The role of Helium plasma in improving the sensitivity of Hydrogen detection in laser induced plasma spectroscopy

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Published 13 August 2014

The experimental studies have been performed on the characteristics of laser induced He plasma that give influence to the sensitivity enhancement and the long lifetime of hydrogen emission line. Under He ambient gas, the emission intensity of spectra of hydrogen and oxygen increase with low background emission. In order to confirm the intensity enhancement, spatial intensity distribution of hydrogen and helium was measured along the plasma expansion direction. The result revealed that the maxima come at the far end of the plasma where the available shock wave generated thermal excitation energy should have been significantly reduced. It implies the time-mismatch effect on the shock wave excitation process and the presence of possible contribution of helium metastable excited state in He plasma.

Keywords: Helium plasma; hydrogen emission line; laser induced plasma spectroscopy.

1. Introduction

Nowadays, Laser-Induced Plasma Spectroscopy (LIPS) method has gained popularity and grown for spectrochemical analysis over a wide range of applications. Refinders are drawn to this particular application by the simplicity of equipment for generating a laser induced plasma, the simple process for sample preparation as well as the possibility of performing local microanalysis. Furthermore, the improvement in optical detection method made possible by the availability of the Optical Multichannel Analyzer (OMA)

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systems that has further enhanced the spectroscopic resolution and accuracy in addition to allowing for real-time acquisition of experimental data.

The LIPS method had been developed in two major directions¹⁻³, one employs a high pressure surrounding gas and is usually referred as Laser Induced Breakdown Spectroscopy (LIBS), which was first proposed by Radziemski et al.⁴⁻⁵ In LIBS, a pulsed Nd-YAG laser with a pulsed energy of approximately several tens of mJ is focused on the sample, resulting in a high temperature and high density plasma. A gated OMA is used to remove the strong background emission emitted from the plasma. The use of LIBS in rapid quantitative analysis has been demonstrated in various fields such as soil analysis⁶⁻⁷, metallurgy and mining⁸⁻⁹, art conservation¹⁰, ceramic analysis¹¹, organic materials analysis¹²⁻¹³ and pharmaceuticals.¹⁴

Another direction is the use of low gas pressure in order to suppress the background emission intensity.¹⁵⁻¹⁸ Our refind group has referred this method as Laser Induced Shock Wave Plasma Spectroscopy (LISPS) which was first proposed by Kagawa et al. In the subsequent series of experiments, the low pressure plasma emission spectra were found to exhibit consistent favourable characteristics for spectrochemical analysis of a variety of samples. In addition, the experimental studies further revealed the formation process of shock wave plasma and its important role in the excitation of the ablated atoms in low pressure plasmas.

Hydrogen analysis is urgently needed in a number of investigations covering the field of material sciences as well as industrial processes and products, such as the detection of hydrogen distribution in high strength steel weldments¹⁹ and particularly the detection of hydrogen trapped in zircaloy fuel vessels in nuclear power plant and hydrogen impurity in titanium for industrial and medical applications.²⁰⁻²¹

We have successfully applied the laser-induced plasma in low-pressure surrounding gas of around 1 Torr to analyze hydrogen in zircaloy used in nuclear power station. However, the low-pressure plasma technique has limitations for practical application in nuclear power station, one of which is the inability for in-situ analysis, which requires atmospheric pressure surrounding gas. It is well known that hydrogen spectrum of laser induced plasma in the atmospheric pressure ambient air invariably suffers from the unfavourable effects of line broadening and intensity diminution. These adverse effects were, on the other hand, practically negligible in the emission spectra of heavier elements, which explain the highly successful application of LIBS nowadays.

Along with the continuing development of LIBS, experiments showing the results of emission spectra enhancement using ambient helium gas were already reported in the early 1990s using various solid metal samples.²²⁻²³ It was demonstrated in each case that a maximum signal to background ratio of plasma emission from solid metals was achieved in the reduced pressure helium atmosphere. Kuzuya et al reported that the emission line to continuum ratios were maximized in a reduced pressure helium atmosphere for the analysis of several solid metals.²³ The promising advantages of using helium ambient gas on hydrogen emission enhancement were recently investigated and confirmed by Kagawa et al in a series of experimental studies on the emission spectra from solid zircaloy

samples containing hydrogen impurity in atmospheric²⁴⁻²⁵ and reduced pressure helium ambient gas.²⁶

The effects of helium and nitrogen ambient gases on the hydrogen and carbon emission intensities from methane gas were comprehensively studied with LIBS by C.A. Henry et al.²⁷ It was shown that increased helium addition on the ambient gas resulted in enhanced helium emission intensity and improvement of its analytical figure of merit measured in terms of peak to base ratios and signal to noise ratios. Meanwhile an opposite quenching effect was exhibited by nitrogen addition. The report went on to show that the electron density in plasma was increased by nitrogen addition, leading to a perceptible shift of the temporal emission decay profile. Based on the analysis of additional data, the authors concluded that the enhancement and quenching effects might also be related to the changes of overall plasma condition induced by the decrease and increase in electron density in the plasma, respectively. In particular, the authors suggested that the previously proposed additional excitation mechanism via helium atom should be relegated to a lesser role in the helium ambient gas with significant nitrogen addition.

This paper will describe our work that aimed to re-examine the relative contributions of the shock wave induced thermal excitation process and the He assisted excitation process in laser-induced plasma. It was previously shown that the former was primarily responsible for emission of the relatively heavier atoms such as Zr, while it is much less effective for hydrogen.²⁸ Given the possible additional contribution of “He-assisted excitation” to hydrogen, this work was expected to provide the important clues as to which of the two different excitation mechanisms were mainly responsible for the different emission lines. In particular, detailed measurements of spatial distribution, in addition to temporal variations of emission intensity, can be readily performed in the spatially more extended low-pressure plasma. These data would reveal the different effects of different ambient gases on the spatial and temporal emission characteristics associated with the different excitation mechanisms mentioned above.

2. Hydrogen Analysis Using Laser Induced Plasma Spectroscopy

2.1. Pressure dependence of hydrogen emission

As mentioned in the introduction, application of LIBS to hydrogen analysis with atmospheric pressure ambient air is known to be less than successful. In an effort to overcome this shortcoming, an initial study of hydrogen emission with low pressure ambient air was conducted on a glass slide sample because it contains hydrogen in the form OH⁻ at rather high concentrations. For this study, TEA CO₂ laser was focused on a glass sample in surrounding air of around 1 Torr. The strong and sharp H I 656.2 nm (H _{α}) emission line was successfully detected displaying a narrow full spectral width of 0.3 nm at half maximum (FWHM) as shown in Fig. 1. It is worth noting that the spectrum features very low background emission.

Fig.1. The spectrum of hydrogen getting narrower at the air of 1 Torr (FWHM= 0.3nm); the spectrum taken from the glass slide.

This experiment is repeated with 1 atmospheric pressure surrounding air just as usually done in the ordinary LIBS. The resulted emission intensity of H_{α} as presented in Fig. 2 is found to be drastically suppressed, with much broader spectral width (FWHM) of 1.1 nm.

Fig.2. The spectrum of hydrogen getting broader at the air of 760 Torr (FWHM= 1.1nm); The spectrum taken from the glass slide

The peculiar phenomenon of H_{α} in respect to its pressure dependence, was examined using an Nd-YAG laser. An optical glass filter was used as the glass sample because of its low transmittance at the laser wavelength of 1,064 nm. The glass contains Mg and Ca on the order of a few weight percentages as the main impurities. At least estimated of 1,000 ppm of hydrogen from OH^{-} analysis using infrared spectroscopy.

The pressure dependence of H_{α} emission intensity is shown in Fig. 3. The H_{α} emission comes from the glass slide sample in surrounding nitrogen gas of 1 Torr to 760 Torr. It is clearly shown that the H_{α} intensity decrease sharply with increasing pressure from 2 Torr up to 100 Torr, followed by a slow decline thereafter, and eventually diminishes to practically zero at 760 Torr. Meanwhile, the profile of the Mg II 279.5 nm emission line clearly exhibits completely different behaviour from that of H_{α} emission. Namely, the emission intensity of Mg II 279.5 nm sharply increases from 2 Torr up to 100 Torr and then slowly increase with pressure up to 760 Torr. A similar tendency of peculiar reduction of H_{α} emission with the increasing gas pressure is invariably observed in other samples such as quartz and fossil stones using TEA CO_2 laser.

Fig.3. Pressure dependence of the emission intensities of H I 656.2 nm and Mg II 279.5 nm under nitrogen as the ambient gas. The emission intensity of spectra taken from a glass sample.

In order to examine the influence of different surrounding gas on the pressure dependence of the H_{α} emission intensity, helium gas was used in place of nitrogen gas. It was found that the reduction of hydrogen emission intensity with gas pressure took place at a lower pace.

2.2. Mismatching effect of hydrogen atom (light element)

The unfavourable pressure effect of hydrogen line, as shown in Fig. 3, was explained on the basis of the shock wave excitation model. Namely, an irradiation of the laser beam will take atoms gush out from the primary plasma with high speed to form shock wave. There is a time lag between the laser bombardment and the starting time of the shock wave and that the shock wave induced by propelling atoms of the host elements, which

are heavier than hydrogen. It is assumed that the time lag increase with increasing pressure. Therefore, at high pressures hydrogen atoms would gush out with very high speed earlier than other elements, because its mass is extremely light than others, and when the shock wave starts the hydrogen already locates forward of the shock front. We call this phenomenon as the “mismatching effect”. This mismatching effect also can explain the reason why H_{α} emission is more sensitive to the laser power density. In the case of low pressure of around 1 Torr, it is supposed that the time lag is short, and therefore the hydrogen gush out time and the shock wave starting time is almost synchronous, resulting in effective excitation of the hydrogen atom. Therefore, the strong hydrogen emission only takes place at low pressure.

2.3. Spatial distribution of hydrogen and helium emission intensity

In order to know the possible relationship between hydrogen and helium emission, we carried out the measurement of time-integrated spatial distributions of the hydrogen emission intensities employing the “plasma slicing technique”²⁹⁻³⁰, namely a movable lens imaging system was scanned along the plasma expansion axis, start from the zero point at the target surface till at the far end of the plasma (~ 30 mm), as shown in Fig. 4(a).

Fig. 4. (a) The feature of the plasma with size about 30 mm, was scanned using imaging system start from zero point at the target surface till the far end of plasma; (b) Spatial distribution of hydrogen and helium emission intensity normalized by the host calcium emission intensity measured from the black stone sample in 20 Torr ambient helium gas.

The result is presented in Fig. 4(b) in which both the hydrogen and helium emission intensities exhibit qualitatively similar distributions featuring more diffused distributions or more extended profiles. Additionally, both intensities appear to rise to their maxima

near the far end of the plasma at about 20 mm from the target surface, where the plasma temperature is supposed to approach its minimum with the correspondingly reduced thermal energy barely sufficient for the excitation of H atoms in the plasma.

It is important to recall that the excitation energies of both helium and hydrogen are known to be around 23.5 eV and 12 eV respectively, which are considerably higher than the 4 eV excitation energy of the calcium host element associated with its emission at 649.3 nm. This means, according to the shock-wave-induced thermal excitation mechanism, that the H and He emission intensities should be more pronounced closer to the target, with the calcium emission becoming relatively more favoured farther away from the target. However, the extended curves of normalized He and H emission intensities displayed in Fig. 4, especially the rises to their maxima near the far end of the plasma clearly contradict the result expected from the excitation mechanism described above. Therefore, an additional process other than the direct thermal excitation process must be responsible for the “unexpected” observation.

2.4. Helium induced excited (HIE) mechanism

It is worthwhile at this point to recall that the He I 667.9 nm emission is associated with one of the cascaded radiative transitions terminating at the metastable 2^1S_0 excited state of He, which may provide the needed excitation energy for the delayed and persistent emission of H. Unfortunately, in view of the large energy difference between the hydrogen excited state associated with H I 656.2 nm (12 eV) emission and the 2^1S_0 helium metastable excited state (20.8 eV), a direct collision-induced energy transfer involving only recoil kinetic energies of He and H is deemed highly unlikely. Instead, a more complicated process must be at work. It was proposed that the process might involve the release of an electron from the excited helium atom and transfer its energy to the hydrogen atom through a Penning-like ionization process such as

This is quickly followed by the recombination process leading to the neutral excited H and the subsequent radiative transition processes. It is also interesting and indeed remarkable to note that when the same measurement was repeated for zircaloy sample, the same general features of H and He intensity distributions were also reproduced. This result clearly provides an additional experimental support of He assisted excitation hypothesis.

In order to prove the role of helium in excitation of H, a special experimental setup as shown in Fig. 5 is devised, namely two Nd: YAG lasers system, both operated in the Q-switched mode with a repetition rate of 10 Hz, were configured to produce the laser beams in mutually perpendicular directions³¹.

Fig.5. The experimental setup used to examine the role of helium gas in the excitation of H. Two lasers are used, the fundamental one (1,064 nm) was used to generate the He plasma at point 5 mm in front of the target, and the second harmonic laser (532 nm) was used for ablation of the solid target.

One of the laser operating at its fundamental wavelength of 1,064 nm and a fixed energy of 110 mJ was focused onto a spot within the He ambient gas in the chamber to generate the He plasma at a point 5 mm in front of the target. The He gas flow rate was 2 L/min. The second laser was employed at the second harmonic wavelength 532 nm and a fixed energy of 37 mJ for ablation of the solid target. This second laser irradiation was started 10 μ s after the generation of He plasma by the first laser, in order to allow the small He plasma. By this experimental setup, the results showed the dramatic intensity enhancement effect of H emission that entirely due to the presence of the excited He atoms, which are supposed to serve as a temporary energy source for the subsequent excitation and emission of the H atoms. This experimental setup also demonstrated the exclusive He-induced H emission excitation (HIE) in the cooled plasma.

3. Conclusion

The peculiar pressure dependence of the hydrogen emission in terms of the new concept of mismatching effect was explained using the shock wave model; namely no synchronization of the shock wave generation and the super speed gushing of hydrogen atoms from the target. This unfavourable time mismatch effect was more severe for higher ambient gas pressure. Therefore at this stage, the thermal excitation mechanism induced by the shock wave doesn't contribute to hydrogen emission, otherwise the hydrogen intensity should be more pronounced closer to the target. Conversely, in low ambient gas pressure, the spectrum of hydrogen has very low background emission with high intensity.

The employment of He ambient gas offers the advantage of providing the additional and separate excitation mechanism in the He gas plasma via the metastable excited state of He atoms in the plasma. As a result, the hydrogen lines can be detected in atmospheric pressure He plasma with sharp emission line and low background emission.

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