amount changes due to the difference in the surface height gradient of the sample. There is an urgent need for a device to calibrate the amount of laser defocus. Li et al [23] identified the focus position through two-beam cross positioning. This method generally focuses at the mm level and the accuracy is poor. Motto-Ros et al [24] compared the determined cross center position produced by a red laser pointer with a reference position to measure eventual deviations from the initial height of the sample surface, where a precision of better than 5 μm in the determination of the sample surface height has been obtained. In order to achieve higher focusing accuracy, a simple and fast focusing control method that achieves focusing accuracy better than 3 μm in μLIBS is proposed in this paper.

2. Experimental description

The experimental setup used for LIBS analysis is shown in figure 1. The ablation pulse was generated from a Q-switch Nd:YAG laser (Bigsky Ultra, USA) at 1064 nm with a pulse width of 10 ns. The beam was attenuated to work with an adjustable energy (0–1 mJ). A beam shutter followed by a beam expander system was used to shape the laser and obtain a good beam profile to gain spatial resolution. The laser beam is reflected by a 1064 nm mirror and focused on the surface of the sample by a 20× objective. This 1064 nm reflector can reflect 90% of the laser energy. In addition, a laser pointer with a beam expander can adjust the size of the focusing spot. It can produce a red light and passes through a spectroscope with a transmittance of 3:7, by which 30% of the beams of light converge on the sample to form a spot through the 20× objective. When the distance between the sample and the focus lens changes, the size of the focused spot changes accordingly. Therefore, the CCD camera and focusing objective lens were used to form an optical system to detect the change of the spot. For the sake of regulating the focusing control more accurately, a 3D motorized stage with 1 μm accuracy was used, to drive the sample to move up or down so as to correct the defocus of the laser.

The LIBS signal was collected through a quartz lens with a focal length of 12 mm. This quartz lens was 65 degrees from the direction of the laser beam. The acquired plasma emission spectrum was coupled to the spectrometer (AvaSpec-2048 from Avantes, 190–305 nm) through a fiber. In order to obtain a stronger spectral line with less continuous background, the

Figure 1. Experimental assembly of μLIBS. (1. Laser 2. Attenuator 3. Beam shutter 4. Beam expander 5. Laser pointer 6. CCD camera 7. Splitter 8. Photodiode 9. 1064 nm reflector 10. Objective lens 11. XYZ stage 12. Collection device 13. Optical fiber 14. Spectrometer 15. Trigger 16. Computer).
The delay time of the spectrometer was about 0.13 μs relative to the laser by optimizing the trigger time of the spectrometer. The laser energy was set to about 366 μJ per pulse (500 ms delay between pulses) and was monitored by a photodiode (DET10A/M Thorlabs, USA) next to the 1064 nm reflector in real time. Mapping was achieved by controlling the movement of an XYZ stage step by step. A software was developed to operate all the devices (laser, XYZ stage, CCD camera, spectrometer, etc) and to realize automatic 2D scanning on the sample surface. With this setup, we can achieve a crater with an inner diameter of about 35 μm. The crater and an acquired spectral line are shown in figure 2.

3. Methods

Ideally, when the beam passes through a convex lens, the propagation path of the beam is as shown in figure 3. The angle between the focused beam and the main optical axis is θ. In the direction perpendicular to the main optical axis, at a distance h from the focal plane, the resulting spot area S can be expressed as:

\[ S = \pi h^2 \tan^2 \theta \]  

It can be seen from equation (1) that the spot area obtained perpendicular to the main optical axis exhibits a quadratic function relationship with the distance from the focal plane. Therefore, we wonder whether we can use the camera to observe the focal spot area of the sample surface to realize the automatic adjustment of μLIBS laser defocus. For this purpose, we have done the following research.

3.1. Establishment of an automatic focusing model

In the experiment, samples were polished by using 500#, 1000# and 2000# sandpaper, respectively, so that the...
The surface roughness of the sample was about 0.05–0.2. In order to reduce the interference of stray light on the experiment, we set the exposure time of the camera to be 50 $\mu$s and adjusted the Y-axis of the stage to find the minor spot focused by the laser pointer. The minor spot size obtained was approximately 10 $\mu$m. Then, at this position, the stage was moved up and down 80 times in steps of 1 $\mu$m. In order to weaken the influence of the vibration of the experiment table and the stability of the light source, three pictures were taken at each position. The number of pixels in the spot was calculated as follows: the median filter was used to process the salt and pepper noise in the picture first. Then, image pixels were normalized and the threshold of 0.05 was set to binarize the picture, making the pixel values of the image 0 and 1. Finally, the average number of pixels with the pixel value of ‘1’ in the picture was selected to estimate the size of the bright spot area in the picture. As shown in figure 4, the graph is drawn from the 161 height positions and the corresponding number of pixels.

When the laser beam and the red beam pass through the focusing objective, in the direction parallel to the focal plane, the defocus amount of the beam is first negative and then positive. In addition, when the laser beam is in a negative defocus state, the collected spectral lines are relatively stable, so the left focus model in figure 4 is selected. In order to make the model have a more reasonable adjustment range, it was prepared to set the laser energy stabilization point (laser negative defocus 20 $\mu$m) at the position where the red line is shown in figure 4, at a relative position of the model of 40 $\mu$m. First, the number of pixels in which the spot pixel

---

**Figure 5.** Number of pixels of the focusing spot over the relative position of the Y-axis in the intra-group test (a) and the inter-group test (b).

**Figure 6.** Model fitted by the average of the number of pixel points obtained in the seven sets of experiments.
value obtained by the above-described picture processing method was ‘1’ at the relative position of 40 μm was recorded. Then, we adjusted the laser energy attenuator to minimize the laser energy and found the sample point that the laser beam could excite on the sample as the focus of the laser, and moved the Y-stage up 20 μm. Finally, the beam expander next to the laser pointer was adjusted so that the number of pixels of the obtained spot focused on the sample substantially coincided with the number of spot pixels previously obtained at a relative position of 40 μm. In this way, we can make the relative position of the stage 40 μm and the laser negative defocusing amount of 20 μm in the same position.

To explore the light source stability, ‘scratches’ on the surface of the sample, and the effects of the external environment on the experimental model, experiments were conducted between the intra-group test and the inter-group test. The intra-group test was to take three pictures with the camera every 1 μm by the Y-stage, when the relative horizontal position of the sample was unchanged. The obtained images were processed by the above image processing method. The relationship between the number of points whose pixel value was ‘1’ and the corresponding relative position of the obtained picture is as shown in figure 5(a). It is shown that the relative error of the experiment is small and has good repeatability. A total of seven groups were tested in the inter-group test. In each set of the inter-group test, the stage was moved horizontally by 50 μm. The number of pixel values of the seven sets of picture pixels with the relative position of Y-stage changes is shown in figure 5(b). It is indicated that the ‘scratches’ on the surface of the sample have an effect on the experiment, but using this method, the model can achieve a focusing accuracy higher than 3 μm within error permissibility.

The model was fitted using the average of seven sets of experimental data from the inter-group test (in figure 5(b), indicated by ‘*’). As shown in figure 6(a), the cubic function can be used to fit the model well. However, in the specific experiment, solving the cubic function needs to be filtered from the obtained solution and it takes so much time, which increases the complexity of the system. The method shown in figure 6(b) was adopted. This model used a linear function to perfectly fit the number of pixels corresponding to the relative position of 20–60 μm and the complexity of the system was reduced without losing the accuracy of the system in a certain range. The block diagram of the automatic defocusing adjustment in this experiment is shown in figure 7.

As shown in figure 7, in the specific focusing process, first, three pictures are taken by the camera, and the average number of pixels of the spots in the three pictures is calculated by using the method for solving the number of pixels of the spot, and is recorded as S. Second, the relative height position in the focus model established in figure 3 is solved for the average number of pixel points S, and is represented by D1. Then, the focus amount D2 is calculated by the distance value at which D1 subtracts the reference position point. If D2 is greater than 0, the lens-to-sample distance is reduced by D2. If D2 is less than 0, the lens-to-sample distance is increased by D2. The above steps are repeated until the absolute value of the focusing amount D2 is less than 1 μm, and the focusing has ended.

4. Results and discussions

4.1. Quantitative analysis of Mn and Ni elements in low-alloy steel

Spectral data acquisition was performed on ten Japanese low-alloy steel samples (element concentration is shown in table 1) under the premise of using the focusing method to ensure the same surface height. Each sample was 25 craters ablated by the laser with an interval of 50 μm between each crater to form a 5 × 5 matrix. Each crater was generated by ten laser pulses, the first five lasers being used to clean the impurities on the surface of the samples. In order to ensure the stability of the spectrum, the average value of the spectral lines generated by the sixth to tenth laser pulses was taken as a spectrum. In the first and second samples, the content of the
Ni element is relatively less, as there was no high characteristic line. Therefore, in the process of analyzing the Ni element, only the remaining eight samples were used for calibration. With the rise of the concentration of elements in the sample, the self-absorption effect of the elements is aggravated [25, 26], so the calibration curve was fitted using a quadratic function. The Mn II (257.6 nm) and Ni I (300.2 nm) lines were analyzed using the basic calibration curve, and the

![Calibration curves of the Mn element and Ni element in (a) and (c), and the relationship between the actual concentration and predicted concentration of the sample drawn by leave-one-out cross-validation in (b) and (d).](image)

| Table 1. Low-alloy steel sample concentration table. |
|-----------------------------------------------|
| Element concentration (%) | C   | Si  | Mn | P  | S   | Cu  | Ni  | Cr  | Mo  | V   |
|-----------------------------|-----|-----|----|----|-----|-----|-----|-----|-----|-----|
| Number                      | 1   | 2   | 3  | 4  | 5   | 6   | 7   | 8   | 9   | 10  |
| 1   | 0.0009 | <0.01 | 0.01 | 0.001 | 0.002 | 0.01 | 0.01 | 0.01 | 0.001 | 0.001 |
| 2   | 0.1 | 0.6 | 0.15 | 0 | 0.0032 | 0.07 | 0.05 | 4.02 | 0.5 | 0.4 |
| 3   | 0.149 | 0.4 | 0.75 | 0 | 0.006 | 0.69 | 0.1 | 3.22 | 0.4 | 0.027 |
| 4   | 0.21 | 0.06 | 2 | 0.008 | 0.016 | 0.11 | 0.5 | 2.51 | 0.3 | 0 |
| 5   | 0.26 | 0.25 | 1.6 | 0.013 | 0.0071 | 0.4 | 1.05 | 2.02 | 0.092 | 0.3 |
| 6   | 0.34 | 0.34 | 1.29 | 0.048 | 0.0013 | 0.49 | 1.55 | 1.49 | 0.2 | 0.058 |
| 7   | 0.5 | 0.3 | 1.02 | 0.038 | 0.026 | 0.2 | 2.02 | 1.02 | 0.6 | 0.11 |
| 8   | 0.64 | 0.15 | 0.51 | 0.028 | 0.02 | 0.3 | 2.53 | 0.53 | 1.02 | 0.16 |
| 9   | 0.8 | 0.2 | 0.31 | 0.018 | 0.0029 | 0.17 | 3.26 | 0.12 | 0.82 | 0.2 |
| 10  | 0.99 | 0.11 | 0.1 | 0.003 | 0.009 | 0.05 | 4.06 | 0.05 | 0.059 | 0.49 |

Ni element is relatively less, as there was no high characteristic line. Therefore, in the process of analyzing the Ni element, only the remaining eight samples were used for calibration. With the rise of the concentration of elements in the sample, the self-absorption effect of the elements is aggravated [25, 26], so the calibration curve was fitted using a quadratic function. The Mn II (257.6 nm) and Ni I (300.2 nm) lines were analyzed using the basic calibration curve, and the
fitted coefficients $R^2$ were 0.9944 and 0.9676, respectively. In order to reduce the influence of the plasma fluctuation, the two elements were calibrated by the internal standard method, and the accuracy of the model analysis was measured by the leave-one-out cross-validation method. The reference lines of the selected Fe elements were Fe II (256.7 nm) and Fe II (298.5 nm). In figure 8, (a) and (c) are calibration curves of the Mn element and Ni element, respectively, and the error bars represent standard deviation of the intensity of 25 position points collected. We can find that the $R^2$ of the fitting curves of the Mn and Ni elements are all above 0.997 and the relative standard deviations of the line intensity of Mn (257.6 nm)/Fe (256.7 nm) and Ni (300.2 nm)/Fe (298.5 nm) are 2.44% and 4.38%, respectively. Figures 8(b) and (d) show the relationship between the actual concentration and predicted concentration of samples drawn by leave-one-out cross-validation. The error bars represent the standard deviation of the predicted concentrations of the 25 spectral data collected for each sample. The root-mean-square errors represent the root-mean-square error of predicted concentration and actual concentration. From this, we can draw the conclusion that the calibration model can accurately calibrate the content of Mn and Ni in low-alloy steel samples. The experimental result shows that with the above-mentioned automatic adjustment of the laser defocus amount, a relatively accurate analysis of some elements in the low-alloy steel can be performed at a crater diameter of about 35 μm.

4.2. Automated controls during a surface mapping

In this section, we present the ability of the automatic focusing control system to work with an inclined plane sample and a curve sample. The experimental parameters described previously were used. Prior to the scanning analysis, we used the above-mentioned focusing method to lock the sample height to the position where the laser can generate a stable plasma (laser negative defocus 20 μm). The measurements were performed on the sample surface, which moved along the X- and Z-axis in a 20 × 20 matrix of 400 craters. Ten spectra were acquired for each crater, and the average of the sixth to tenth spectra is taken as a spectrum. Two series of measurements were performed, one with the focusing control system to fixed lens-to-sample distance and one without. The inclined plane used was a low-alloy steel sample with a slope of about 1.1°. The sample concentration is shown in table 1 and No. 3. The curved surface used was a high-alloy steel sample with an iron content of approximately 85% with a curvature of about 60.8 m⁻¹. The change in the height gradient of the samples and the placement position are shown in figure 9. We randomly chose the spectral lines of the Fe elements at wavelengths of 302.0575, 298.4797, 294.8, 278.4092, 276.2334, 272.7983, 269.3336, 244.5374, 234.8867 and 232.8 nm, respectively. The spectral positions of these lines are shown in figure 10. The mapping started with a line along the X-axis of 20 craters in steps of 200 μm. At the end of the 20th crater, the sample was shifted by 200 μm along the Z-axis. It was then scanned back along the X-axis. The round-trip scan continued to accomplish the matrix of 20 × 20 craters. The linear displacement of the sample along the X-axis induced a variation of the lens-to-sample distance, resulting in a change in the intensity of the spectrum. In figures 11(a) and (c), it can be seen that in the absence of focusing control, the fluctuations in the spectrum are very strong. However, when using this focusing control method, the stability of the spectrum was greatly improved, as shown in figures 11(b) and (d). The fluctuation of relative standard deviation of these lines is shown in table 2. Compared to focusing and non-focusing, the average relative standard deviation on the inclined plane was reduced by about three times and the average relative standard deviation on the curved surface was reduced by about eight times. The average relative standard deviation of these lines calculated by focusing was less than 5%.
5. Conclusion

In this article, we proposed a method for laser focusing control in micro-laser-induced breakdown spectroscopy. The accuracy of the laser focusing control could achieve 3 μm. On the scale of the crater diameter of about 35 μm, Fe II (256.7 nm) and Fe II (298.5 nm) characteristic spectral lines were selected as the internal standard lines for the analytical lines, Mn II (257.6 nm) and Ni I (300.2 nm), respectively, to analyze the concentrations of Mn and Ni in low-alloy steel samples. The values of $R^2$ of Mn and Ni were 0.9974 and 0.9993, respectively. The average root-mean-square errors of Mn and Ni were 0.0133 and 0.0395; and the values of $R^2$ of Mn and Ni were 0.9995 and 0.9990, respectively, through leave-one-out cross-validation. The results demonstrate that after using the proposed method, the internal standard method can further attenuate the interference of the laser sample fluctuation and the amount of each laser ablation.
substance on the spectral acquisition. In addition, using this automatic focusing method, a $20 \times 20$ matrix was analyzed for a low-alloy steel sample surface with a slope of about $1.1^\circ$ and a high-alloy steel sample with a curvature of about $60.8 \text{ m}^{-1}$. For ten analytical lines of Fe selected randomly, focusing and non-focusing results were compared. The average relative standard deviation on the inclined plane was reduced by about three times and the average relative standard deviation on the curved surface was reduced by about eight times. For both the inclined plane and curved surface, the average relative standard deviations of these lines with focusing control were less than 5%. The experimental results show that the use of the focusing method proposed in this paper can greatly enhance the stability of the spectral line. The proposed focusing control method provides a new idea for the consistency of non-planar in spectral micro-domain analysis of metal structural parts, bones and ceramics.

Acknowledgments

This work was supported by the National Key Research and Development Program of China (Grant No. 2017YFF0106202), National Natural Science Foundation of China (Grant No. 61473279), the Key Research Program of Frontier Sciences, CAS (Grant No. QYZDJ-SSW-JSC037) and the Youth Innovation Promotion Association, CAS.

References

[1] Rieger G W et al 2002 Appl. Spectrosc. 56 689
[2] Freedman A, Iannarilli F J Jr and Wormhoudt J C 2005 Spectrochim. Acta B 60 1076
[3] Cristoforetti G et al 2006 J. Anal. At. Spectrom. 21 697
[4] Wang X Z et al 2017 Spectrosc. Spect. Anal. 37 1254 (in Chinese)
[5] Liu J et al 2015 Plasma Sci. Technol. 17 644
[6] Wang F J et al 2017 Spectrosc. Spect. Anal. 37 236 (in Chinese)
[7] Algan M S, Hou Z Y and Wang Z 2017 J. Anal. At. Spectrom. 32 1905
[8] Godwal Y et al 2008 Opt. Express 16 12435
[9] Menut D et al 2003 Appl. Opt. 30 6063
[10] Bette H and Noll R 2004 J. Phys. D Appl. Phys. 37 1281
[11] Wessel W et al 2010 Eng. Fract. Mech. 77 1874
[12] Liu X N et al 2015 Plasma Sci. Technol. 17 904
[13] Vadillo J M et al 1996 Fresenius J. Anal. Chem. 355 909
[14] Fabre C and Lathuiliere B 2007 Spectrochim. Acta B 62 1537
[15] Yang C et al 2015 Plasma Sci. Technol. 17 671
[16] Ashrafkhani B, Bahreini M and Tavassoli S H 2015 Opt. Spectrosc. 118 841
[17] Han Z Y et al 2015 Spectrosc. Spect. Anal. 35 304 (in Chinese)
[18] Zhang S et al 2018 Front. Phys. 13 135201
[19] Godwal Y et al 2008 Laser Part. Beams 26 95
[20] Lu Y et al 2013 J. Anal. At. Spectrom. 28 743
[21] Gornushkin I B et al 2004 Appl. Spectrosc. 58 762
[22] Hwang D J et al 2007 Appl. Phys. Lett. 91 251118
[23] Li Y D et al 2016 Spectrosc. Spect. Anal. 36 2238 (in Chinese)
[24] Motto-Ros V et al 2014 Spectrochim. Acta B 92 60
[25] Golik S S et al 2015 Plasma Sci. Technol. 17 975
[26] Wang Z et al 2011 J. Anal. At. Spectrom. 26 2289