Characteristics of Helium Microwave-Induced Atmospheric Pressure Plasma for Fine Particle Analysis

Tetsu OKAMOTO and Yukio OKAMOTO*

Section No.1, Technology & Engineering Department, Lamp Company, Ushio Inc, 1194, Sezuchi, Bessho-cho, Himeji, 671-0224, Japan

**Department of Electronics & Communications Eng., Faculty of Eng., Toyo University, 2100 Kujirai, Kawagoe, 350-8585, Japan*

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Helium microwave-induced plasma (He-MIP) for trace element analysis is generated by a 2.45 GHz microwave power (~ 1 kW) with the Okamoto cavity of the surface wave mode at atmospheric pressure, and an iron excitation temperature and an electron density of the plasma are measured. With 0.8 kW input microwave power, an excitation temperature of 8000 K and the electron density of 2 x 10^{14}/cm^3 are obtained. The sample particles in an Al plate which are ablated by a Q-switched Nd:YAG laser (266 nm) or the nebulization of the suspension of Al_2O_3 powder are introduced into the center of the annular He-MIP through an inner tube of the torch along with the carrier gas (He or Ar). A time-resolved atomic emission spectrometry (AES) is studied for the particulate composition analysis by the laser ablation and the nebulization of suspension. Atomic emission signals derived from the single particles in the size of submicron are observed. The He-MIP AES is detected the non-metal elements with sufficient sensitivity.

Keywords: helium plasma, atmospheric pressure plasma, microwave-induced plasma, fine particle analysis, atomic emission spectrometry, excitation temperature, laser ablation, nonmetal detection

1. Introduction

Particulate contaminations in ultra-pure water, reagents, gases and solids etc. have a significant impact on production quality, and must be tightly controlled. The accurate determination of trace elements (particulate) in steel is an important and challenging task in analytical chemistry [1]. The variation of the contents of non-metal elements (particulates) such as C, P and S in steel have a significant influence on the mechanical and physical properties. A sensitive and accurate method for the determination of these elements in steels is therefore required. Over many years, laser ablation atomic emission spectrometry (LA-AES) has been receiving increased attention for the direct determination of trace elements in various types of soil samples [1, 2]. Analysis of airborne dust is an essential aspect of environmental studies and pollution control. Especially, the detection of increasing lower levels of nonmetals (e.g. F, Cl, Br, I, C, P, etc.) in the various materials (solid, liquid, and gas) is of great environmental and material importance [2].

Takahara et al., developed a particle analyzer system, which can analyze the composition of just one particulate using helium microwave-induced plasma (He-MIP) with Beenakker cavity and provides simultaneous three dimensional on the number of particulates and the size distribution [3]. He-MIP is better suited for the determination of nonmetals, because He has the highest ionization potential. However, Beenakker cavity has a low tolerance to aqueous solution samples, because the input microwave power was limited up to 150 watt [3]. The low-power MIP does not provide sufficient plasma energy to atomize and ionize the particulates, and is the higher detection limits [4].

The purposes of this work are to present the characteristics (excitation temperature and electron density) of the high-power (~ 1 kW, 2.45 GHz) He-MIP generated by the Okamoto cavity of the surface wave mode at atmospheric pressure [4, 5] and to develop a particle analyzer using the high-power He-MIP for the determination of nonmetals in the gas, liquid and solid samples. The preliminary results of the particle analyzer will be presented.

2. Experimental

2.1 Instrumentation

A schematic diagram of the experimental system is shown in Fig.1. The Okamoto cavity with surface wave mode is a non-resonant cavity without cooling and

* *Author to whom correspondence should be sent. E-mail: okamoto@toyonet.toyo.ac.jp*

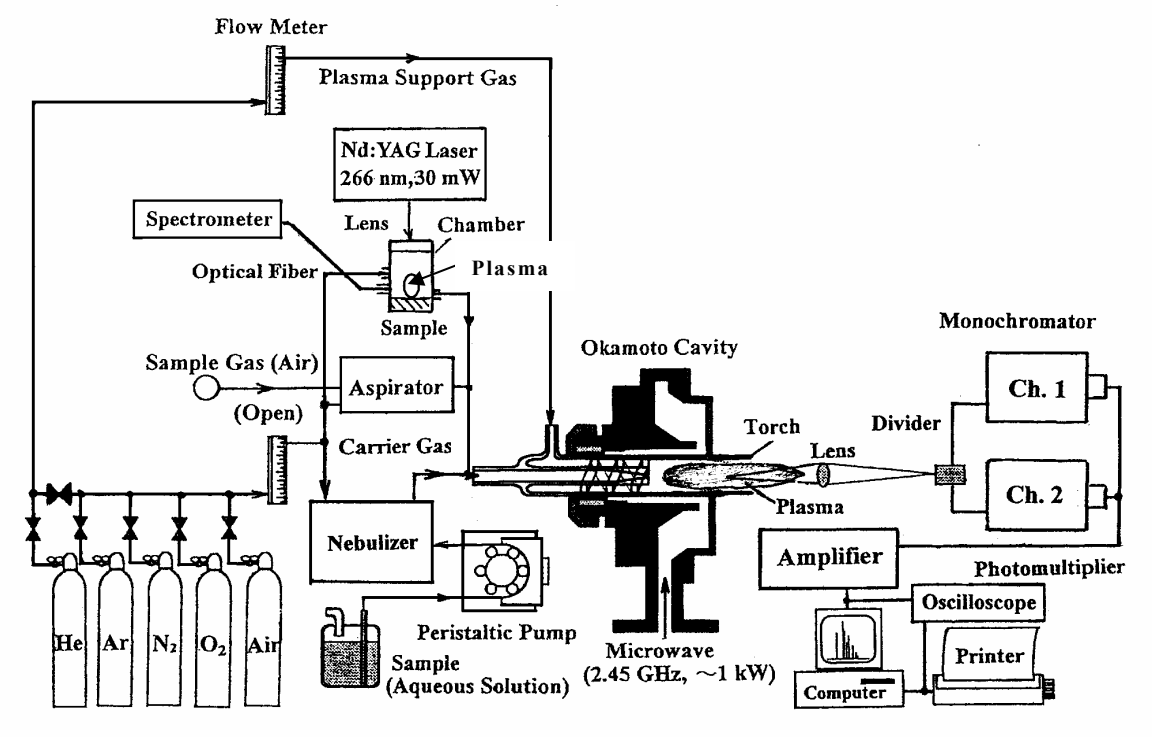

Fig.1. Experimental setup of the laser-ablation / helium microwave-induced plasma atomic emission spectrometry (LA/He MIP AES) for the particle analysis.

consists of two parts [4, 5]. One section is a flat rectangular waveguide with a reduced height (electric field plane; 6 mm) for impedance matching between the resultant impedance of the cavity and that of the He plasma in order to absorb the power for plasma efficiently. The other section is a mode transformer which consists of an inner conductor and an outer cylindrical conductor terminated by a front plate. The ring-gap distance between the front plate and the front edge of the inner conductor is 5 mm. The axial symmetric surface wave is excited in the ring-gap and is coupled to the discharge tube (quartz) placed inside the cavity. Then the annular He plasma is generated in the discharge tube and run with 300 ~ 1,000 watt (power source limit) of forward microwave power and zero reflected power after tuning with a three-stub tuner.

The torch (discharge tube : 10 mm o.d., 8 mm i.d.) with tangential flow makes of quartz and consists of two concentric tubes, as well as two gas flows. A central carrier-gas flow for the sample introduction and a outer plasma-support-gas flow with a spiral trajectory, for the plasma support, are used. These flow rates are referred to as *G*c and *G*p, respectively. The gas used is helium (purity: 99.995 %). The inner tube is tulip-shaped and the gap between the two concentric tubes is 0.3 mm which affects the production of annular-shaped plasma and the value of *G*p.

The microwave-induced Helium plasma (He MIP) is observed in an “end-on” mode where the axis of the plasma is perpendicular to the slit of a monochromator. The monochromator (Ebert type) has a focal length of 1 m and is equipped with a 1200 lines/mm grating. Thedetector is a photomultiplier tube (Hamamatsu, R955). The signal from the tube is amplified by a preamplifier and process by a digital storagescope, and/or convert to a voltage and the analog-voltage is digitized an analog-to-digital converter, and process by a computer. The emission signals form the sample particles are observed as single pulses if the particle concentration is sufficiently low and the content of a given element in the particles is large enough to produce pulses sufficiently high above shot noise. The background signal due to the continumun is suppressed by an offset adjuster in the pre-amplifier.

An aqueous solution sample (Fe: 500 ppm or Al: 100 ppm) is introduced into the He plasma using an ultrasonic nebulizer with a desolvation and condensation system (Cetac:U-5000 AT^{+}) and a peristaltic pump. During sample introduction, the mist produced by the transducer is carried by He flow through a heating tube (desolvation temperature: 150 ℃) and condenser (temperature : - 2 ℃) which are used for the droplet desolvation and condensation, respectively. The sample aerosol is introduced into the center of the annular He plasma through the inner tube

along with the carrier-gas.

A solid sample is ablated by a Q-switched Nd:YAG laser (New Wave Research, Tempest-10 Hz, forth harmonic: 266 nm, power: 30 mJ, repetition: 10 Hz, duration: 3-5 ns). The laser beam is focused on the aluminum (Al) plate with the use of a fused-silica spherical lens (focal length : 150 mm). A standard aluminum plate containing the 9 ppm carbon (JSS-410-2) is set in a stainless steel ablation chamber. When the laser beam is focused on the target, the irradiation in the focal spot can be lead to rapid local heating and the intense evaporation of the material. The evaporated materials (particles) are injected into the He-MIP by the carrier gas of helium passing through the ablation chamber and the inner tube of the torch.

Particles of Al_2O_3 (mean diameter : 1 μm) in aqueous suspension are introduced into the He-MIP by the use of a cross-flow type nebulizer with Scott-type double-pass spray chamber. Signal is monitored using a digital storagescope serving the wavelength of Al I(396.2 nm) for the time-resolved. In this case, the carrier gas is Ar. The signal will be calibrated by using the nebulization of aqueous solution of Al.

Electron density of He plasma is measured using the Stark broadening of H_β(486.1 nm) from the sample solution [2, 6]. The Stark full-width at half maximum ε (Å) and the electron density *Ne* [cm^3] are related by $Ne = \{\varepsilon / 2.50 \times 10^{-9}\alpha\}^{3/2}$, where α is the half-width parameter (7.87×10^{-2}) [2, 6].

The excitation temperature is calculated from the Boltzmann plot of $\log(I\lambda^3/gf)$ vs. *E*u, giving a slope equal to - 0.434 *kT*, where *I* is the emission intensity of Fe line (arb. units), λ is the wavelength (nm), *g* is the statistical weight of the upper state, *f* is the oscillator strength, *E*u is the energy of the upper state in the transition (cm^{-1}), *k* is the Boltzmann constant and *T* is the excitation temperature (K) [2, 6].

3. Results and Discussion

3.1 He-MIP production

Figure 2 shows the photograph of the He-MIP at atmospheric pressure with aqueous solution nebulization. Here, the microwave power, *P,* is 600 watt, and *G*p and *G*c are 10.5 l/min and 0.3 l/min, respectively [5]. By increasing the microwave power, the higher temperature and the longer tail flame plasma is generated.

3.2 Excitation Temperature & Electron Density

Figure 3 shows an example of the Boltzmann plot for iron twelve lines (370.9, 372.0, 372.3, 372.8, 373.3, 373.5, 373.7, 374.8, 375.0, 375.8, 376.4 and 376.6 nm)

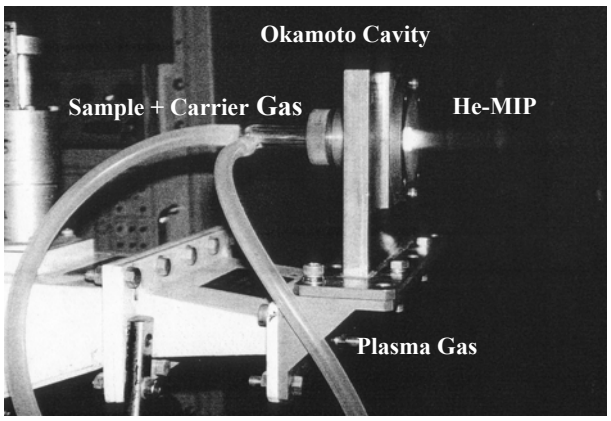

Fig.2. Photograph of the He-MIP at atmospheric pressure generated by the Okamoto Cavity with aqueous fluoride, NaF nebulization. Microwave power = 600 watt, plasma and carrier gas flow rate *G*p = 10.5 l/min and *G*c = 0.3 l/min, respectively [5].

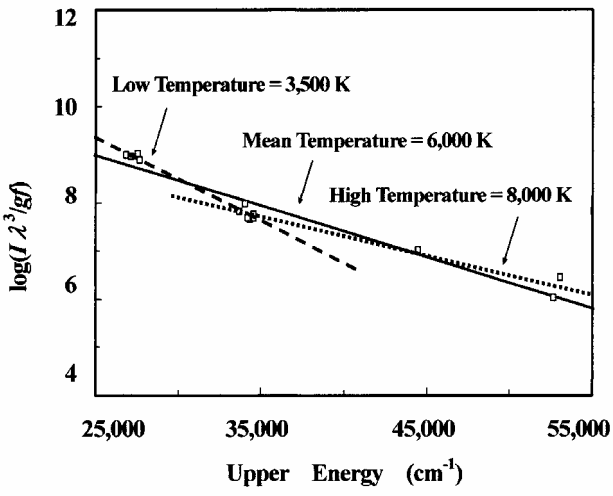

Fig.3. Boltzmann plot for Fe I upper levels with He-MIP. Mirowave power is 800 watt.

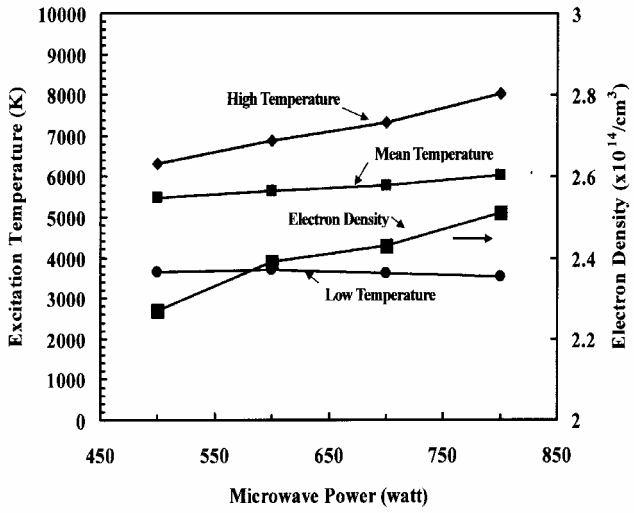

Fig.4. Effects of microwave power on the excitation temperature and the electron density.

intensities. Here, the emission is measured with "end-on" viewing, where microwave power *P* is 0.8 kW, and *G*p and *G*c are 11 l/min and 0.2 l/min, respectively. The Boltzmann plot for these lines yields not a single straight line as shown in Fig.3. The He-MIP consists of two elements, i. e., the low energy component (25000 ~ 35000 cm^{-1}) and high energy component (35000 ~ 55000 cm^{-1}). The line slop of the low energy component is 3500 K (low temperature) and the high energy one is 8000 K (high temperature). As shown in Fig.4, in the case of a single line (25000 ~ 55000 cm^{-1}) for these lines is 6000 K (mean temperature). Under the same conditions, the electron density was 2.1 x $10^{14}/cm^3$.

Figure 4 shows the dependence of the excitation temperature (high, mean and low temperature) and the electron density on the applied microwave power, where *G*p and *G*c are 11 l/min and 0.2 l/min, respectively. The high and mean temperatures, and the electron density increase with increasing applied power, if all other parameters are kept constant. With higher microwave power, more intense plasma is formed. While the lower temperature decrease with increasing applied power. The increase of the excitation temperature and the electron density with the microwave power suggest that the detection limit for the He-MIP will be improved. This expectation is demonstrated experimentally in He-MIP AES .

3.3 Solid & Powder Sample

By ablating the standard Al plate, the particulate contamination of carbon (9 ppm) in the sample is detected. Figure 5 shows the temporal behavior of (1) Al I(396.2 nm) and (2) C I(247.9 nm) emission signals for the aluminum ablation. The signal is observed by a digital storagescope. Some strong pulses may be due to the emission of large particle simultaneously introduced into the He-MIP. Particulate contamination of carbon in the aluminum plate is detected as shown in Fig.5-(2). The carbon signal is not detected with a spectrometer (Ocean Optics inc. USB2000) connected to the ablation chamber shown in Fig.1. A study of these developments is currently in hand.

Atomic emission signals derived from the particles with mean diameter of 1 μm size is observed after injection of Al_2O_3 particles into the He-MIP by the nebulization of dilute suspensions using argon as the carrier gas. Figure 6 shows the typical temporal behavior of the emission signal of Al I(247.9 nm). Intensity of the signal is proportional to the particle diameter cubed. Here, the microwave power is 600 watt, and *G*p and *G*c

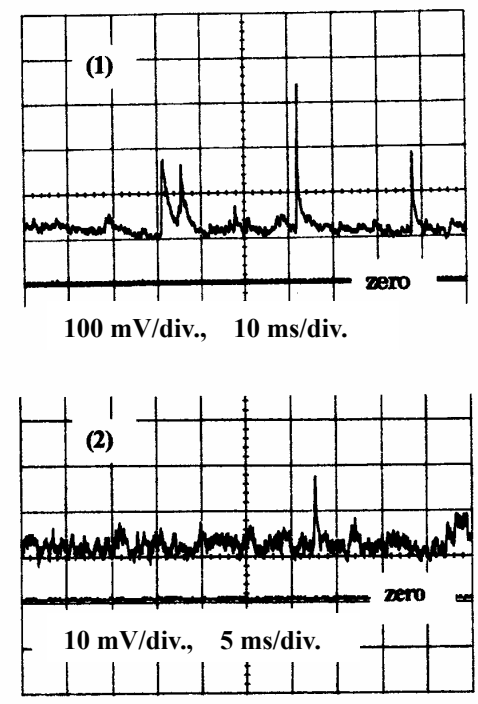

Fig.5. Sample output (1) Al I(396.2 nm) and (2) C I(247.9 nm) emission obtained when aluminum plate was ablated by the laser.

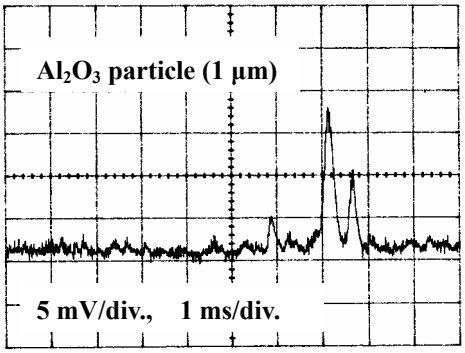

Fig.6. Temporal behavior of Al (396.2 nm) emission from the Al_2O_3 particle.

are 10.5 l/min. and 0.3 l/min., respectively. The intensities increases exponentially with increasing the power. The smallest diameter of particles that can be detected by this method is limited by the signal to noise ratio. The noise arises mainly from the shot noise of the continuum of the He-MIP.

4. Conclusion

Characteristics of the high-power He-MIP at atmospherics pressure for trace element analysis are presented and the feasibility is demonstrated of collecting usable analytical signals from single particles introduced into the He-MIP by the laser ablation or by the nebulization of suspensions.

This analytical method will be used in the field of

analysis of atmospheric environments, powder industries, and the high-performance materials such as ultra-pure water, reagents, and gases. A study of these developments is currently in hand.

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