Quantitative emission from femtosecond microplasmas for laser-induced breakdown spectroscopy

MT Taschuk, SE Kirkwood, YY Tsui and R Fedosejevs

Department of Electrical and Computer Engineering, University of Alberta, Edmonton, Alberta, Canada T6H 2V4

E-mail: mtaschuk@ece.ualberta.ca

Abstract. An ongoing study of the scaling of Laser-Induced Breakdown Spectroscopy (LIBS) to microjoule pulse energies is being conducted to quantify the LIBS process. The use of microplasmas for LIBS requires good understanding of the emission scaling in order to maximize the sensitivity of the LIBS technique at low energies. The quantitative scaling of emission of Al, Cu and Si microplasmas from 100 μJ down to 100 nJ is presented. The scaling of line emission from major and minor constituents in Al 5052 alloy is investigated and evaluated for analytical LIBS. Ablated crater volume scaling and emission efficiency for Si microplasmas are investigated.

1. Introduction

Laser-Induced Breakdown Spectroscopy (LIBS) is a rapid, flexible and robust material characterization technique that makes use of the optical emission from a laser-induced plasma. LIBS has been applied as a quality control technique for steel manufacturing [1], in-situ testing of steam tubes in a nuclear power plant [2], as a diagnostic for laser cleaning of historic buildings and statues [3, 4] and investigation of the composition of archaeological samples [5]. A recent development in LIBS is the investigation of micro-LIBS or μLIBS, which utilizes pulse energies below 100 μJ [6-11]. This reduction of pulse energy allows the probing of smaller spots on the surface and reduces the damage caused by a LIBS measurement. However, the use of lower energies for LIBS measurements requires a good understanding of the emission scaling from microplasmas in order to optimize the sensitivity of detection and ascertain the analytical limits of μLIBS.

An ongoing study of the scaling of emission from LIBS plasmas to microjoule pulse energies is being conducted [12]. It is expected that as one scales to shorter pulses the energy required to initiate breakdown will decrease, allowing the extension of the μLIBS technique to sub-microjoule pulse energies. In the present work, the scaling of emission from Al, Cu and Si microplasmas generated by femtosecond laser pulses is quantified. The application to analytic detection of major and minor elements in aluminum alloys is discussed and the emission efficiency of Si microplasmas is investigated.
2. Experimental Setup
The experimental setup is similar to that used to characterize the absolute emission from ns and ps KrF microplasmas [12]. In this case, a Ti:Sapphire laser at 800 nm and a pulsewidth of ~ 120 fs was used. The emission from the microplasmas is monitored by a photomultiplier tube (PMT) coupled to interference filters, and with a 1/4 m, f/3.9 spectrometer (Oriel MS260i) coupled to an intensified CCD (Andor iStar DH720). PMT signals were measured for peak and full-width at half-maximum (FWHM) to estimate the area under the curve. Signal to noise ratios (SNR) for spectral lines are defined by equation 1 where background noise $\sigma_b$ is defined as the standard deviation of the pixel to pixel variation in a neighbouring spectral region with no spectral lines and $N_{\text{channels}}$ is the width of the spectral line in channels.

$$\text{SNR} = \frac{\int I(\lambda)d\lambda}{3\sigma_b \sqrt{N_{\text{channels}}}}$$

The PMT used in these experiments has been calibrated using a pulsed laser together with a barium sulphate diffuser plate to provide a known intensity source with an absolute error of ± 15 %. The spectrometer/ICCD combination has also been calibrated with the same source, as well as with a Hg lamp with known brightness [13], and compared to the manufacturer specifications. The three calibration sources for the spectrometer/ICCD agree to within about 40%, and the absolute error in spectral intensity values is estimated at that value. Interference filters were used to reduce the response of the PMT to background continuum from the microplasma.

3. Experimental Results
The energy scaling of microplasma emission is presented in Fig. 1 for Si (a), Cu (b) and Al (c). Observation wavelengths, bandwidth and target reflectivities are summarized in Table 1. For the microplasma emission, single shot data was acquired at various energies. For Al and Cu a 10 cm lens was used to focus the laser light, while in the case of Si both a 10 cm lens and a 10X objective were used. For measurements of the emission from air breakdown, 16 shot averages were taken with the target removed from focus using the 10X objective in all cases. Power law fits were applied to the data sets and the resulting coefficients are summarized in Table 1.

In the case of Si microplasmas, the energy scaling is preserved across the transition from the 10 cm lens to the 10X objective. There is no difficulty detecting the Si microplasma down to ~ 100 nJ per pulse, where the emission trend approaches the noise floor of the PMT. The solid angle observed by the PMT is ~ $9 \cdot 10^{-3}$ Sr, so a noise floor of ~ $10^3$ photons Sr$^{-1}$ corresponds to a detection limit of ~ 9 photons. The noise floor varies with observation wavelength due to the quantum efficiency of the PMT and the transmission of the interference filters used. The emission levels per unit energy for Cu (Fig. 1b) and Al (Fig. 1c) are much lower than that of Si. In both cases, the higher noise limit of the PMT is met even before the 10X objective can be used. In addition, if the emission trends for Al and Cu were to continue across a transition to the 10X objective, one would expect to start having
Table 1. Observation Conditions and Emission Scaling Power Law Coefficients.

|                      | Al       | Cu       | Si       |
|----------------------|----------|----------|----------|
| Observation Wavelength| 400 nm   | 326 nm   | 288 nm   |
| Observation Bandwidth | 25 nm    | 10 nm    | 10 nm    |
| Target Reflectivity  | N/A *    | 96%      | 33%      |
| Microplasma Emission | 3.0 ± 0.3  | 3.0 ± 0.3 | 1.98 ± 0.04 |
| Air Background       | 2.6 ± 0.2 | 2.25 ± 0.06 | 2.53 ± 0.09 |

* Reflected light too scattered to measure reflectivity

Figure 1. Quantitative emission levels from (a) Si, (b) Cu and (c) Al microplasmas. The line fits are power law with the coefficients summarized in Table 1. Material data points in (a) - (c) are single shot, while air breakdown points in (a) - (c) are an average of 16 shots. The horizontal line in plots (a) - (c) represents the equivalent noise power of the PMT at the appropriate wavelength. (d) SNR for major and minor elements in Al 5052 alloy from ICCD measurements. Each data point is an average of 100 shots with 1σ error bars.
difficulty differentiating the microplasma signal from the background air breakdown. This effect was observed in experiments with the 10X objective for Cu emission, where it was not possible to reliably differentiate between microplasma emission and air breakdown.

Observations were also made with the spectrometer/ICCD for Al 5052 alloy using the 10X objective. In LIBS it is typical to delay the start of acquisition from the laser-matter interaction in order to avoid the noise contribution from the broadband emission of the early time plasma. However, in this case the gate was opened before the initiation of the microplasma in order to capture all of the emission and thus allow comparison with the PMT results. The Al 5052 sample used has matrix concentrations of $\sim 2.3 \pm 0.1\%$ Mg, and $\sim 0.03 \pm 0.01\%$ Mn [10]. The results are presented in Fig. 1d where each data point is an average of 100 spectra with 1 $\sigma$ error bars. Though Al and Mg remain detectable using single shot pulse to $\sim 600$ nJ, the precision of the data near the detection threshold needs improvement. Mn was not reliably detectable at the low concentration present in the Al 5052 sample for this energy range.

The spectrometer/ICCD combination has the advantage of spectrally discriminating between the contribution from the air breakdown and the line emission from the target element. However, narrower line filters could be employed with the PMT, which should help eliminate the difficulties encountered here for Al and Cu microplasmas for the observations using a 10X objective.

Si ablation craters were measured with an optical profilometer (Zygo NewView 5000) for the 10X objective data presented in Fig. 1a. Crater lineouts were fit with a modified gaussian function as given in Equation 2, where $D$ is the nominal depth, $x_0$ is the center of the crater, $\sigma$ is a width parameter, and $d$ is a parameter which governs the flatness of the peak region of the modified gaussian function.

\[
y = -D \exp \left( -\frac{(x-x_0)^2}{2\sigma^2} \right) + y_0
\]  

Best fit curves were numerically integrated to give the ablated volume. The volume ablated was found to be linear with pulse energy, which is consistent with many reports [7, 14, 15]. Ablation efficiency for Si under these conditions is $2.7 \pm 0.1 \ \mu$m$^3$/μJ. Scaling the data presented in Fig. 1a to a 2$r$ Sr emission angle and dividing by the number of atoms ablated for each shot yields an emission efficiency parameter. This efficiency is quite low, with far less than a photon emitted per ablated atom. However, over the range 100 nJ to 2 μJ the efficiency climbs from $\sim 10^{-6}$ to $\sim 10^{-4}$, yielding a power law dependence of 1.9 $\pm$ 0.1.

4. Conclusion
While Al and Cu emission approached the PMT noise limit of $\sim 10^4$ photons Sr$^{-1}$ with pulse energies of $\sim 1$ μJ, the emission from Si microplasmas was detectable to $\sim 100$ nJ. For Al 5052 alloy it was found that minor elements are only detectable in favourable cases such as Mg, while the major constituent element Al could be detectable with a single shot of $\sim 600$ nJ. The emission efficiency of Si was found to be quite low and followed a power law dependence on laser energy of 1.9 $\pm$ 0.1.

Acknowledgments
This work funded by the Natural Sciences and Engineering Research Council of Canada, MPB Technologies, Inc. and the Canadian Institute for Photonics Innovations.
References

[1] R. Noll, H. Bette, A. Brysch, M. Kraushaar, et al. *Spectrochim. Acta, Part B*, Vol. 56:637 – 649, 2001.
[2] A.I. Whitehouse, J. Young, I.M. Botheroyd, et al. *Spectrochim. Acta, Part B*, Vol. 56:821 – 830, 2001.
[3] S. Klein, F. Fekrsanati, J. Hildenhagen, K. Dickmann et al. *Appl. Surf. Sci.*, Vol. 171:242 – 251, 2001.
[4] P. Maravelaki-Kalaitzaki, D. Anglos, V. Kilikoglou et al. *Spectrochim. Acta, Part B*, Vol. 56:887 – 903, 2001.
[5] B. Al Ali, D. Bulajic, M. Corsi, G. Cristoforetti, S. Legnaioli et al. *SPIE 4402*, pages 25 – 31, 2001.
[6] H. Häkkänen and J.E.I. Korppi-Tommola. *Appl. Spectrosc.*, Vol. 49:1721 – 1728, 1995.
[7] C. Geertsen, J-L Lacour, P. Mauchien, L. Pierrard. *Spectrochim. Acta, Part B*, Vol. 51:1403 – 1416, 1996.
[8] M. Hidalgo, F. Martin and J.J. Laserna. *Anal. Chem.*, Vol. 68:1095 – 1100, 1996.
[9] W.F. Ho, C.W. Ng and N.H. Cheung. *Appl. Spectrosc.*, Vol. 51:87 – 91, 1997.
[10] G.W. Rieger, M. Taschuk, Y.Y. Tsui and R. Fedosejevs. *Appl. Spectrosc.*, Vol. 56:689 – 698, 2002.
[11] I.V. Cravetchi, M. Taschuk, Y.Y. Tsui and R. Fedosejevs. *Spectrochim. Acta, Part B*, Vol. 59:1439 – 1450, 2004.
[12] G.W. Rieger, M. Taschuk, Y.Y. Tsui and R. Fedosejevs. *Spectrochim. Acta, Part B*, Vol. 58:497 – 510, 2003.
[13] C.J. Sansonetti J. Reader and J.M. Bridges. *Appl. Opt.*, Vol. 35:78 – 83, 1996.
[14] A. Semerok, C. Chaléard, V. Detalle, J-L. Lacour et al. *Appl. Surf. Sci.*, Vol. 138-139:311 – 314, 1999.
[15] A. Semerok, B. Sallé, J-F. Wagner, G. Petite, O. Gobert et al. *SPIE 4423*, pages 153 – 164, 2001.