Effect of Plane Mirrors Combined with Au-Nanoparticle Confinement on the Spectral Properties of Fe Plasma Induced by Laser-Induced Breakdown

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ABSTRACT: To overcome the shortcomings of low detection sensitivity and high spectral line background noise of traditional laser-induced breakdown spectroscopy (LIBS), a method of combining flat mirrors with gold nanoparticles (Au-NPs) was proposed. First, independent plane mirror and Au-NPs experiments were performed by using aluminum alloy samples. After that, the samples were placed under four conditions (None-LIBS; Three mirrors-LIBS; 20 nm Au-NPs-LIBS; 20 nm Au-NPs and Three mirrors-LIBS), and the differences between various spectral parameters were analyzed. The experimental results show that the optimal number of plane mirrors is 3, and the optimal size of gold nanoparticles is 20 nm. When 20 nm Au-NPs and Three mirrors are used in combination, the plasmonic spectral intensity can be effectively enhanced. The enhancement factor is up to 2.98 (Fe II 240.45 nm), and the signal-to-noise ratio (SNR) is significantly improved up to 10.03. The variation of the plasma temperature between 1 and 5 μs was also investigated, and the experimental results showed that the plasma temperature could be increased by the flat mirror, while the electron temperature was almost unchanged under the action of Au-NPs. It is shown that the combination of the two enhancement methods can effectively increase the spectral intensity and improve the signal-to-noise ratio, which will help to improve the detection performance of the LIBS system.

1. INTRODUCTION

Laser-induced breakdown spectroscopy is a technology that can qualitatively and quantitatively analyze elements contained in substances. It uses a pulsed laser to focus on the surface of the sample, and when the laser ablates the sample, plasma is generated. The spectrometer collects the spectrum of the plasma radiation, and the computer performs elemental analysis. The technology is simple in sample preparation, easy in operation, and comprehensive in elements detected. Laser-induced breakdown spectroscopy (LIBS) technology is widely used in material detection,1–3 environmental monitoring,4–7 gas composition analysis,8–10 and other fields.11–14

Traditional LIBS has the disadvantages of low detection sensitivity and high spectral line background noise. Therefore, many methods have been proposed to enhance spectral intensity and improve the sensitivity of LIBS systems, such as nanoparticle enhancement,15 increasing sample temperature,16 etc.
multipulse, and other methods. These methods were used in combination with LIBS, and the related spectral enhancement theory was also investigated.

Wang et al. compared the measurement results of stainless steel in air using single-pulse LIBS (SP-LIBS) and DP-LIBS, indicating that DP-LIBS can significantly enhance the emission intensity. De Giacomo et al. found that depositing a layer of nanometal particles with a diameter of 20 nm on the surface of the sample to be tested can effectively reduce the excitation threshold of the plasma. Chen et al. applied LIBS technology to the detection of soil metal elements. Two plane mirrors and three plane mirrors were placed around the sample. The results showed that the temperature and density of the generated plasma electrons were significantly enhanced. At present, no one has studied the effect of Au-NPs with different particle sizes combined with flat mirrors on laser-induced spectroscopy.

In this paper, two and three plane mirrors combined with LIBS were used to obtain the optimal number of plane mirrors, and then Au-NPs with different particle sizes were used to deposit on the surface of the sample to obtain the optimal particle size. The optimal number of plane mirrors combined with the optimal particle size of Au-NPs was used in the LIBS system, and the changes of parameters such as aluminum alloy spectral enhancement factor, signal-to-noise ratio, and plasma temperature were studied.

2. EXPERIMENTAL SETUP

The LIBS instrument used in the experiment is the ChemReveal desktop laser-induced breakdown spectrometer from TSI Corporation of the United States. The laser configured by the instrument is a Nd:YAG laser. The laser wavelength is 1064 nm, the maximum pulse energy can reach 200 mJ, the repetition frequency is adjustable from 0 to 10 Hz, and the pulse width is 10 ns. The detected wavelength range is 190–950 nm with a resolution of 0.05 nm, and the sample is placed on a computer-controlled XYZ three-dimensional sample stage. The experimental setup is shown in Figure 1.

The samples used in the experiment were standard aluminum alloy samples provided by the Standard Sample Research Institute of Fushun Aluminum Factory.

During the plane mirror experiment, two plane mirrors with a width of 40 mm and a height of 20 mm were placed vertically on the surface of the sample; the two mirrors were parallel to each other, and the distance between the mirror surfaces was 6 mm from the central axis of the plasma; the three plane mirrors were set up to reflect on the two planes. At one end of the mirror device, a third flat mirror with a width of 13 mm and a height of 20 mm was placed vertically. The distance between the mirror surface and the central axis of the plasma is still 6 mm, and the optical fiber collects spectral signals at the other end. The schematic diagram of the plane mirror device is shown in Figure 2.

The particle sizes of the gold nanoparticles used in the experiment were 10, 20, 30, and 40 nm, respectively, and the concentration was 1 mg/mL. Except for Au and trace Na elements, the solution contained no other metal elements. When using NELIBS, a spot was struck to clean the sample, and then the Au-NP colloid solution was dropped onto the cleaned sample surface. After natural evaporation, a layer of gold nanoparticles was deposited on the surface, and then the sample was subjected to the deposition of gold nanoparticles. The breakdown schematic diagram of the NELIBS experiment is shown in Figure 3.

3. EXPERIMENTAL METHODS

3.1. Best Flat Mirror Quantity. The laser energy was set to 70 mJ, the laser repetition frequency was set to 5 Hz, the spot size after focusing was 200 μm, and the spectrometer delay time was 1 μs to break down the aluminum alloy sample. Taking the trace element spectral lines Fe II 239.53 nm, II 240.45 nm, and II 240.63 nm in the sample as the analytical lines, the spectral intensities of the two and three plane mirror devices were measured successively.

The measured spectral data were averaged through 10 repeated experiments in each case, and the spectral intensity results are shown in Figure 4. It can be seen that the spectral intensity has been improved to a certain extent after the plane mirror device was added compared with the device without the plane mirror. This is because when the laser-induced plasma expands outward, the initial explosion pressure generates a strong shock wave, and the shock wave diffusion speed is much higher than the expansion speed of the plasma. So when the shock wave hits the flat mirror during expansion, it reflects back into the central region of the plasma, compressing the expanding plasma and confining it to a smaller size. This increases the probability of collisions between fast-moving particles in the plasma, producing more particles in excited states, and ultimately increasing the spectral intensity. In addition, the photons are partially reflected back into the plasma after encountering the flat mirror and generate resonance absorption with the atoms in the sample, which also increases the radiation intensity of the plasma. When three plane mirrors are placed, the spectral intensity is the highest because three plane mirrors can reflect shock waves and light radiation more effectively than two planes, so the enhancement effect is better. Therefore, in this paper, three plane mirrors are the optimal number of plane mirrors.

3.2. Optimum size of Au-NPs. The experimental parameters are set in the same way as the plane mirror experiment. Figure 5 shows the spectral intensity of Fe II 240.45 nm in the sample under Au-NPs with different particle sizes (10 nm, 20 nm, 30 nm, 40 nm). The particle size of 0 represents the spectrum without adding Au-NPs, and the error bar is the standard deviation of the 10th data. Compared with no Au-NPs added, Au-NPs with four particle sizes all have an enhancement effect on the spectrum. The enhancement...
mechanism is that the nanogold particles can effectively reduce the excitation threshold of the plasma. The excitation threshold is the minimum value that can make the sample generate plasma laser energy. When the excitation threshold is lowered, it means that the sample can be excited out of the plasma radiation spectrum with only a small amount of laser energy, or the ablation is deeper with the same laser energy. The gold nanoparticles make the surface of the sample rough. When the laser ablates the rough surface, the efficiency is higher, which can effectively improve the ablation efficiency of the laser, reduce the laser breakdown threshold, and enhance the characteristic spectral line. Relatively speaking, when the particle size of Au-NPs is 20 nm, the spectral enhancement effect is the best. Therefore, under the current experimental conditions, the optimal particle size of Au-NPs is 20 nm.

3.3. Combination of Two Enhancement Methods. When the combination experiment of Au-NPs and plane mirror was conducted, the nanogold was first coated on the surface of the sample, and then the plane mirror was quickly placed so that the coated nanogold area was in the center of the plane mirror. The sample is broken down. Figure 6 shows the spectral intensities at the 240.45 nm line of Fe II in four cases (None-LIBS; Three mirrors-LIBS; 20 nm Au-NPs-LIBS; 20 nm Au-NPs and Three mirrors-LIBS). It can be seen from Figure 6 that the enhancement effect of the combination of Au-NPs and plane mirrors is better than that of Au-NPs or plane mirrors alone because the plasmon is affected by two mechanisms, and the enhancement effect is greatly improved. For spectral lines of the same wavelength, the intensity from strong to weak is the combination of the flat mirror and gold nanoparticles, the intensities of gold nanoparticles, flat mirror confinement, and zero confinement.
4. RESULTS AND DISCUSSION

4.1. Enhancer Factor. The enhancement factor described in this paper refers to the ratio of the spectral intensity under a certain enhancement method to the spectral intensity without any enhancement under the same other experimental conditions. Figure 7 shows the enhancement factors of the Fe II 240.45 nm line under three enhancement methods relative to traditional LIBS. From the Fe II 240.45 nm spectral line, the enhancement factor of Au-NPs and the plane mirror reached the maximum, and the enhancement factor reached 2.98.

4.2. Signal-to-Noise Ratio (SNR). SNR is often used to evaluate the detection sensitivity of LIBS methods. The larger the SNR, the higher the sensitivity and the lower the detection limit. In this paper, the Fe II 240.45 nm emission line was selected to calculate the signal-to-noise ratio, and the results are shown in Figure 8. It can be seen that the signal-to-noise ratio is low without any enhancement method, while the signal-to-noise ratio is improved after using the plane mirror or the Au-NPs method. Consistent with the enhancement factor conclusion, the Fe II 240.45 nm spectral line reaches the maximum signal-to-noise ratio when Au-NPs is combined with a plane mirror, and the signal-to-noise ratio reaches 10.03.

4.3. Plasma Temperature. The plasma temperature is an important parameter to describe the properties of the plasma, and the higher the temperature, the stronger the excitation ability. According to the LTE conditions, the Boltzmann slope method was used to calculate the plasma temperature. According to the saha-Boltzmann equation, it can be deduced that

\[
\ln \frac{\lambda_{mn} I_{nm}}{g_m A_{mn}} = -\frac{E_m}{kT} + \ln \frac{hcN}{U(T)}
\]

(1)

where \( m \) and \( n \) are the upper and lower energy levels of the transition, respectively, \( \lambda_{mn} \) is the wavelength of the characteristic spectral line, \( I_{nm} \) is the spectral line intensity, \( A_{mn} \) is the transition probability, \( g_m \) is the statistical weight of the upper energy level, \( E_m \) is the energy of the upper energy level, and \( k \) is Boltzmann constant, \( T \) is the plasma temperature, \( h \) is Planck’s constant, \( c \) is the speed of light in vacuum, \( N \) is the electron number density, and \( U(T) \) is the partition function. Taking the ordinate as the ordinate and \( E_m \) as the abscissa to draw a graph, and fitting a straight line with a slope of, the plasma temperature \( T \) can be obtained. In this paper, the Fe element is selected to calculate the plasma temperature, and the spectral parameters are shown in Table 1. The data are from the NIST database.

| \( \lambda/\text{nm} \) | \( \frac{g_m A_{mn}}{10^7 \text{s}^{-1}} \) | \( E_m/\text{eV} \) |
|----------------|------------------|--------------|
| 228.72 | 6.69 | 5.50 |
| 237.36 | 4.57 | 5.27 |
| 300.72 | 1.37 | 4.20 |
| 430.79 | 30.40 | 4.43 |

Four spectral lines at 228.72, 237.36, 300.72, and 430.79 nm were selected to draw the Boltzmann diagram to calculate the Fe plasma temperature. Figure 9 is the Boltzmann diagram when the delay time is 1 \( \mu \text{s} \) without any constraints.
Figure 10 shows the temperature changes of Fe plasma when the delay time is 1–5 μs in four cases. It can be seen that the electron temperature in each case decreases with increasing delay time, and the change trend tends to be flat. For the same delay time, the plasma temperature is larger under the two conditions of plane mirror confinement, Au-NPs, and plane mirror combination. There is little difference in plasma temperature between only Au-NPs enhancement and no enhancement. This indicates that the enhancement of plasma temperature is due to the plane mirror confinement. The temperature enhancement is due to the plane mirror confinement. The reason is that when the shock wave is reflected back to the plasma by the confinement of the plane mirror, the plasma is bound, and the collision probability increases. In addition, the resonance absorption also increases the plasma temperature. Comparing Figure 10, panels a and c, it can be seen that the Au-NPs have little effect on the plasma temperature. This is because the plasma temperature is mainly determined by the photon energy absorbed during the electron transition, Au-NPs can only increase the sample ablation efficiency, and the photon energy absorbed by the electrons does not change, so Au-NPs do not change the electron temperature.

5. CONCLUSION

In this paper, the effects of the LIBS technique combined with a plane mirror reflector and gold nanoparticles on the spectral parameters of aluminum alloy samples were investigated. Using two and three plane mirrors to enhance the spectrum, the results show that the spectral enhancement effect of three plane mirrors is better. For Au-NPs with different particle sizes (10 nm, 20 nm, 30 nm, 40 nm), 20 nm Au-NPs is the optimal particle size for enhancing the spectrum. The Fe II 240.45 nm spectral line was selected for spectral analysis. The spectral enhancement factor, signal-to-noise ratio, and plasma temperature were investigated for four cases (None-LIBS; Three mirrors-LIBS; 20 nm Au-NPs-LIBS; 20 nm Au-NPs and Three mirrors-LIBS). When 20 nm Au-NPs was combined with Three mirrors, the spectral enhancement was the most obvious, and the enhancement factor of Fe II at 240.45 nm was the largest, reaching 2.98. The signal-to-noise ratio also reached its maximum at this time, reaching 10.03. In addition, the temperature changes of Fe plasma from 1 to 5 μs were compared under the four conditions, and with a plane mirror reflector, the plasma temperature was higher, while Au-NPs did not have much effect on the plasma temperature. This study shows that the combination of the two enhancement methods can effectively increase the spectral intensity and improve the signal-to-noise ratio, which will help improve the detection performance of the LIBS system.

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Figure 10. Plasma temperature variation under four conditions: (a) None-LIBS; (b) Three mirrors-LIBS; (c) 20 nm Au-NPs-LIBS; (d) 20 nm Au-NPs and Three mirrors-LIBS.
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Notes

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