Comparison of nanosecond and femtosecond LIBS

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Abstract: We report a comprehensive study of the differences in the emission and hydrodynamics expansion features of ns and fs LIBS plumes under both vacuum and atmosphere environments under similar laser fluence conditions.

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1. Introduction

Traditionally, laser-induced breakdown spectroscopy (LIBS) systems have employed using nanosecond (ns) laser systems, but with the recent developments in femtosecond (fs) laser systems, much attention has been turned to development of fs-LIBS systems. Even though the only difference between the conventional ns laser based LIBS and ultrafast LIBS is the difference in laser system, the mechanisms leading to energy absorption and target ablation are entirely different for both cases. Whereas ionization, sample heating, and vaporization all occur during the laser pulse in ns laser ablation, fs laser pulses are so short that these phenomena do not occur until the end or after the laser pulse. Femtosecond pulse duration is shorter than the characteristic relaxation times, such as the electron-to-ion energy transfer time, electron heat conduction time, and hence the hydrodynamic or expansion time; all of which typically occur on the order of several picoseconds after laser absorption. Because of this, ultrafast LIBS offers greatly reduced thermal damage and heat- affected zone (HAZ) in the target due to negligible heat conduction and hydrodynamic motion during the laser pulse duration. Moreover, the spatial resolution obtained by fs pulses is better than ns pulses. Other advantages of fs-LIBS include reduced continuum and atmospheric plasma mixing and generation of atomic plume in comparison with ns LIBS [1-3].

In this paper we examined the dynamics of ns and fs LIBS plumes in both atmosphere and vacuum conditions using an array of diagnostic tools at similar laser fluence levels. The plume diagnostics employed are fast-gated imaging, spectroscopic techniques, ion emission studies using Faraday cup, and mass ablation rate using quartz crystal microbalance (QCM). Our results show several advantages for fs-LIBS over ns-LIBS which include reduced continuum and atmospheric plasma mixing and generation of atomic plume, higher mass ablation rate, and narrower ion emission.

2. Experimental

Plasma creation was accomplished either in vacuum or at 1 atmospheric pressure using a Nd:YAG laser (1064 nm, 6 ns FWHM) or using a Ti-Sapphire laser (800 nm, 40 fs FWHM). Laser energy used for both ns and fs lasers was 6 mJ and a 100 μm spot size was maintained to keep the same laser fluence (76.4 Jcm^{-2}) and hence, energy deposited per unit area on the target was the same for both lasers. Images of the expanding plasma were obtained using an intensified CCD (ICCD) to demonstrate the effect of the ambient environment on plasma expansion and identify key differences between fs and ns LPP plume expansion. Emission spectra from both lasers in both pressure environments were studied at different delays after the laser pulse and particular emission features specific to each have been identified. Excitation temperature and density of the plumes were then estimated using Boltzmann plot and Stark broadening techniques, respectively, allowing us to better understand the differences in the dynamic properties from different pulse duration lasers and in different pressure environments. A systematic comparison of analytical performance (S/N and S/B ratios) is also performed for both ns and fs LPPs in vacuum and ambient air atmosphere.

3. Results and Discussion

LIBS experiments are normally performed in ambient air atmosphere. The presence of ambient air affects the hydrodynamic expansion properties of laser ablation plumes. Figures 1 shows ICCD time-integrated images of emission in the visible region (350 nm – 800 nm) from ns and fs laser-produced plasmas (LPP) in 1 atmosphere. Intensities have been normalized to the maximum intensity seen from both figures. We see significant differences in expansion of emitting species between ambient atmosphere and vacuum environments. For the case of ns LPP emission, spherical expansion of the plume is observed. In vacuum, expansion of the emitting species is significant and emission can be seen at distances greater than 10 mm from the target. However in atmosphere conditions, where plume expansion is confined by the ambient gas, expansion of emitting species is limited to a distance of ~2.5 mm from the target, creating a smaller source, which is beneficial for light-collection optics in LIBS systems. Higher emission intensities are seen in the atmosphere case due to confinement, as emission is concentrated in a smaller region. Expansion dynamics of fs LPP are significantly different from ns LPP. Instead of spherical expansion noticed in ns LPP, fs LPP plumes are found to expand with a much stronger forward bias in directions normal to the target surface, as seen in Figure 1. Our studies showed that fs LPP provided narrower angular distribution of ions and evaporated mass in comparison with ns LPPs. Like the ns LPP case in vacuum, expansion of emitting species in fs LPP can also be seen at distances greater than 10 mm, while in atmosphere, stronger emission can be seen at farther distances from the target surface in the case of fs LPP due to the pinching and cylindrical expansion of the plasma compared to ns LPP, though like ns LPP, emission is limited to a distance of ~2.5 mm. Forward directed expansion of fs laser plumes can be understood by considering pressure confinement due to strong overheating in the laser impact zone. Lower visible emission intensities were observed from the fs LPP than those observed from the ns LPP despite similar laser fluence conditions. In both ns and fs LPP cases, strongest emission was observed closest to the target surface, as this region of the plasma is hottest.

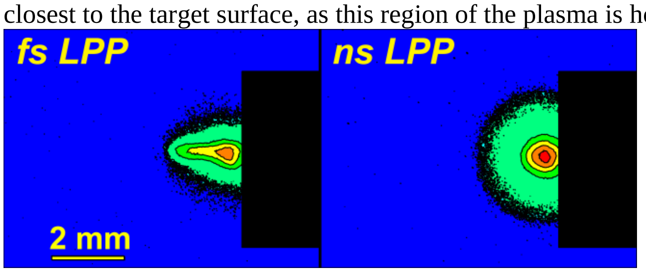

Figure 1 – ICCD time-integrated images of visible emission from fs LPP and ns LPP in 1 atmosphere.

We investigated the angular distribution of ions and ablated mass of femtosecond and nanosecond laser-produced metal plasmas. The ion flux and kinetic energy studies of the fs laser plasmas show narrower angular distribution while ns laser plasmas provide narrower energy distribution. The kinetic ion profiles of fs LPP showed a faster broad kinetic peak followed by a slower peak. The observation of multiple kinetic energy peaks in the fs laser plumes is associated with different ablation mechanisms (Coulomb explosion and thermal vaporization). The deposited mass studies at similar laser fluence levels showed fs laser mass ablation to be significantly higher compared to ns laser. Angular dependence of mass deposition profiles showed forward biasing for fs plume compared to the ns plume. The peak deposited mass is nearly 15 times higher for fs LPP compared to ns LPP for the parameters used in our study.

We also compared the spectral features from both LPP at different times after the laser pulse to see how the spectral shapes change with time and change with decreasing laser pulse width. It was observed that fs LPP emission spectra showed similar characteristics in both atmosphere and vacuum environments, while ns LPP emission spectra appeared to excite different ionic transitions in atmosphere and vacuum. In both environments, it was shown that continuum emission from ns LPP dominates at early times, while fs LPP demonstrated negligible continuum emission. Another important observation is that all ns LPP emission spectra showed transition lines from lower-charged ions, while fs LPP emission spectra were dominated only by neutral species emission. This can be explained by the different ablation processes for the two lasers, as ns lasers tend to generate lower-charged ion populations that through recombination, produce neutral species, while fs lasers create highly-charged ions emitting at much shorter wavelengths followed by thermal vaporization of the target, producing mostly neutral species. S/N and S/B ratios were calculated at different delays after the laser pulse to identify the importance of the delay time when collecting plasma emission for LIBS-related analysis. However, the signal to noise (S/N) and the signal to background (S/B) ratios obtainable for ns and fs LIBS are comparable with proper time discrimination of the spectral emission.

The important plume parameters, *viz.* plasma excitation temperature and electron density were calculated using the Boltzmann plot and Stark broadening methods, respectively. These important plasma parameters are necessary to optimize a plasma emission source, as they are directly related to the emission characteristics of the plume species. It was shown that confinement by the ambient environment plays a significant role in maintaining plasma temperature and density and hence, emission at later times. This was the case for both ns and fs LPP, though ns LPP maintained these properties approximately two times longer than fs LPP, which can be attributed to the faster expansion of the fs plume. Power functions were fit to this data to characterize the rapid decays seen in vacuum and to identify the more rapid decay exhibited by the fs LPP.

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