OPTICAL MEASUREMENTS OF NANO-ALUMINUM COMBUSTION IN A HETEROGENEOUS SHOCK TUBE AND IN A FLAT FLAME BURNER

BY

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THESIS

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ABSTRACT

Metal additives are commonly used in combustion based devices such as high explosives and solid rocket motors. Of these, aluminum is the most common due to its availability, high energy density, and low toxicity; however, many aspects of nano-aluminum combustion are still not well understood. Depending upon the type of measurement, nano-aluminum burntimes can vary greatly and any reaction occurring at later burntimes is ignored. Also, much of the nano-aluminum work has been done using a heterogeneous shock tube, leaving hot post-combustion gas environments largely unstudied.

The purpose of this study was to determine the burntime of nano-aluminum by measuring the heat release of the particles rather than relying on photon emission by the burning particles. By tracking the temperature of the ambient gases within the shock tube, specifically the OH radical chosen for its limited participation in the combustion event, a comparison can be made between the transient heat release of the particle and the luminosity curve giving a better understanding of nano-aluminum burntime.

Also, similar burntime measurements were made in the hot ambient gases of a one dimensional flat flame burner. Three different particle sized were studied (50, 80, and 110 nm). The burntimes of each were
measured using high speed CMOS imaging allowing for a comparison of burntimes in various types of environments.

The results found OH could be used as an indicator of ambient temperature within the shock tube environment; however, the addition of nano-aluminum into the shock tube altered the signal of the absorption spectroscopy measurement. Also, the burntime results from the flat flame burner indicated that both single particles and larger agglomerations were present during testing and that the burntimes of single particles were consistent with burntimes observed in alternate environments.
To my family,...
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CHAPTER 1

INTRODUCTION

The primary purpose of this study is to investigate the burning of nano-aluminum focusing specifically on the burntime. To do this, both the heterogeneous shock tube facility and a one dimensional flat flame burner were employed. Optical measurements were used in order to categorize the nano-aluminum burntime both within the shock tube and the flat flame burner. The following sections will discuss the motivation for the work and the mechanisms of aluminum combustion and photon emission.

1.1 Research Motivation

Metal powders, because of their high heat capacity and ability to react with post combustion gases, are commonly used to enhance the performance of devices such as high explosives (HE) and solid rocket motors (SRM) [1]. Aluminum is one of the more common metal additives used due to its restively high energy density, availability, and low toxicity when compared to some other metal additives. The burntime of aluminum has been a subject of interest because of the need to match the overall energy release of the burning particle to the desired combustion event duration. Any energy release of the particle outside of this event is wasted, unable to enhance the performance of the device.

Current methods of measuring burntime include the constant intensity cutoff method, the percent peak
height method, and the percent total area method [2]. Each of these methods rely on photon emission by the burning aluminum particles, resulting in luminosity traces as illustrated by Figure 1.1; however, the method chosen for experimentation is often arbitrary, and the different methods can lead to significant variability in the calculated results. Also, these methods often ignore the decreased intensity tail indicated in Figure 1.1.

![Figure 1.1 - Example Nano-Aluminum Burntime Plot](image)

By using noninvasive optical measurement that study the environment around the burning aluminum particles, a better understanding of the relationship between burntime and luminosity can be achieved.

Also, there have been many studies categorizing the combustion of single aluminum particles within hot
ambient gases [2,8], but these studies have focused largely on micron sized aluminum particles. The study of nano-aluminum particles within the hot ambient gases of a burner supported flame has been somewhat limited with much of the work occurring in simulated environments within a heterogeneous shock tube [7]. By studying the combustion of nano-aluminum in hot ambient gases with varying amounts of oxidizing agent available, a deeper knowledge can be attained of how nano-aluminum burns in different types of environments.

1.2 Aluminum Combustion

Nano-aluminum combustion has been studied extensively due to its potential to improve the performance of combustion based devices [1]. This work has led to an increase in the understanding of the aluminum combustion mechanism. Aluminum particles exposed to air at room temperature develop a thin amorphous oxide layer that is varies between 0.5 nm to 4 nm in thickness [3]. The ignition point, the point at which conditions are sufficient to allow for an exothermic chemical reaction that raises the local temperature and increases the reaction rate, can vary greatly depending on the size of the particle.

For larger particles (~100 μm) temperature is the limiting factor for ignition. These particles cannot ignite until the particle has reached a temperature sufficient to melt the oxide layer surrounding the particle. The melting point of the Al₂O₃ oxide layer occurs at approximately 2300 K at atmospheric
conditions. Until this temperature is reached diffusion of aluminum through the oxide layer is limited, rendering the heat release from the chemical reaction too small to sustain a local temperature and reaction rate increase. However, ignition of nano-aluminum particles has been observed at temperatures well below the melting temperature of the oxide layer with some studies suggesting nano-aluminum can be ignited at temperatures of 1000 K [3]. As the particle diameter decrease the ratio of the surface are to the volume increases resulting in a shift away from the constant temperature model and the 2300 K ignition limit. Two models have been suggested to describe the burning mechanism for nano-aluminum particles. The shrinking core model predicts diffusion of the oxidizing agent through the oxide layer to the surface of the aluminum core [4]. An alternative model suggests that mechanical stresses resulting from rapid heating and the differences in thermal expansion coefficients of the oxide layer and aluminum core cause fragmentation of the particle and allow the aluminum to react [5]. Although the validity of either of these models will not be discussed in this work, it has been shown previously that as size decreases, a larger percentage of the particle mass is allowed to react at the surface resulting in ignition [6]. This is illustrated in Figure 1.2.
Because the reaction of small particles occurs close to the particle surface, the temperature does not rise much beyond the boiling point of aluminum. The particle itself and aluminum evaporation near the surface help to pull heat away from the particle preventing a large temperature rise. The limiting factor with regards to burntime may be a combination of both the reaction rate and the rate of diffusion at the surface [7].

1.3 Aluminum Emissivity

Extensive studies have been done in order to categorize the combustion characteristics of aluminum particles seeded in a burner stabilized flame;
however, much of this work such as that done by Freedman et al has focused largely on micron sized aluminum particles [8]. This is due in part to the difficulty of observing single nano-aluminum particles burning individually within a flame because of both the decreased diameter and decreased emissivity.

The number of emitted photons emitted at a specific wavelength by a particle of any composition or size is given by the following equation [9]:

\[
N_{\nu} = \frac{2 \pi v^2}{c^2 \exp \left( \frac{\nu}{kT} \right)} \frac{\varepsilon A t}{\lambda^4} \quad (1.1)
\]

Integrating equation 1.1 over all possible frequencies results in the total number of photons emitted for a single particle. Also, by inspection of equation 1.1 it can be shown that the relative number of photons between any two particles at the same temperature is directly proportional to the product of the emissivity of the particle and the particles emitting area. By doing this analysis for aluminum particles of different sizes, the relative number of emitted photons can be deduced.

The emissivity of a 2 μm aluminum particle is on the order of 0.1 based on calculations done using the Mie scattering code published by Bohren and Huffman. Doing a similar calculation for a 50 nm aluminum particle yields an emissivity of 0.001. This calculation was done using the complex refractive index of aluminum oxide at 3000 K published by Perry et al. [10].
By doing comparative analysis on the 2 μm aluminum particle and the 50 nm particles, it can be shown that the relative number of emitted photons of the 2 μm aluminum particles is 165,000 times greater than that of the 50 nm aluminum particles based on the differences in the emissivity and the area. This difference in photon emission greatly increases the difficulty in observing single nano-aluminum particle burning and means steps must be taken to ensure any observed particle is in fact a single nano particle and not an agglomeration of many particles.

1.4 Previous Work

Much of the work done has been done by studying the luminous event during nano-aluminum combustion and has showed a deviation of the burntime away from the d² law observed in larger aluminum particles. This is important because it shows the nano-aluminum particles are burning for much longer durations than would otherwise be expected; however, most of these measurements preclude the possibility of continued particle burning at later times on the luminosity curve.

Also, while single particle burning in hot ambient gases has been done with larger micron sized particles, the work done to categorize nano-aluminum combustion in ambient hot gases has been limited.
CHAPTER 2

EXPERIMENTAL METHODS

The experimental methods used to study nano-aluminum particles are described in detail below. The University of Illinois-Urbana Champaign (UIUC) shock tube facility has operated since the early 1990s under multiple advisors including Professor Herman Krier, Professor Rodney Burton, and Professor Nick Glumac. The operation of the shock tube has been described in previous publications, most recently by Allen et al. [11]. The shock tube dimensions, operation, particle injection, and test conditions are outlined below followed by a description of the diagnostics, instrumentation, and setup used to make combustion measurements. Similarly, a description of the flat flame burner and its operation, particle injection, test conditions, and the relevant diagnostics are outlined below.

2.1 Shock Tube

Shock tube theory is well understood and has been presented in several texts devoted to the topic [12]. The UIUC shock tube is termed heterogeneous due to the mixture of gases and condensed phases present in the test section. The shock tube is capable of generating temperatures of up to 5000 K and pressures of 30 atm in a highly repeatable manner with test times of approximately 2 ms making it ideal for the study of metal combustion. Previously the shock tube has been
used to study aluminum combustion in a variety of oxidizing environments including \( \text{O}_2 \), \( \text{CO}_2 \), and \( \text{H}_2\text{O} \) mixed with either \( \text{Ar} \) or \( \text{N}_2 \) [13]. The test condition chosen for this study was 2000 K and 5 atm, a condition for which nano-aluminum combustion has been shown previously [14].

The shock tube consists of three sections, a low pressure driven section (test section), an intermediate pressure diaphragm section, and a high pressure driver section. The driven section measures 8.4 m in length and has an inner diameter of 8.9 cm. The driver section has a diameter greater than that of the driven section and has a conical converging section that mates with the diaphragm section and accelerates the shock into the driven section. Both the driver section and diaphragm section are filled with helium. Once the test pressure is reached, the diaphragm section is vented allowing for diaphragm rupture and shock passage. The incident shock travels the length of the shock to the end wall where it reflects and raises the temperature and pressure of the shock tube to the desired test conditions. The temperature and pressure inside the shock tube can be controlled nearly independently of one another and are dependent only on the test gas composition and the ratio of the absolute pressure of the driver gas and the absolute pressure of the driven gas.

The test time mentioned above refers to the time between the moment the incident shock reflects off the end wall and the instant when the reflected wave reaches the end wall a second time after reflecting.
off of the contact discontinuity. This time varies depending on the shock velocity but is typically 2 ms in the facility described. After the second reflection of the shock off the end wall the conditions inside the shock tube can no longer be accurately described.

Figure 2.1 shows a schematic of the shock tube operation using the sapphire window end section. Particles are injected radially into the shock tube just before diaphragm rupture. As the incident shock passes the particles, they are entrained in the flow behind the shock and swept to the end wall where they are stagnated by the reflected shock. Due to the low Stokes number of nano-sized particles, any remaining velocity is negligible. After being stagnated at the end wall, the aluminum particles burn in the elevated temperature and pressure behind the reflected shock. Sapphire windows in the end section of the shock tube allow for light from the 310 nm LED to pass through the shock tube and into the spectrometer.
Figure 2.1 - Schematic of Shock Tube Operation

The ambient conditions behind the reflected shock are calculated by measuring the shock velocity using three piezoelectric pressure transducers located a known distance from the end wall. Figure 2.2 is an example plot of the pressure transducer output. Because of the fast response time of each transducer, the arrival of the incident shock is accurately known at each location. An average velocity can then be calculated between each pair of transducers. Friction with the walls of the shock tube causes a decrease in the shock velocity of approximately 10 m/s as it moves towards the end wall. A first order approximation of the decrease is extrapolated to the end wall to find the final shock velocity. This value and the initial pressure and temperature are then input into the Gordon-McBride chemical equilibrium solver to find the temperature and pressure behind the incident shock and reflected shock.
Figure 2.2 - Example Pressure Transducer Response

Particles are injected radially into the shock tube using a pneumatically driven piston shown in Figure 2.3. Typically between 1-5 mg of powder is injected. This amount of powder ensures there is adequate separation between the particles allowing for each to burn independently of the others and preventing a significant rise in the ambient temperature of the test gas. The piston system is triggered electronically prior to diaphragm rupture. The signal opens the solenoid valve allowing high pressure air to pass through the valve and force the piston forward. Particles are entrained into the flow created by the piston movement. They pass through a 60 μm mesh and then enter the shock tube where they
are suspended in the test gas until incident shock passage.

Prior to testing, the test gases are allowed to mix in a mixing tank while the shock tube is being vacuumed down. This ensures the gas mixture is homogenous throughout the shock tube during the test. Once the driven section reaches vacuum, the test section is purged with the premixed gases, vacuumed again, and then filled to the desired test pressure.

2.2 Shock Tube Diagnostics

The shock tube is used to generate high temperatures and pressures in a highly controlled and repeatable environment that is used to combust energetic particles. Absorption spectroscopy and photometry were used as diagnostic tools in order to determine the temperature of the ambient gas around the burning nano-particles and to relate the
temperature increase, heat release, to the luminous signal measured during combustion. Figure 2.4 shows the setup used to take the absorption measurements. The path of the 310 nm light is highlighted in blue.

![Image of Absorption Spectroscopy Setup](image)

**Figure 2.4- Image of Absorption Spectroscopy Setup**

### 2.2.1 Absorption Spectroscopy

Absorption spectroscopy is an optical technique typically used to determine the presence of a specific species by passing a light of a particular wavelength through the specimen. If multiple absorption lines are present, as with the $A^2Σ^+ \rightarrow X^2Π_i$ rotational band of the OH radical investigated in this study [16], a temperature can be fit to the observed spectrum. This particular OH transition is well understood and has been categorized previously [17]. In absorption the molecule absorbing the light emitted from the source and is excited from a lower energy state to a higher energy state. The degree to which each transition
absorbs light varies with temperature, pressure, and with the amount of the molecule present.

The LED used for testing was supplied by Rothiner LaserTechnik. The AlGaN LED is a narrow bandwidth 310 nm LED with an optical power of 1.1 mW at the rated 40 mA of current and a full width half max (FWHM) of 10 nm [18]. Initially the LED was operated at the recommended 40 mA; however, this was found to be insufficient for absorption measurements. In order to increase the optical output of the LED, a pulse circuit was constructed, consisting of a 10 ohm resistor and a mosfet, which would allow for much higher currents to pass through the LED. After receiving the input TTL signal from a digital delay generator, the circuit would close for 50 μs allowing up to 1.5 A to flow through the LED thereby greatly increasing is optical output. Also, the divergence of the light leaving the LED was relatively large, approximately 60 degrees. In order to prevent the loss of useful light, a 5 mm fused silica ball lens was placed 1 mm from the front surface of the LED which collimated the emitted light.

Absorption measurements were taken using an f/6 spectrometer with a focal length of 470 mm and a diffraction grating that had 3600 gr/mm. The resulting wavelength range was 10 nm, the FWHM of the LED, and the resolution was approximately 0.03 nm. The spectrometer was used in conjunction with an Andor iDus-420 CCD camera that has 1024 x 255 pixels each 26 μm square. The minimum capture time allowed by the camera was 1.6 ms, much larger than the desire 50 μs
pulse width. To limit the collection of extraneous light, 1.6 ms was chosen.

The acquired spectra were calibrated using a combination of nickel and aluminum calibration lamps. No less than three emissions lines were fit using the Origin Lab peak fitting software. The wavelengths of the three lines were then mated to the appropriate pixel and a polynomial equation was generated to give the appropriate pixel vs. wavelength calibration. The then calibrated spectra were input into the LIFBASE software where a temperature was fit to the observed OH absorption.

2.2.2 Photometry

Typical burntime measurements rely on the emission of photons from the burning metal particles [12]. In order to replicate this result, photometry was used to observe the luminous event of the burning nano-aluminum particles. A single photodiode was placed 10 mm from the end wall ensuring burning will be observed despite the particle cloud’s location within the shock tube. The silicon photodiode used is a Thorlabs model PDA 55 and has a switchable gain. The intensity curves taken with the photodiode could be compared to the spectroscopic measurements taken in order to determine at what point during the luminous event the spectrum was captured.

The initiation of the camera, LED pulse, and photodiode was controlled using a digital delay generator. Upon incident shock passage, a signal was
sent from the delay generator to the diagnostics so that each would start at the appropriate time during the test.

2.3 Flat Flame Burner

The flat flame burner used in the UIUC facility is a premixed burner capable of using a variety of fuel, oxidizer, and diluent mixtures. It is termed a one dimensional burner due to the pseudo 1-D nature of the flow streamlines, especially near the burner surface. The burner used here is 3.8 cm in diameter and has an array of 0.75 mm holes in the burner surfaces. Gases come together prior to entering the bottom of the burner and are encouraged to mix further by passing through a layer of 1 mm tungsten spheres that rested on a 60 μm mesh before passing through the burner surface into the flame. A separate section within the burner allows for the flow of water to cool the burner during operation. Figure 2.5 gives a cross section view of the flat flame burner.
Figure 2.5- Flat Flame Burner Cross Section

For this study the flame used was a methane-oxygen flame with argon used as the diluent. The flow of each gas was controlled independently using three MKS Instruments Mass-Flo Controllers. Three different equivalence ratios were chosen: $\phi = 0.5$, $\phi = 1$, and $\phi = 1.2$, giving conditions both above and below stoichiometric burn. Gases were kept separate until just before insertion into underside of the flat flame burner.

Before mixing with the other gases, the argon gas would pass through a fluidized bed feed where nano-aluminum particles were entrained into its flow. The fluidized bed feeder was a 2.54 cm diameter cylinder that is 10.2 cm long. This was much larger than the diameter of the tubes used to deliver the argon gas, approximately 0.64 cm. The increase in area decreased
the flow speed of the argon helping to prevent larger particles and agglomerations from being captured by the argon. The aluminum particles (~5 mg) were placed on a 60 μm mesh near the bottom of the cylinder. During testing, the fluidized bed feeder would be excited mechanically to encourage the particles to be entrained into the argon where they would be carried vertically to the exit of the feeder. Before exiting the feeder, the particles passed through another 60 μm mesh helping to further discourage large particles and agglomerations from leaving the feeder. Figure 2.6 gives a cross sectional view of the fluidized bed feeder.

Figure 2.6- Fluidized Bed Feeder Cross Section
The entrained particles were then carried through the flat flame burner into the flame where they would ignite and could be observed by the high speed CMOS camera for burntime measurements. The particles continued to follow the quasi one dimensional stream lines away from the burner surface.

2.4 Flat Flame Burner Diagnostics

The UIUC flat flame burner is a one dimensional premixed gas burner that can be operated at a wide range of fuel, oxidizer, and diluent concentrations. In this study, aluminum particles were imaged with a high speed CMOS camera in order to quantify burntime data for different particle sizes and equivalence ratios. Figure 2.7 shows the one lens setup used during the first phase of testing.

![Figure 2.7- Example Flat Flame Burner Setup](image-url)
Two different lens setups were used to quantify burntime in this study. The first made use of the typical one lens and camera setup. In order to maximize the amount of light captured by the camera, the lens was set to its minimum f-number, f/1.4, and minimum focal length, 51 cm. In addition to the one lens setup, a second setup was used to increase the magnification near the burner surface. For this configuration, a second f/1.4 lens was placed in front of the lens attached to the CMOS camera. This two lens setup allowed for the camera to be moved much closer to the flat flame burner (~18 cm) to further increase the amount of light captured by the camera and to aid in observing the burning of nano-sized aluminum particles.

The camera used for burntime testing in this study was the Vision Research Phantom v7.0 which can record up to 4,800 frames per second using the full 800x600 pixel SR-CMOS sensory array, and faster framing rates can be achieved by frame size [19]. For this study the aspect ratio used was 256x512 giving a maximum framing rate of 15000 fps. The corresponding exposure time per images was 63 μs, and the total interval between individual frames was 66 μs. The Phantom 675 software was used for image capturing and processing.

2.5 Particle Description

Three different sized of nano-aluminum particles were used in the study: 50 nm particles purchased from SkySpring Nanomaterials and 80 nm and 110 nm particles
purchased from NovaCentrix. The 50 nm particles were used for both the shock tube testing and for testing with flat flame burner. Testing of the 80 and 110 nm particles was limited to the flat flame burner. The SkySpring particles were specified as being 99.9% pure, and the NovaCentrix particles were specified as being 80-90% aluminum with an oxide thickness of approximately 2 nm. The particles have been used in previous test at the UIUC shock tube facility and have been categorized previously by Allen et al [11].

In order to characterize the size distribution of the aluminum particles, they were analyzed using the Hitachi S-4700 high resolution SEM. The diameter of 100 particles for each of the three sizes was measured to obtain an accurate distribution. Imaging showed that the particles from each of the samples were weakly agglomerated, and very little particle necking was present. Figure 2.8 shows a histogram of the particle distributions and an image of the NoveCentrix 80 nm particles.
Figure 2.8- Particle Characterization

(a) Particle size distribution for the SkySpring Nanomaterials 50 nm particles
(b) Particle size distribution for the NovaCentrix 80 nm particles
(c) Particle size distribution for the NovaCentrix 110 nm particles
(d) Sample Scanning Electron Microscopy (SEM) image of the NovaCentrix 80 nm particles
CHAPTER 3

RESULTS AND DISCUSSION

The following sections present the results of the OH absorption and photometry measurements taken in the heterogeneous shock tube facility and the burntime measurements taken using the flat flame burner. The results will be divided into sections, one for the shock tube measurements and another for the flat flame burner measurements, each with the appropriate subsections.

3.1 Shock Tube Results

OH absorption measurements were taken using the UIUC shock tube. The spectra could then be fit to an equilibrium temperature. The temperature was used as an indicator of the ambient temperature inside the shock tube both with and without the presence of nano-aluminum particles. Any rise of the ambient temperature above the shock temperature when aluminum particles were present could then be related to the heat release of the particles in order to determine at what point the particles ceased to burn. Also, this result could be compared to the luminosity trace taken with the photodiode in order to compare the heat release burntime measure to the typical luminosity curve burntime measurement.
3.1.1 OH Absorption without Added Nano-Aluminum

Because shorter LED pulse widths result in temperature measurements that better reflect the instantaneous ambient temperature within the shock tube, the LED was pulsed in order to determine the minimum pulse necessary for effective OH temperature fitting. A plot of the results can be found in Figure 3.1.

![LED Pulse Results](image)

**Figure 3.1- LED Pulse Results**

The shorter 10 and 20 μs pulses were found to be insufficient for high resolution temperature fitting, but because the 50 μs would give an adequate signal to noise ratio and would still give a temperature measurement an order of magnitude shorter than the
aluminum burntime, the 50 μs pulse was chosen for further experimentation.

Absorption measurements were taken without the addition of nano-aluminum in order to determine the effectiveness of using OH absorption as an indicator of the ambient conditions within the shock tube. Initially, water vapor was added to the driven gas to ensure adequate OH absorption. A plot of the observed absorption plot is given in Figure 3.2.

![OH Absorption Spectrum with Added H2O](image)

**Figure 3.2- OH Absorption Spectrum with Added Water Vapor**

The maximum absorption for this experiment was approximately 30%, a value which could prove problematic for accurate temperature fitting as optical depth becomes a factor. To prevent complications, further spectra were taken without
adding water vapor to the shock tube driven section. Sufficient amounts of residual water vapor remained in the shock tube during the vacuuming process which allowed for an adequate amount of OH absorption for temperature fitting. A plot of the OH spectrum without the addition of water vapor is given in Figure 3.3.

![OH Absorption with No Added Water Vapor](image)

**Figure 3.3- OH Absorption without Added Water Vapor**

The maximum absorption value for this measurement was approximately 15% which helped to avoid any optical depth issues and ensured an accurate temperature fit.

The data taken without added water vapor was then imported into the LIFBASE software to compare the reflected shock temperature calculated using the
Gordon-McBride chemical equilibrium software and the temperature found using the LIFBASE fitting software. It is important to note that the absorption spectra in the LIFBASE software uses a normalized value of one minus the intensity ratio instead of the typical I/I₀ value depicted above. The plot of the temperature fit is given in Figure 3.4.

![OH Fit 1810 K](image)

**Figure 3.4- LIFBASE Temperature Fit at Calculated 1810 K Shock Temperature**

There was good agreement between the LIFBASE temperature fit and the calculated Gordon-McBride temperature. Also, the lines indicated in Figure 3.4 were found to be the most sensitive to changes in temperature and were the primary lines used in further
temperature fitting. To illustrate the effect of changes in the temperature and the response of the indicated lines, the same experimental spectrum shown in Figure 3.4 was fit at a higher, incorrect temperature. The incorrect fit is shown in Figure 3.5 with the same lines indicated with arrows.

![OH Fit 2300 K](image)

**Figure 3.5-LIFBASE Temperature Fit at Higher, Incorrect Temperature**

While some lines exhibited little to no change in their relative heights, especially those to the left of the 309 nm line, the indicated lines displayed a noticeable shift in their heights. This result helped to demonstrate that the OH absorption signal taken over 50 μs intervals is a good indicator of the
ambient temperature within the shock tube and is sensitive to changes of the ambient condition.

3.1.2 OH Absorption with Added Nano Aluminum

Having successfully fit a temperature to OH absorption spectrum, the test was repeated with nano-aluminum being injected into the shock tube. However, the addition of the nano-aluminum particles made it difficult to obtain an appropriate reference single due to the scattering off of the aluminum particles and emission by the burning aluminum particles. This caused a shift in the peak value of the spectroscopic signal and made an accurate temperature fit impossible. Figure 3.6 is a plot of the comparison between the reference signal and the observed signal taken during testing.
Figure 3.6- Comparison of the Reference Signal to the Test Signal

Another potential source of this shift away from the reference is the total collection time of the camera, 1.6 ms, being much greater than the 50 μs pulse of the LED. Any additional light emitted from the burning aluminum particles after the LED pulse would be collected by the camera and shift the signal away from the reference. Figure 3.7 shows the luminosity curve taken with the photodiode and illustrates the difference in the LED pulse and the camera collection time.
Figure 3.7- Comparison of LED and Camera Collection Durations with respect to the Aluminum Luminosity Curve

As is illustrated by the blue line in Figure 3.7, the duration of the camera collection is much greater than the actual LED pulse, represented by the red line. Also, while much of the camera collection occurs while the aluminum particles are emitting at a background level, a portion of the collection occurs while the luminosity curve is still decreasing which increases the amount of light collected during the test. The disparity between the duration of the LED pulse and camera collection helps account for the shift in the signal and greatly increases the
difficulty in obtaining an accurate temperature measurement.

3.2 Flat Flame Burner Results

Aluminum burntime measurements were made using the UIUC flat flame burner by imaging the burning nano-aluminum particles with a high speed CMOS camera. Three different particle sizes were entrained into the pre-mixed gases prior to entering the burner and observed in a methane flame operating at three different equivalence ratios. By imaging at a speed an order of magnitude greater than the burntime of the particles, frame to frame intensities of the observed particles were compared in order to obtain the appropriate burntime.

3.2.1 One Lens Camera Setup

As stated previously, initial testing with the flat flame burner was done using the standard camera and one lens setup. These images were taken in 63 μs intervals with an exposure of 61 μs while the burner was operating with a 5 slm flow rate and equivalence ratio of 0.5 and a diluent fraction of 0.5. Figures 3.8 and 3.9 show two examples aluminum particles that were observed during testing.
Figure 3.8 - Example 1 of an Observed Particle Using 50 nm Aluminum Powder

Figure 3.9 - Example 2 of an Observed Particle Using 50 nm Aluminum Powder
The observed particles using the one-lens setup displayed large variability and included many that persisted for times of up to 1 to 2 ms, times that were much larger than expected [13]; therefore, in order to determine the nature of the observed particles, tests were performed using H2 aluminum powder manufactured by Valimet, Inc. The H2 particles are spherical aluminum particles with an average diameter of 3.2 μm and 90% of the particles being less than 6.8 μm [20]. The spherical shape of these aluminum particles makes them less prone to agglomeration which made them a good basis for comparison. The results for the H2 aluminum powder testing are depicted in Figure 3.10.

<table>
<thead>
<tr>
<th>t=0 μs</th>
<th>t=150 μs</th>
<th>t=650 μs</th>
</tr>
</thead>
</table>

Figure 3.10- Example of Observed H2 Aluminum Particle

The H2 particles observed during testing burned for a much shorter duration of time, ~650 μs, than the
50 nm particles, and the total emitted light was observed over a fewer number of pixels. This result seemed to indicate the particles observed initially were not single 50 nm aluminum particles but were instead large agglomerations of many 50 nm particles. Also, due to the already decreased area of the H2 particles, the validity of observing single nano-aluminum particles was called into question and necessitated the two-lens camera setup that was used for further testing.

3.2.2 Two-Lens Camera Setup

The two-lens camera setup greatly increased the magnification of the burner surface and allowed for the observation of particles smaller than the previously used one-lens setup. Using the two-lens setup, the three selected particle sizes were tested at the fuel rich, stoichiometric, and fuel lean test conditions. An example particle from each condition is given in the figures that follow.
Figure 3.11 - 50 nm Aluminum Particle at $\phi=0.5$

Figure 3.12 - 50 nm Aluminum Particle at $\phi=1.0$
It is important to note that larger agglomerations of particles can clearly be seen in Figures 3.13 and 3.14. These particles were ignored when processing burntime results.
Figure 3.14 - 80 nm Aluminum Particles at $\phi=1.0$

Figure 3.15 - 80 nm Aluminum Particles at $\phi=1.2$
Figure 3.16 - 110 nm Aluminum Particles at $\phi=1.0$

Figure 3.17 - 110 nm Aluminum Particles at $\phi=1.2$
The particles observed during testing with the two-lens setup had much shorter burntimes and emitted light in a significantly smaller area seeming to indicate the observed particles were in fact nano-particles and not larger agglomerations as previously observed. Also, the burntimes of the tested particles increased both with increased diameter and as the amount of available oxygen decreased or as the equivalence ratio increased. Table 3.1 gives a summary of the burntimes for all of the observed particles at the three conditions.

<table>
<thead>
<tr>
<th>Nano-Aluminum Burntime Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle Size (nm)</td>
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<tr>
<td>--------------------</td>
</tr>
<tr>
<td>50</td>
</tr>
<tr>
<td>50</td>
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<tr>
<td>50</td>
</tr>
<tr>
<td>80</td>
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<tr>
<td>110</td>
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<td>110</td>
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</tbody>
</table>

*Particles were tested at this condition, however, turbulence near the burner surface prevented an accurate measure of the burntime.

Table 3.1- Nano-Aluminum Burntime Results

The values of burntime for the $\phi=1.0$ and $\phi=1.2$ case were then fit using the power law to determine the relationship between the particle diameter and the average burntime. Figure 3.18 is a plot of the results.
Figure 3.18 - Particle Burntime vs. Particle Diameter

The particle diameter dependence was found to have an exponent of 0.31 for the stoichiometric test condition and 0.36 for the $\phi=1.2$ test condition. These values correspond well with data taken previously for particles of diameter less than 2 μm [21].
Chapter 4

CONCLUSIONS AND RECOMMENDATIONS

A large quantity of work has been presented detailing the combustion of nano-aluminum particles both within the UIUC heterogeneous shock tube and the flat flame burner facility. Measurements made include spectroscopic measurements, photometry, and high speed imaging. The following conclusions can be drawn from the results presented.

4.1 Shock Tube

• Conclusions based on spectroscopic measurements taken within the shock tube:

  - OH absorption measurements can be made and provide an accurate and reasonably responsive measurement of the ambient temperature within the shock tube.

  - The addition of nano-aluminum particles into the shock tube proved problematic with regards to absorption measurements. The burning aluminum particles caused a shift of the absorption signal away from the reference signal preventing an accurate measure of the ambient temperature.

• Recommendations for future work on the direct measure of nano-aluminum heat release:
One possible solution to the problem of excess light with aluminum present would be to employ a camera with a capture time equal to or less than pulse width of the 310 nm LED. However, because many fast kinetics CCD cameras are line scan camera, the total collection area would be deceased significantly necessitating an increase in the signal from the LED.

Another possible solution would be to make use of a fast shutter that would work on the desired time scale for camera collection.

4.2 Flat Flame Burner

- Conclusions with regards to burntime measurements taken using the flat flame burner setup:

  - Agglomerations within the flat flame burner setup are prevalent and can skew data if not taken into account.

  - There is a regular increase in the burntime of nano-aluminum particle burning in hot ambient gases both because of increased particle diameter and increased equivalence ratio.

  - The increase in burntime due to increased particle diameter followed a power law with a coefficient of between 0.3 and 0.4, values
which have been observed for nano-aluminum in other combusting environments.

• Recommendations for future work measuring burntimes of nano-aluminum in the flat flame burner:

  Further experimentation of nano-particles burning in hot ambient gases can be done to better categorized the combustion of these small particles in various types of fuels, equivalence ratios, and for differing types of metal additives.
References


Champaign. Dept. of Mechanical and Industrial Engineering, 2006.


