Estimation of Temperature and Electron Density in Stainless Steel Plasma using Laser Induced Breakdown Spectroscopy

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Graphical abstract
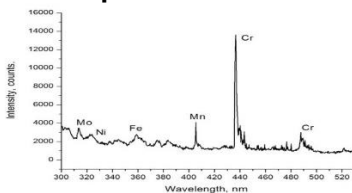
Abstract

LIBS plasma produced by a 1064 nm Q-switched Nd:YAG laser in an atmospheric pressure was studied for the stainless steel sample. The laser output energy 150 mJ with pulse duration of 6 ns. The plasma emission spectrum was recorded by the LR1 Spectrometer connected to the fibre optic. The plasma temperature and electron density of each element were estimated by time-resolved spectroscopy of neutral atom and ion line emission. The plasma temperature was obtained from the Boltzmann plot method and their electron density was determined by using Saha-Boltzmann equation method. The preliminary qualitative LIBS analysis shows that several elements contained in the stainless steel. The element detected was Cu, Fe, Mn, Ni, and Cr. The results shows that Mn and Fe has the highest plasma temperature of 1.2 eV, but the electron density of Mn was the highest with value 4.6×10^{20} cm^{-3}, while the Cu has the lowest temperature that is 0.73 eV with the electron density 2.8×10^{17} cm^{-3}. The results are discussed.

Keywords: Nd:YAG laser, plasma temperature, electron density, LIBS

Abstrak

Plasma LIBS yang dihasilkan oleh laser Q-switched Nd:YAG yang mempunyai panjang gelombang 1064 nm pada tekanan atmosfera di kaji pada sampel keluli tahan karat. Tenaga keluar laser ialah 150 mJ dengan tempoh denyutan laser 6 ns. Pelepasan plasma di rekod oleh spektrometer LR1 yand disambungkan dengan fiber optik. Suhu plasma dan ketumpatan elektron bagi setiap unsur yang di kesan di anggar menggunakan spektroskopi masa di selesaikan atom neutral dan ion pelepasan garis. Suhu plasma di perolehi dari kaedah plot Boltzmann manakala ketumpatan elektron plasma di tentukan dari kaedah kiraan Saha-Boltzmann. Kualitatif awal untuk analisis LIBS menunjukan terdapat beberapa element di dalam keluli tahan karat. Elemen yang di kesan ialah Cu, Fe, Mn, Ni dan Cr. Keputusan menunjukan Mn dan Fe mempunyai suhu plasma paling tinggi iaitu 1.2 eV, dengan ketumpatan elektron Mn adalah tertinggi dengan nilai 4.6×10^{20} cm^{-3}, manakala Cu mempunyai suhu terendah iaitu 0.73 eV bersama ketumpatan 2.8×10^{17} cm^{-3}. Keputusan di bincangkan.

Kata kunci: Laser Nd:YAG, suhu plasma, ketumpatan elektron, LIBS

1.0 INTRODUCTION

Plasma is an ionized particle form results from high temperature heating in instant. It is very similar to gas and carry charges. It is also a form of matter that exist when atom are in excited state. They are excited and jump to an energy level after that fall back and produced light [1]. Laser was one of the techniques that can produce plasma. The laser wavelength affects the formation of plasma, such as the laser plasma interaction and the plasma ignition threshold [2]. The plasma formed contains atoms and ions in different excited states, free electron and radiation.

The analysis of plasma includes the spectral lines characteristics and the relationship between plasma properties. The plasma temperature and the electron density are related to the line widths [3]. When the wavelength longer, the Bremsstrahlung plasma shielding inversed, the ablation rate reduced, the plasma temperature increased and the elemental fractional increase [4].

Several research were done on plasma parameters of aluminium sample at different wavelength of visible and a UV laser [5], Nd:YAG laser [6] and its harmonic [7-9] and Er:YAG laser [10] and some research on carbon plasma by using Nd:YAG laser [11]. Recently the researchers are interested to investigate the influence of Nd:YAG laser at a fundamental wavelength of 1064 nm on ferrous metal for example zinc plasma, [12] steel plasma [13] and nonferrous metal lead plasma by using Nd:YAG laser [14]. Stainless steel is a metal iron that consists of nickel, chromium and many other elements. Its application was widely used in industry depend on their properties such as magnetic, non-magnetic, hardness and strength, and its corrosion resistance. As the result, the product quality control and it can be achieved by examining its element composition.

This research will focus on investigating the plasma temperature and the electron density of ferrous metal at different wavelength in air at atmospheric pressure. The Q-Switched Nd:YAG laser is used as a laser source at 1064 nm fundamental wavelength. This research is using multiple Q-switch Nd:YAG laser to vaporize the material from solid state to induce a plasma. Some of the researches use various types of procedure to determine the plasma parameter. (Sattmann *et al.*, 1995) is using single, double and multiple Q-Switched to determine the plasma parameter and it shows that each parameter increase with multiple pulse compare to single pulse. The ablation and plasma excitation cannot be optimized separately if single pulse LIBS is used and it may interfere the analysis and reduced its flexibility.

2.0 ADVANTAGES AND CONCEPT OF LASER INDUCED-BREAKDOWN SPECTROSCOPY (LIBS)

The advantages of this system are that it can be used for elemental detection in samples in any states, i.e., solid, liquid or gas. The other advantages of this system are portable and easy to use. The preparation for the sample is minimal and sometime does not need to be prepared. The best feature of LIBS system is it gives a great advantage in term of analytical time and minimum cost. LIBS can be used as a qualitative and quantitative analytical technique by using auto-calibration technique based on the theoretical model builds up on LTE, it also suitable for

in situ for real time analysis, in vacuum and at atmosphere [15].

The LIBS efficiency as analytical tools is based on a set on the assumption to be verified concerning both the laser matter interaction and the laser-induced plasma dynamics. The observed emission lines are directly correlated to the species energy distribution in the expanding plasma and the actual species concentration in the sample is already known [15]. The nature of particle making up the plasma, the kinetic, excitation, ionization and radiation are expected to contribute to the system state description. This description is mention by Maxwell, Boltzmann, Saha and Plank. The temperature, T defined as the particular form of energy and it can determine the equilibrium distribution of energy among the different state of the particle assembled. It may happen that the equilibrium distributions exist for one form of energy but not for another. Thermodynamic equilibrium will exist when all form of energy distribution is described by the same temperature.

In the case of Local Thermodynamic Equilibrium (LTE), the excitation temperature, T_{exc} is equal to temperature of electron, T_e and T_H temperature of heavy particle i.e., atom and ions,

$$T_{exc} = T_e = T_H \neq T_\upsilon$$

where T_υ is the temperature describing the photon distribution. The escape of photon is associated with spatial gradient in the plasma and to time-dependent regimes, so that LTE can be established [16-18]. In LIBS plasma the ionization degree is sufficiently high, this completion dominated by the electron, i.e., $T_{exc} \sim T_e$ and just a small perturbation that is usually be neglected can be expected from the temperatures of electron and heavy particle [19].

In typical LIBS plasma only neutral atom and singly charged ion are presents to a significant degree. Therefore, only neutral and singly ionized particle will be considered. Under LTE condition, the population of the excited level for each species follows a Boltzmann distribution [20]. The condition of atomic and ionic state should be populated mainly by electron collision other than radiation, to ensure it has high collision rate the electron density must be sufficient. The minimum limit for electron density n_e is,

$$n_e = 1.6 \times 10^{12} T^{1/2} (\Delta E)^3 \qquad (1)$$

where ΔE is the highest energy to hold the LTE condition, and T is the plasma temperature. This limit is given by McWhirter criterion to fulfill during the first stage of plasma lifetime. This criterion is necessary even though it insufficient for the condition [20].

The excitation temperature control the population of atomic and ionic energy level must be same as the ionization temperature. It resolved the distribution of atom of the same element in the different ionization stages. It describe in Saha equation where the neutral and singly ionized species of the same element can be written as,

$$n_e \frac{n^{II}}{n^{II}} = \frac{2(2\pi m_e kT)^{\frac{3}{2}}}{h^3} \frac{2U^{II}(T)}{U^{I}(T)} e^{-\frac{E_{ion}}{kT}} \quad (2)$$

where n_e is the plasma electron density, n^{I} and n^{II} are the number densities of the neutral atomic species and the single ionized species, respectively, E_{ion} is the ionization potential of the neutral species in its ground state, m_e is the electron mass, and h is Planck's constant. In accurate calculations, the ionization potential lowering factor E_{ion} should be taken into accounts for the typical value being on the order of 0.1 eV.

In the measurement of plasma temperature, many methods have described it based on the absolute or relative line intensity (line pair ratio or Boltzmann plot), the ratio line to the continuum intensity. The method was depending on the experimental condition whether it is suitable or not [21]. Boltzmann equation is use to relate the population of an excited level to the total number density of the species in the plasma. After the linearization, the formula of Boltzmann plot obtained was:

$$ln \frac{I_{ij}}{g_i A_{ij}} = ln \left(\frac{n^s}{U^s(T)}\right) - \frac{E_i}{kT} \quad (3)$$

The left hand side of the equation (3) versus E_i was plotted and has a slope of $-1/kT$. The plasma temperature can be calculated without n^s and $U^s (T)$. The gradient usually gives negative slope. The electron can be derived from the intensity ratio of the two lines corresponding to the different ionization stages of the same element when the plasma is near to LTE condition.

The formula of Saha equation refer to the ratio of the total number densities of two ionization stages of the same element, a similar expression holds for the population ratio of the two excited levels i and m of different ionization stage of the same element that is singly ionized and neutral atom [20]. After rearranging the equation, and consider the insertion the excluded the ionization potential lowering factor. The equation given to calculate the electron density is

$$n_e = \frac{2(2\pi m_e kT)^{\frac{3}{2}}}{h^3} \frac{I^I_{mn}}{I^{II}_{ij}} \frac{A_{ij}g^{II}_i}{A_{mn}g^I_m} e^{-\frac{E_{ion}+E^{II}_i-E^I_m}{kT}} \quad (4)$$

Most of the research is using Stark broadening method and use the line intensity ratio to determine the electron density of plasma [22-26].

3.0 EXPERIMENTAL DETAILS

Figure 1 show the schematic diagram of LIBS experiment. The Q-Switched Nd:YAG laser (Nd:YAG Laser Cosmetic System) was operated at fundamental wavelength of 1064 nm, the repetition rate of 1 Hz and pulse width of 6 ns. The stainless steel sample was placed on the target holder 12 cm away from the focusing lens and the experiment was performed at atmospheric pressure in air. The sample position was adjusted so that every laser pulse was incident on a fresh location of the target.

The plasma emission was collected and recorded by using an optical fibre-based collection system and LR1 spectrometer. The detector range for the LR1 spectrometer is from 200 – 1200 nm, with the spectral resolution < 2 nm. The exposure time for the spectrometer was from 2.5 ms to 10 s.

The fibre optic was position 8 cm from the sample and the angle was 45^0 to the laser beam. The detector was synchronized with the Nd:YAG laser by using custom made Trigger Control Unit. The delay between the spectrometer and Nd:YAG laser pulse was set at 100 microseconds.
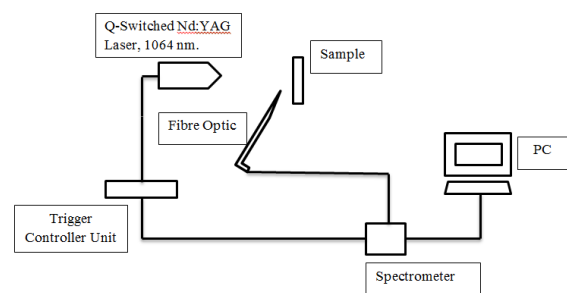

Figure 1 The schematic diagram of the experiment

The sample use for this experiment is stainless steel. The sample placed parallel to the target source to react with the plasma.

4.0 RESULT AND DISCUSSION

Figure 2 shows the plasma emission spectra of the stainless steel sample. The element detected was copper, manganese, iron, nickel, and chromium.
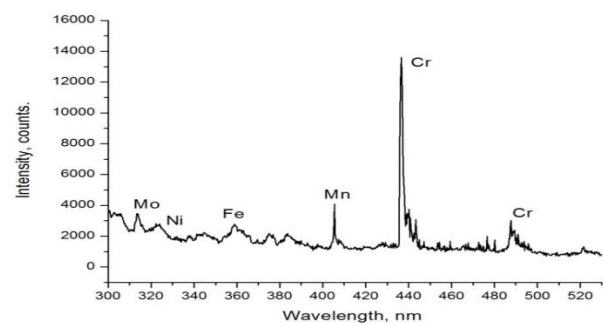

Figure 2 The LIBS plasma emission spectra of sample stainless steel for wavelength 1064 nm

Table 1 Spectroscopic data of iron lines

Wavelength, λ(nm)	Lower level of energy, E_i (cm^{-1})	Upper level of energy, E_k (cm^{-1})	(g_k)x (A_k) Ag	Lower level configuration	Upper level configuration
230.01417	704.007	44 166.206	3.49e+07	3d64s2	3d6(3F2)4s4p(3P°)
243.930114	25 428.7893	66 411.712	3.15e+09	3d6(3G)4s	3d6(3G)4p
247.066913	22 810.3459	63 272.981	9.24e+08	3d6(3F2)4s	3d6(3F2)4p
248.015734	22 637.1950	62 945.045	1.24e+09	3d6(3F2)4s	3d6(3F2)4p
254.874389	21 812.0454	61 035.285	4.8e+08	3d6(3P2)4s	3d6(3P2)4p
255.068286	26 170.1810	65 363.607	1.28e+09	3d6(3H)4s	3d6(3H)4p
268.92121	7 376.764	44 551.335	1.18e+08	3d7(4F)4s	3d6(3F2)4s4p(3P°)
344.38763	704.007	29 732.736	2.38e+07	3d64s2	3d6(5D)4s4p(3P°)
372.76735	20 874.482	47 693.239	1.54e+07	3d64s2	3d6(3G)4s4p(3P°)
392.7920	888.132	26 339.696	1.30e+07	3d64s2	3d6(5D)4s4p(3P°)

*Reference [28]

Based on the plasma emission line in Figure 2, there were several elements found in the stainless steel. The elements were iron, chromium, copper, manganese, and nickel. There were other elemental composition detected but their intensity were small, exist in one or two lines such as carbon, nitrogen and silicon. These elements are identified by comparing their wavelength with NIST database as shown in Table 1.
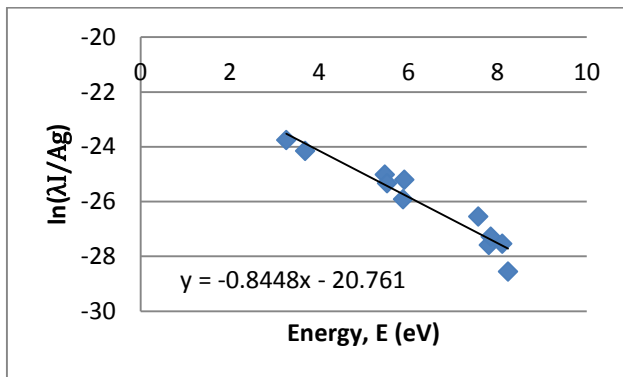

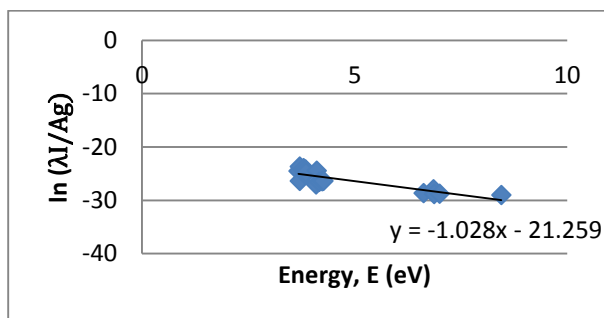**Figure 3** Boltzmann plot of iron

Figure 4 Boltzmann plot of nickel

In this spectroscopic analysis, the electron temperature was estimated by using Boltzmann plot method. Figure 3 shows the Boltzmann plot for iron element. λ and I are the wavelength and the intensity of the spectral lines. The temperature was obtained from the slope of the lines. The plasma temperature of iron was 1.2 eV. As for manganese, chromium, nickel and copper composition, temperature was 1.2 eV, 0.99 eV, 0.97 eV and 0.73 eV respectively.

Saha-Boltzmann equation or equation (3) was used to measure the electron density of the element in the stainless steel. Figure 4 shows the Boltzmann plot for nickel element. Based on the calculation in this research, the electron density of iron and manganese were 1.1×10^{19} cm^{-3} and 4.6×10^{20} cm^{-3} respectively. The electron density of the copper was 2.8×10^{17} cm^{-3}. As for nickel and chromium, the electron density was 1.29×10^{19} cm^{-3} and 5.8×10^{19} cm^{-3} respectively.

5.0 CONCLUSION

In this research, the elemental temperature of stainless steel plasma using LIBS technique was successful estimated from the Boltzmann plot. In addition, the electron density of the element was estimated using Saha-Boltzmann in which relates the intensity ratio of atomic and ionic emission lines. Comparing the value obtained in this research with others is difficult because of the different environment, condition and types of the method used.

Acknowledgement

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