1. Introduction

In the refining process for steel-making, direct analyses of minor elements provide important information for controlling various properties of manufactured steels. For this purpose, spark discharge optical emission spectrometry is now extensively employed due to the rapid response of analytical results as well as the capability of multi-element analysis. However, because the refining techniques are recently advanced, impurities in steel materials can be reduced down to a content range of several ppm.1) This advance must require analytical methods having better detection ability for quality control of the highly-purified materials.

Glow discharge optical emission spectrometry (GD-OES) is an analytical method for the direct analysis of solid samples, and a powerful tool for the quality control of various manufactured materials.2) Also in GD-OES, a study to improve the detection sensitivity is needed for the analytical applications in steel-making processes. Higher discharge powers increase the emission intensities emanated from a glow discharge lamp, but this does not always improve the detection ability for quality control of the highly-purified materials.

Glow discharge optical emission spectrometry (GD-OES) is an analytical method for the direct analysis of solid samples, and a powerful tool for the quality control of various manufactured materials.3) Also in GD-OES, a study to improve the detection sensitivity is needed for the analytical applications in steel-making processes. Higher discharge powers increase the emission intensities emanated from a glow discharge lamp, but this does not always improve the detection sensitivities. At a fixed pressure of the plasma gas, the discharge current changes along with the discharge voltage supplied. Higher discharge currents lead to an increased density of charged particles in the plasma and thus increased amounts of the sputtered particles, causing higher background levels as well as self-absorption. Generally, very high discharge voltages decrease the short-term stability of the emission intensities due to larger background fluctuations and irregular spark-like discharges and also the long-term stability because the sputtered particles re-deposit on the electrodes. In a Grimm-style glow discharge lamp with Ar gas, these negative effects appear especially at discharge voltages of more than 1 kV3). Optimum discharge conditions depend on the anode diameter, the kind of samples and the Ar pressure. Kruger et al. carried out the analysis of steel samples at discharge parameters of 1.1 kV/200 mA.4)

In GD-OES, argon is commonly employed as the plasma gas due to the low running-cost as well as good performance as the emission source. The plasma gas plays an essential role in the characteristics of the discharge and in the excitation of sample atoms; however, few studies on the analytical application using different gases are presented5). Changing the plasma gas could be a possible option to improve the detection sensitivity. Helium has higher ionization potential (24.48 eV) compared to argon (15.76 eV),6) thus leading to lower density of charged particles in the plasma. It also has a lower sputtering yield.7,8) Thus helium would not be a suitable plasma gas for GD-OES because the sputtering rate would be too low. However, argon–helium mixed gas plasmas are interesting.9–12) Rare gas atoms have the metastable energy levels: 11.55 eV and 11.72 eV in Ar, and, 19.82 eV and 20.61 eV in He.9) Atoms in such metastable levels have relatively long lifetimes especially at low pressures and thus can cause excitation of sample atoms through various collisions. In addition, in the argon–helium mixed gas plasma, the helium metastables could principally contribute to excitations of species having larger excitation energies.9) As considered that the helium metastables have larger internal energies, sample atoms requiring higher excitation energies may be more readily excited by helium than by argon, thus leading to intensity increase in the emission lines.

In this paper, the analytical performance of argon–helium mixed gas plasmas is investigated for the determination of carbon in steel samples. Carbon is an important element to

For the sensitive determination of carbon in steel samples, an argon–helium mixture plasma gas was employed in glow discharge optical emission spectrometry. The emission lines of carbon have relatively high excitation energies, which implies that the excitations by helium whose ions and metastable atoms have larger internal energies could produce the excited states of carbon more readily. Comparison in the calibration curves yields the detection sensitivity obtained with the argon–helium mixture was enhanced than with the argon gas alone by a factor of 3.

KEY WORDS: glow discharge optical emission spectrometry; carbon determination; argon–helium mixed gas plasma; steel.
be strictly controlled in the steel-making and is less easily excited because excited states of carbon have high excitation energies. It is therefore expected that the use of argon–helium mixed gases could contribute to more sensitive detection of carbon in GD-OES.

2. Experimental

The structure of the glow discharge lamp,\textsuperscript{13)} the spectrometer and the power supply device,\textsuperscript{14)} the procedure for gas mixing\textsuperscript{12)} have been described elsewhere. The lamp was made according to the original model by Grimm.\textsuperscript{15)} The inner diameter of the hollow anode was 8.0 mm and the gap between the electrodes was adjusted to be ca. 0.3 mm. High-purity argon (99.9995\%) and helium (99.9999\%) was used as the plasma gas. Standard reference materials of Fe-based low alloys (NBS-1160 Series) containing 0.54, 0.26, and 0.11 mass\% C were employed for measurements of the emission characteristics as well as the calibration curves.

3. Results and Discussion

The carbon spectrum comprises some intense atomic lines: C I 131.1363 nm, C I 156.1438 nm, C I 165.7008 nm, C I 193.0905 nm (vac.\textsuperscript{16}) and C I 247.8573 nm (air).\textsuperscript{17)} The emission lines in a vacuum ultraviolet region cannot be observed on the spectrometer employed, and the intensity of the C I 193.03 nm (air) is several times larger than that of the C I 247.86 nm. Therefore, the C I 193.03-nm line is employed as the analytical line.

Figure 1 shows spectral scans of the Fe–0.54mass\%C sample in the neighborhood of the C I 193.03 nm line emitted by a pure argon plasma (a) and an argon–helium mixed gas plasma (b). Whereas no emission lines of iron appear, some argon ionic lines such as Ar II 193.08 nm and Ar II 193.16 nm are in this wavelength region. The intensity of the C I 193.03-nm line becomes larger by using the argon–helium mixture gas. On the other hand, introduction of helium to the argon plasma results in a decrease in emission intensities of the argon ionic lines. The reason for this is that the corresponding excited states (4f electron configuration) of argon ion are de-populated as a result of collisions between excited argon ions and helium atoms.\textsuperscript{9,16)} Such collisions can also produce the helium metastables probably contributing to excitation of carbon.\textsuperscript{9)} Hence the helium mixture could lead to a favorable change of the glow discharge plasma suitable for carbon determination.

Figure 2 shows variations in the emission intensities of the Fe I 374.59-nm line and C I 193.03-nm line (a), the signal-to-background ratio (SBR) of the carbon line (b), and the intensity ratio (c), as a function of the helium partial pressure added. In this case, the pressure of argon and the discharge voltage are both fixed. The emission intensity of iron decreases with the helium pressure added, which could be explained from a decrease in the sputtering rate caused by the addition of helium.\textsuperscript{18,19)} In fact, the sputtering rates...
were measured to be $1.0 \times 10^{-4}$ g cm$^{-2}$ min$^{-1}$ for 530-Pa argon alone and $0.51 \times 10^{-4}$ g cm$^{-2}$ min$^{-1}$ for 530-Pa argon and 530-Pa helium mixed gas. It is likely to consider that the intensities of the iron line having smaller excitation energy (3.43 eV)$^6$ correspond to the sample atom density in the plasma more closely. However, the intensity of the carbon line having larger excitation energy (7.68 eV)$^6$ gradually becomes larger even if the number of sample atoms in the plasma are reduced. This effect is due to any additional excitations by helium. The SBR also increases with the helium pressure, which is caused by the increased intensity of the carbon line as well as by decreases in the background level. The lowering of the background is mainly due to a decrease in the emission intensities of the adjacent argon lines. These could contribute to an improvement of the detection sensitivity for carbon determination.

**Figure 3** shows intensity changes of the iron line and the carbon line as a function of the discharge voltage when pure argon and argon–helium mixed gases are employed. In the argon plasma, the discharge voltages of up to 800 V were employed because the higher voltages worsen the stability of the emission intensities. It should be noted that stable discharges can be maintained at higher voltages in the mixed gas plasma compared to in the pure argon plasma. This is probably because the sputtering rate as well as the discharge current is reduced by adding helium to argon glow discharge plasmas.$^{18}$ In the mixed gas plasma, the SBR is much improved along with increasing discharge voltage. It is expected that, at higher discharge voltages, the plasma with argon–helium mixtures gives better analytical performance in the carbon determination.

**Figure 4** shows calibration curves of their intensity ratio when pure argon and argon–helium mixed gases are employed. In both the plasmas, linear relationships passing through the origin point are obtained, and the sensitivity for carbon determination in the argon–helium mixed gas plasma is enhanced by a factor of 3.

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