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Comparative study on contribution of charge-transfer collision to excitations of iron ion between argon radio-frequency inductively-coupled plasma and nitrogen microwave induced plasma

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This paper describes an ionization/excitation phenomenon of singly-ionized iron occurring in an Okamoto-cavity microwave induced plasma (MIP) as well as an argon radio-frequency inductively-coupled plasma (ICP), by comparing the Boltzmann distribution among iron ionic lines (Fe II) having a wide range of the excitation energy from 4.76 to 9.01 eV. It indicated in both the plasmas that plots of Fe II lines having lower excitation energies (4.76 to 5.88 eV) were fitted on each linear relationship, implying that their excitations were caused by a dominant thermal process such as collision with energetic electron. However, Fe II lines having higher excitation energies (more than 7.55 eV) had a different behavior from each other. In the ICP, Boltzmann plots of Fe II lines assigned to the higher excited levels also followed the normal Boltzmann relationship among the low-lying excited levels, even including a deviation from it in particular excited levels having an excitation energy of ca. 7.8 eV. This deviation can be attributed to a charge-transfer collision with argon ion, which results in the overpopulation of these excited levels, but the contribution is small. On the other hand, the distribution of the high-lying excited levels was non-thermal in the Okamoto-cavity MIP, which did not follow the normal Boltzmann relationship among the low-lying excited levels. A probable reason for the non-thermal characteristics in the MIP is that a charge-transfer collision with nitrogen molecule ion having many vibrational/rotational levels could work for populating the $3d^64p$ ($3d^54s4p$) excited levels of iron ion broadly over an energy range of 7.6–9.0 eV, while collisional excitation by energetic electron would occur insufficiently to excite these high-energy levels.

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1. Introduction

Several electric discharge plasmas have been employed as an excitation source for optical emission spectrometry (OES) [1]. Various inter-particle collisions occurring in these plasmas determine the excitation and ionization of the supporting gas as well as analyte species introduced into them, thus affecting the emission characteristics and eventually the analytical performance. The collision phenomena are classified into the first kind and the second kind [2], where the former results from an energy transfer of the kinetic energy between collision partners, such as fast electrons, and the latter accompanies an energy transfer of the internal energy from a particular particle such as a metastable atom of argon. It can be general to say that the first-kind collisions enable the plasma to be in a local thermodynamic equilibrium (LTE) [3], whereas the second kind collisions make the plasma to deviate from an LTE condition. A criterion for the LTE thus is an important key to determine whether the ionization and excitation in a plasma can be understood totally and statistically or they must be treated individually and non-statistically. For this consideration, an analysis on Maxwell/Boltzmann statistics would provide useful information not only for combining the complicated processes of collisions with several statistical parameters such as an excitation temperature, but for finding any specified excitation which is caused by a second-kind collision.

A microwave induced plasma (MIP) excited with Okamoto-cavity [4,5] has a unique feature for an excitation source in OES, being superior to conventional MIPs such as a Beenaker cavity[6] and a Surfatron [7]. The plasma has a doughnut-like structure so that sample aerosol can be easily introduced through a central tube of the plasma torch [4]; furthermore, it can be operated at high incident powers up to 1.5 kW enabling the plasma to be highly tolerant to loading of wet aerosols, as similar to radio-frequency inductively-coupled plasma (ICP). The MIP-OES with Okamoto-cavity also has several features beyond a conventional ICP-OES. The Okamoto-cavity MIP can be maintained with various gases, such as nitrogen, nitrogen–oxygen, and helium [8–12], each of which can be available for OES, and it can be also operated by using an air compressor without any cylinder gas [10]. As an analytical application, organic solvents can be introduced directly when using nitrogen–oxygen mixed gas[12]. The analytical performance of the Okamoto-cavity MIP has been found in several scientific papers [10–13], and also the diagnostics of this plasma have been carried out to measure the characteristic temperature and the electron density

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[10,14], indicating that the electron density of the MIP was one or two orders lower than that of an argon ICP [10]. However, few papers were published on the fundamental excitation/ionization processes occurring in the Okamoto-cavity MIP. On the other hand, several studies of this kind have been found in the field of argon ICP [15–24]. They indicated that ICP was not in LTE condition completely but had some deviation from normal Boltzmann statics in a specific range of the excitation energy [15–20], and that a non-thermal collisional process with argon ion: $M + Ar^{+} \rightarrow M^{+*} + Ar$, called an asymmetric charge-transfer reaction [25], also contributed to the excitation in ICP [21–24] but its effect was exerted to a small degree [16,24]. Farnsworth et.al investigated a contribution of the charge-transfer reaction to excitations of the third row metals from calcium through copper in an argon ICP [23]. Chan and Hieftje suggested a mechanism why the charge-transfer reaction worked insufficiently in the ICP [24]. On the other hand, a contribution of the charge-transfer collision in MIPs has not been elucidated in previous research. The Okamoto-cavity MIP has been operated using nitrogen plasma gas for normal analytical use, while the ICP using pure argon plasma gas. It is therefore interesting to investigate the excitation mechanism in the Okamoto-cavity MIP, which is sustained with a different plasma gas from the argon ICP, especially focused on such non-thermal collisions with excited species of nitrogen gas.

It is well known that the charge-transfer reaction may be a dominant ionization/excitation mechanism in the case of a glow discharge plasma (GDP), which results in large intensity enhancement of emission lines originated from the corresponding excited energy level [26]. Typical instances have been reported in the emission spectrum of copper, nickel, and iron [26–33]. The GDP is a typical plasma in which the charge-transfer reactions predominantly contribute to the excitation of emission spectra, because it can be maintained at reduced pressures and thus collisional exchanges in kinetic energy occur insufficiently. We reported on Boltzmann plots for lots of ionic lines of iron in glow discharge plasmas when argon or neon was employed as the plasma gas, indicating that particular emission lines relating to charge-transfer collision largely deviated from a normal Boltzmann distribution among emission lines having low excitation energies [34,35]. An enhancement factor, which was defined as a ratio of the observed intensity to the expected value extrapolated from the corresponding linear Boltzmann plot, could provide quantitative information for estimating the charge-transfer collision [35].

In this paper, a spectrochemical analysis using the enhancement factor estimated from Boltzmann plots of iron ionic lines (Fe II) is described when an Okamoto-cavity MIP with nitrogen gas and a conventional ICP with argon gas are compared on their excitation mechanisms. Larger contribution of the charge-transfer collision was observed in the MIP than in the ICP, probably because there was a difference in the excited levels of their plasma gases which could take part in the collision of this kind.

2. Experimental

The Okamoto-cavity for MIP has been described elsewhere [4,36], consisting of an inner conductor and an outer cylindrical conductor terminated by a front plate to conduct microwave power to surrounding gas being in a plasma state, as the schematic diagram illustrated in previous papers [36]. The microwave power, which was generated with a high-voltage power supply (KN-153-3T-LR-PS, Nippon Koushuha Ltd., Japan) and a 2.45-GHz microwave generator (MKN-153-LA-OSC, Nippon Koushuha Ltd., Japan), was loaded to the Okamoto-cavity through a wave guide equipped with a three-stub tuner. The reflected power is minimized by adjusting the tuner, and then a traveling surface wave of the loaded microwave can be generated at the gap between the inner and outer conductors, so that the electric field can be the maximum to couple with the plasma gas most effectively. The resulting plasma has an annular shape like ICP. A plasma torch (300-8352, Hitachi Corp., Japan) comprises two coaxial quartz tubes enabling each individual gas flow: one is a tangentially-introduced gas flow as the plasma gas through the outer tube and the other is introduced through the central inner tube to carry sample aerosol to the plasma. In this study, pure nitrogen gas was employed as the plasma gas under the conditions that the flow rate of nitrogen was fixed at 14.0 dm^3/min for the outer gas and 0.5 dm^3/min for the central carrier gas. The forward power of the microwave was adjusted in the range of 0.80–1.15 kW. The observation height was adjusted to be 20 mm above the front plate.

An ICP system was employed (P-5200, Hitachi Corp., Japan). The ICP was driven through a 3-turn load coil by a 27.12-MHZ radio-frequency generator. A Fassel-type quartz torch (No. 306-1418, Hitachi Ltd.) was employed with a pneumatic concentric-type nebulizer (No. 306-1582, Hitachi Ltd.). Argon flow rates of the plasma and the intermediate gas were fixed at 11.5 and 0.50 dm^3/min, respectively, and a flow rate of the carrier gas was selected to be 0.55 dm^3/min. The incident forward power was varied in a range from 0.80 to 1.20 kW. The observation height was adjusted to be 14 mm above the load coil.

The emission signal was focused with a biconvex lens on the entrance slit of a scanning spectrometer (P-5200, Hitachi Corp., Japan), comprising a modified Czerny–Turner mounting monochromator and a photomultiplier tube (R955, Hamamatsu Photonics Corp., Japan), and then dispersed to estimate the averaged intensity of a particular emission line over triplicate measurements. The focal length is 0.75 m and the grating has 3600 grooves/mm at a blaze wavelength of 200 nm.

A stock solution of iron (10 g/dm^3) was prepared by dissolving a high-purity iron metal (99.98%) with 6-M/dm^3 hydrochloric acid. Test solutions for estimating the emission characteristics, having an iron concentration of 1.0 g/dm^3, were prepared by diluting the stock solution with de-ionized water.

The background level (spectrum) for the emission line was estimated from each blank spectrum in a nitrogen Okamoto-cavity MIP and an argon ICP, which was measured by aspirating de-ionized water instead of the sample solution of iron. Especially in the MIP, several of iron emission lines were partly overlapped with band spectra of nitrogen species; in this case, they were not included in the analysis of Boltzmann plot.

3. Results and discussion

3.1. Analytical lines of iron ion

In order to estimate a Boltzmann plot for singly-ionized iron, we selected a set of the ionic lines (Fe II) in a wavelength range of 234–264 nm, comprising 90 emission lines having excitation energies from 4.76 to 9.01 eV. These Fe II lines are classified into three groups: $3d^64p$–$3d^64s$, $3d^64p$–$3d^7$, and $3d^54s4p$–$3d^54s^2$ optical transitions [37]. The $3d^64s$ electron configuration gives the ground state of iron ion, including the lowest energy level of $^6\mathbf{D}_{9/2}$ (0.00 eV) [37]. The $3d^64p$ electron configuration is the first excited state, which splits into lots of energy levels having excitation energies of more than 4.77 eV. Their energy levels have different spin multiplicities of doublet, quartet, and sextet terms [37]. The details have been published as a table in our previous paper [35]. All the assignments were determined based on an energy level table complied by Suger and Corliss [37], and their transition probabilities were cited from a wavelength table published by Wiese et al. [38].

3.2. Boltzmann plot of Fe II lines in argon ICP

Fig. 1 shows plots of the Boltzmann factor of the Fe II lines emitted from an argon ICP as a function of the excitation energy, at an r.f. forward power of 1.0 kW. Triplicate intensity measurements were conducted for each emission line, whose relative standard deviation ranging from 0.4 to 9.0% was estimated to be 3.5% on the average. Error bars of these plots were omitted in Fig. 1, because they might complicate the graph and also their intensity variations hardly changed the following discussion. The data points in excitation energies of 4.7–5.9 eV

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