The Effect of Selective Vaporization on TEA CO₂ Laser Induced Shock Wave Plasma

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Synopsis

TEA CO₂ laser (130 mJ, 100 ns) and Nd-YAG laser (50 mJ, 8 ns) pulses were employed to generate secondary plasma from brass samples in air under a reduced pressure of 1 Torr. The vaporization effects on Zn and Cu were studied in terms of their emission characteristics for the two cases. In the case of TEA CO₂ laser, the emission intensities of copper spectral lines are extremely low, compared to the zinc spectral lines, indicating a highly selective-vaporization effect. The time-profiles of the emission intensities of ZnI 481.0 nm and CuI 327.4 nm spectral lines observed near the target surface clearly showed that vaporization of Cu atoms occurred later and continued for a long time at a relatively low gushing speed, while the vaporization of Zn atoms took place sooner with a higher gushing speed. It was shown that only Zn atoms form a shock front, and Cu atoms are left behind the shock-wave and are not excited. This selective vaporization process does not occur at a laser power density considerably higher than the threshold for the plasma generation as demonstrated by the use of Nd-YAG laser of higher power density. This phenomenon of selective vaporization described in the present paper also supports our laser-induced shock wave model.

1. Introduction

In conventional laser microprobe analyses¹⁻³⁾, solid-state laser pulses are focused onto a target surrounded by gas at 1 atm pressure. In such a case, a high temperature and high-density plasma is generated, resulting in high intensity of the emission with a continuous spectrum; the situation is further complicated by an occurrence of self-absorption effect. As a

consequence, precision and sensitivity are limited in the case of ordinary laser ablation emission spectrochemical analysis (LAESA). For this reason, LAESA is not in widespread use, in spite of its potential application for in situ measurement.

Thanks to the increasing variety of laser systems available recently, researches of the LAESA method have again attracted considerable interest for its application in the field of spectrometry. It is becoming clear now that some of the disadvantages which are

inherent in the ordinary LAESA techniques can now be overcome, to some extent, by the use of new laser sources and modern spectral detection systems. Presently, two strategies are being pursued in LAESA developments. One of them adopted a high pressure surrounding gas, and is usually called Laser-Induced Breakdown Spectroscopy (LIBS), which has been developed by Cremers et al.⁴⁻⁶ In this method a high peak power laser with short duration, such as a pulsed Nd-YAG laser, is focused onto a sample at the atmospheric pressure. In order to remove the interfering background from the high continuous emission spectrum due to the high density plasma, a gated OMA system is incorporated into the detection system. The development of LAESA method along the other direction involves the use of low gas pressures. With the laser plasma produced under a reduced gas pressure, the intensity of background emission is expected to be reduced as well⁷⁻¹⁴.

In the mean time, we have shown in previous experiments that a laser-induced shock wave plasma is generated when a pulsed gas laser, such as an N₂ laser, a TEA CO₂ laser, or an excimer laser, is focused onto a solid target at a reduced gas pressure around 1 Torr¹⁵⁻²⁵. It was found in either case, the laser plasma invariably consists of two distinct parts. The first part occupies a small region of high temperature (the primary plasma), which provides an intense and continuous emission for a short time, just above the surface of the target. The second part (the secondary plasma) expands with time around the primary plasma emitting sharp atomic spectral lines with negligibly low background emission. By means of time-resolved measurements in our experiments using a TEA CO₂ laser¹⁵ and an excimer laser¹⁶, we were able to demonstrate that atoms in this secondary plasma were excited by the shock wave, while the primary plasma acts as a source of explosion energy source. We have referred to this method as laser-induced shock wave plasma spectroscopy (LISPS).

Generally speaking, the characteristics of a laser generated plasma depend on many factors involved in the process. Aside from the fact that it is influenced by the properties of the target material and the surrounding gas employed, the characteristics of the plasma can be affected by the type of a laser used and various parameters of the laser itself, such as its wavelength, pulse width, total energy and power density. We have clearly shown, in our previous experiments of LISPS using an N₂ laser²⁵ and an excimer laser¹⁶, that there was a good linear relationship between the atomic emission intensities and the contents of the associated elements in the sample such as steel and brass, and that so called selective vaporization was practically negligible. In a separate experiment, TEA CO₂ laser induced shock wave plasma also exhibited excellent characteristics for a highly sensitive spectrochemical analysis using glass

samples^{21,22}, alkali halide pellet samples²³ and low-alloy steel samples²⁴. However, some serious problems remain, depending on the type of samples. For examples, when a 500 mJ TEA CO₂ laser with 100 ns pulse width was focused onto a brass sample, the characteristic bright green color associated with the copper atoms was only seen for the several initial laser shots repeated on a fixed position of the sample. While the green color disappeared completely thereafter, the blue color associated with zinc remained very bright throughout the repeated irradiation and over the entire hemispherical region occupied by the plasma. This was an unexpected new phenomenon unknown in the case of an ordinary laser plasma produced at the atmospheric pressure. A selective vaporization effect was suspected to be responsible for this phenomenon.

Selective vaporization was also observed by Baldwin²⁶ and Russo²⁷ in laser atomization on brass. This effect should be taken into account generally when a quantitative analysis is carried out for brass samples using ordinary LAESA or laser ICP. The same effect is expected in LISPS using a TEA CO₂ laser and should therefore be examined in some detail. As pointed out in our previous paper, in the case of LISPS, atoms were expected to gush out at very high speeds and compress the surrounding gas to produce the secondary plasma^{16,22}. It was assumed that in the case of brass samples, the vaporization of Cu atoms and Zn atoms did not take place simultaneously, and that the Cu atoms gushed out of the sample later and at a lower speed, than the Zn atoms. This was suspected to be a consequence of insufficient power density of the laser due to difficulties in precise focusing of the TEA CO₂ laser beam. We have referred to this phenomenon as selective vaporization process, a term commonly used in ordinary LAESA. However, the mechanism and the actual effects of selective vaporization have yet to be studied thoroughly.

The present study is undertaken to clarify how this selective vaporization takes place in our Laser-Induced Shock-Wave Plasma and how it influences spectrochemical analyses. For this purpose, various factors affecting the process are examined by employing a TEA CO₂ laser and a Nd-YAG laser on different target materials. The results of the analysis will be discussed in connection with the physical mechanism of LISPS, specifically with the assumption of a shock wave model.

2. Experimental Procedure

The experimental arrangement is shown in Fig. 1. The laser radiation from a TEA CO₂ laser or Nd-YAG laser was focused by a focusing lens ($f=100$ mm) through a window onto the surface of the target. The TEA CO₂ laser (Lumonics, multi gas laser, HE 440 B) with a setting of 130 mJ pulse energy,

Fig. 2 Relationship between total emission intensity (time and spatially integrated) of ZnI 481.0 nm and CuI 515.3 nm as a function of the number of shots of laser irradiation for a TEA CO₂ laser and a Nd-YAG laser at 1 Torr.

laser shots observed for Zn as seen in Fig. 2 are correlated with the form and depth of the crater produced by the repeated bombardment of the laser pulses. A similar phenomenon was already observed for steel samples²⁴.

A different result was obtained when a Nd-YAG laser was used, as shown by the corresponding curves in Fig. 2. Emission intensities of both Zn and Cu spectral lines remained nearly constant under the repeated irradiation at the same position. The power density for Nd-YAG laser employed was 5 times stronger (20 GW/cm²) than the case of TEA CO₂ laser due to the much higher beam quality of the Nd-YAG laser.

It is important to stress here that time-gating method was not employed in the space and time integrated measurements as the continuum background in the spectrum is practically negligible. As

Fig. 3 Relationship between the time-integrated emission intensity of (a) ZnI 481.0 nm and (b) CuI 515.3 nm as a function of position using the TEA CO₂ laser.

described in our previous reports, the emission from the primary plasma continued for only a short period, about twice the duration of the laser pulse, and the total emission intensity of the associated continuous spectrum was relatively very weak, while the secondary plasma mainly emits sharp and strong atomic emission lines. In fact, when the setting of the monochromator was shifted away from the emission lines of Cu and Zn, the total intensity dropped to nearly zero, strongly confirming the negligible contribution of the continuous spectrum. The same thing can be said for the results presented in Fig. 3 and Fig. 4.

Fig. 3(a) and (b) provide a comparison of Cu and Zn emission intensities for the case of rotating sample at 2 rpm under the successive irradiations by TEA CO₂. In this case the secondary plasma was imaged on the plane of the slit, and the time-integrated emission intensity was plotted as a function of distance from the sample surface and presented in Fig. 3(a) and 3(b) for Cu and Zn respectively with comparable intensity scale. It is clearly seen that in the case of standard brass sample, the Cu emission intensity (Fig. 3(b)) is extremely low, as compared to the Zn emission intensity (Fig. 3(a)) and the spatial distribution of the time-integrated Cu emission inten-

sity is much narrower than that of Zn emission.

The total emission intensity of ZnI 481.0 nm and CuI 515.3 nm spectral lines was derived from the curves shown in Fig. 3 according to the following equation:

$$I_{\text{total}} = \int I(y) dy \quad (1)$$

where $I(y)$ is the emission intensity at position y . The result shows that the total emission intensity of ZnI 481.0 nm is about 23 times higher than that of CuI 515.3 nm for the brass sample. The emission intensities of ZnI 481.0 nm obtained from brass and pure Zn sample are also compared in Fig. 3(a). The total emission intensity of ZnI 481.0 nm obtained for the brass sample is one fifth of that for the pure zinc sample. It should also be noted that the total Cu emission intensity for pure commercial copper is much lower than that for brass. These differences are mostly the consequences of the different heat characteristics among these samples.

The time-integrated emission intensities of Cu and Zn are plotted in Fig. 4(a) and (b) as functions of position for the plasmas induced by the Nd-YAG laser irradiation on brass and pure Zn targets. The experimental condition was the same as that for the results given in Fig. 3(a) and (b). It can be clearly seen that emission of CuI 515.3 nm is comparable to that of ZnI 481.0 nm. This result is in marked contrast to the result shown in Fig. 3(a) and (b). The calculated total emission intensity of ZnI 481.0 nm is only about 2.4 times stronger than that of CuI 515.3 nm. It should also be noted that the Cu emission intensity for the commercial copper sample is nearly the same as that for the brass sample, which is again different from the result obtained by means of a TEA CO₂ laser. A comparison between the total emission intensities of ZnI 481.0 nm from pure zinc and brass samples was also made by using eq. (1). The result shows approximately 3 fold difference between them. This ratio is also different from the above mentioned result for the TEA CO₂ laser induced plasma.

It is well known that in the laser-induced shock wave, the front position of the atomic emission moves characteristically with time. Fig. 5 shows the relationship between time and the front position of the Zn emission for the TEA CO₂ laser as well as the Nd-YAG laser on the brass sample. These data were obtained by measuring the time between the initiation of the laser irradiation and the rising point of the emission of ZnI 481.0 nm at various positions of the slit settings. The result for the case of the TEA CO₂ laser as depicted in Fig. 5 gives a time versus distance slope of around 0.6. It should be noted that the rise in the Cu emission in this case could not be clearly located and was therefore not presented here. In contrast to this, for the Nd-YAG laser induced plasma, the rising point of Cu emission could be clearly

Fig. 4 Relationship between the time-integrated emission intensity of (a) ZnI 481.0 nm and (b) CuI 515.3 nm as a function of position using a Nd-YAG laser.

Fig. 5 Relationship between the front position of emission and time for ZnI 481.0 nm using both the TEA CO₂ laser and the Nd-YAG laser.

observed to share the same time profile with the Zn emission. The slope of the log-log curve for the relationship between the time and the emission front position for Nd-YAG laser induced plasma is 0.47 as shown in Fig. 5. Comparison of the two curves in Fig. 5 indicates that the speed of Zn atoms observed in Nd-YAG laser generated plasma is much higher than that in the TEA CO₂ laser generated plasma.

In order to see more clearly the different process involved in the plasma generated by the TEA CO₂ laser on the brass target, a comparison of time profiles for ZnI 481.0 nm and CuI 327.4 nm emission intensities was conducted using a dual channel measurement of the emissions at 5 mm from the surface. The result is shown in Fig. 6. It is perceptibly clear that the emission of Cu took place later and continued for a long time. The Zn emission, on the other hand, started earlier and lasted only a short time.

It is believed that the degree of selectivity is highly dependent on the physical form and composition of the sample, due to the differences in the heat characteristics of the samples. For instance, selective vaporization is not expected to occur on a film target even when the TEA CO₂ laser is used, because the threshold for vaporization of the atoms from the film is relatively low. To prove the above hypothesis, a film of brass was deposited on a glass substrate by the TEA CO₂ laser bombardment (6000 laser shots) on a brass target in a manner shown schematically in Fig. 7. The film was then irradiated using the TEA CO₂ laser. As expected, the Cu green emission was strong enough to be noticeable by naked eye. The emissions of both Zn and Cu were analyzed at 3

Position	1	2	3
Emission line			
Zn I 481.0 nm	62	250	893
Cu I 515.3 nm	39	44	38

Fig. 7 Relationship between the total emission intensity of ZnI 481.0 nm and that of CuI 515.3 nm for different positions of the film.

Fig. 6 Time-profile of the emission intensity of CuI 327.4 nm and ZnI 481.0 nm using a TEA CO₂ laser. Data was collected at 5 mm above the sample surface at a reduced pressure of 1 Torr.

different points (point 1, just on the surface; point 2, 3 mm from the surface and point 3, 8 mm from the surface). The results listed in the table of Fig. 7 show a comparison between the total emission intensities due to Cu and Zn. It is observed that Zn emission intensity increases with increasing distance from the sample surface, while Cu emission intensity remains nearly constant with respect to the distance from the sample surface. This was further substantiated by microscope inspection showing only limited droplets left on the film. This observation indicated that Cu was vaporized in the gas phase, rather than being merely melted into droplets.

4. Discussion

As reported in our previous work²¹⁾, on a TEA CO₂ laser induced plasma under a reduced pressure of 1 Torr, it was observed that a shock-wave plasma could be generated on various types of targets. On the other hand, in the case of low-melting-point glass samples, the shock-wave plasma could not be generated by the TEA CO₂ laser (power density 0.6 GW/cm²) because of a lack of expulsion from the sample surface. In the present experiment the shock-wave

plasma was readily generated by a TEA CO₂ laser of higher power density (4 GW/cm²) even for low-melting-point glass samples. However, a problem remained unsolved for the case of alloy targets, such as brass. It seems likely that selective vaporization takes place because Cu and Zn have different melting and boiling temperatures.

On the basis of the experimental results obtained in this study we may conclude that selective vaporization does take place to a remarkable extent on brass target when a TEA CO₂ laser is used. To be specific, the ratio between the totally integrated emission intensities of the two elements is about 23 in favor of the Zn emission. On the other hand, the total emission intensity of ZnI 481.0 nm is about 2.4 times that of CuI 515.3 nm when the Nd-YAG laser is employed instead on the same target. This means that in the case of the TEA CO₂ laser the vaporization process of Cu is strongly suppressed on the brass sample. A more decisive evidence was provided by the result of repeated irradiation at a fixed position on the target as shown in Fig. 2, which showed no Cu emission from the plasma after only a few initial laser shots.

As proposed in our previous work, a secondary plasma is produced through adiabatic compression of the surrounding air as a result of atoms gushing from the primary plasma at a supersonic speed¹⁶. These atoms are excited in a limited region just behind the shock wave where the plasma attains its highest temperature. As a consequence, atoms of elements with lower boiling points are evaporated sooner and gush out from the target surface with high velocities to form a shock wave in the surrounding gas. This shock wave is, in turn, responsible for the excitation of the evaporated atoms. In the meantime, atoms of elements with higher boiling points are evaporated more slowly. Being unable to produce its own shock wave and being left behind the shock wave generated by the more volatile atoms of the first batch, these atoms are not expected to be excited.

The experimental result shown in Fig. 6 could be viewed as a direct evidence that Cu atoms gush out from the target at lower speed as compared to Zn atoms. It is natural to expect on the basis of the argument presented above that the Cu atoms are unable to generate their own shock wave, and are left behind the shock-wave generated by the Zn atoms without undergoing effective excitation.

An additional case of "selective-vaporization" was provided by the TEA CO₂ laser-induced shock wave plasma on high speed steel samples containing W with a concentration of about 10%²⁴. In this case only a limited region emitting W spectral line was faintly observed near the primary plasma, while the emission lines of Fe were clearly observable over the entire region occupied by the secondary plasma. In contrast to this, even for LISPS using an N₂ laser of

6 mJ pulse energy, a good calibration curve for the WI 400.9 nm emission line could be obtained for high speed steel samples²⁵.

The selective vaporization and the selective excitation observed in this experiment is likely to take place when the power density of the focused laser light is comparable to the threshold for plasma generation. In other words, if the power density of the laser is far higher than the threshold, no selective-vaporization would take place. For this reason, selective vaporization is hardly expected to play a significant role in the cases plasmas generated by Nd-YAG, excimer and nitrogen lasers. In fact, as described in the experiment shown in Fig. 5, when the Nd-YAG laser is focused on the brass target Cu atoms and Zn atoms gush out almost simultaneously and move together at more or less the same speed. We have already confirmed in another experiment that Sn and Pb gush out simultaneously and move together at high speed to generate a shock wave when TEA CO₂ laser was focused on Sn-Pb alloy samples²⁰. In the light of present study, this result can be interpreted as a consequence of the much lower threshold energy for generating primary plasma on Sn-Pb sample compared that required for plasma generation on the brass sample.

As shown in the table of Fig. 7, the Zn emission intensity observed at different positions of the film increases with increasing the distance from the sample surface, while Cu emission intensity remains almost constant with respect to its distance from the sample surface. This difference can also be interpreted in terms of the difference between the gushing speeds of Zn and Cu atoms during the plasma deposition process. Namely, Zn atoms gushing out from the primary plasma at a very high speed, tend to accumulate at far end of the deposited film (8 mm from the target surface). On the other hand, the Cu atoms evaporate from the target in the primary plasma tend to spread out by diffusion process at a relatively lower speed, and thereby resulting in a more uniform distribution in the film.

By comparing the emission intensities of the film with that of the bulk, it was observed that the emission efficiency for Cu is far higher in the film than in a bulk form. Therefore one of the effective ways to overcome the selective vaporization effect in a sample with high threshold for vaporization is to prepare the analytical samples in the form of film. This presents a great prospect for the practical development of a laser plasma generating system capable of carrying out two different tasks successively, one for the film preparation and the subsequent one for the spectrochemical analysis.

Experiments on material removal in a series of copper-zinc alloys by Q-switched pulsed laser has already been reported by Baldwin²⁶. The report noted that selective vaporization did take place to some extent, but it was overcome by employing an auxiliary

spark to excite the vaporized atoms. In an experiment on laser atomization, Russo²⁷⁾ reported that selective vaporization also took place on a brass sample containing 60% copper (bp. 2567 K) and 40% zinc (bp. 907 K). However, in his work, the evaporated atoms were excited via the ICP. Besides, in the case of ordinary LAESA, the surrounding gas near the focusing point acts as a heat reservoir¹²⁾. Therefore even if the evaporated Cu atoms moved out at low speed, excitation would still take place with high efficiency by absorbing the thermal energy from the reservoir. Unfortunately we were not able to prove this point using the TEA CO₂ laser. We have in fact demonstrated that breakdown would take place above the sample surface even at a gas pressure above 10 Torr, and as a consequence the laser light could not reach the target for the generation of plasma.

Finally, it should be emphasized that the occurrence of the strong selective vaporization effect observed in this study complies with the plasma generation mechanism embodied by the laser induced shock wave model which has been proposed previously by the present authors.

5. Conclusion

It was demonstrated in this experiment that selective vaporization had a significant effect on the total emission intensities observed in our laser-induced shock wave plasma. Based on our model, the adiabatic compression of the gas surrounding the target is induced by atoms gushing out of the primary plasma at very high speed. The rapid compression is in turn required for the creation of blast-wave as well as the subsequent secondary plasma. Consequently, atoms of elements with higher melting points which are not readily evaporated are unable to generate their own shock wave and hence are left behind the shock-wave generated by the evaporated atoms of the low-melting-point element. As a result, these atoms would not be expected to experience excitation. We have demonstrated however, that this undesirable selective-vaporization process in a TEA CO₂ laser-material removal can be suppressed by using a film as the target. Experiments are in progress for the preparation of film samples by means of laser plasma ablation technique in connection with the potential application for the Laser Ablation Emission Spectrochemical Analysis.

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References

- 1) K. Laqua: *Analffical Laser Spectroscopy*, N. Omenetto, Ed. (Wiley, New York, 1979), pp. 47-118.
- 2) E. H. Piepmeier: *AnalSical Applications of Lasers* (Wiley, New York, 1986), pp. 627-669.
- 3) D. A. Cremers and L. J. Radziemski: *Laser Spectroscopy and Its Application*, R. W. Solarz and J. A. Paisner, E. (Marcel Dekker, New York, 1987), pp. 351-415.
- 4) T. R. Loree and L. J. Radziemski: *Plasma Chem. And Plasma Proc.* 1, 271 (1981).
- 5) L. J. Radziemski and T. R. Loree: *Plasma Chem. And Plasma Proc.* 1, 281 (1981).
- 6) D. A. Cremers: *Appl. Spectrosc.* 41, 572 (1987).
- 7) E. H. Piepmeier and D. E. Osten: *Appl. Spectrosc.* 25, 642 (1971).
- 8) G. Dimitrov and V. Gagov: *Spectrosc. Lett.* 10, 337 (1979).
- 9) A. F. Gibson, T. P. Hughes, and C. L. M. Ireland: *J. Phys. D.* 4, 1527 (1971).
- 10) M. Kuzuya and O. Mikami: *Jpn. J. Appl. Phys.* 29, 1568 (1990).
- 11) Y. Iida: *Spectrochim. Acta*, 45 B, 1353 (1990).
- 12) F. Leis, W. Sdorra, J. B. Ko, and K. Niemax: *Microchim. Acta* II, 185 (1989).
- 13) Y. I. Lee, T. L. Thiem, G. H. Kim, Y. Y. Teng, and J. Sneddon: *Appl. Spectrosc.* 46, 1597 (1992).
- 14) J. D. Wu, Q. Pan, and S. C. Chen: *Appl. Spectrosc.* 51, 883 (1997).
- 15) H. Kurniawan, M. O. Tjia, M. Barmawi, S. Yokoi, Y. Kimura, and K. Kagawa: *J. Phys. D: Appl. Phys.* 28, 879 (1995).
- 16) K. Kagawa, K. Kawai, M. Tani, and T. Kobayashi: *Appl. Spectrosc.* 48, 198 (1994).
- 17) K. Kagawa, M. Ohtani, S. Yokoi, and S. Nakajima: *Spectrochim. Acta B* 39, 525 (1984).
- 18) H. Kurniawan, T. Kobayashi, and K. Kagawa: *Appl. Spectrosc.* 46, 581 (1992).
- 19) M. Tani, H. Kurniawan, H. Ueda, K. Mizukami, K. Kawai, and K. Kagawa: *Jpn. J. Appl. Phys.* 31, 1213 (1992).
- 20) H. Kurniawan, T. Kobayashi, S. Nakajima, and K. Kagawa: *Jpn. J. Appl. Phys.* 31, 1213 (1992).
- 21) H. Kurniawan, K. Kagawa, M. Okamoto, M. Ueda, T. Kobayashi, and S. Nakajima: *Appl. Spectrosc.* 50, 3, 299 (1996).
- 22) H. Kurniawan, S. Nakajima, J. E. Batubara, M. Marpaung, M. Okamoto, and K. Kagawa: *Appl. Spectrosc.* 49, 1067 (1995).
- 23) H. Kurniawan, N. Ikeda, T. Kobayashi, and K. Kagawa: *J. Spectrosc. Soc. Jap.* 41, 21 (1992).
- 24) K. Kagawa, H. Hattori, M. Ishikane, M. Ueda, and H. Kurniawan: *Anal. Chim. Acta* 299, 393 (1995).
- 25) K. Kagawa, S. Yanagihara, and S. Yokoi: *J. Spectrosc. Soc. Jpn.* 34, 306 (1985).
- 26) J. M. Baldwin: *Appl. Spectrosc.* 24, 429 (1970).
- 27) R. R. Russo: *Appl. Spectrosc.* 49, 14A (1995).
- 28) H. Kurniawan, Y. Ishikawa, S. Nakajima, and K. Kagawa: *Appl. Spectrosc.* 51, 1769 (1997).