The Effect of Laser Wavelength on the Selective Vaporization of Cu–Zn Alloy in Laser Ablation at Low Pressure

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1. Introduction

Laser induced plasma emission spectrometry (LIPS) is an analytical method suitable for direct and rapid determination of various types of solid samples. The application to process control of manufactured materials is much concerned due to its direct sampling without any pretreatment. LIPS under evacuated pressures further can yield better analytical performance because of the low fluctuation of the emission intensity as well as the large signal to background ratio.1–7) However, selective vaporization of sample atoms often cause serious problem during the laser ablation process, so that the analytical result involves large errors. Selective vaporization was observed by Baldwin8) and Russo9) in laser atomization on brass. Recently, selective vaporization in laser-induced plasma at reduced pressures was reported when using TEA CO2 laser and Q-switched Nd:YAG laser.10,11) However, the mechanism on the selective vaporization should be further investigated to get accurate analytical data in LIPS. In this study, the effect of laser wavelength on the selective vaporization of a metal sample is discussed.

2. Experimental

The experimental setup is shown in Fig. 1. Four different wavelengths of a Q-switched Nd:YAG laser (LS-2135 LOTIS TII, Japan) equipped with a harmonic assembly (YHG-34 LOTIS TII, Japan): 1064 nm (12 mJ/pulse), 532 nm (5 mJ/pulse), 355 nm (5 mJ/pulse), and 266 nm (5 mJ/pulse), were employed for laser irradiation. All measurements were conducted in He atmosphere of 400 Pa. The laser beam was condensed on a sample surface (~Ø0.7 mm) by a plano-convex lens with a focal distance of 200 mm. Cu (~60wt%)–Zn (~40wt%) alloy was selected as the test sample considering the large difference in the boiling point of its constituents; i.e. Zn (1180 K) and Cu (2843 K). Cleaning of the sample surface was performed with 100 shots of laser irradiation, and the emission spectrum was measured by accumulating subsequent 100 shots on a spectrograph (Ritsu Oyo Kogaku MC-25N, Japan) equipped with a CCD detector (Hamamatsu Photonics M6296, Japan). The exposure time of the detector was 19 ms. The emission signal was directly collected by an optical fiber.

3. Results and Discussion

Figure 2 shows the typical spectra containing several Cu I and Zn I lines when changing the wavelength of irradiated laser. After cleaning of sample surface with 100 shots of laser irradiation, emission intensity of LIP produced by 1064 nm laser irradiation was greatly reduced. It is found from Fig. 2 that the emission intensities become larger with shorter wavelength of the laser. The observed intensity ratios of Cu I 521.8 nm to Zn I 481.0 nm (I_{521.8}/I_{481.0}) were es-
Colombant and Tonon derived a formula relating the length of laser and the excitation of sample atoms.

Both the reflectivity and the penetration depth (determined by the skin effect) of a metal sample on laser irradiation are generally reduced when the wavelength of laser becomes shorter, as a result, absorption of the laser energy to the sample could occur more effectively with shorter wavelengths of the laser. Since larger energy can be absorbed and concentrated only at the surface of the sample when lasers with the shorter wavelength are employed, the temperature of the sample surface could be easily and quickly elevated up to boiling temperatures of elements in the sample (independent of the kind of the elements). It is therefore assumed that selective vaporization of Zn relative to Cu is not predominant in the brass alloy sample when the 266-nm laser is employed. Especially for the 1064-nm laser, the laser energy was elevated to 12 mJ/pulse because ablation of the sample was hardly caused at 5 mJ/pulse.

Now, we consider the relationship between the wavelength of laser and the excitation of sample atoms. Colombant and Tonon derived a formula relating the electron temperature of laser-produced plasma and the laser wavelength as follow:

$$ T(eV) = 5.2 \times 10^{-6} A^{1/3} [\lambda^2 \phi]^{1/5} $$

Here, $A$ is the atomic number of the element considered (e.g. 29 for Cu and 30 for Zn), $\lambda$ (in $\mu$m) is the laser wavelength, and $\phi$ is the laser power density (in W/cm$^2$). This equation suggests that for approximately the same laser power density, brass plasma produced by the longer wavelength of laser radiation will have a higher electron temperature than those produced by the shorter wavelength of laser. Recently, Khater et al. observed the strong emission lines of highly ionized carbon emissions such as C(II), C(III), C(IV) in Fe plasma produced by Nd:YAG laser radiation at 1064 nm, while those emission lines could not be observed in the plasma produced by the third and fourth harmonics at 355 and 266 nm, respectively. Usually, excitation energies of atomic emission lines used for elemental analysis are relatively low (ca. 3–5 eV). In such a case, too much high electron temperature of laser-produced plasma will be harmful and relatively cold plasma produced by the shorter wavelength lasers will be suitable for the excitation of usual analytical emission lines having low excitation energy.

When the laser ablation was performed with the 1064-nm laser (12 mJ/pulse), the LIPS emission intensities of the Zn and Cu lines decreased rapidly with the progress of laser shots. Figure 3(a) is the averaged spectrum of 1st to 100th laser shot and this period corresponds to the cleaning process of sample surface. First emission intensity of the Zn and Cu lines decreased rapidly with the progress of laser shots. Since LIPS could not be observed when the 1064-nm laser (12 mJ/pulse) was irradiated on pure Cu sample, it was considered that the laser ablation threshold of pure Cu was more than 12 mJ/pulse. When the laser irradiation is quit for some time, diffusion of Zn to the surface would occur and then the surface has the bulk composition of the brass alloy, which leads to laser ablation to yield the LIPS spectrum again.

In conclusion, the 266-nm wavelength laser is effective to obtain the LIPS emission intensity of the brass alloy with a high precision, because the selective vaporization of Zn is suppressed. This effect should be noticed when a sample comprising elements having different thermal properties is analyzed by LIPS. Kagawa et al. also reported that the selective vaporization negligibly take place when UV laser with a short pulse duration is focused on a target at reduced pressure.

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