Emission spectroscopy of ablation plumes in liquid for analytical purposes

Tetsuo Sakka, Hisayuki Oguchi and Yukio H Ogata
Institute of Advanced Energy, Kyoto University, Uji, Kyoto 611-0011, Japan
E-mail: t-sakka@iae.kyoto-u.ac.jp

Abstract. The emission intensity of Ag(I) lines obtained by the laser ablation of an Ag plate immersed in water was examined. Due to an intense self-absorption in the plume, the spectral intensity of the emission approaches the Planck distribution, which is a function of temperature, but not a function of the population of the levels involved in the transition. The temperature obtained by assuming the Planck intensity agrees well with the previous study on the plume temperature in water. The result that the emission suffers from the intense self-absorption is a disadvantage for the use of emission spectra from the laser ablation plume in liquid as a quantitative elemental analysis of solid surfaces in liquid.

1. Introduction
Wet processes for solid surface modification, such as electrodeposition, electroless deposition, and chemical surface modifications have been widely studied and applied to various industrial processes. The process parameters are adjusted on the basis of the characterization of the resultant surfaces after the processing. For these ex situ characterizations, various techniques are available, such as those based on electron spectroscopy, X-ray analysis, and mass spectroscopy. On the other hand, in situ monitoring technique of the surface processes in wet environments is very limited.[1] We have studied the laser-ablation plume formed on a solid target immersed in liquids, principally by using emission spectroscopy of the species originating from the target.[2-7] The findings in the previous studies [2-10] suggest that an elemental analysis of the target surface might be possible even in wet environments. However, additional difficulties should be overcome to obtain quantitative results for the surface analysis in the wet environment, in contrast to the laser-induced breakdown spectroscopy (LIBS) in gaseous environment.[10] One of them is that a self-absorption due to a high population density in the plume, as a result of a strong confinement effect in water, gives a spectral intensity which is not proportional to the population of the emitting species.

The luminous intensity from the plasma at the extreme of intense re-absorption gives the intensity of the black-body radiation.[11] In this case, the emission intensity is not related to the population density anymore, but dependent only on the plasma surface temperature. Therefore, the information on the population density is absent in the spectral intensity. Also, the spectral feature tends to be broad and white, and the lines characteristic to each element will be ambiguous. On the other hand when the self-absorption is negligible, or in other words, the optical density is low enough, the emission intensity of spectral lines is proportional to the
population of the upper level of the transition multiplied by the transition probability. Specifying the mechanism which the measured spectra follow is important from the point of view of the surface elemental analysis.

In the present work, we examined the self-absorption effect observed in the line spectra of Ag atoms in the plume. Ag(I) $^2S_{1/2} - ^2P_{3/2}$ ($^2P_{1/2}$) doublet appearing at 328.068 nm and 338.289 nm was examined. As a result, the relative intensity of the fine structure doublet gave reasonable temperatures by assuming the Planck formula rather than assuming the intensity proportional to the population densities with the Boltzmann distribution. This may be a disadvantage for analytical purposes. A possible solution for this problem is also discussed.

2. Experimental

A multimode Nd:YAG laser with the pulse duration of 20 ns, pulse energy of 80 mJ, and the wavelength of 1064 nm was used as an ablation laser. The original beam diameter was ca. 5 mm. The laser beam was focused by a lens with a focal length of 100 mm, and irradiated onto a silver metal plate (99.98%, Nilaco Co.) placed horizontally in a glass cell filled with pure water. The depth from the water surface to the target surface was ca. 15 mm.

The lateral emission from the ablation plume was introduced into the entrance slit of a spectrograph. A 27.5-cm-focal-length spectrograph (Acton, SpectraPro275) equipped with a 1200 grooves/mm diffraction grating was used. The slit was set to be 20 μm in width. The spectral range of the measurement from 310 nm to 360 nm was employed in order to cover appropriately the emission of an Ag(I) $^2S_{1/2} - ^2P_{3/2}$ ($^2P_{1/2}$) fine-structure doublet. An intensified charge coupled device (ICCD) (Princeton Instrument, ICCD-1024MDG/1) was attached to the spectrograph and used as a detector. The spectral resolution of this system was 0.5 nm. The time delay from the laser pulse to drive the ICCD detector was varied from 29 ns to 3500 ns, and the gate width was varied from 50 ns to 200 ns according to the delay time.

3. Results and Discussion

Typical spectra obtained for the Ag(I) $^2S_{1/2} - ^2P_{3/2}$ ($^2P_{1/2}$) fine-structure doublet are shown in Fig. 1. In an early time range the spectral lines were seen as absorptions in a continuous spectrum. This feature changes with time. Later in the delay time we see clear emission lines, while they still have an absorption dip, or a self-reversed structure, in an emission feature. The appearance of the absorption dip in the spectra shown in Fig. 1 is consistent with the previous observations [7, 12]. It is attributed to a temperature gradient in the direction normal to the plume surface and also to the dense optical thickness. Because of this effect, it is not easy to

![Figure 1. Typical spectra obtained in water for the Ag(I) $^2S_{1/2} - ^2P_{3/2}$ ($^2P_{1/2}$) fine-structure doublet.](image)
discuss the population density from the intensity of the lines.

In the present work, the line intensity was defined as shown in Fig. 1(c). This definition of the line intensity may have been affected by the contribution from the true continuum, such as the one originated from the plasma electrons, to the whole spectra. The continuous spectrum, however, follows the Planck distribution. If both the Ag atomic lines and the continuum follow the Planck distribution with the same temperature, the overlapping of the continuum should not affect the resultant temperature obtained by fitting the line intensities to the Planck formula. Furthermore, the contribution of the true continuum emission is limited to very early stages of the delay time, i.e., much earlier than 500 ns. At short delay times this intensity definition given in Fig. 1(c) cannot be applied straightforwardly, since they do not have a clear intensity maximum. We regarded the intensity of the continuous spectrum interpolated into the center of absorption dip as representing the emission intensity of the spectral line (Fig. 1(b)). Even in the case that the continuous spectrum is dominant, the 328 nm line was always weaker than the 338 nm line. The two lines of the Ag(I) atoms have almost the same transition probability, but the degeneracy of the upper level of the 328 nm transition is 4 while that of the 338 nm line is 2. This means that the intensity ratio of the 328 nm line to the 338 nm line should be 2, if there were no re-absorption effect. The results that the 338 nm line is always more intense than 328 nm line suggest that the actual intensity is not reflecting the population density determined by the Boltzmann distribution, but likely to be dominated by the self-absorption effect, i.e., by the intensity of the black body radiation.

The intensities of the two lines were compared with the intensity of the Planck distribution, as illustrated in Fig. 2. By assuming that the line intensity is controlled by the black body radiation, black body temperature can be estimated from the intensity of the two lines, i.e., the Planck distribution which satisfies the intensity of both lines can be determined by adjusting the temperature. The temperatures thus obtained are given in Fig. 3. They were roughly the same as those reported for the rotational and vibrational temperature of the C2 molecules produced by the laser ablation of graphite in water [5, 6]. Also in Fig. 3, a gradual decrease of the temperature is seen.

The present results suggest that the intensity is governed by the black body radiation, and therefore the emission line maximum is not a function of the population density but the function only of the plume temperature. This is a disadvantage for the application of emission-line intensities to a quantitative elemental analysis. To avoid the deformation of the line profile by the self-absorption effect, it is probably effective to minimize the temperature gradient in
the plume and also to minimize the population density of the levels involved in the transition. For the former attempt the re-heating of the plume may be effective [8, 9], while for the latter attempt a low-energy-pulse ablation by controlling the pulse width may be effective, since the density of the plume is expected to be lowered by using a low energy pulse. Further experiments should be performed to verify these ideas.

4. Conclusion
The emission spectra of 328 nm and 338 nm lines of Ag(I) from the laser ablation plume produced by targeting a silver plate in water was examined. The experimental results show that the relative intensities of the two lines are far from that expected directly from the Boltzmann distribution. If we assume the Planck distribution, the results gave a temperature ranging from 2500 K to 5000 K, which is reasonable in comparison with the previous temperature estimation studies. We therefore conclude that even the though line spectra are observed, the intensity is explained mainly by the black-body radiation as a result of a strong self-absorption effect. This conclusion is not favorable for the application to the in situ elemental analysis of the solid surface immersed in liquid.

Acknowledgments
The authors would like to acknowledge Hideki Furusawa and Kohichi Hirata for their support in experiments.

References
[1] Bockris JO’M and Khan SUM 1993 Surface Electrochemistry (New York, Plenum Press) p 37
[2] Sakka T, Iwanaga S, Ogata YH, Matsunawa A and Takemoto T 2000 J. Chem. Phys. 112 8645-53
[3] Sakka T, Takatani K, Ogata YH and Mabuchi M 2002 J. Phys. D: Appl. Phys. 35 65-73
[4] Saito K, Takatani K, Sakka T and Ogata YH 2002 Appl. Surf. Sci. 197 56-60
[5] Sakka T, Saito K and Ogata YH 2002 Appl. Surf. Sci. 197 246-50
[6] Saito K, Sakka T and Ogata YH 2003 J. Appl. Phys. 94 5530-36
[7] Saita T, Saito K and Ogata YH 2005 J. Appl. Phys. 97 014902
[8] De Giacomo A, Dell’Aglio M, Colao F, Fantoni R and Lazic V 2005 Appl. Surf. Sci. 247 157-62
[9] Pichahchy AE, Cremers DA and Ferris MJ 1999 Spectrochim. Acta B52 25-39
[10] Casavola A, Di Giacomo A, Dell’Aglio M, Taccogna F, Colonna G, De Pascale O and Longo S 2005 Spectrochim. Acta B60 975-85
[11] Griem HR 1997 Principles of Plasma Spectroscopy (Cambridge: Cambridge University Press) p 23
[12] Sakka T, Nakajima T and Ogata YH 2002 J. Appl. Phys. 92 2296-303

Figure 3. Black-body temperature obtained by fitting the Planck distribution to the experimental relative line intensities.