Estimation Using an Enhancement Factor on Non Local Thermodynamic Equilibrium Behavior of High-lying Energy Levels of Neutral Atom in Argon Radio-Frequency Inductively-Coupled Plasma

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This paper describes a plasma-diagnostic method using an enhancement factor on the Boltzmann distribution among emission lines of iron atom in an argon radio-frequency inductively-coupled plasma (ICP). It indicated that Boltzmann plots of the atomic lines having lower excitation energies (3.4 to 4.8 eV) were well fitted on a straight line while those having more than 5.5 eV deviated upwards from a linear relationship. This observation could be explained by the fact that ICP is not in a complete thermodynamic equilibrium between direct excitation to energy levels of iron atom, ionization of iron atom, and radiative decay processes to the ground state. Especially, the recombination of iron ion with captured electron should accompany cascade de-excitations between closely-spaced excited levels just below the ionization limit, the rates of which become slower as a whole; as a result, these high-lying levels might be more populated than the low-lying levels as if a different LTE condition coexists on the high energy side. This overpopulation could be quantitatively estimated using an enhancement factor (EF), which was a ratio of the observed intensity to the expected value extrapolated from the normal distribution on the low energy side. The EFs were generally small (less than 3); therefore, the cascade de-excitation process would slightly contribute to the population of these excited levels. It could be considered from variations of the EF that the overpopulation proceeded to a larger extent at lower radio-frequency forward powers, at higher flow rates of the carrier gas, or at higher observation heights. The reason for this is that the kinetic energy of energetic particles, such as electrons, becomes reduced under all of these plasma conditions, thus enabling the high-lying levels to be more populated by cascade de-excitation processes from iron ion rather than by collisional excitation processes with the energetic particles. A similar Boltzmann analysis using the EF was also carried out in emission lines of nickel atom, which confirmed the conclusion concerning the atomic lines of iron.

Keywords Radio-frequency inductively-coupled plasma, Boltzmann plot, enhancement factor, excitation mechanism, iron atomic line

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the resultant iron atoms, thus leading to an overpopulation of the high-lying excited levels. This effect would appear in ICP predominantly because iron atom can be highly ionized in the plasma; this ionization enhances the population of iron ion from which the recombination/step-wise de-excitations occur to emit many non-resonance lines of iron atom. It is thus interesting to investigate a Boltzmann plot of the atomic lines that are assigned to higher excited levels in more detail, when experimental parameters regulating ICP such as r.f. forward power are varied.

We reported on Boltzmann plots for many atomic lines of iron in glow discharge plasmas when argon or neon was employed as the plasma gas, indicating that emission lines having higher excitation energies largely deviated from a normal Boltzmann distribution that emission lines having low excitation energies (< 4.8 eV) followed. A large overpopulation was observed in the high-lying excited levels of iron atom in both the argon and neon glow plasmas. It was suggested that this effect would be attributed to recombination/step-wise de-excitations from iron ion that was favorably populated through Penning-type collisions with metastable atoms of argon or neon, rather than collisions with fast electrons. We also investigated Boltzmann plots of iron ionic lines in a nitrogen microwave-induced plasma as well as the glow discharge plasmas, and found abnormal behaviors of these plots that could be explained by charge-transfer collisions with the plasma gas species. In our previous studies, an enhancement factor, which was defined as a ratio of the observed intensity to the expected value extrapolated from a corresponding linear Boltzmann plot, could provide quantitative information on the excitations of the high-lying excited levels.

This paper discusses the relative population of excited levels of iron and nickel neutral atoms on a quantitative scale of an enhancement factor, when a conventional argon ICP is employed as the excitation source. This indicates a slight overpopulation of high-lying excited levels in nickel as well as iron, suggesting that the thermal ionization and the recombination/de-excitation processes are not fully controlled in an LTE condition between ionic and atomic states of iron or nickel, but that the cascade de-excitation process contributes more to the population of the high-lying excited levels.

**Experimental**

An argon ICP measuring system (P-5200, Hitachi Corp., Japan) was employed to measure the emission intensity of iron atomic lines. Figure 1 represents the block diagram schematically. The ICP was driven through a 3-turn load coil by a 27.12-MHz radio-frequency generator at forward powers of 0.7 – 2.0 kW. A Fassel-type quartz torch (No.306-1418, Hitachi Ltd.) was employed with a pneumatic concentric-type nebulizer (No.306–1582, Hitachi Ltd.). The argon flow rates of the plasma and the intermediate gas were fixed at 11.5 and 0.50 dm³/min, respectively, and those of the carrier gas were varied from 0.50 to 0.70 dm³/min. The incident forward power was selected in a range from 0.80 to 1.20 kW. The observation height was adjusted to be from 14 to 42 mm above the load coil, so as to measure the plasma in the radial direction (side-on view), as indicated in Fig. 1.

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, yielding a reciprocal linear dispersion of 0.29 nm/mm.

Stock solutions (10 g/dm³) of iron and nickel were prepared by dissolving a high-purity iron metal (99.98%) and a high-purity nickel metal (99.9%) with 6-M/dm³ hydrochloric acid and 7-M/dm³ nitric acid, respectively. Test solutions for estimating the emission characteristics, having iron or nickel concentration of 1.0 g/dm³, were prepared by diluting the stock solution with deionized water.

Subtraction of the background level for estimating the emission intensity, if necessary, was carried out by using each blank spectrum, which was measured by aspirating deionized water instead of the sample solution of iron. Typical signal-to-background ratios at an r.f. incident power of 1.0 kW were estimated to be 800 in the most sensitive line (Fe I 371.99 nm) and 0.60 in the weakest line (Fe I 374.26 nm), in measurement of the Fe I emission lines.
Results and Discussion

Analytical lines of atomic iron and nickel

Emission lines of iron atom (Fe I) were selected to estimate the Boltzmann distribution of the corresponding excited energy levels, for the excitation phenomenon in the argon ICP to be discussed comprehensively. Iron is the most suitable element for investigating the Boltzmann relationship, because lots of Fe I lines are included. An energy level table compiled by Wiese et al.16 These Fe I lines are classified into three groups: 3d^24p-3d^4s, 3d^4s4p-3d^4s (3d^4s^3), and 3d^4s4d-3d^4s4p optical transitions.

In Boltzmann analysis for nickel, 38 emission lines of nickel atom (Ni I) having excitation energies from 3.68 to 7.68 eV were selected in a wavelength range of 300 - 339 nm. The assignment was based on an energy level table complied by Suger and Corliss,14 and their transition probabilities were cited from a table published by Corliss and Bozman.17 These Ni I lines are classified into three groups: 3d^34p-3d^4s, 3d^4s4p-3d^4s^2, and 3d^4d-3d^4p optical transitions.

General aspect of Boltzmann plot

Figure 2 shows Boltzmann plots of the Fe I lines when an argon ICP is operated at an r.f. forward power of 1.0 kW. Their emission intensities were estimated from triplicate measurements. Average values of the relative standard deviation were 2.2% for Fe I lines having excitation energies of 3.4 - 4.8 eV, and 4.5% for Fe I lines of more than 5.5 eV. Error bars of these plots were not added in Fig. 2, because they might complicate the graph and also their intensity variations hardly change the following discussions. The data points in excitation energies ranging from 3.4 to 4.8 eV well followed a linear relationship with a negative slope of -1.72 whose correlation coefficient was -0.9961, and the standard error of the slope was calculated to be 0.035 (2%) in the linear regression analysis. This statistical estimation implies that these excited levels are populated by a dominant thermal process, being in an LTE condition. The LTE condition is generally obtained as a result of frequent collisions with energetic particles to give their kinetic energies to other particles in the plasma; electron collisions are the most probable excitation mechanism for obtaining the LTE plasma because ICP has a high number density of electrons. In this situation, one can define an excitation temperature that is principally determined by the average kinetic energy of electrons in the ICP. On the other hand, as shown in Fig. 2, Boltzmann plots in excitation energies of more than 5.5 eV deviated upwards from the straight line, where their excited levels would be overpopulated compared to the expected values from the Boltzmann distribution among the low-lying excited energy levels. One should notice that most of the data points over 5.5 eV appear above the straight line, which is extrapolated towards higher excitation energy from the linear relationship on the lower energy side, as drawn with a dotted line in Fig. 2. It can therefore be considered that there may be any additional process responsible for the overpopulation, in addition to thermal excitation such as electron collisions.

A feasible mechanism to explain their deviation from a Boltzmann relation is that some imbalance could occur between thermal excitation processes to energy levels of iron atom, ionization of iron atom and the recombination processes, and then the overall radiative decay processes.10 It is the most important to note that the neutralization by electron capture should accompany cascade de-excitations between closely-spaced excited levels just below the ionization limit of iron atom, so that these high-lying levels can likely be populated to have longer lifetimes as a whole. This effect changes the excitation/de-excitation equilibrium as a whole, which might be dependent on the excitation energy of the excited levels:

\[
\text{Fe} + e^- \text{(fast)} \rightleftharpoons \text{Fe}^* + e^- \text{(slow)} \quad (1)
\]

\[
\text{Fe}^* \rightarrow \text{Fe}^{*1} + h\nu \rightarrow \text{Fe}^{*2} + h\nu \quad \ldots \quad (2)
\]

\[
\text{Fe} + e^- \text{(fast)} \rightleftharpoons \text{Fe}^+ + e^- \text{(slow)} + e^- \quad (3)
\]

\[
\text{Fe}^* + e^- \rightarrow \text{Fe}^{**} \rightarrow \text{Fe}^{**} + h\nu' \rightarrow \text{Fe}^{*''} + h\nu'' \quad \ldots \quad (4)
\]

Here, the asterisk denotes an excited state of iron atom and \( h\nu \) means light emission at a frequency of \( \nu \). The reaction depicted in Eq. (1), called a collision of the first kind,18 is caused by transfer of the kinetic energy of a fast electron; in a similar reaction, argon species having large kinetic energies can also work as the energy supplier in the plasma. Radiative decay of an excited iron atom is generally depicted in Eq. (2), and can occur through possible de-excitation channels as almost simultaneously as the electron-impact excitation, so that the excited atom can rapidly fall down to the ground state while emitting the characteristic radiation.9 Collisions with long-lifetime species, such as argon metastable atom, called a...
processes with recombination with an electron, and then step-wise de-excitation finally returns to the ground state of iron atom through collision of the second kind, contribute less to the overall excitations of iron atom than does the electron collision. It is therefore considered that, when collisions with energetic electrons would be a dominant process for excitations of iron atom, the Boltzmann plot should follow a linear relationship over a wide range of the excitation energy, which is mainly determined by the average kinetic energy of the electrons. However, the experimental result did not support this situation. The reaction depicted in Eq. (3) means an ionization of iron atom by electron impact; also, Eq. (4) shows that the iron ion finally returns to the ground state of iron atom through recombination with an electron, and then step-wise de-excitation processes with radiative decay. The excited level that is first neutralized by the recombination, as denoted with double asterisks in Eq. (4), might be one of unidentified higher excited levels of iron atom. Such highly-excited levels are densely distributed just above or below the ionization limit of iron atom, and thus have longer lifetimes as a whole; therefore, the stepwise de-excitations, as denoted in Eq. (4), would result in an overpopulation of the high-lying excited levels. We can consider that this mechanism is a probable reason why the Boltzmann plot, as shown in Fig. 2, deviates upwards from a linear relationship on the higher excitation energy side. It is known that this effect can be observed much more predominantly in the spectrum of iron emitted from a glow discharge plasma, because iron atom is predominantly ionized by the second-kind collision with argon metastable atom rather than any thermal collision.

**Effect of radio-frequency forward power**

As shown in Fig. 2, the Boltzmann plots in excitation energies of more than 5 eV slightly deviated from a straight line, and thus the data of these plots did not completely follow the Boltzmann statistics among the low-lying excited energy levels. When the linear relationship on the lower energy side was extrapolated towards higher excitation energy, as denoted by a dotted line in Fig. 2, deviations of the data points over 5.5 eV from the extrapolated line (the dotted straight line in Fig. 2) were estimated by defining an enhancement factor (EF), as follows: EF = I_{obs}/I_{bolz}, where I_{obs} and I_{bolz} are the observed and the extrapolated emission intensity of an iron atomic line, respectively. Figure 3 shows a semi-log plot of the enhancement factor for the Fe I lines as a function of the excitation energy at an r.f. forward power of 1.0 kW. Such a plot should have a linear relationship, where the EFs for all emission lines are unity, if their excitations fully follow a Boltzmann distribution obtained among the low-lying excited levels; therefore, a contribution of the additional excitation for the high-lying excited levels is roughly estimated with the EF. It was found from Fig. 3 that the enhancement factors exceeded unity, but all of them were less than 2 at higher excitation energies over 5.5 eV. On the other hand, our previous study on an argon glow discharge plasma (GDP) indicated a large overpopulation of the high-lying excited levels of iron atom, in which several of the EFs exceeded 100. Indeed, the deviation from the LTE condition would be limited to a small extent in the ICP, for which the reason is that the direct excitation by energetic electron, as indicated in Eq. (1), could work as a dominant mechanism in the whole range of the excitation energy, whereas the GDP was in a non-LTE condition, where the high-lying levels of iron atom are less populated through electron collisions due to lower kinetic energy as well as lower number density of electrons in the negative glow region compared to ICP. It is thus probable in the GDP that the recombination/step-wise de-excitation process from ionic iron can appear dominantly. Furthermore, as shown in Fig. 3, the EF gradually became larger due to lower kinetic energy as well as lower number density of electrons in the negative glow region compared to ICP. It is thus probable in the GDP that the recombination/step-wise de-excitation process from ionic iron can appear dominantly.
semi-log plots of the EF, can be an effective parameter for estimating the deviation from the normal Boltzmann relationship. The slope should be zero if all the excited levels are populated in an LTE condition, and may be any positive value if the de-excitation occurs spontaneously from a certain higher level. Figure 4 indicates a variation in the slope of the log(EF), calculated under a linear regression fitted to data points of the high-lying excited levels over 4.8 eV, when the r.f. forward power is varied from 0.80 to 1.20 kW. In this measurement, the flow rate of the carrier gas was fixed at 0.55 dm$^3$/min and the emission signal was observed at a plasma position of 14 mm above the load coil. It was observed that the slope value was reduced and then reached constant with increasing r.f. forward powers. This result is probably because direct and thermal excitations by energetic electrons, as depicted in Eq. (1), contribute to the population of the high-lying excited levels more largely beyond the recombination/step-wise de-excitation processes, as depicted in Eq. (4), due to the increased kinetic energy of the electrons at higher fo.

As a conclusion, the plasma characteristics of the ICP would become closer to an LTE condition when the r.f. forward power is elevated; therefore, the excitation temperature becomes meaningful over atomic and ionic excited levels of iron as well as over a wide range of the excitation energy. In such a case, the excitation temperature can be considered to be determined by the average kinetic energy of energetic particles in the plasma.

**Effect of carrier gas flow rate**

Boltzmann plots for the Fe I lines were investigated when a flow rate of the carrier gas was varied from 0.50 to 0.70 dm$^3$/min. In this measurement, the r.f. forward power was fixed at 1.0 kW and the emission lines were observed at a plasma position of 14 mm above the load coil. All of the Boltzmann plots were well fitted to each linear relationship in excitation energies of 3.4 - 4.8 eV, even when the carrier gas flow rate was largely varied. Figure 5 shows semi-log plots of the EF for all the Fe I lines as a function of the excitation energy at different flow rates of the carrier gas. In a range where the excitation energy exceeds ca. 5.5 eV, the EFs generally became larger by increasing the flow rate of the carrier gas. This indicates an increase in the slope value with increasing flow rates, leading to larger deviation from the Boltzmann relationship among the low-lying excited levels. This result is probably because the kinetic energies of energetic particles become reduced at higher flow rates of the carrier gas. In fact, the excitation temperature, which was estimated from each Boltzmann plot in an excitation energy of 3.4 - 4.8 eV, was measured as follows: 7690 ± 150 K at 0.50 dm$^3$/min, 7290 ± 100 K at 0.55 dm$^3$/min, 6350 ± 70 K at 0.60 dm$^3$/min, 5200 ± 120 K at 0.65 dm$^3$/min, and 4930 ± 70 K at 0.70 dm$^3$/min. Such a large decrease in the temperature would be attributed to cooling of the central channel of the ICP, thus resulting in thermal collisions with the energetic particles insufficient to excite the high-lying levels of iron atom; in this case, the step-wise de-excitation process becomes relatively obvious to determine their population. As a summary, the plasma characteristics of the ICP would become closer to an LTE condition when the flow rate of the carrier gas is gradually reduced, where the thermal collisions with energetic particles could populate higher excited levels of iron atom more dominantly than the step-wise de-excitations from iron ion.
ICP at the tail position would deviate from an LTE condition this measurement, some deviation from a linear relationship was different observation heights from 14 to 42 mm, when the r.f. the plasma. The variation of the log(EF) curve implies that the high-lying excited levels more largely along with higher observed in Boltzmann plots of the Fe I lines having higher the non-thermal collisions would contribute to excitations of the more predominantly than that at the normal analytical position, as similar to cases where the RF power is lower (see Fig. 4) or at higher flow rates of the carrier gas (see Fig. 6).

Effect of observation height
Boltzmann plots for the Fe I lines were also investigated at different observation heights from 14 to 42 mm, when the r.f. forward power and the flow rate of the carrier gas was fixed to be 1.0 kW and 0.55 dm³/min, respectively. The observation height was determined as a position above the load coil, which is indicated as a caption in Fig. 1, thus providing spatial information on the Boltzmann statistics in the plasma. Also in this measurement, some deviation from a linear relationship was observed in Boltzmann plots of the Fe I lines having higher excitation energies over 5.5 eV. Linear-regression curves for the log(EF) versus the excitation energy had positive slopes, which were predominantly elevated with increasing the observation height as shown in Fig. 7. In general, ICP would be apart from an LTE condition at a tail portion of the plasma, because both the average kinetic energy and the number density of electrons become largely decreased. In our observation, the excitation temperature, which was estimated from each Boltzmann plot in an excitation energy of 3.4 – 4.8 eV, was drastically reduced as the following: 6940 ± 180 K at 14 mm, 6380 ± 110 K at 21 mm, 5630 ± 120 K at 28 mm, 5140 ± 50 K at 35 mm, and 4740 ± 100 K at 42 mm. Therefore, the result of Fig. 6 could be explained by the fact that various recombination collisions, such as non-thermal collision with metastable argon atom, occur more dominantly than thermal collision with energetic particles at the tail zone of the plasma. The plots of the EF can indicate such a change in the plasma characteristics of the ICP, in which the non-thermal collisions would contribute to excitations of the high-lying excited levels more largely along with higher observation positions from the induction zone to the tail zone of the plasma. The variation of the log(EF) curve implies that the ICP at the tail position would deviate from an LTE condition more predominantly than that at the normal analytical position, as similar to cases where the RF power is lower (see Fig. 4) or at higher flow rates of the carrier gas (see Fig. 6).

The 300-nm system of nickel atomic lines
A Boltzmann-statistics analysis of Ni I lines similar to the 370-nm Fe I lines was carried out in the emission lines of nickel atom in a 300-nm wavelength range. The Boltzmann plots of the Ni I lines included a larger variance compared to those of the Fe I lines, probably due to the uncertainty of their transition probabilities; however, the data points in excitation energies ranging from 3.6 to 4.5 eV generally followed a linear relationship (the correlation coefficient ranged from –0.6578 to –0.7310), implying that these excited levels were populated by a dominant thermal process, such as collision with a fast electron. On the other hand, Boltzmann plots in excitation energies of more than 7 eV deviated upwards from the straight line, where their excited levels would be overpopulated compared to the expected values from the Boltzmann distribution among the low-lying excited energy levels less than 4.5 eV. Figure 8 shows semi-log plots of the EF for the Ni I lines as a function of the excitation energy at r.f. forward powers of 0.8 and 1.2 kW, indicating that the EFs are more than unity in excitation energies of more than 7 eV and that a relation between the log(EF) and the excitation energy may be roughly fitted to a linear-regression curve, like the results of the Fe I lines (see Fig. 4). Figure 9 indicates a variation in the slope of the log(EF) versus the excitation energy, based upon a linear regression fitted to data points of the high-lying excited levels between 4.5 and 7.8 eV, when the r.f. forward power is varied from 0.80 to 1.2 kW. In this measurement, the flow rate of the carrier gas was fixed at 0.55 dm³/min and the emission signal was observed at a plasma position of 21 mm above the load coil. We could find that the slope of the log(EF) curve changed in a similar manner to the observation for the Fe I lines as shown in Fig. 4, where the slope values were elevated with a decrease in the RF incident power. This result of Ni I lines supports the excitation mechanism suggested in the case of the Fe I lines; that is,
However, the EFs were generally small (less than 3) in the case of iron, meaning that the overpopulation occurred to a small extent. The other experimental conditions are the same as in Fig. 8.

the high-lying excited levels of nickel atom would be excited through the non-LTE processes to a certain degree, in which step-wise de-excitation among high-lying excited levels of a nickel atom occurred just after electron capture of the ion. The observation confirms the usefulness of the EF parameter in plasma diagnostics.

Conclusions

The excitation mechanism occurring in an argon ICP was investigated in cases of excited energy levels of iron and nickel atoms having a wide range of the excitation energy. For this purpose, Boltzmann plots for many atomic lines were evaluated when the r.f. forward power as well as the flow rate of the carrier gas was widely varied in the ICP. The plots using the low-lying atomic lines, in excitation energies of 3.4 – 4.8 eV for iron and 3.6 – 4.5 eV for nickel, followed each linear relationship obtained among the low-lying excited levels. In addition to direct excitations by fast electron, their energy levels could be overpopulated through stepwise de-excitations between the high-lying excited levels, which are located just below the ionization limit, after the electron capture of the ion species. However, the EFs were generally small (less than 3) in the case of iron, meaning that the overpopulation occurred to a small extent principally because the first-kind collision with electron always worked as a major excitation process in the whole range of the excitation energy. Therefore, the ICP does not deviate from an LTE condition so largely, in excitation/de-excitation processes of the excited levels of iron atom. It was understood from changes in the EF that the overpopulation exerted smaller effect on the overall excitation with increasing the r.f. power, with decreasing the flow rate of the carrier gas, or in the normal analytical zone of the plasma. All of these plasma conditions elevated the kinetic energy of energetic particles in the plasma; in these cases, they could contribute to the thermal ionization/excitation of iron atom over the wide range of the excitation energy, beyond the step-wise de-excitations from iron ion. The enhancement factor, which quantitatively estimates the deviation from a normal Boltzmann distribution, can provide useful information for discussing the state of the plasma for emission spectrometric analysis.

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