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Simultaneous Particle Flow-Field Characterization and Metal Speciation in the Reaction Zone of Metalized AP/HTPB Propellants

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Abstract

Inhaling air-borne metal particles is known to cause adverse health effects such as cancer, pulmonary heart disease, and asthma. Metal particles can be released to air from various additives often used to augment the combustion characteristics of propellants, pyrotechnics and explosives. The objective of this study is to, characterize the gas-phase reacting flow field of burning ammonium perchlorate/hydroxyl-terminated polybutadiene (AP/HTPB) propellants seeded with different metal additives, using simultaneous digital in-line holography (DIH) and laser-induced breakdown spectroscopy (LIBS). Recent developments in DIH method enables quantification of particle size, density, velocity and three-dimensional position, while LIBS enables identification of elemental species, in particular metals. The present study is focused on micron-sized Al added to solid AP/HTPB strands. The particles imaged were found to be 100–200 microns in size, with an average velocity of 3 m/s. As the ejected particles spread out in different directions, the spatial locations closest to the burning surface contains the highest density of particles. Simultaneous LIBS experiments were capable of detecting Al signals from propellants strands doped with 5–15% Al by mass and generated time histories of Al in the flame zone. The work presented here is a significant step forward in simultaneous reacting flow-field characterization and chemical speciation in propellants and explosives using combined DIH and LIBS techniques.

Key Words

Laser Induced Breakdown Spectroscopy, Digital In-line Holography, Propellant Combustion, Aluminum Combustion, Metal Particle Emissions.

1. Introduction

Energetic materials are compounds that release energy rapidly when reacted. These materials are the basis of explosives, propellants, and pyrotechnics [1]. Depending on the practical application of these materials, different combustion and heat release properties are desired. Metal particulates, most often aluminum, are added to propellant materials to enhance desired performance characteristics. In ammunition powder, for example, aluminum particles can be added to raise the reaction temperature, enhance the air blast, and increase the heat of detonation [2]. The solid rocket boosters of NASA's Space Shuttle utilize aluminum powder to enhance the energy content of the propellant [3]. In these applications, portion of the added metal particulates are ejected into the atmosphere during the combustion process. This particle release can be concerning in cases where humans are in the close proximity to the combustion products. Inhaling metal particulates, whether aluminum, lead, copper or mercury for example, is known to cause adverse health effects such as asthma, cancer, pulmonary heart disease [4]. In order to fully assess the adverse health effects and derive mitigation strategies, it is vital to first understand metal particle release mechanisms and quantify the emissions during the combustion in these compounds.

Laser inducted breakdown spectroscopy (LIBS) is a powerful analytical technique capable of these concentration measurements. In LIBS, a pulsed laser beam is focused onto a small special location. At this location, the beam irradiance becomes so high that a small plasma is formed out of the material at the focal point [5]. The LIBS plasmas can be formed by solid, liquid, or gaseous medium. This plasma emission contains spectral characteristics of elemental species of the materials present in the medium. The atoms are excited to higher energy states and as they relax, they emit light at characteristic wavelengths. This light can then be dispersed using a spectrometer, which then can be used to determine the elemental composition within the medium [6]. Using LIBS, the intensity of light captured can then be correlated to the concentration of the elemental species. Previous experiments conducted in our laboratory has revealed the possibility of using a 10-Hz nanosecond (ns)-duration Nd: YAG laser pulses to measure concentrations of metal particles within the gas-phase reaction zone of solid rocket propellant samples [7]. However, the detected LIBS signal was very intermittent, indicating a strong dependence on the nature of the particle flow filed, in particular, the size, density, velocity and the spatial location of metal particles in the reaction zone. A clearer understanding of reacting flow field is needed to better interpret the LIBS data, enabling comprehensive model development to predict the combustion chemistry and flow physics of metalized energetic materials.

The goal of the present work is to combine two laser diagnostics approaches to fulfil the above objective. In particular, digital inline holography (DIH) combined with LIBS enables the detection of particle size, velocity, particle density and spatial location along with the chemical composition of these particles. This work shows promise of utilizing these laser diagnostics together and provides a basis for future detailed characterization experiments.

2. Methods

In order to simulate the combustion reaction of an energetic compound in the laboratory, small propellant strands are used. As these strands burn down, the resulting flame becomes the zone where the concentration of metal particles is measured. The propellant strands used are ammonium perchlorate (AP), with a hydroxyl-terminated polybutadiene (HTPB) binding material, made in an in-house facility. Additional additive materials can be added to these strands during initial mixing process based on the material release to be studied. AP is a necessary ingredient in the strands, as without AP, the binding material reaction becomes slow and intermittent. In that case, the added metal powder would not react in a fashion that would cause the particles to eject into the surrounding air. The propellant strands are hand-mixed and are created in 20-gram batches. After all components are added together, they are mixed according to a process that has been tested to provide repeatable results. This process produces the same results recorded in prior work that used mechanical mixers instead of a hand-mixing process [8, 9]. The uncured propellant mixture is then drawn into Teflon tubes of diameters and lengths approximately 4.76 mm and 30 mm, respectively. Once cured, the Teflon tubing was cut away to remove the propellant strands. A mounting platform was made of shop-metal to allow for consistent placement of propellant strands in the probe region for simultaneous DIH and LIBS.

Figure 1 shown the experimental apparatus, where L1 is referring to the laser for the LIBS diagnostics. A Continuum Powerlite Nd: YAG laser is used to generate the laser sparks for LIBS. This laser system can produce two different wavelengths, 532 nm and 1064 nm, each operating at a 10-Hz pulse repetition rate. The 1064-nm wavelength was chosen for the LIBS experiments, because the desired detection wavelength for aluminum is 396 nm. If the 532 nm wavelength was used, the scattered intensity of light from the laser beam becomes very bright and hence interferes with LIBS detection system. Using a half-wave plate and a polarizer, the energy of the laser pulses can be tuned to the specific range desired. A collimating lens is then placed about 100 mm away from the LIBS plasma site. The light collected is routed through a fiber optic cable and fed into a Princeton Instruments IsoPlane 160 spectrometer. This spectrometer is a compact module that offers the resolution of approximately a 1/3-m spectrometer. Using a 300-g/mm grating at 300-nm blaze angle, the collected light is diffracted to the constituent wavelengths. A Princeton Instruments PI-Max 4 ICCD camera is used to record the emission spectra. The camera has an imaging array is 1024 pixels by 1024 pixels, with a pixel size of 13 x 13 μm. The detection limits for this camera is approximately from 200 to 900 nm.

Figure 1 also displays the DIH optical setup and how it is located with reference to the LIBS setup. For the DIH apparatus, a continuous wave laser beam used, instead of a pulsed laser beam. An Oxxius diode laser that operated at 532 nm was used. This beam needs to be expanded before it can be used as a holography beam. In the case of DIH, the object beam and the reference beam are on the same axis. Thus, several diverging lenses are placed in the optical path to expand the beam to approximately 50 mm in diameter. A positive lens is then placed to produce a collimated beam with the of that diameter. This expanded beam illuminates both the particles to be imaged, and the imaging camera. Before the beam illuminates the camera, it passes through a neutral density filter to cut down the intensity and prevent the camera from saturating. The camera used for these experiments is a Photron SA-Z Fastcam high-speed CMOS camera. It has the ability to image up to 2 million frames per second; however, to achieve higher frame rates, the camera bins the CMOS chip to use less pixels. For the purpose of the current experiments, the camera is operated at 20,000 frames per second (fps), with an exposure setting of 40 μs. Attached to the Photron SA-Z camera is a high-magnification video lens and objective. The Infinity K2/DistaMax long distance video microscope paired with a CF-4 objective can achieve high magnification at a working distance of 55 mm.

Prior LIBS experiments conducted in a similar configuration in our laboratory have been well documented [7, 10]. It was determined that a laser energy of 100 mJ/pulse for a 532 nm beam allowed for a desirable signal-to-noise ratio (SNR) without increasing intensity levels that would lead towards saturation. However, as mentioned above, the 1064 nm laser beam was chosen for the current experiments. In order to maintain a similar SNR, a laser energy of 200 mJ/pulse was used at 1064-nm wavelength.

The cameras are triggered using the LIBS laser. Utilizing an output TTL signal from the flash lamps firing, the spectrometer ICCD camera can record spectra at the same rate as the laser pulses, 10 Hz. This output signal, however, is synchronized with the flash lamps, and therefore is not aligned with the LIBS breakdown event. In order to have the camera exposed during the LIBS breakdown, a delay needs to be utilized. For this setup, a delay of 256.5 µs was used, with an exposure time of 300 ns and ICCD gain of 8.

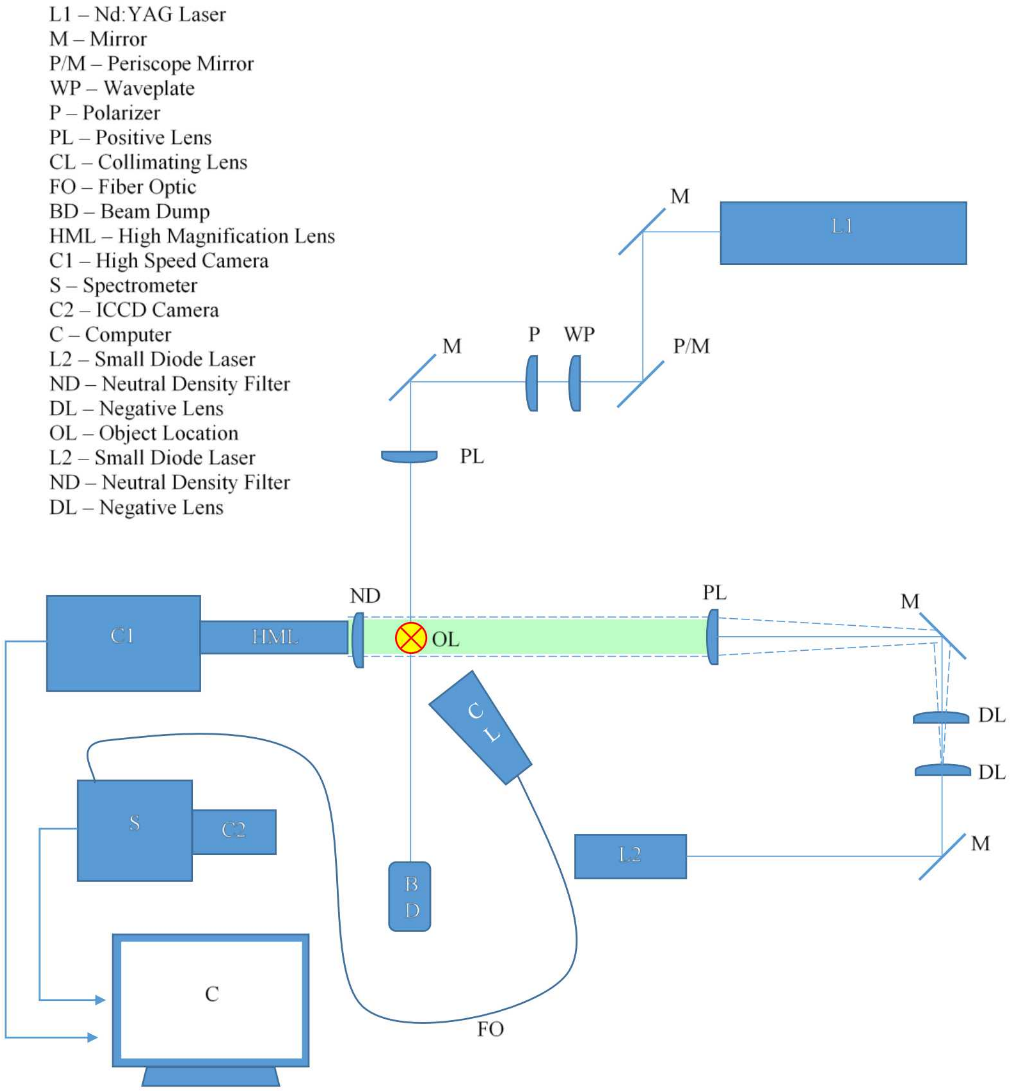


Figure 1. Experimental Apparatus.

The small diode laser used for DIH experiments had no power control. The laser outputted a continuous wavelength of 532 nm light with a power of about 25 mW. However, if the total power of this laser beam illuminated the camera, it would saturate the CMOS chip. Therefore, a neutral density (ND) filter of OD=2.0 was used to cut down the intensity of light illuminating the camera. Before each experiment, the imaging lens was focused to a plane about 50-mm in front of the lens using a 1951 United States Air Force resolution test target.

The propellant strands are placed in the strand holder such that the strand exceeds both above and below the field of view of the camera. The propellant strands are placed like this so that when ignited using a hand-held torch, the camera can be manually triggered to start recording once the strand top is in view of the camera. Setting up the Photron SA-Z camera to image at 20,000 fps, with an exposure timing of 40 µs per frame, allows for approximately 10 seconds of data to be collected. Only certain portions of the total image sequence are saved, depending on the phenomena observed. The small objects in view are the particles that are under study in these experiments. Classification of the size, spatial location, velocity, and density of these objects will help to understand the particle field that future LIBS signals will study. The DIH experimental data were analyzed using a series of MATLAB scripts, written by Guildenbecher et al. at Sandia National Laboratories. These scripts are well documented several papers [11, 12]. Knowing where these particles are in three-dimensional space, and their location in sequential frames at a known frame rate also enables extraction of particle velocity. Coupled with LIBS, these particles can be analyzed and chemically characterized.

3. Results and Discussion

The LIBS spark has to be placed within the field of view of the high-speed camera so that the DIH imaging system can visually see the LIBS spark. The preliminary experiments involved using the pin-head of a push-pin to align the LIBS spark to the DIH system. The push-pin was placed at the focal point of the camera so that the tip was clearly in focus. Then, with the DIH lens partially covered so as to not risk saturating the system, the LIBS spark was placed to ablate the tip of the push-pin. In this fashion, the LIBS spark was placed to be in the field of view of the camera. Figure 2 displays the DIH camera imaging a LIBS breakdown plasma in atmospheric air next to the push-pin tip. The illumination of the plasma is not enough to visualize the push-pin, which is in the center of this image. Note that although this is imaging with the DIH camera, this is not a DIH experiment. The DIH laser is not illuminating the object field during this test. Rather, the light captured is only from the LIBS plasma. Once the LIBS plasma was observed to be at the focal plane of the DIH imaging lens, the LIBS spark was shifted back to the plane of the propellant strand, again using the push-pin as a guide. Figure 3 demonstrates the LIBS spark being imaged in a DIH experiment. Each image in Figure 3 is a subsequent frame in the experiment, with 50 µs separation between the frame. Frame number 1 is in the top left-hand corner, and frames proceed sequentially to the right and then to the next row starting on the left. In frame 1, the top half of the frame has more illumination than the bottom half, resulting from the LIBS plasma. In subsequent frames shock waves generated from the plasma can be visualized.

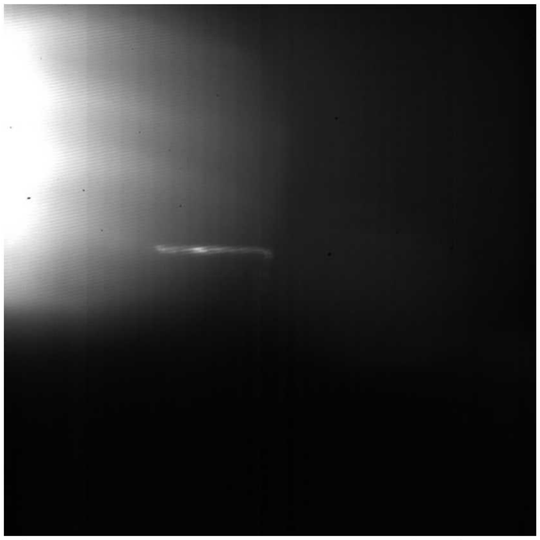


Figure 2. High-speed camera imaging a LIBS spark. The DIH laser is turned off.

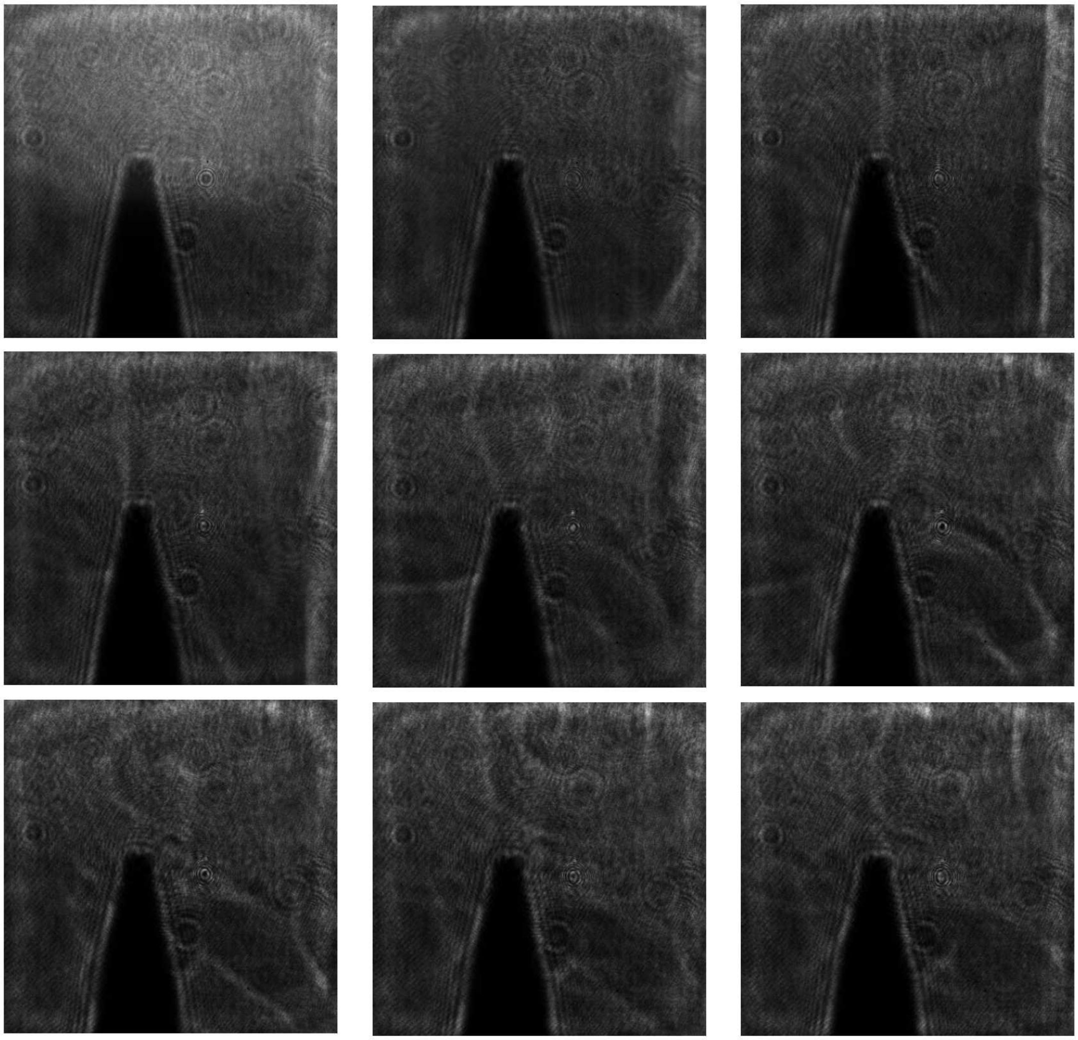


Figure 3. High-speed camera capturing a LIBS spark ablating a push-pin. The DIH laser is on.

Figure 4 shows a timing diagram displaying how DIH system collects data with respect to the LIBS apparatus. The laser beam is shown to be pulsing at a rate of 10 Hz. Each laser pulse lasts approximately 10 ns, which is not to scale on this plot, but each pulse arrives at every 100 ms. Both the LIBS imaging system and the DIH camera are triggered to start taking data by the user with a mouse click; however, each system is connected to a different laptop computer. At the present configuration, an unknown delay, x, between the collection of data between LIBS and DIH presents as shown on Figure 4. The LIBS system is triggered to record 30 spectra, one per each laser shot, for 30 laser shots. The DIH system on the other hand is only phase locked with the laser pulse. This means that the first laser shot after the user triggers the DIH camera to start imaging causes the camera to start taking data. At this point, however, the camera takes images at 20,000 frames per second, irrespective of the laser pulse. It was observed that after several laser shots, although the DIH system was phase locked with the laser pulse, the DIH images started to slightly drift away from the laser pulse. An improved triggering circuit will be implemented during future studies.

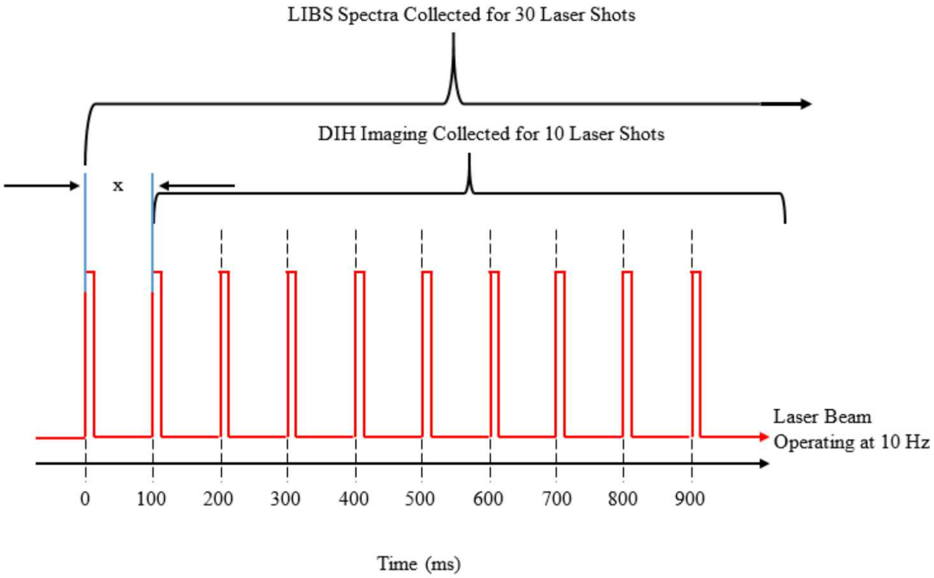


Figure 4. Timing diagram of simultaneous LIBS and DIH experimental scheme. In the present configuration, the delay 'x' is user defined.

In the propellent burning experiment, both LIBS and DIH were conducted simultaneously. The LIBS spark takes place at every 100 ms, and therefore can be observed by the DIH camera once every 2,000 frames. When the DIH system is turned on, but the propellant strand is not burning, the high-speed camera can image the LIBS event every 2,000 frames. Once the propellant strand is burning, however, the laser plasma is unnoticeable in the DIH camera frame. It is expected that the breakdown threshold is much lower in the atmospheric air as compared to the hot, hence less dense propellant flame region. Initial experiments were conducted with a LIBS pulse energy of 200 mJ, and then increased to around 230 mJ per pulse to determine if the plasma could be observed. The plasma still could not be seen with this higher laser pulse energy. Higher pulse energies are a concern, though, because although this higher energy causes an adequate plasma that can be seen within the combustion flame, once the flame extinguishes the plasma occurs in atmosphere at a much higher intensity, which could saturate the imaging camera. Although a higher OD neutral density filter could be used, that would adversely affect the DIH experiments, making metal particles difficult to distinguish. However, based on above characterization in atmospheric air cases, it is concluded that the series of LIBS signals recorded corresponds to every 2000th frame in the DIH image series. The analyzed results from simultaneous DIH experiments shown in Figures 5–10. The observed particle diameter is on the order of several hundred micrometers, which is in good agreement with similar experiments conducted in the literature [11, 12].

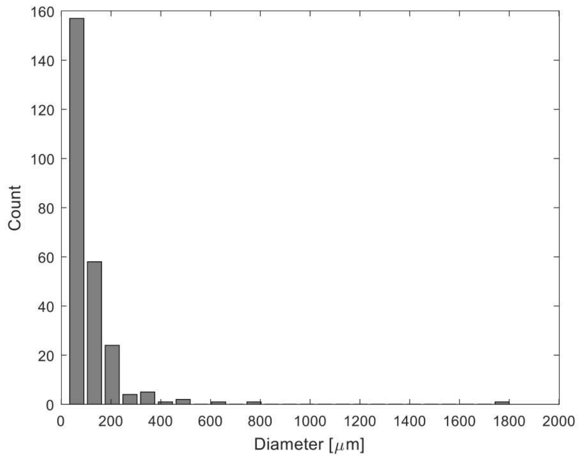


Figure 5. Particle diameter histogram from 16% Aluminum propellant strand burn.

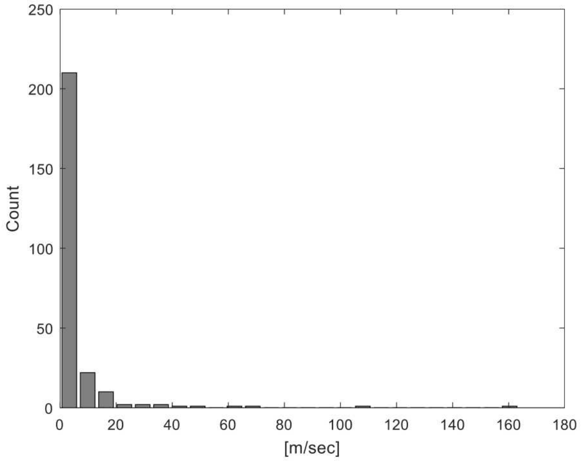


Figure 6. Histogram of total particle velocity.

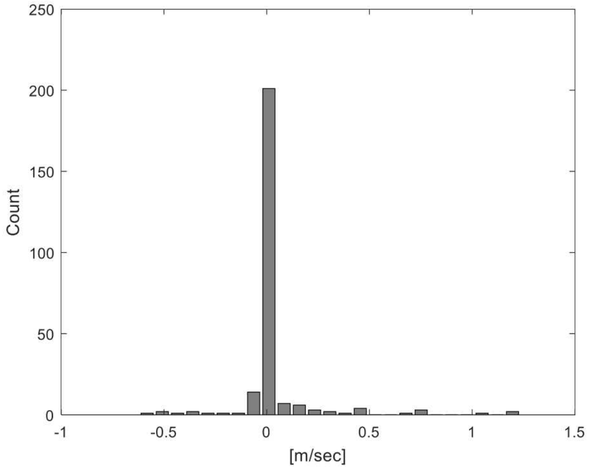


Figure 7. X-velocity histogram.

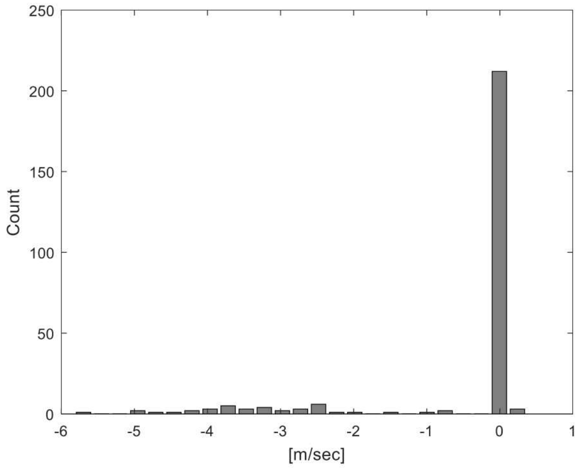


Figure 8. Y-velocity histogram.

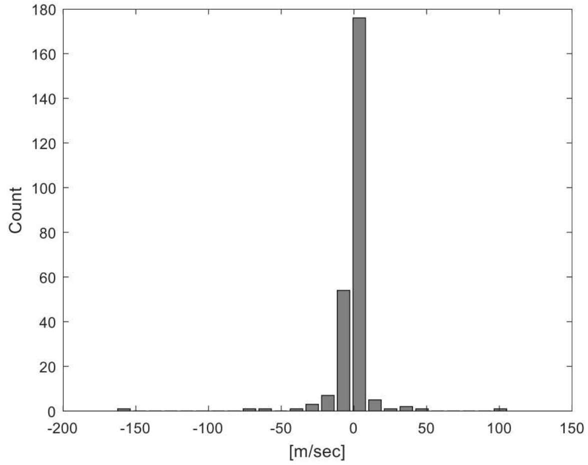


Figure 9. Z-velocity histogram.

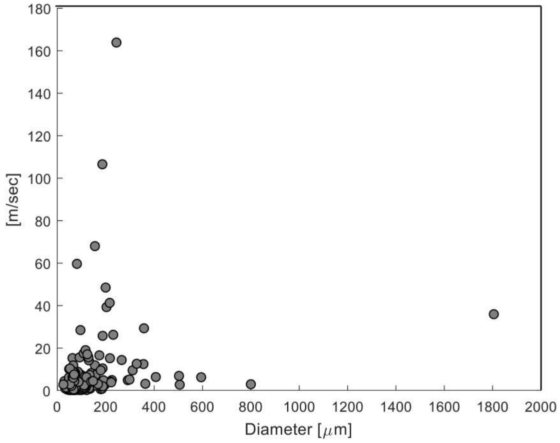


Figure 10. Total particle velocity as a function of particle diameter.

Figure 10 displays a comparison between the total velocity of a particle and its diameter. Most of the particles that were captured are 200 µm or less and are moving at speeds under 20 m/s.

Figures 6-9 display the velocity components of the particles that were captured. These plots indicated how these particles moved across the field of view of the imaging camera. In Figure 7, most of the particles moved at some speed between -0.5 and 0.5 m/s. Most of these particles were not moving completely to the left or right directions in the field of view, but rather moving straight up or down in the field of view. Figure 8 displays the y component of these particles. Most of the particles were moving either less than 1 m/s in the upward direction, or with significant velocity in the downward direction. These are most likely the particles that were falling back down through the field of view. Figure 9 shows the z component of the velocity. Most of the particles had a positive z velocity between -50 and 50 m/s, with a symmetrical number of particles both going in the positive and negative depth directions. Simultaneous LIBS data recorded are shown in Figs 11 & 12.

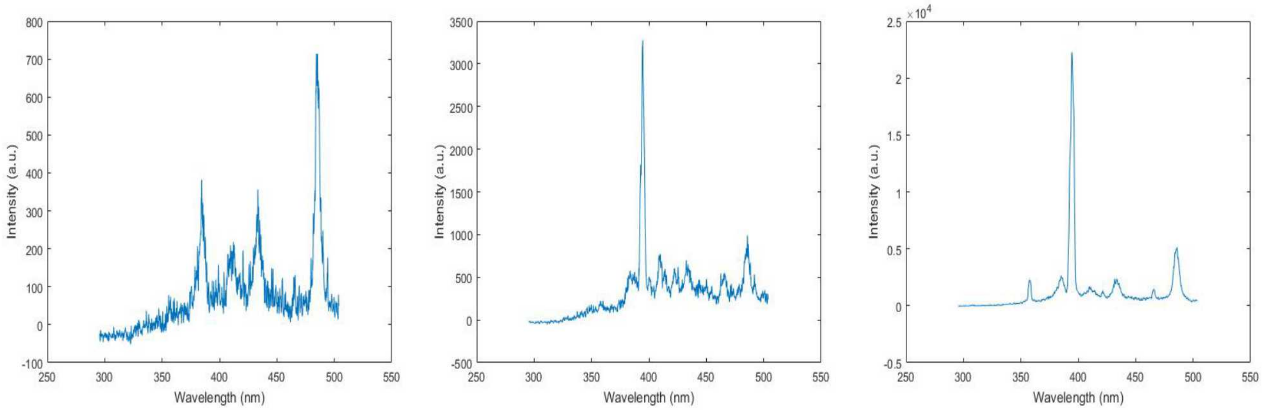
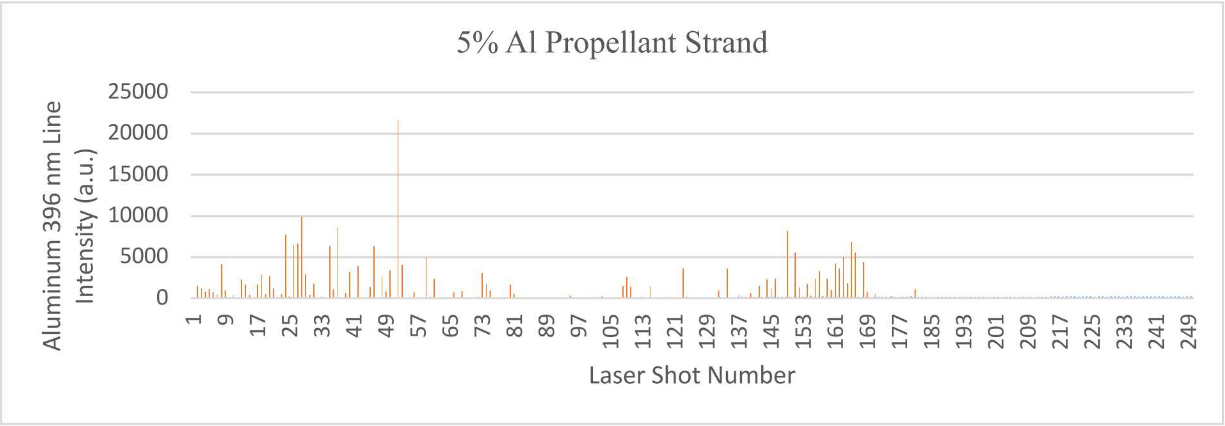


Figure11. Sample LIBS spectra where LIBS spark not detecting any aluminum (left), LIBS spark detecting a moderate aluminum emission signal (middle), and LIBS spark detecting a strong aluminum emission signal (right), indicating the intermittent nature of hitting Al particles and the effects of particle size and morphology, when using a 10-Hz excitation laser pulse.



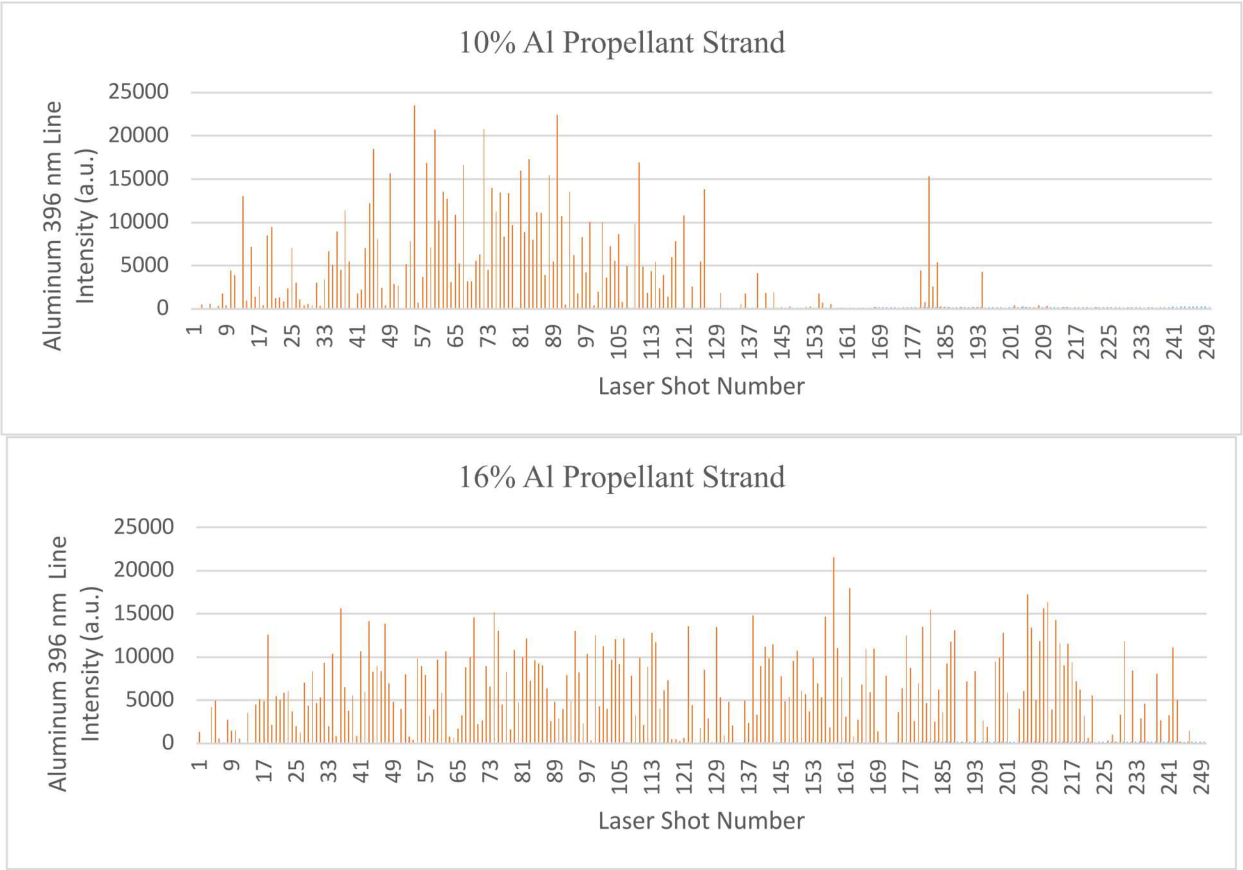


Figure12. Single-laser-shot Al LIBS signal collected from burning propellant strands with different quantities of added Al, 5% (top), 10% (middle), and 16% (bottom), by mass in AP/HTPB propellant strands.

4. Conclusion

Metal particulates are often added to propellant and explosive materials to change the combustion characteristics, tailoring the combustion for specific requirements in terms of blast pressure or heat release rate. The initial research project is geared towards studying the use of LIBS for conducting concentration measurements of metal particles within a combustion flame, which is simulated by a AP/HTPB propellant strands burning at atmospheric air. These initial experiments with LIBS show promise, but in order to make measurement capture more likely, an understanding of the particle flow field within the combustion flame is needed. Hence, simultaneous DIH and LIBS experiments are conducted in the reaction zone of burning metalized AP/HTPB propellent strands.

The particles imaged using DIH were found to be on the order of 100–200 microns in diameter. The total velocity of these particles is mostly under 10 m/s, with most of this velocity being observed in the positive and negative z-directions. Combining LIBS and DIH diagnostics in this study enabled histograms of Al particles at different seeding levels. Simultaneous DIH and LIBS diagnostics are shown to have a strong potential for complete characterization of the paticle flow field and elemental composition in reaction zone of complex energetic compounds.

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