

Imaging of Thermal Propagation in Combustion of Al/CuO Core-Shell Nanothermite Film

by

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Author's Declaration

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Statement of Contributions

This thesis encompasses one manuscript that is intended for publication. Dr. Anqi Wang was the other main contributor to this work, apart from my supervisors. He was co-author for [Chapter 1 Introduction](#) and [subsection 4.2.1 Film Preparation](#).

Abstract

Nanoenergetics have been a topic of great discussion over the past few decades due to their extraordinary combustive properties. In particular, heavy investment has been put into researching nanothermites due to the low cost of their components and high energy release of the products. However, much is still unknown about the kinetics and thermodynamics of nanothermites on both the spatial and temporal micro-scale. Here, we report the design and implementation of a high-speed thermographic facility (“pyrometry setup”) as well as the investigation of the combustion mechanism and flame propagation of Al/CuO nanothermite films at such scales using an alternate high-speed thermography ($3.75\text{ }\mu\text{m px}^{-1}$, 2.5 ms resolution) and videography ($2.8\text{ }\mu\text{m px}^{-1}$, 50 μs resolution) system. Sub-millimeter films of both **Physically-Mixed (PM)** and **Core-Shell (CS)** Al/CuO nanothermite were fabricated and subsequently ignited by hot wire, and the combustion event was recorded onto footage. This work demonstrates the differences between the combustion of **PM** and **CS** films with respect to temperature, flame propagation, and particle ejection. Discussions have been made on the so-called “reactive sintering” mechanism — in which reacting particles amalgamate before burning — and its effects on micro-scale combustion behavior. It has been shown that the self-contained nature of the **CS** film promotes spatio-thermometric uniformity within the pre-combusted regions of the film (uniform temperature banding), whereas the **PM** film exhibits irregularities within those regions as well as notable “hot spots” along the flame front. Additionally, the flame propagation from the **CS** film has been recorded to be faster than that of the **PM** film by a factor of 1.4 (~ 10.80 vs. $\sim 7.44\text{ cm s}^{-1}$, respectively), which may bear a relationship with the particle ejection seen in both samples. In the **CS** film, it is revealed to be more akin to a particle “exhaust” rather than an “ejection” of aggregated particles as displayed by the **PM** film (presumably caused by the hot spots), resulting in a hotter post-combustion region of space. This suggests that for **CS** films, the energy from the reaction remains relatively local to the reaction zone rather than being carried away by distantly ejected particles. Temperature measurements using an emissivity correction value of 0.15 indicate that the maximum temperature along the flame front for the **PM** film is $\sim 3400\text{ K}$ and the

distance (“conduction distance”) between that and the unburned film (room temperature) is $\sim 645 \mu\text{m}$, giving an average spatial temperature gradient of $4.8 \text{ K } \mu\text{m}^{-1}$. For the [CS](#) film, the maximum temperature and conduction distance were found to be $\sim 2500 \text{ K}$ and $\sim 600 \mu\text{m}$, respectively, giving an average spatial temperature gradient of $3.7 \text{ K } \mu\text{m}^{-1}$.

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List of Abbreviations

3DOM Three-dimensionally Ordered Macroporous [7](#), [55](#)

CS Core-Shell [iv](#), [v](#), [4](#), [5](#), [7–9](#), [32](#), [36](#), [38–41](#), [43–55](#), [57](#)

EDS Energy-Dispersive X-Ray Spectroscopy [4](#), [46](#), [50](#), [52](#), [54](#)

ER Equivalence Ratio [46](#)

FPS Frames Per Second [4](#), [24](#), [29](#)

IBI In-Band Irradiance [37](#)

LUT Lookup Table [37](#)

MIC Metastable Intermolecular Composite [1–4](#), [7](#), [10](#), [11](#), [54](#), [55](#)

NIR Near-Infrared [21–23](#), [25](#), [27](#)

PM Physically-Mixed [iv](#), [2](#), [4](#), [5](#), [7](#), [8](#), [32](#), [36](#), [38–51](#), [54–56](#)

QE Quantum Efficiency [24–26](#)

SEM Scanning Electron Microscopy [4](#), [46](#), [50](#), [52](#), [54](#)

UHS Ultra High Speed [3](#), [4](#), [21](#), [33](#), [40](#), [44](#)

Chapter 1

Introduction

1.1 Motivation

Nanothermites, also called [Metastable Intermolecular Composites \(MICs\)](#), have been one of the most attractive reactive materials in recent years due to their rapid reactivity, high energy density, ease of fabrication, storage, and operation, as well as their affordability [2, 37, 67]. [MICs](#) are typically solid mixtures comprised of a reductive fuel, such as Al or Mg particles, and an oxidizer, such as metal oxides, oxygen-rich salts, and fluoropolymers [54, 64, 17, 16, 62]. Upon ignition, redox reactions occur between the solid-phase fuel and oxidizer, forming chemically stable substances such as Al/MgO₂ or Al/MgF₂, and releasing a considerable amount of energy [68, 6, 42, 15]. The rapid combustion of [MICs](#) generates a large amount of energy in a very short period of time, thus reaching temperatures of over 3000 K, allowing for various applications such as propellants, pressure generation, heater materials, and welding [44, 33, 32, 8]. In order to optimize combustible materials for potential applications, it is crucial to understand the nature of their combustion. Experimental and computational methods have both been utilized to investigate the combustion from the micro- to macroscopic scale [12, 28, 49, 38, 55, 46, 30]. Complex processes at different scales, such as heat transfer, mass transport, and chemical diffusion are key factors that contribute to the initiation and propagation of the flame front [43, 23, 11, 21, 45]. Compared to the extensively investigated properties of bulk combustion, where the fuel

and oxidizer are well-mixed, the multi-scale and heterogeneous reaction of MICs serves to obfuscate the understanding of its combustion even further [51, 41]. As the combustion of MICs propagate, multiple physical and chemical reactions occur simultaneously due to the rapid heating rate (on the order of 10^9 K s^{-1}), including the decomposition, melting, and/or vaporization of raw materials and products; sintering of Al nanoparticles; and intermolecular diffusion between the reactants [61, 10, 4]. While the complex reaction pathways mystify the ignition mechanisms of MICs, two competing theories have stood out—reactive sintering and melt dispersion—but without concrete evidence [20, 45, 36, 26]. In a recent paper by Wang et al. [57], a 3D printed polymer-assisted Al/CuO nanothermite showed unique, discrete, local reactions at a higher speed than global propagation due to the occurrence of reactive sintering, which is a crucial parameter determining the rate of combustion. Another recent publication by Kim et al. [23] also hinted at the non-uniform combustion nature of the polymer-assisted Al/CuO nanoenergetic composite at the flame front, where they found that the propagation occurs in both tangential and normal directions, as pre-ignition sites are heated and readily ignited with lower ignition energy. In both papers, reactive sintering of Al nanoparticles was found to be a dominating process during the combustion of a physical mixture of (referred herein as “Physically-Mixed” or “PM”) Al/CuO samples with the addition of polymer. However, it is not yet clear how large a role reactive sintering plays in the combustion propagation rate, and what would happen if reactive sintering of Al is minimized while the chemical reaction between fuel and oxidizer is observed. In previous research, it was found that ordered structures, such as self-assembled or Core-Shell (CS) structures, could enhance the surface contact between fuel and oxidizer, leading to more complete reaction and boosted reactivity [65, 56]. The ordered structures are also assumed to reduce reactive sintering as the surface contact between Al particles is reduced by minimizing phase separation. Therefore, it is important to see how MICs with different structures combust to determine the importance and order of different processes.

1.2 Objective

Given that the direct imaging of the reaction between MICs is extremely challenging due to their nanometric sizes and reaction rates, observation at the micro-scale is critical in discovering the nature of their combustion [10]. The observation of the combustion of MICs using Ultra High Speed (UHS) cameras at high frame rate is commonly adopted as a straightforward method to present the characteristics of nanothermites. Different parameters, including ignition delay, flame speed, and local propagation behaviors are often analyzed as key properties of MICs. For example, the ignition delay when using a controllable ignition source, such as hot wire or laser, indicates the energy threshold to trigger the reaction of the sample; the flame speed indicates the reactivity of the sample; and the local propagation behaviors can be surveyed to show the reaction pathways and mechanisms of the local reaction [6, 23, 57, 13]. The usage of UHS cameras has been vital in today’s research into MICs and has significantly progressed its development. However, to better understand these processes, thermal data during the propagation is also desired for capturing the temperature of different events and extracting valuable information during the combustion/propagation, especially with regards to heat transfer and local reactions [57, 5]. Researchers have performed pyrometry using UHS color camera footage; however, due to Planck’s law, this method is most viable for measuring the temperature of surfaces that become hot enough to emit visible light ($\gtrsim 2000$ K), thus limiting its ability to capture thermal behaviors in regions before the sample is ignited (“pre-heating zone”) or after it has cooled. As noted by Wang et al. [57], the sample undergoes a burn region cycle of heating/conduction, followed by combustion, followed by cooling during combustion—however, only the combustion period when the temperature was over 2000 K was recorded using the UHS camera. Therefore, infrared thermal cameras can be a useful tool to further investigate the combustion. Certain characteristics of the combustion event such as the shape and local propagation speed of the flame front, particle ejection, heat conduction in the pre-combusted sample, and the temperature of the post-combustion area may shed light on said combustion mechanisms [59, 58].

1.3 Overview and Contributions

In this thesis, the design and construction of a high-speed microscopic thermography facility (or “pyrometry setup”), along with an in-depth thermophysical analysis of the combustion of Al/CuO nanothermites with different structures, is reported. The pyrometry setup consists of an objective lens, two wavelength filters, three high speed cameras, and various other optical components, which enable it to capture footage at a resolution of $2\text{ }\mu\text{m px}^{-1}$ and frame rates of over 10,000 [Frames Per Second \(FPS\)](#). For the thermophysical analysis, both [PM](#) and [CS](#) structured Al/CuO [MICs](#) were packed into thin sheets with the addition of 10% polymer and ignited by “hot wire”. The propagation was recorded simultaneously by a [UHS](#) camera and a high-speed thermal camera. Crucial reaction parameters, such as propagation rate, peak temperature, and thermal gradient were investigated to understand the roles of different physical and chemical processes during the propagation of the combustion. It was found that while the [PM](#) film burned at much higher temperatures than the [CS](#) film did—with over double the maximum temperature gradient—the [CS](#) film burned at about 1.4 times the rate of the [PM](#) film. One might believe that higher temperatures are indicative of a more vigorous reaction and therefore a greater burn rate, but this is not necessarily the case. It is believed that the exhaust-like nature of the particle ejection from the [CS](#) film contributes energy to the flame front that would normally exit the system if large particles were ejected, thus accelerating the propagation of the flame front. [Scanning Electron Microscopy \(SEM\)](#) and [Energy-Dispersive X-Ray Spectroscopy \(EDS\)](#) were utilized to compare the post-combustion morphologies of the two sample types. It was seen that the post-combustion [CS](#) debris was about half the size of and displayed a greater degree of combustion completeness than the [PM](#) debris. It is hypothesized that the reaction mechanism for the [PM](#) structured Al/CuO sample is reactive sintering-dominated, leading to the formation of local hot spots across the flame front. Conversely, it is believed that the combustion behavior of the [CS](#) sample is characteristic of the theorized melt dispersion mechanism.

This work admits the following contributions to the [MIC](#) research community:

- Design for a ratio pyrometry setup that allows for accurate, [UHS](#) thermographic

measurements at the spatial and temporal micro-scale

- Method for defining the boundary of the flame front using a gradient-based weighted mean approach
- Insights into the reaction pathways of both [PM](#) and [CS](#) nanothermites

Chapter 2

Literature Review

2.1 Nanothermite

As the name implies, nanothermites are just nano-sized versions of thermites. They are composed of a simple mixture of a metal **A** and metal oxide **BX** which, given enough input energy, react as described by the following equation:



Metal **A** being more reactive than metal **B** (i.e., higher in the reactivity series of metals), it becomes oxidized and metal **B** is reduced, resulting in a tremendous release of enthalpy. Fischer and Grubelich [14] tabulated the theoretical energy releases of thermites in their technical report for Sandia National Laboratory. Five of these reactions, as well as those of three different organic energetic materials [37] are relayed in Table 2.1 below.

Notably, the Al/CuO reaction has a large energy density with the added benefit of its constituents being relatively cheap and accessible. As explained by Rossi et al. [37], Al, and in particular, *nano*-Al, is widely used because it is:

- Cheap and abundant
- Generally safe to handle due to its passive oxide layer preventing spontaneous combustion

Energetic Material	ρ_{TMD} [g cm ⁻³]	Adiabatic flame temperature (T_{af}) [K] with phase changes	Enthalpy (ΔH) [kJ g ⁻¹]	ΔH [kJ cm ⁻³]
2Al + Bi ₂ O ₃	7.188	3253	2.12	15.22
2Al + 3CuO	5.109	2843	4.08	20.82
2Al + Fe ₂ O ₃	4.175	3135	3.96	16.51
2Al + MoO ₃	3.808	3253	4.70	17.90
2Al + 3NiO	5.214	3187	3.44	17.94
PETN	-	4140	6.00	-
HMX	-	3255	5.65	-
NC	-	3000	4.02	-

Table 2.1: Table of energetic materials

- Easy to produce as nanoparticles
- Highly thermally conductive, enhancing the combustion
- Of low melting point and vapor pressure, making it easier to reach ignition conditions

Additionally, Aumann et al. [1] note that, at least with Al and MoO₃ powder mixtures, the nano-scale version react more than 1000 times faster than their conventional macro-scale counterparts due to the reduced diffusion distances between individual reactant species. To reduce the diffusion distance even further, the structure of the nanoparticles may also be augmented; hence, the development of ordered-structure MICs such as CS nanothermites. While MICs can take many forms such as in nanolaminates (alternating nano-sized layers of reactants) [38] or Three-dimensionally Ordered Macroporous (3DOM) [66] structures, the two being contrasted in this work are PM and CS nanothermites.

Physically-Mixed Particles

Since a physical mixture is the simplest way to combine the reactant powders, PM particles serve as a good baseline to compare with other types of nanothermite. The typical procedure for combining the reactants in PM samples, as described by Rossi et al. [37], is

as follows: First, the reactants are dispersed in a solvent (e.g., ethanol, hexane). Next, the mixture is sonicated to break agglomerates and ensure homogeneous mixing. Then, the mixture is heated to evaporate the solvent. Finally, the mixture is passed through a fine mesh to break agglomerates formed in the previous step.

As noted by the authors, while this is a simple method to perform, it is difficult to achieve a mixture with a highly homogeneous distribution of fuel and oxidizer with it. A diagram of the size and distribution of stoichiometric [PM](#) particles is shown in [Figure 2.1](#).

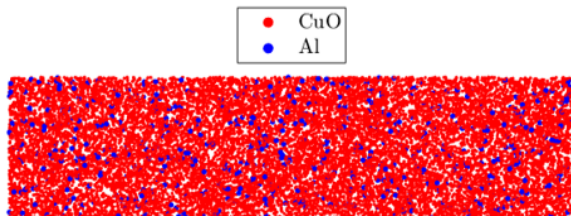


Figure 2.1: Diagram of stoichiometric Al/CuO nanoparticles with [PM](#) structure. Relative size and distribution of particles are to scale.

Core-Shell Particles

As previously noted, it has been found that ordered structures can enhance the surface contact between fuel and oxidizer, promoting both higher reactivity and a greater degree of reaction completion [\[65, 56\]](#). [CS](#)-structured thermites were chosen with the understanding that, in addition to having an ordered structure, they have demonstrated promising properties in previous investigations conducted within our research group, making it an ideal candidate for further exploration [\[65, 56\]](#). In a [CS](#) structure, each fuel particle is surrounded by an oxidizer shell, as shown in [Figure 2.2](#).

Notably, this minimizes the distance between the fuel and oxidizer, and in doing so minimizes the ability for the Al/Al₂O₃ core to sinter with nearby particles. This is important for observing the nanothermite in a context where reactive sintering may not be a dominating reaction mechanism. However, as can be seen in [Figure 2.3](#), the process of covering Al with CuO is not perfect and there may still be gaps where the Al core is exposed.

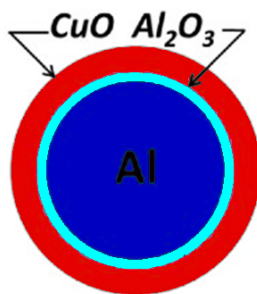


Figure 2.2: Diagram of Al/CuO nanoparticles with CS structure, adapted from [65]

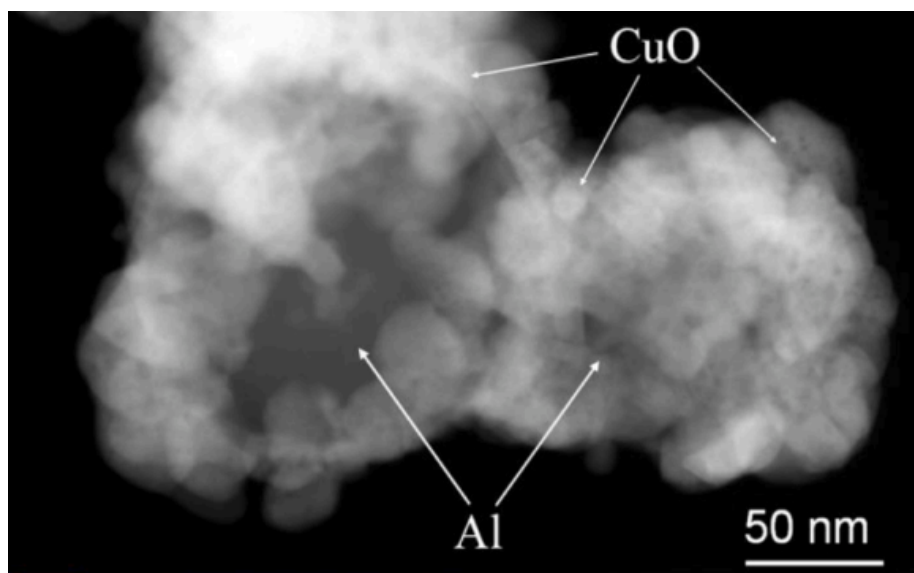


Figure 2.3: SEM image of Al/CuO nanothermite with CS structure [56]

As will be discussed in the next section, the reduced ability for CS particles to sinter may shed some light on our understanding of the reaction mechanism taking place when these particles combust.

2.2 Ignition Mechanisms

One of the great mysteries about Al thermites is the disparity between the ignition temperatures of nano-Al and larger, macro-Al particles—nano-Al ignites much closer to the melting point of pure Al (933 K) while macro-Al ignites closer to the melting point of its Al_2O_3 shell (2327 K) [52]. Which begs the question: if a prerequisite to the initiation of the thermite reaction is the melting of either the Al or the Al_2O_3 shell, why is the ignition

temperature partial to the size of the particle? The cause of this disparity is a critical gap in our understanding of the ignition mechanisms of nano-Al MICs. As previously mentioned, two competing theories that attempt to explain this phenomenon are the “melt dispersion” and “reactive sintering” mechanisms.

Reactive Sintering

The mechanism of reactive sintering has been discussed at great length by Sullivan et al. [45]. In brief, reactive sintering is what happens when an exothermic reaction causes particles to sinter, releasing supplemental energy into the system. It is theorized that in Al MICs, the supplementary energy provided by reactive sintering leads to large amounts of melting (and therefore ignition) below the bulk melting temperature. Wang et al. [57] goes further to say that the reactive sintering mechanism plays a key role in the combustion performance of MICs by causing aggregated metal nanoparticles to combine and form larger sintered particles *before* burning. It is thought that this loss of nano-structure (i.e., surface energy [53]) and subsequent energy gain accelerates the thermite reaction. As noted by Sullivan et al. [45], this mechanism would be evidenced by the morphology of the combustion product. Large, highly spherical particles would suggest the coalescence of the aforementioned aggregates caused by reactive sintering.

In the same paper, Sullivan et al. performed rapid heating “T-jump” tests ($\lesssim 10^6 \text{ K s}^{-1}$) on various nano-Al MIC mixtures. They estimated that the sintering time scale was on the order of $10^1 \mu\text{s}$ while the reaction time scale was on the order of $10^3 \mu\text{s}$. Egan et al. [10] conducted in-situ observations of Al/CuO under rapid heating conditions ($\sim 10^{11} \text{ K s}^{-1}$) at the temporal and spatial *nano*-scale by using a nanosecond laser with a dynamic transmission electron microscope (DTEM). They showed that within 235 ns, the central CuO region of a 500 nm diameter aggregate was completely molten and spherical in shape, while the Al particles remained a similar morphology as at the beginning. By 615 ns, the Al was seen to have coalesced with the CuO and formed the particle seen in Figure 2.4.

While it is unusual for CuO to melt before Al, it was determined that this was because CuO was three times more absorptive of the energy of the 532 nm light from the laser than

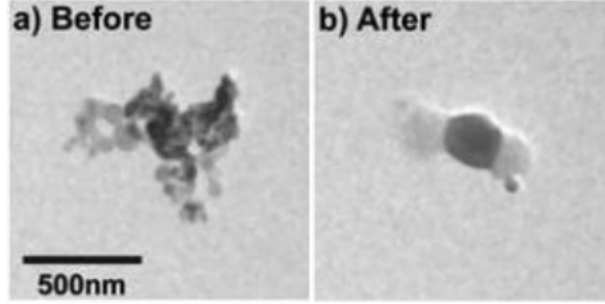


Figure 2.4: DTEM image of ignited Al/CuO agglomerate (a) pre- and (b) post-ignition, adapted from [10]

the Al particles. Through these tests, it was concluded that the combustion was likely a condensed-phase reactive sintering process.

Melt Dispersion

In 2006, Levitas et al. [26] described a mechanism in which **spallation** (stress-induced fragmentation and ejection), is the driving force behind the increased reactivity of nano-Al MICs. In this mechanism, the difference in thermal expansion coefficients between the Al core (as it melts) and its oxide shell is thought to cause a tremendous pressure differential (0.1–4 GPa) within the particle. This in turn causes the oxide shell to burst, ejecting molten Al and pieces of its oxide shell at high velocity. While there has been little if any experimental evidence of such a mechanism occurring, the advantage of this theory is that it is not limited by the diffusion of oxygen through the oxide shell to the pure Al core, which is a known limiting factor for particles of diameters larger than $20\text{ }\mu\text{m}$ [25]. However, three key conditions are necessary for this to occur: a high heating rate ($\gtrsim 10^6\text{ K s}^{-1}$), a core temperature that exceeds the melting temperature of Al, and an oxide shell that is homogeneous enough that it can withstand the pressure built by the melting Al core [61].

Levitas et al. [27] made further observations in 2007, noting that the ratio $M = \frac{R}{\delta}$ between the radius of the core R and the thickness of the oxide shell δ is a crucial parameter in predicting the flame speed in nano-Al combustion. According to them, $M \approx 19$ is the critical ratio, above which the flame speed decreases with increasing M , but below which the flame velocity does not change with M . They argue that in a diffusion-controlled

regime, the flame speed is expected to increase if: R increases, since surface-area-to-volume ratio increases; δ decreases, since length of the diffusion path decreases; or the absolute Al content increases, since Al_2O_3 does not participate in the reaction. Figure 2.5 shows the measured flame speed against various radii and shell thicknesses of nano-Al mixed and combusted with MoO_3 , as adapted from their paper. The size of the markers indicate the

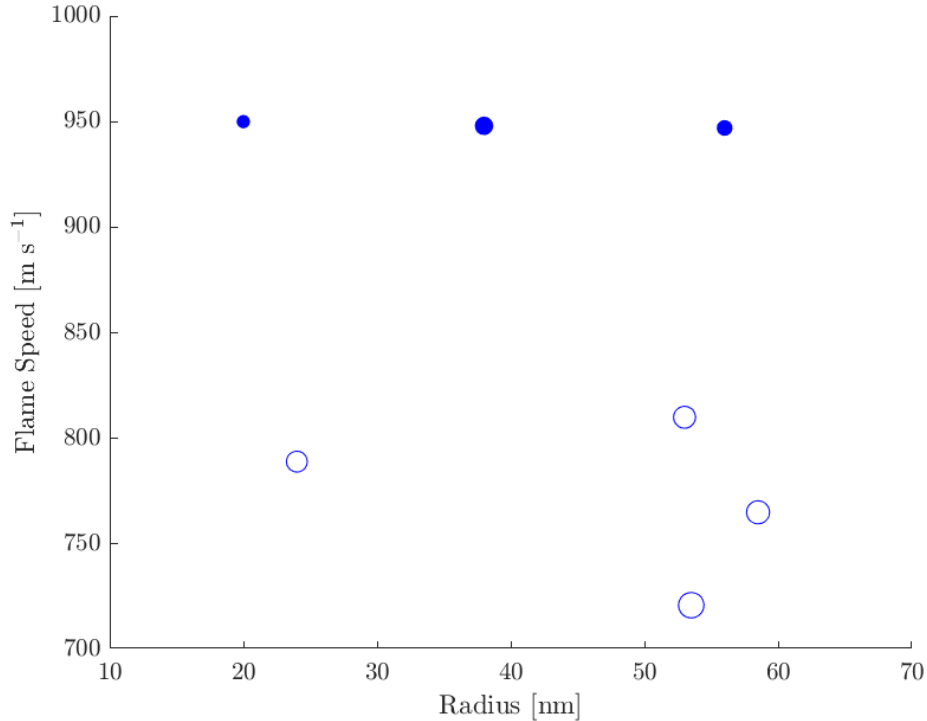


Figure 2.5: Measured flame speed for various radii and shell thicknesses of nano-Al, adapted from [27]

relative M of each data point and filled markers indicate data points where $M \leq 19$. This shows that while there does not seem to be any relationship between the flame speed and particle radius, there is a strong relationship between flame speed and M .

However, the greatest criticism facing this mechanism is that there has yet to be any solid evidence of spallation occurring. While there have been copious studies showing the presence of sintered particles, spallated particles have yet to be reported, despite the numerous rapid heating tests conducted by Sullivan et al. [10] and Egan et al. [45].

Chapter 3

Thermometry: Background and Theory

Obtaining high-accuracy and precision temperature data is crucial to support the evidence of reaction mechanisms. However, this can be extremely difficult to accomplish at microscopic scales—miniaturization of instrumentation is often both necessary and complicated. [Table 3.1](#) lists a few of the methods reviewed by Brites et al. [3].

Typical Resolution				
Method	Principle	∂x (μm)	∂T (K)	∂t (μs)
Radiation	Planck's law	10	10^{-1}	10
Thermocouple	Seebeck effect	10^2	10^{-1}	10
Fluorescence	Temperature dependence of quantum efficiency/lifetime/intensity	10^{-1}	10^{-2}	10

Table 3.1: Methods of thermometry [3]

The following is an overview of the named methods, with emphasis on radiation-based techniques.

3.1 Thermocouple

As mentioned, thermocouples operate on the principle of the Seebeck effect. The effect itself is quite simple: in 1821, Thomas Seebeck discovered that if you take a length of wire with a temperature difference between the two ends, then the voltage difference across the two ends is proportional to that temperature difference [35]. Equation 3.1 describes this relationship in its simplest implementation.

$$V_{NL} = \alpha_{te} \Delta T_{te} \quad (3.1)$$

where V_{NL} is the no-load or open-circuit voltage [V]; α_{te} is the Seebeck coefficient [V K⁻¹] (dependent on probe material); and ΔT is the temperature difference [K].

Although it can be extremely small, by using highly sensitive instruments, it is possible to probe the temperature of an object by measuring the voltage difference. It is important to note that this is considered an *intrusive* technique in that it requires physical contact with the measured object to make measurements. Advantages of this technique include that the temperature calibration is precise and the spatial resolution (1D) can be as small as 25 nm; while disadvantages include the difficulty of fabricating such small and sensitive probes and that signal processing time limits the timescale for transient measurements by the device [3].

Zhu et al. [69] demonstrate the use of a spherical thermocouple to study the combustion performance of SiO₂-added nano-Al with CO₂. The thermocouple was embedded into the Al/SiO₂ powder mixture and placed in the middle of a tube furnace with a constant feed of CO₂. They found that, in the control sample of pure nano-Al, the ignition and peak temperatures were 719 K and 1622 K, respectfully. However, with the SiO₂, the peak temperature was found to be around 1900 K with roughly the same ignition temperature. It should be noted here that Rossi et al. [39] reported the adiabatic flame temperature of (macro) Al in CO₂ to be 3273 K while Fischer and Grubelich [14] report the theoretical adiabatic flame temperature of the Al/SiO₂ reaction (with phase changes) to be 1889 K. Hence, it is unclear whether or not thermocouples are accurate and sensitive enough to capture the dynamic nature of the nanothermite reaction.

3.2 Fluorescence

As described by Dowell [9], fluorescence thermometry uses the temperature-dependence of the fluorescence (and fluorescent lifetime) of certain materials for the measurement of temperature. Equation 3.2, modeled by Inokuti and Hirayama [19], describes the time evolution of the fluorescence of an excited state by an energy pulse.

$$S(t) = A \exp \left(-\frac{t}{\tau} - \gamma \left[\frac{t}{\tau} \right]^\theta \right) \quad (3.2)$$

where S is the fluorescence amplitude [a.u.], measured by sensing the fluorescent spectral line of excitation and emission; A is the initial fluorescence amplitude [a.u.]; t is the time [s]; τ is the lifetime [s], a scaling parameter for time that characterizes the exponential rate of decay of the luminescence that would occur if there were no energy transfer; θ is the scaling factor [a.u.] that characterizes the effect of energy transfer mechanisms depending on the molecular interaction; and γ is another scaling factor [a.u.] that is a function of the effective energy-transfer distance and of the acceptor concentration. Of these parameters, A , τ , and γ are dependent on temperature[9].

Figure 3.1 shows the lifetime τ of the ceramic Eu : Y₂O₃ as a function of temperature for two excitation sources.

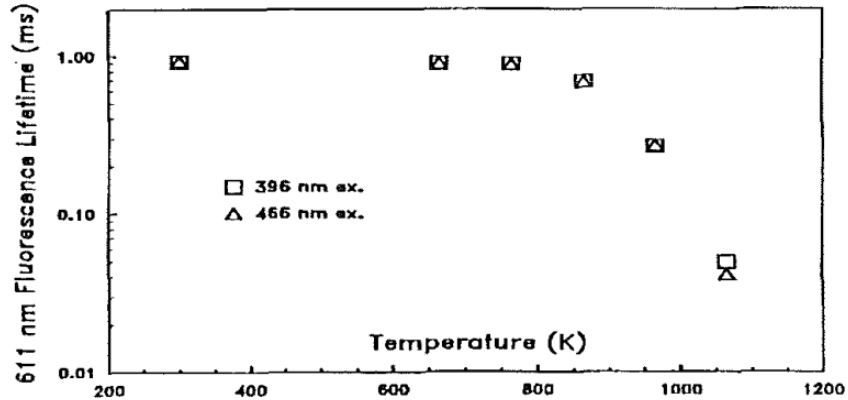


Figure 3.1: Fluorescence lifetime of 1% Eu : Y₂O₃ [9]

Advantages of this technique include that it has high temperature sensitivity and that radiometric algorithms are independent of the illumination source; while disadvantages

include that photobleaching limits long-term intensity and lifetime determination and the high expense of excitation sources (e.g., lasers) and detectors [3].

Zakiyyan et al. [60] utilized the principles of this technique to determine the thermal response of nano-Al on different substrates (flat silver and plasmonic grating) when heated by a 808 nm wavelength laser. They mixed rhodamine 6G (R6G) dye with nano-Al and a polymer to form a micron-thick nanocomposite film. The calibration parameters for R6G were determined by steadily heating the sample using a temperature-controlled microplate reader, all the while measuring the fluorescence spectrum. Using this setup, they were able to find that the heating rate of the nano-Al was enhanced by over 24 times by using the plasmonic grating over the flat silver substrate.

Emission Spectroscopy

A more state-of-the-art implementation with similar principles to fluorescence thermometry involves the measurement of the emission spectra of combustion intermediates such as AlO to determine the temperature. A benefit of this method is that it does not require that additional chemical components (i.e., fluorescent dye) be added. However, this comes at the cost of needing to find or model the emission spectra of the combustion product in question, which may not be as robustly characterized as those of commercial dyes. Ruesch et al. [40] used this method to study the influence of Al particle size on the temperature of composite-propellant flames. Using a spectrometer, they measure the B-X, $\Delta v = -1$ emission band of AlO near 515 nm. Implementing a least-squares fitted model against measured spectra, they were able to infer the temperature of the AlO. Figure 3.2 shows the measured and modeled emission spectra of AlO at 2820 K.

Using the same propellant formulation across three nominal Al diameters (31 μm , 4.5 μm , and 80 nm), they measured the temperature of AlO at various heights above the flame. They found that the temperature of AlO remained similar between the two micro-Al propellants, while the temperature of nano-Al was lower than that at all heights—at a height of 4 cm, the temperatures were approximately 2900 K and 2700 K for the micro-Al and nano-Al, respectively. The authors suggest that this is caused by the nano-Al

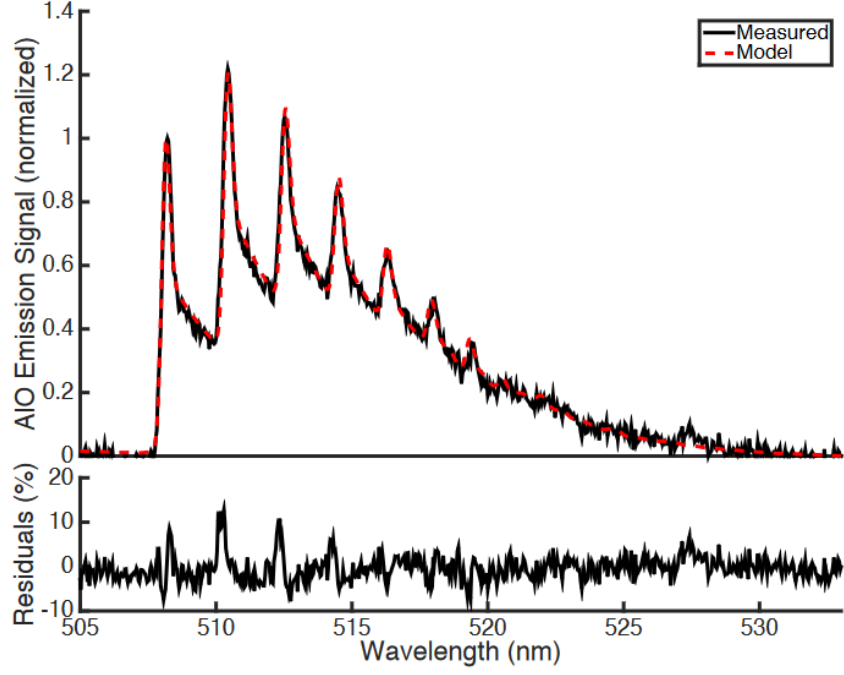


Figure 3.2: AIO emission spectra at 2820 K, measured vs. best-fit model [40]

being in thermal equilibrium with the surrounding flame while the micro-Al burned in a diffusion-controlled regime [40].

3.3 Radiation Thermography

As previously mentioned, radiation-based thermometry methods operate on the basis of Planck's law of blackbody radiation, wherein the spectral irradiance that is emitted by an object is a function of the emitted electromagnetic wavelength, the temperature of the object, and the emissivity of the object (which, in the case of a black body, is unity). Using a sensor to record the light intensity, one may use Equation 3.3 to determine the temperature of the object emitting the light (assuming that the emissivity of the object is also known).

$$B(\lambda, \varepsilon, T) = \frac{2\pi hc^2}{\lambda^5} \frac{\varepsilon(\lambda, T)}{\exp\left(\frac{hc}{\lambda k_B T}\right) - 1} \quad \text{or} \quad B(f, \varepsilon, T) = \frac{2\pi hf^3}{c^2} \frac{\varepsilon(f, T)}{\exp\left(\frac{hf}{k_B T}\right) - 1} \quad (3.3)$$

where B is the spectral irradiance [$\text{W m}^{-2} \text{ nm}^{-1}$ or $\text{W m}^{-2} \text{ Hz}^{-1}$]; h is the Planck constant $= 6.626 \times 10^{-34} \text{ [J s]}$; c is the speed of light $= 2.998 \times 10^8 \text{ [m s}^{-1}\text{]}$; k_B is the Boltzmann constant $= 1.381 \times 10^{-23} \text{ [J K}^{-1}\text{]}$; λ is the wavelength of light [m]; f is the frequency of light $= \frac{c}{\lambda} \text{ [Hz]}$; ε is the emissivity of the object [1]; and T is the temperature [K]

By integrating Planck's law with respect to the wavelength range used to record the data, one may compute the power radiated from an object given the object's temperature and emissivity.

$$I = \frac{2\pi k_B^4 \varepsilon}{h^3 c^2} T^4 \int_x \frac{x^3}{\exp(x) - 1} dx, \quad x = \frac{hf}{k_B T} \quad (3.4)$$

where I is the radiant exitance [W m^{-2}] emitted by the object.

In the special case of *all* wavelengths being used as the limits of integration, one is left with the Stefan-Boltzmann law [50].

$$I = \varepsilon \sigma T^4 \quad (3.5)$$

where σ is the Stefan-Boltzmann constant $= \frac{2\pi^5 k_B^4}{15h^3 c^2} = 5.670 \times 10^{-8} \text{ [W m}^{-2} \text{ K}^{-4}\text{]}$

Advantages of this method include that it is well implemented and commercialized and that it can create a 2D thermographic image; while disadvantages include the difficulty in the precise estimation of the emissivity of the object in question and that the spatial resolution is diffraction-limited and proportional to the wavelength of light used for measurement [3].

Infrared Thermography

Thermal cameras capture the radiation emitted by an object and translate it into a temperature value on a pixel-by-pixel basis, creating a thermographic image. For typical thermal cameras, the wavelength range used in Planck's law is small. The wavelength range is limited by the capability of sensors to detect photons of certain wavelengths. As such, various types of sensors with an equally various number of working wavelength ranges have been developed for commercial use. Additionally, through software, the emissivity may be set

or “corrected” (assumed unity by default) to adjust the temperatures measured by the camera.

Ratio Pyrometry

Ratio pyrometry, also known as dual- or multi-wavelength pyrometry, takes a slightly different approach in order to remove the emissivity-dependence of [Equation 3.3](#). This is done under the common “grey body” assumption that the emissivity of an object/surface is constant over all temperatures and wavelengths. As demonstrated by Densmore et al. [7], if one were to isolate the spectral irradiance emitted by an object to two wavelengths, it is possible to take a ratio of the irradiances. This is shown in [Equation 3.6](#).

$$R_{i,j} = \tau_{i,j} \frac{B_i}{B_j} \approx \tau_{i,j} \left(\frac{\lambda_j}{\lambda_i} \right)^5 \exp \left(\frac{hc}{k_B T} \left[\frac{1}{\lambda_j} - \frac{1}{\lambda_i} \right] \right) \quad (3.6)$$

$$\therefore T = \frac{\frac{hc}{k_B} \left(\frac{1}{\lambda_j} - \frac{1}{\lambda_i} \right)}{\ln \left(\frac{R_{i,j}}{\tau_{i,j}} \left[\frac{\lambda_i}{\lambda_j} \right]^5 \right)} \quad (3.7)$$

where $\tau_{i,j}$ is a parameter that represents the optical efficiencies, detector sensitivities, etc. of the system (obtained through calibration).

While ratio pyrometry is extremely accurate if performed properly, there is still a dependence on: a) the energy that is able to be captured at specific wavelengths and b) a sensor’s ability to capture photons at that wavelength.

[Figure 3.3](#) depicts the wavelength dependence of spectral irradiance at various lines of constant temperature. From this, it can be seen that the amount of signal that can be captured within the visible spectrum greatly diminishes at lower temperatures. As such, pyrometry using color cameras, as noted in [Chapter 1](#), is most suitable for measuring temperatures of $\gtrsim 2000$ K.

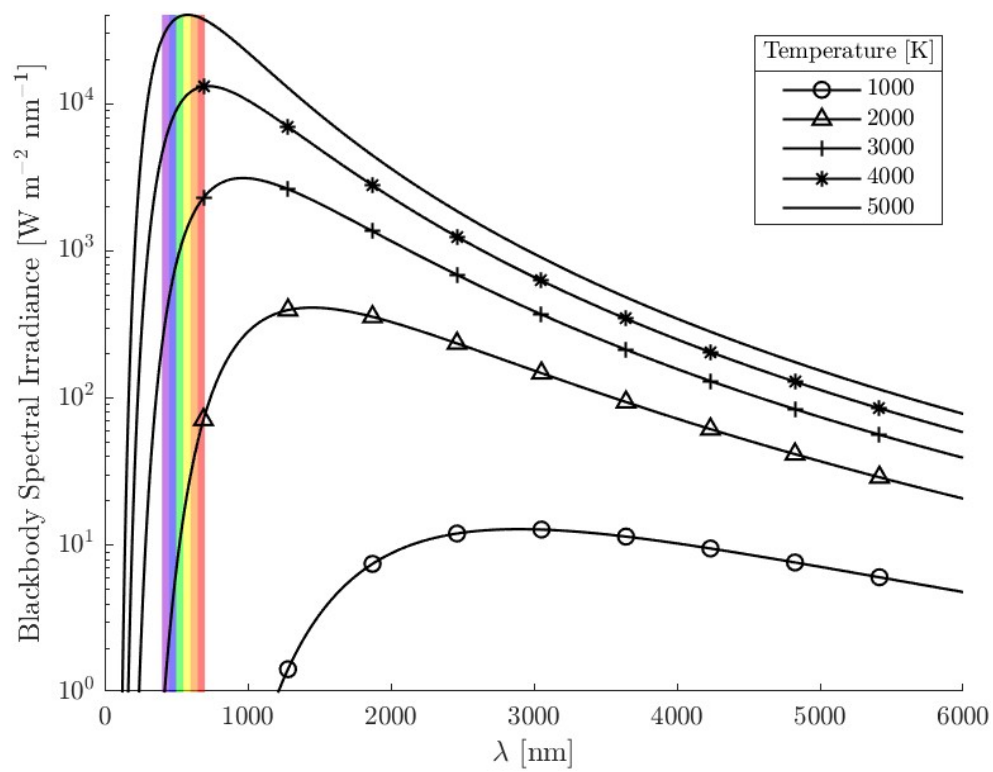


Figure 3.3: Blackbody irradiance by λ at select temperatures

Chapter 4

Methods

4.1 Application of Theory: Pyrometry Setup

4.1.1 Overview

Based on the principle of ratio pyrometry, the design and construction of a system that can be used to measure temperatures at the temporal and spatial micro-scale is presented. The system consists of the following major components:

- Photron FASTCAM MINI AX200 High Speed Camera (x2)
- Phantom v2012 [UHS](#) Camera
- 10x Mitutoyo Plan Apochromat Infinity-Corrected [Near-Infrared \(NIR\)](#) Objective [Thorlabs: MY10X-823]
- Infinity-corrected tube lens, 400–2000 nm (x2) [Thorlabs: TTL200-A]
- Infinity-corrected tube lens, 400–750 nm [Thorlabs: TTL200-S8]
- 700 nm wavelength bandpass filter [Thorlabs: FB700-10]
- 905 nm wavelength bandpass filter [Thorlabs: FL905-10]
- Shortpass dichroic mirror (or “beam splitter”), 650 nm cutoff [Thorlabs: DMSP650R]
- Shortpass dichroic mirror/beam splitter, 805 nm cutoff [Thorlabs: DMSP805R]

- 45° aluminum mirror [Thorlabs: CCM1-G01/M]
- Various mounts and adapters used to connect the components

The basic diagram of the setup can be seen in [Figure 4.1](#) and the CAD rendering in [Figure 4.2](#).

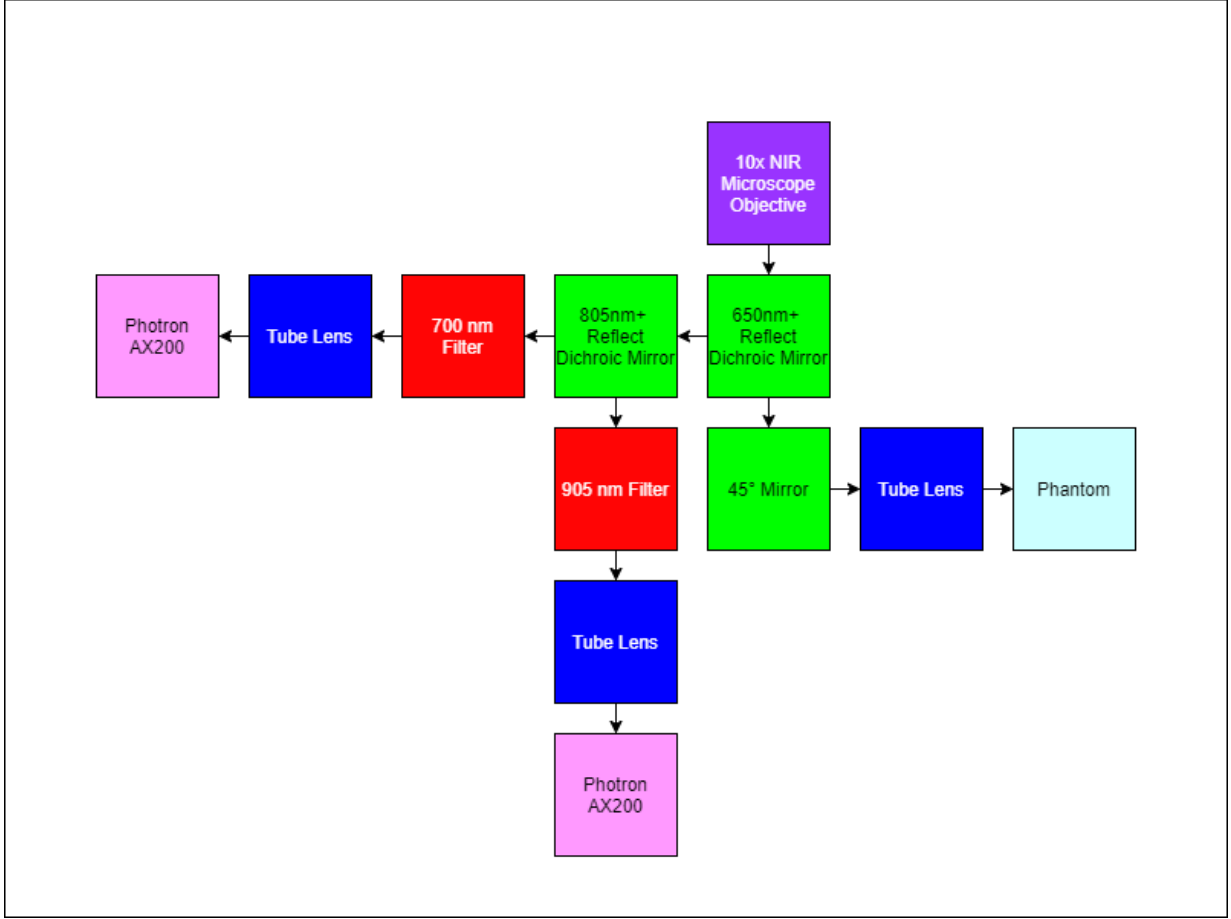


Figure 4.1: Diagram of pyrometry setup

Starting from the 10x [NIR](#) objective, the light being recorded (coming from above) is directed follows:

- First, it passes through the 10x [NIR](#) infinity-corrected objective lens
- Then, it gets split into two paths by the 650 nm dichroic mirror, one straight downwards and the other oriented horizontal (parallel to the optics table):

Path 1: Light of $\lambda < 650$ nm gets sent to the 45° mirror so that it is oriented horizontal

Path 2: Light of $\lambda > 650$ nm gets split once again by the 805 nm dichroic mirror

Path 2a: Light of $\lambda < 805$ nm gets filtered so that only 700 nm light passes through to the Photron camera

Path 2b: Light of $\lambda > 805$ nm gets filtered so that only 905 nm light passes through to the other Photron camera

- All three paths terminate at an infinity-corrected tube lens, which focuses the light into its respective camera sensor

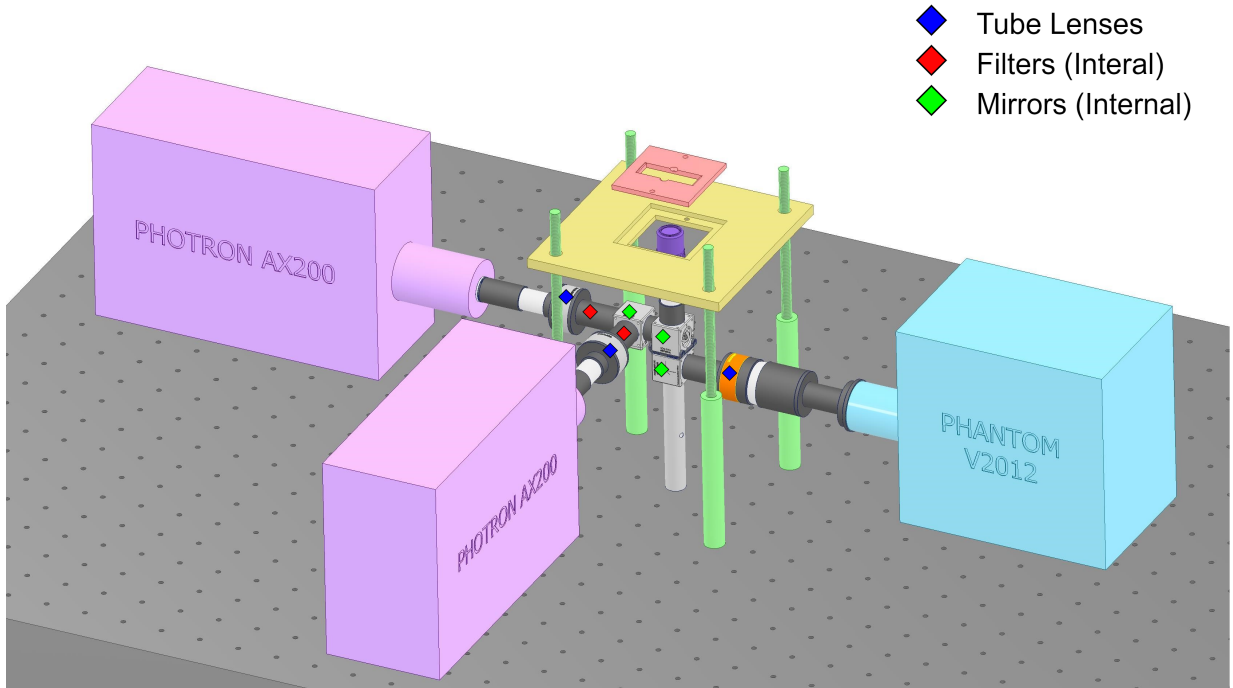


Figure 4.2: CAD rendering of the pyrometry setup. In cyan: Phantom camera; lilac: Photron cameras; violet: 10x NIR objective lens; red: sample mount

Notably, the wavelengths used to conduct the ratio pyrometry are 700 and 905 nm; the reasoning for which will be discussed further below.

4.1.2 Design Choices

The goal of this setup was to be able to render thermographic images from the light collected by the “pyrometry” (Photron) cameras while simultaneously capturing normal footage using the Phantom camera. The following subsections will go into the choice of materials in more detail.

Cameras

While the Photron cameras were chosen to be incorporated into the setup, the Phantom camera was already owned by the lab and needed only to be incorporated. The following minimum criteria were used to find the pyrometry camera that best fit our needs within budget constraints:

- $\gtrsim 10\%$ [Quantum Efficiency \(QE\)](#) at $\lambda = 905 \text{ nm}$ —[QE](#) is the measure of a sensor’s ability to convert photons to electrons and a reasonable [QE](#) is needed so that enough light is able to be read by the camera sensor despite losing much of its intensity through the optical path(s). [QE](#) at $\lambda = 700 \text{ nm}$ was not a concern since this is usually inclusive of the former condition.
- $\gtrsim 10,000 \text{ FPS}$ ($100 \mu\text{s}$ per frame) frame rate—to observe as much of the reaction as possible
- $\lesssim 28 \mu\text{m}$ pixel size—to match the resolution of the Phantom, which has a $28 \mu\text{m}$ pixel size

The chosen Photron camera has the following specifications:

- $20 \mu\text{m}$ pixel size
- $6,400 \text{ FPS}$ at full resolution ($1024 \times 1024 \text{ px} = 20.48 \times 20.48 \text{ mm}$) and $216,000 \text{ FPS}$ at $128 \times 16 \text{ px}$ resolution

The plot showing the [QE](#) (from the Photron AX200 manual) as a function of wavelength is seen in [Figure 4.3](#). It can be seen that the [QE](#) is approximately 42% and 12% at $\lambda = 700$ and 905 nm , respectively



Figure 4.3: QE of Photron camera by wavelength

Filters

Great care needed to be taken in order to choose the wavelengths used to conduct the ratio pyrometry (and consequently the filters). One thing to note is that while cameras are typically able to “see” into the NIR spectrum, $\lambda \approx 1000$ nm is the upper limit. Although, even at that point (as seen in Figure 4.3), the efficiency may be too poor to be effective. This needs to be balanced with the fact that, as seen in Figure 3.3, as one decreases the wavelength being probed, less of the lower end of the temperature spectrum is able to be measured.

According to Llull et al. [29], cameras commonly capture on the order of 100×10^{-12} W per pixel. Using the pixel size of the Photron ($20 \times 20 \mu\text{m}$) and assuming that the amount of light lost through the system is 50%, that is equivalent to an irradiance of $100 \times 10^{-12} \div (20 \times 10^{-6})^2 \div 0.5 = 0.5 \text{ W m}^{-2}$ that is needed to capture an image. Figure 4.4 is similar to Figure 3.3, but with the roles of temperature and wavelength swapped and multiplied by both the wavelength in question and the QE of the Photron camera at those wavelengths. It shows the lower limit of the temperature that is able to be measured by

various wavelengths, limited by the 0.5 W m^{-2} needed to capture an image.

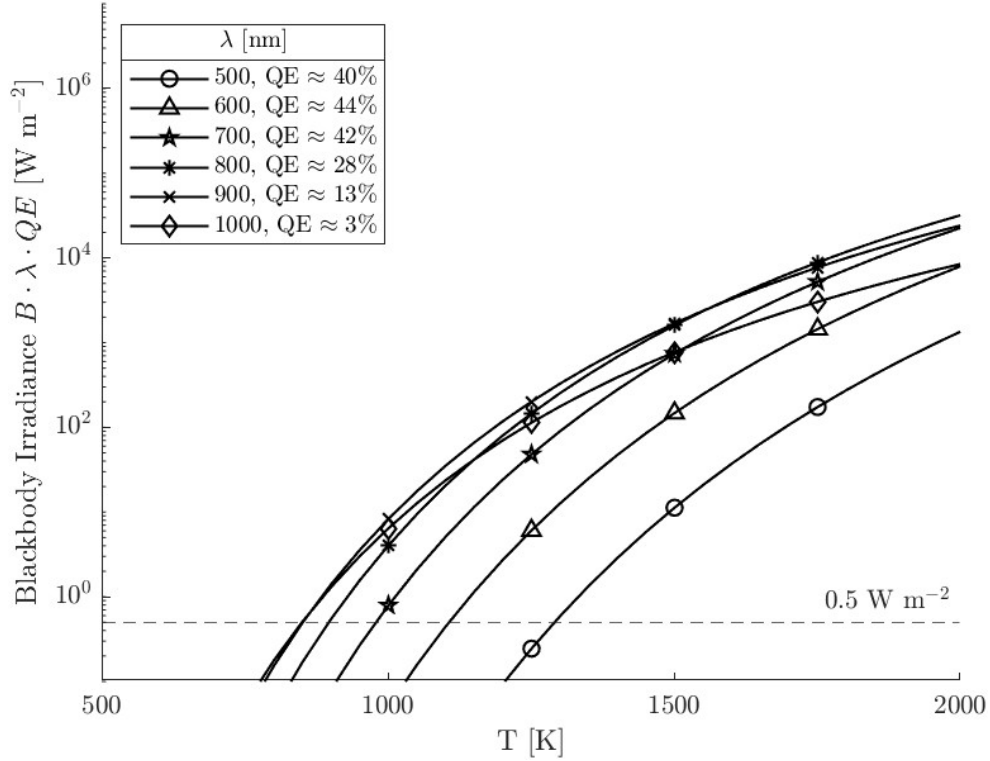


Figure 4.4: Blackbody irradiance by temperature at select λ , multiplied by λ and the QE of the Photron camera at each λ

It can be seen that while there is some temperature to be gained by increasing λ from 800 to 900 nm, there is no benefit beyond that. Thus, 905 nm was chosen as one of the wavelengths, due to the superior specifications of the 905 nm model over other variants in the 900 nm wavelength range.

Another factor to consider is that it is beneficial for the second wavelength to be far from the first wavelength. This is for two reasons: 1) Since a ratio is being taken, if the two wavelengths are too close together, so too will the intensities being measured, leaving more room for precision/rounding errors; and 2) Dichroic mirrors were to be used to split the light into the 2a and 2b paths, and it is more difficult to find mirrors that will efficiently split light into wavelength bands that are close together. Additionally, care must be taken to avoid noise that may come from the thermite reaction itself. Known values for the emission spectra related to the combustion of Al/CuO are: 473, 485, 513, 578, 596, 608, 627, and

655 nm [63]. Thus, the second wavelength of 700 nm was chosen as it is far away from both the first chosen wavelength and the known emission spectra of the Al/CuO reaction. The choice of mirrors just followed in suit of what was appropriate for the given wavelengths.

Lenses

An objective lens was desired so that observations could be made at the microscopic scale. The objective also needed to be able to transmit light into the NIR range so that ratio pyrometry could be performed. Another key feature is the infinity-correction property of the lens. Infinity-correction is the property of a lens that allows it to transmit light as parallel beams instead of focusing it behind the lens. At the end of its path, the beams are accepted by a compatible tube lens, which then focuses the light into an image onto the sensor. This property is useful because it allows additional optical equipment (filter, mirrors, etc.) to be placed in the optical path between the objective and the tube lens with relative ease compared to if the objective were finite [18]. Unsurprisingly, the selection of microscope objectives that were both NIR and infinity-corrected was minimal and only the chosen 10x Mitutoyo NIR Objective was viable.

Lastly was the choice of tube lens. Granted that the TTL200-S8 tube lens has a 400–2000 nm design range, it would have been acceptable to use this same tube lens in conjunction with all three cameras. However, the transmission efficiency of TTL200-S8 is relatively poor in the visible spectrum ($< 95\%$), so it was decided that the TTL200-A was more suitable for the Phantom with its efficiency being over 95%. Conveniently, the TTL200-A and TTL200-S8 have the same specifications in terms of working distance, focal length, etc.

4.1.3 Construction

The optical components can be assembled in any number of ways, barring two conditions: the ordering of the optical components must follow the design and the spacing between the optical components must be within the specified working ranges. The reason for keeping

the ordering of the components is self-explanatory—the ordering was designed to modify the light path in very specific ways such that pyrometry could be performed. The spacing however, while being somewhat flexible in the paths between the objective lens and the tube lenses, is rigid between the tube lens and the camera sensor. According to the specifications of the tube lenses, the distance between the tube lens and the objective lens must be between 70 and 170 mm—this flexibility owing to the infinity correction. However, the distance between the rear shoulder of the tube lens and the sensor must be exactly 151.8 mm to avoid any loss of image quality. Understanding this, it was in best practice to use an extensible coupling between the tube lens and the camera so that this distance may be adjusted as necessary. Another extensible coupling was used between the objective lens and the first mirror mount to allow for focusing adjustments.

Finally, it should be noted that the 45° mirror mount required the tapping of at least one #8-32 hole in order to allow for an optical post to hold it in the orientation specified by the design. A second hole was tapped to allow for further flexibility should the user decide that they want to change the orientation. The changes made to the mirror mount can be seen in [Figure 4.5](#).

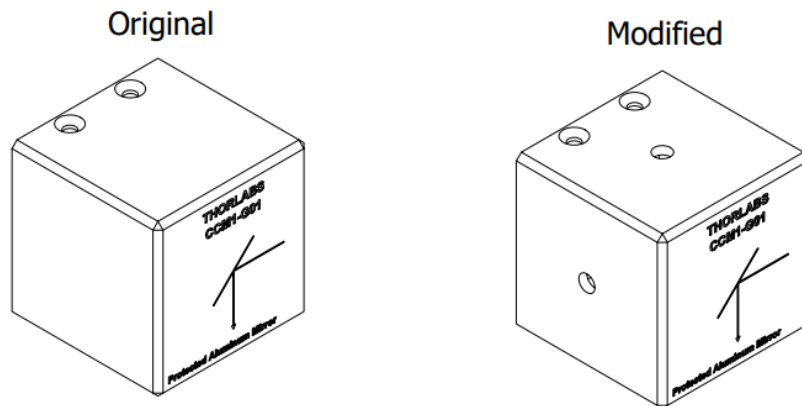


Figure 4.5: Modification made to mirror mount

4.1.4 Experimental Workflow

The process of recording footage using the pyrometry setup follows four major steps: synchronize the cameras, capture a registration image, capture a calibration image, and record the event you wish to capture.

First, all three cameras must be turned on and synchronized using the BNC-connector Sync and Trigger ports located on the rear side of the cameras along with the sync and trigger settings in the cameras' respective softwares. When the desired FPS and resolution have been chosen, a registration image must be captured with all cameras. The registration process will be discussed in detail in [Section 4.2.3](#), but in brief: since each camera will have a slightly shifted view of the object being transmitted through the optical paths, the images need to be adjusted or “registered” such that the view is unified on a pixel-by-pixel basis. Next, a calibration image must be captured using both pyrometry cameras. To do so, a calibrator must be placed in view of the cameras (i.e., in front of the objective lens). While a blackbody calibrator rated for extremely high temperatures would be ideal, it may not be feasible to use one due to the short working distance of the objective lens (31 mm)—a heat source of (e.g.) 1200 K placed only 31 mm away from the objective lens could risk damage to the lens. Instead, McNesby et al. [\[31\]](#) have demonstrated the utilization of a stabilized calibrated light source [Thorlabs: SLS201L] with a color temperature of 2796 K in place of a blackbody calibrator. Taking this latter approach, the light source need only be pointed at the objective lens and an image taken of the light beam. An optical diffuser is recommended to be used to smooth the beam coming from the light source. After registration, the calibration images can be used to determine $\tau_{i,j}$ from [Equation 3.6](#).

As an example, consider the same 2796 K light source being used in this pyrometry setup. In the ideal case, $\tau_{i,j}$ would be unity, and the resultant ratio $R_{i,j} = R_{i,j,ideal}$ should be equal to

$$\begin{aligned} R_{i,j,ideal} &= \tau_{i,j} \left(\frac{\lambda_j}{\lambda_i} \right)^5 \exp \left(\frac{hc}{k_B T} \left[\frac{1}{\lambda_j} - \frac{1}{\lambda_i} \right] \right) \\ &= (1) \left(\frac{905}{700} \right)^5 \exp \left(\frac{hc}{2796 k_B} \left[\frac{1}{905 \times 10^{-9}} - \frac{1}{700 \times 10^{-9}} \right] \right) = 0.6813 \end{aligned}$$

$\tau_{i,j}$ can then be calculated as $R_{i,j,ideal} = 0.6813$ divided by the ratio between the measured intensity from the calibration images. To clarify, the intensity of the image is just the intensity value at each pixel in the image, given when the image is read into memory such as in MATLAB. Ideally, the intensity ratio would be the same value at every pixel in the image, but in a non-ideal case, the mean value across all pixels should suffice.

$$\tau_{i,j} = \frac{R_{i,j,ideal}}{R_{i,j,meas}} = \frac{R_{i,j,ideal}}{B_{i,cal}/B_{j,cal}}$$

Once data recordings have been captured and registered, $\tau_{i,j}$ may be used in [Equation 3.7](#) with other $R_{i,j} = R_{i,j,data}$ to calculate the 2D temperature map at each timestamp.

Example

The following is an example of the workflow using the “M83 spiral galaxy” (`'m83.tif'`) stock image from MATLAB. Starting from after the images have been registered, assume that $\tau_{i,j} = 0.87$ (chosen arbitrarily). Let **A** be the image recorded by the camera that is filtered for 700 nm wavelength; and **B** the 905 nm filtered image. **A** and **B** are the same image of the M83 spiral galaxy with intensities modified to simulate what they would look like from the perspective of their respective wavelengths. [Figure 4.6](#) shows **A** and **B** with a color bar indicating the intensity at each pixel. Note that **A** and **B** are 16-bit (maximum intensity value of $2^{16} - 1$) monochrome images which have been loaded into MATLAB as numerical arrays.

Applying [Equation 3.7](#) to **A** and **B** as an element-wise operation where $R_{i,j} = \frac{\mathbf{A}}{\mathbf{B}}$, the result is an array of temperatures, indexed by the pixel locations. The resulting temperature map can be seen in [Figure 4.7](#). It should be noted that the temperatures shown here are not true to life, but are a representation of what a temperature map might look like.

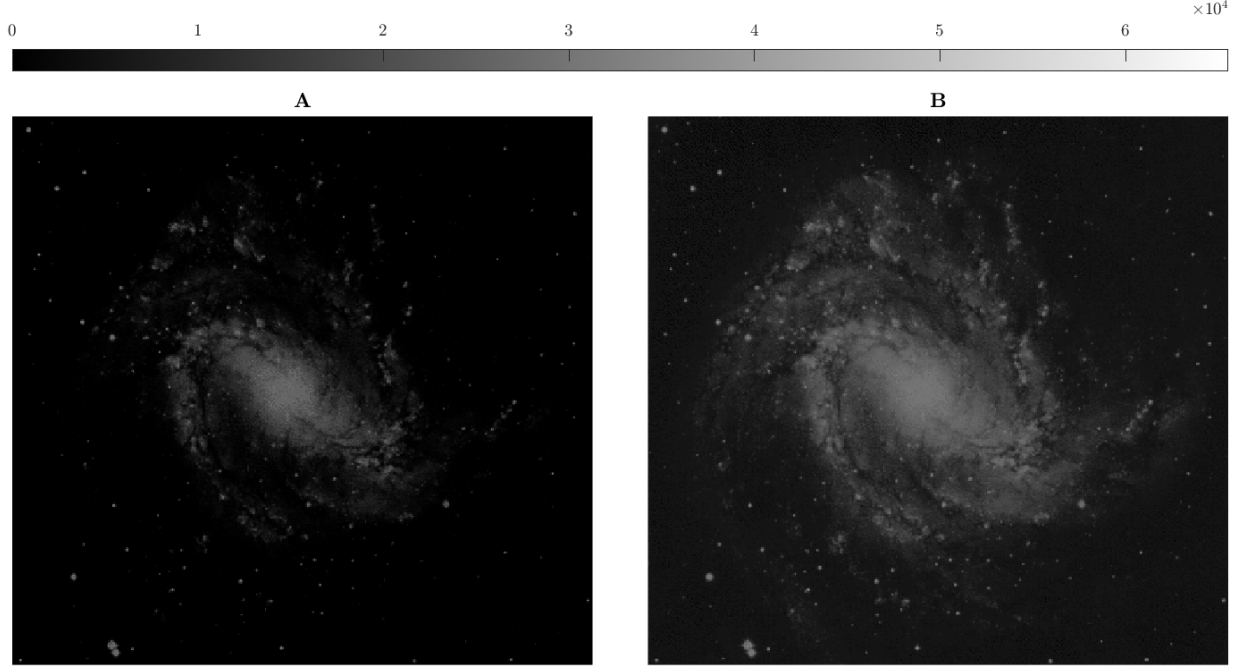


Figure 4.6: **A** and **B** displaying the M83 spiral galaxy as “seen” by their respective wavelengths

4.2 Experimental Methodology

4.2.1 Film Preparation

The fabrication of the film followed a procedure previously described by Kim et al. [23]. In brief, 62.5 mg each of hydroxypropyl methylcellulose (HPMC, 86kDa, Sigma-Aldrich, St. Louis, MO) and poly(vinylidene fluoride) (PVDF, $\overline{M}_w \sim 534,000$, Sigma-Aldrich, St. Louis, MO) were dissolved into 4 mL of dimethylformamide (DMF, Sigma-Aldrich, St. Louis, MO) under rigorous stirring. Upon dissolving, 1125 mg of solid thermite powders were added to the solution. Two different types of powders were used to make two samples. One sample simply utilized the mixture of Al (100 nm, US Research Nanomaterials, Houston, TX) and CuO (40 nm, US Research Nanomaterials, Houston, TX) nanoparticles, which is referred to as **PM**. The other sample used core-shell Al/CuO composite synthesized by the method described by Wang et al. [56], which is referred to as **CS**. After the addition of the thermite powder, the mixture was sonicated in a water bath for two hours before magnetically stirring for 24 hours in preparation of the final slurry.

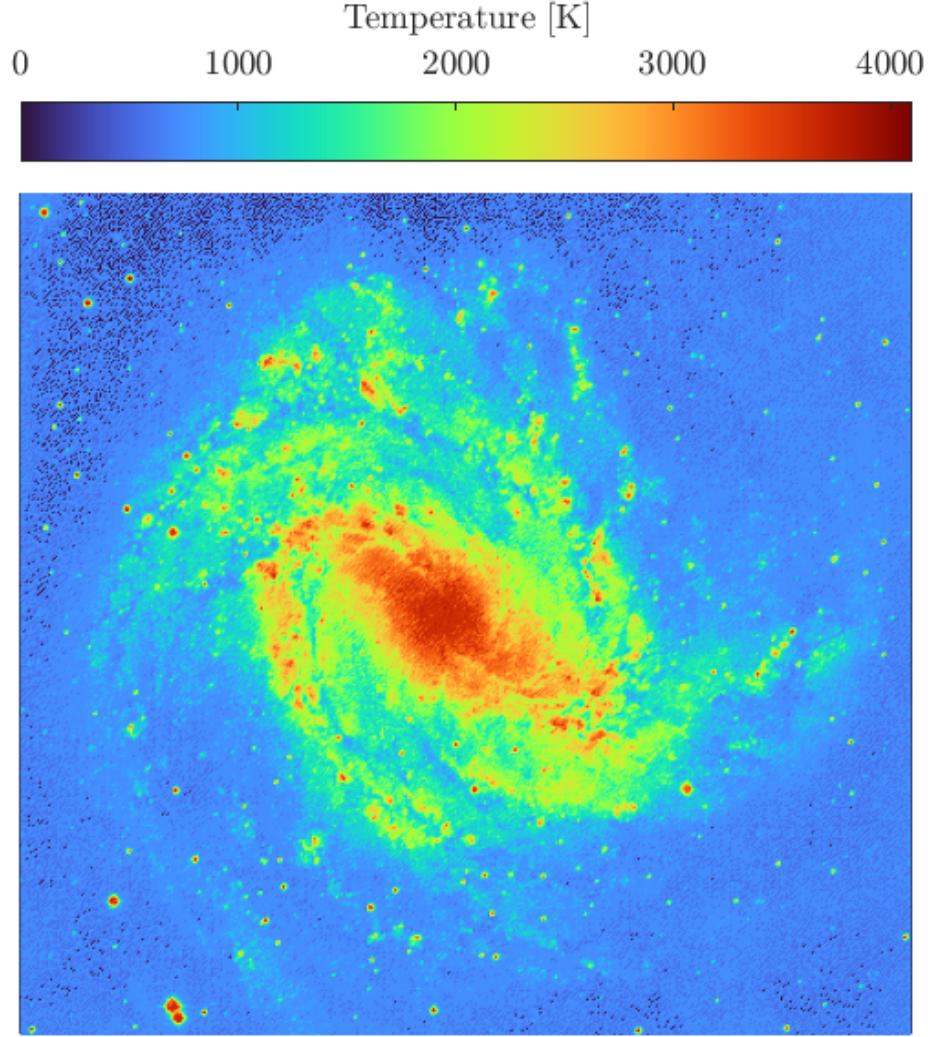


Figure 4.7: Resultant temperature map from processing **A** and **B**

Polytetrafluoroethylene (PTFE) sheets and pieces of Kapton tape of 0.001 in. (25.4 μm) thickness were used to fabricate the film for combustion tests. Segments of Kapton tape were cut and adhered to the PTFE sheets to make a rectangular well of approximately 2 cm $\times$ 0.4 cm, acting as a mask for the films. The PTFE sheets were then placed on a hot plate at 85°C. A droplet of the slurry was placed at one end of the well, and a film applicator with a nominal thickness of 25 μm was pushed across the well to form the droplet into a thin layer of slurry within the well. Once the first layer was dried, an additional layer was applied by repeating the process. A total of 5 to 8 depositions were made to allow the thickness of the film reach the nominal thickness of the film applicator. [Figure 4.8](#) shows the film at this stage after it has dried.



Figure 4.8: Prepared film on PTFE substrate

The Kapton tape mask was then removed and the fabricated thin film was peeled carefully from the PTFE sheets to be mounted onto the sample holder, which was a 2 in. $\times$ 2 in. acrylic sheet with a $\frac{3}{8}$ in. hole cut into it. To mount the sample, a fuse wire (Parr, Moline, IL) was first adhered to the acrylic sheet, followed by the film, which was placed across the hole, as seen in [Figure 4.9](#). The purpose of the hole was to enable free-surface combustion. From there, the sample could be ignited by applying a voltage across the ends of the fuse wire.

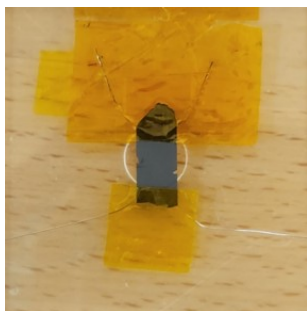


Figure 4.9: Peeled film adhered to acrylic sample holder

4.2.2 High-Speed Imaging

Two high-speed cameras were used to observe the flame propagation of the nanothermite film. Firstly, a Telops FAST M350 infrared camera was used with a 4x magnification lens (final pixel size of $3.75 \mu\text{m px}^{-1}$) to measure the temperature gradients within the film as it burned. Secondly, a Phantom v2012 [UHS](#) camera was used with a 10x magnification lens (final pixel size of $2.8 \mu\text{m px}^{-1}$) to observe the behavior of the combustion reactants

and products as the flame propagated across the film. Due to the thickness of the film, the combustion event is considered to be approximately 2D, making the view from both sides of the film virtually identical. With the two cameras aligned to and facing each other, the film was mounted between them atop an XYZ translational stage, which allowed for fine-tuning of the cameras' focuses. It was then ignited by using a DC voltage source to apply a voltage across the fuse wire. The experimental setup and workflow are shown in Figure 4.10.

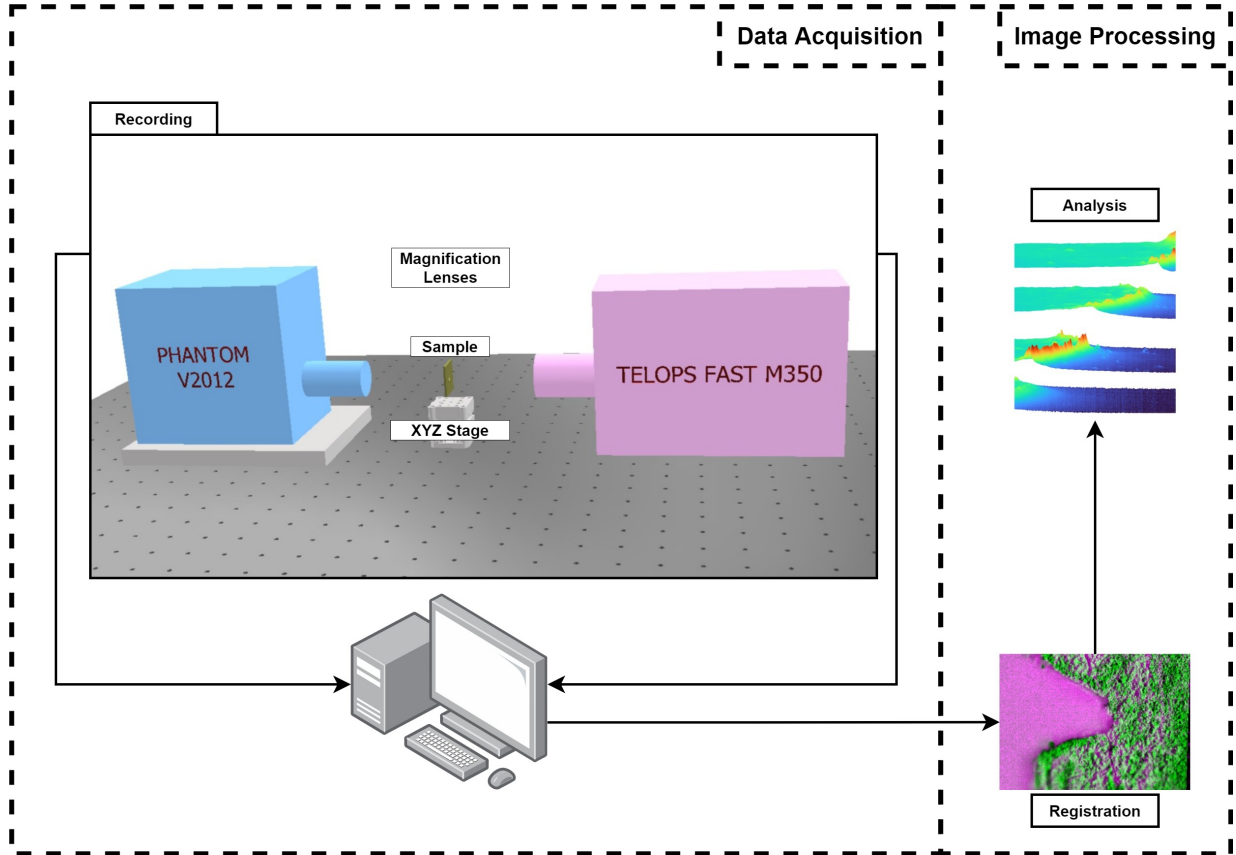


Figure 4.10: Experiment workflow: 1) Sample is placed on holder and cameras are aligned; 2) Registration/calibration snapshots are taken using both cameras; 3) Cameras record to memory while sample is ignited using hot wire; 4) Recorded images are registered using calibration snapshots; 5) Data is extracted from images and analyzed

4.2.3 Image Processing

Image Registration

In order to correlate the footage taken from the cameras, image registration was performed using MATLAB. Since the Phantom had a larger field of view, its images were chosen as the “moving” images with regards to the registration process. An image snapshot of the nanothermite film was taken with both cameras, and the features seen in the image were used to register the “moving” image from the Phantom to the “fixed” image from the Telops. In doing so, the processed images from the Phantom attain the same frame and pixel size as the Telops images (henceforth referred to as “UHS” and “thermal” images or footage, respectively). The results of the registration process can be seen in [Figure 4.2.3](#) below.

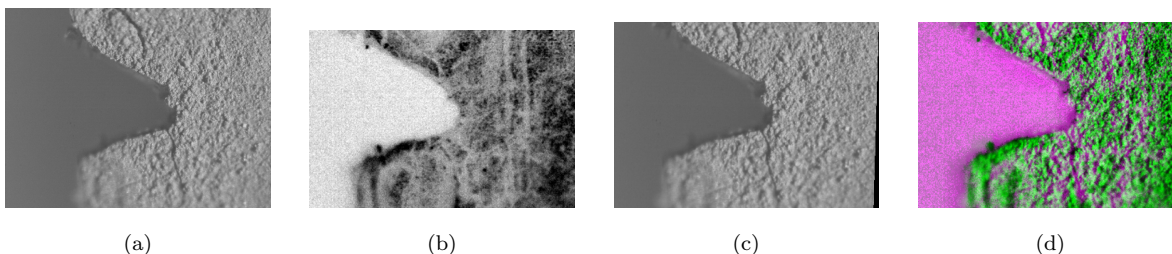


Figure 4.11: Image registration process: (a) Original Phantom registration snapshot; (b) Telops snapshot; (c) Registered Phantom snapshot—image has been rotated, cropped, and resized according to features matched between **a** and **b**; (d) Composite image of the two snapshots

Flame Front

While much discussion has been made about the flame front, there still does not exist a robust definition for the region in which the flame front exists. Thus, we propose and utilize a gradient-based weighted mean (WM) approach to assess the boundary at which the flame front may be defined. Since the flame front is the area within which the reaction occurs, it is also the area at which the temperature is greatest and temperature gradients are relatively high. As such, temperature and gradient thresholds ($\bar{T}$ and $\bar{G}$, respectively) may be defined, where any region that has values above these thresholds may be considered

part of the flame front. The proposed approach considers the temperatures and gradients at each pixel location and uses them as weights to determine these thresholds as follows:

$$\bar{T} = \frac{\sum T_i G_i}{\sum G_i}, \quad \bar{G} = \frac{\sum T_i G_i}{\sum T_i} \quad (4.1)$$

where T_i is the temperature at each pixel location [K] and $G_i = \sqrt{G_{x,i}^2 + G_{y,i}^2}$ is the temperature gradient as the magnitude of the central distance gradients in the x- and y-directions at each pixel location [K px⁻¹].

Using the condition that the temperatures and gradients must be greater than the thresholds, a “mask” is created to segment the flame front from the rest of the image. The benefit of using this approach is that regions of low gradient are penalized (i.e., contribute negligibly) to the temperature threshold, resulting in in-boundary temperatures that are more representative of the flame front. Figure 4.12 shows the results of this approach. The temperature peaks at which the gradient is small have been included within the mask for aesthetic reasons.

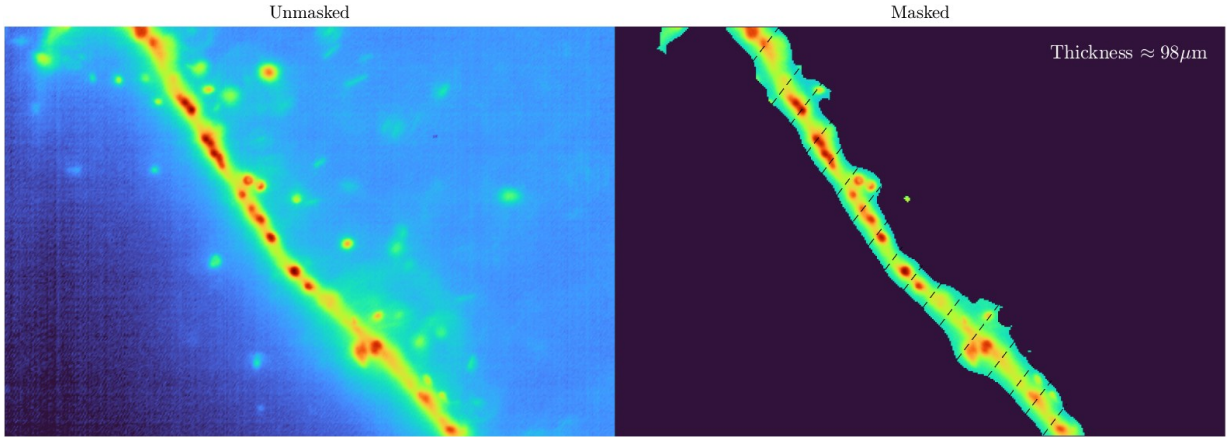


Figure 4.12: Masking of the flame front as defined in Equation 4.1

Emissivity Correction

Although the “true” emissivity of our samples is unknown and is also assumed to vary as the reaction propagates, for the purpose of this study, the value of 0.15 has been chosen as it is a common value that is used in simulations [70, 48]. The goal of this study was to

contrast the combustion behaviors of the [PM](#) and [CS](#) films with only some regards to the “true” temperature observed in the reaction.

Emissivity correction can be done in the “RevealIR” software for the Telops thermal camera. However, it is inconvenient to access the data through the software, manually change the emissivity, and export the data every time one wishes to see the data under different emissivity values. Thus, I wrote a script in MATLAB that will take the exported data and perform the emissivity correction. [Equation 3.4](#) can be solved using numerical methods for the wavelength range used by the thermal camera (3–5.4 μm). In doing so, I generated a [Lookup Table \(LUT\)](#) to index and match temperatures with their corresponding [In-Band Irradiance \(IBI\)](#). Note that this is not the “true” [IBI](#) that would be reported by the camera, but differs from it by some scalar value that takes into account the view factor of the camera sensor. As it is a scalar, this difference is inconsequential since it would just scale the [IBI](#) values recorded in the [LUT](#) and would not change the emissivity-corrected temperature.

As an example, consider a radiometric temperature of $T = 1000$ K as read by our camera, which assumes $\varepsilon = 1$. Referencing the [LUT](#), this corresponds to an [IBI](#) of 22495 W m^{-2} . Using an emissivity value of $\varepsilon = 0.15$, the adjusted [IBI](#) is just $22495 \div 0.15 = 149967$ W m^{-2} . Referencing the [LUT](#) again, this corresponds to an emissivity-corrected temperature of $T = 1912$ K.

Chapter 5

Results and Discussion

This work attempts to contrast the different combustion behaviors between PM and CS nanothermites. As noted, the structure of the CS particles discourages sintering by minimizing the opportunity for Al to sinter with other Al particles. In addition, it is possible that the outermost shell composed of the CuO oxidizer may increase the structural integrity of the particle. In the case that the melt dispersion theory holds true, this would provide an even greater pressure differential within the core of the particle. Given this, the results of this work may contribute evidence to support or refute either of these theories.

The key facets of each theory that should be observed for are:

Reactive Sintering	Melt Dispersion
Sintering of aggregated particles	Explosion of individual particles
Sintering time $\leq$ reaction time	Heating rate $\gtrsim 10^6$ K s ⁻¹
Highly spherical morphology (post-combustion)	High velocity particle ejection

Table 5.1: Key aspects of competing ignition models

To observe the nanothermite reaction, a film of nanothermite was placed on top of an acrylic square with a circular hole cut into it. The hole provided an unobstructed view of the thermite and also enables open-air combustion as the reaction propagated across the hole. A wire was placed between the film and the acrylic and everything was held together using Kapton tape. Supplying the wire with sufficient power resulted in the ignition of the

film.

5.1 Propagation and Flame Front

Figure 5.1 shows the propagation of the flame front in four sequential frames from the thermal footage. The thermal camera also captured scattered hot spots along the flame front, which indicate regions of significantly higher temperatures. These hot spots may be related to inhomogeneities in the micro-structure of the sample and/or the heat transfer mechanisms. The shape of the flame front was also observed to be highly irregular, implying nonuniform heat transfer.

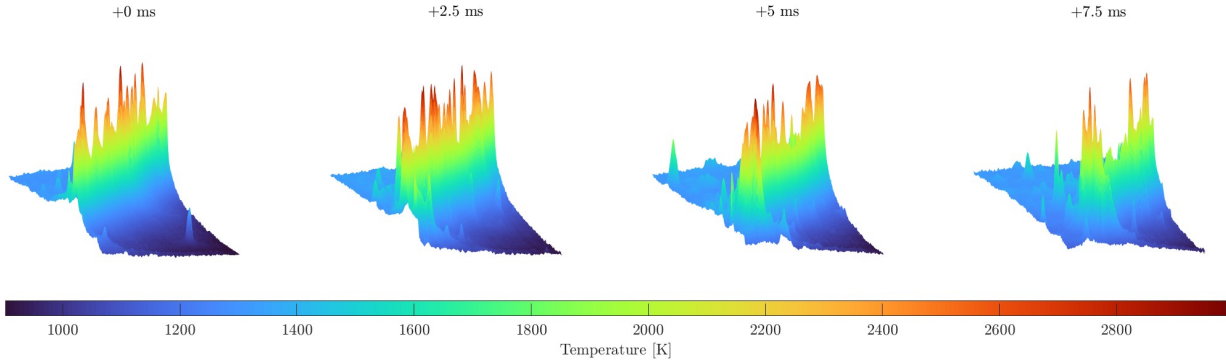


Figure 5.1: PM thermal images, oriented such that the propagation direction is southeast with respect to the figure. Large independent spikes can be seen in the flame front

Figure 5.2 shows the same, but for the CS sample. Unlike in the previous case, highly localized hot spots were hardly seen along the flame front and the shape of the flame front was also observed to be very uniform. Additionally, the hot regions appear to spread out and travel along the flame front itself, which indicates a tangential component to the propagation similar to the one observed by Kim et al. [23]. However, as will be shown later, this propagation is not only of the flame front but of the reactants as well. These observations may indicate a more stable and controlled combustion process and greater efficiency with regards to heat transfer.

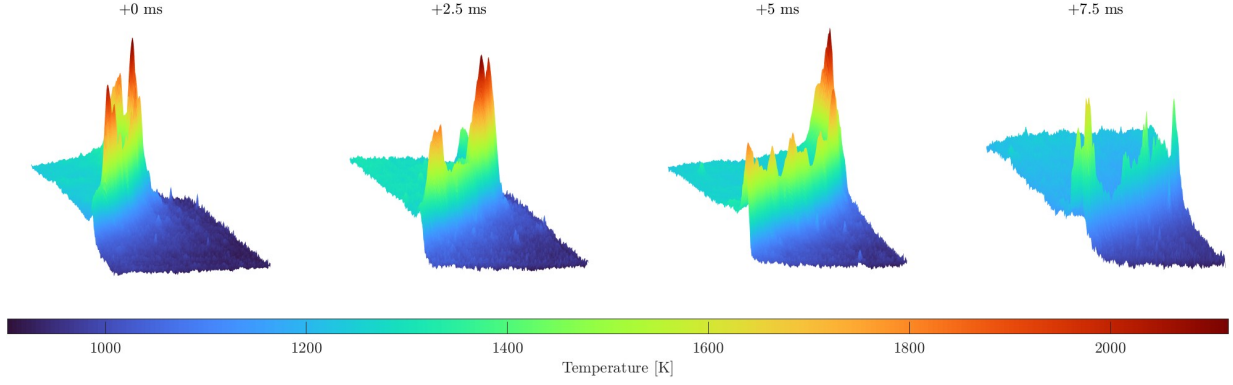


Figure 5.2: [CS](#) thermal images, oriented such that the propagation direction is southeast with respect to the figure. Independent spikes are hardly seen; high temperature regions are more coalescent

Velocity Maps

Furthering the discussion of the propagation of the flame front, [Figure 5.3](#) and [Figure 5.4](#) show propagation and velocity maps of the flame front processed from the [UHS](#) data.

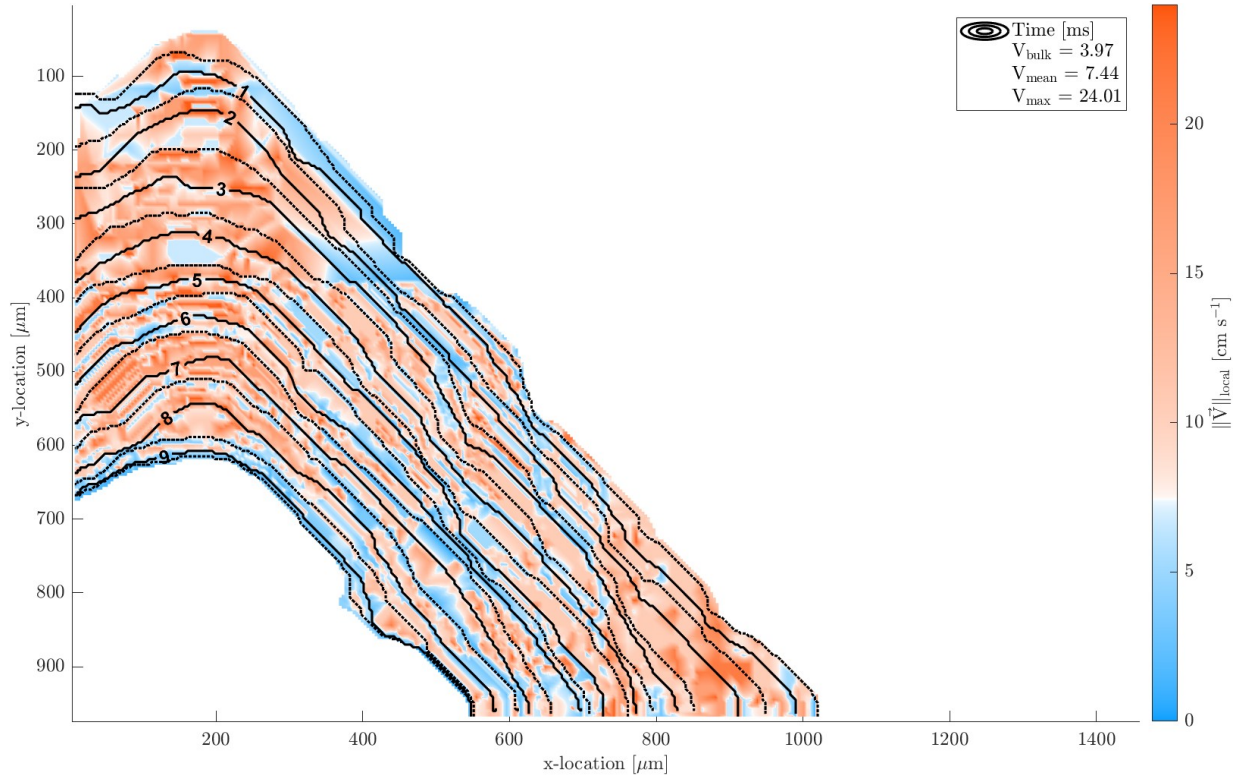


Figure 5.3: Propagation and velocity map of the flame front at times and locations indicated by the contour lines for the [PM](#) sample. The color map is shifted such that the mean velocity appears as “white”

For the **PM** sample, the flame front is seen to propagate erratically. The spacing between the contour lines is somewhat irregular, indicating the nonuniformity in the propagation rate along the flame front. The mean speed of the flame front across the map was found to be 7.44 cm s^{-1} with a maximum speed of 24.01 cm s^{-1} and bulk propagation rate of 3.97 cm s^{-1} .

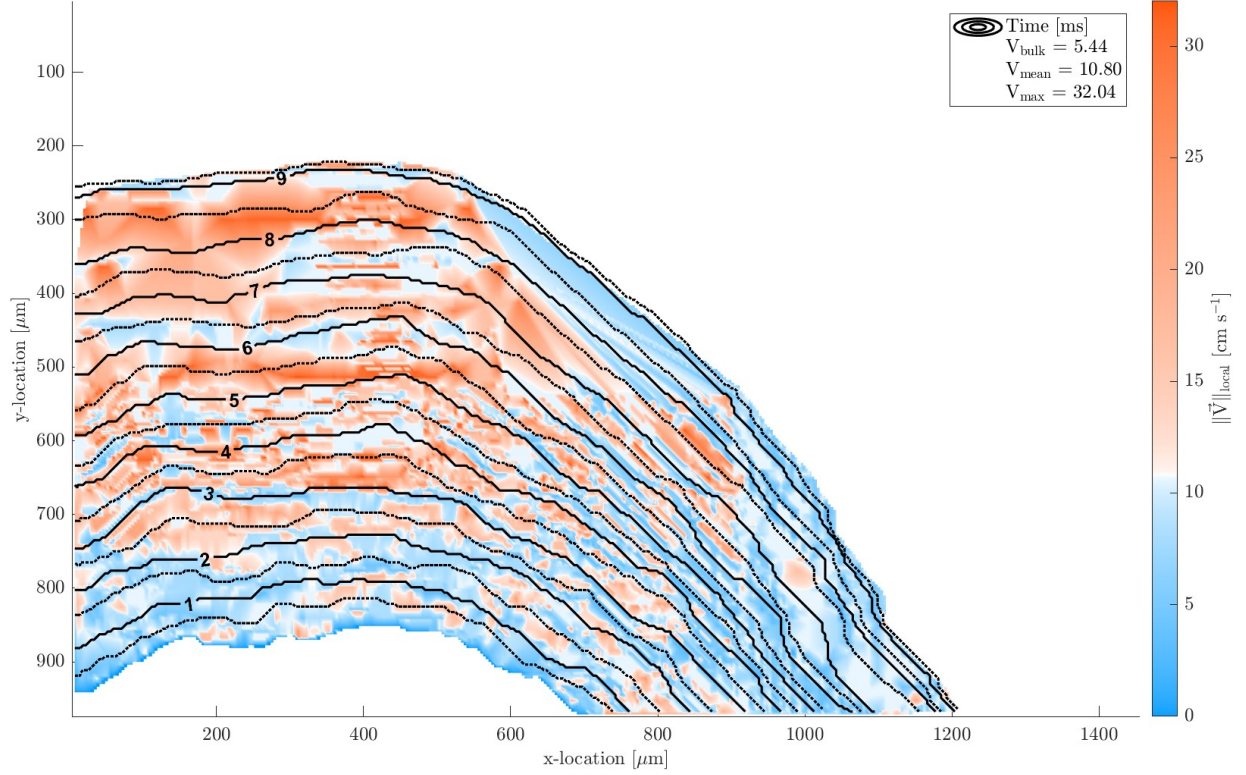


Figure 5.4: Propagation and velocity map of the flame front at times and locations indicated by the contour lines for the **CS** sample. The color map is shifted such that the mean velocity appears as “white”

For the **CS** sample, the flame front is seen to propagate rather uniformly with consistent spacing between the contours. The mean speed of the flame front here was found to be to be 10.80 cm s^{-1} with a maximum speed of 32.04 cm s^{-1} and bulk propagation rate of 5.44 cm s^{-1} .

Both data sets corroborate the findings of Wang et al. [57] in that the local flame front velocities are an order of magnitude greater than the bulk propagation rate.

5.2 Temperature Banding

Figure 5.5 and Figure 5.6 give a closer look at one of the frames from each set of footage.

Figure 5.5(a,b) clearly shows irregular shape of the flame front with distinctive hot spots

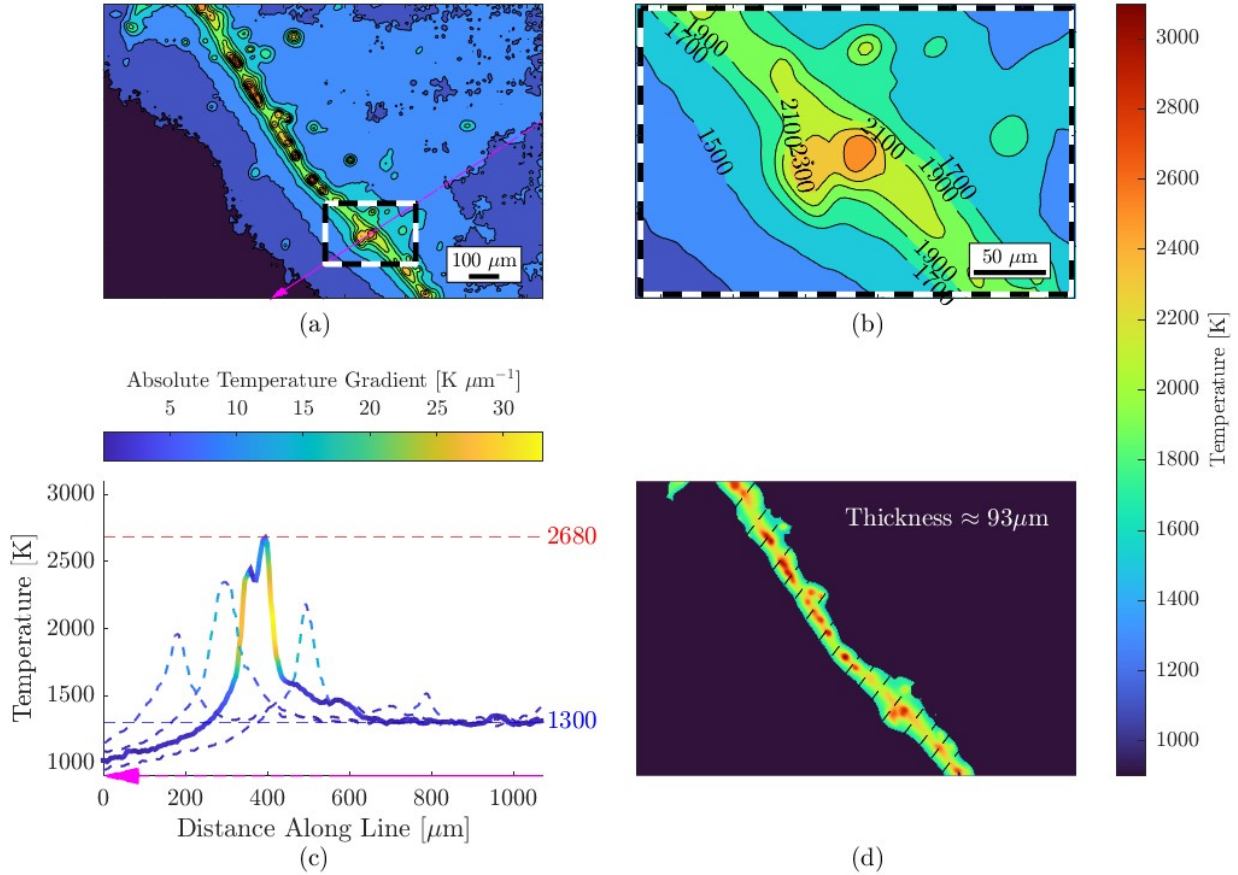


Figure 5.5: A closer look at one of the thermal images of the PM film (propagation direction indicated by magenta arrow): (a) the full-sized image, contoured at 200 K intervals; (b) contours zoomed into the 300 $\mu\text{m} \times 200 \mu\text{m}$ rectangle found in **a**; (c) temperature profiles measured along the magenta arrow found in **a** with additional profiles from neighboring frames (dashed lines); (d) Masked flame front displaying approximate thickness

along it, indicating extremely nonuniform heat transfer. The distance between the center of the flame front to the unburned film (“conduction distance”) was measured to be $\sim 645 \mu\text{m}$. In addition, the extreme heat of and close proximity between the temperature spikes may be indicative of the sintering process. Taking a closer look at Figure 5.5(b), it can be seen that the hot spots lie on top of the flame front. This suggests that these extreme temperature

peaks—some larger than the theoretical adiabatic flame temperature ($T_{af} = 2843$ K)—happen *before* the thermite reaction is completed and generates the gas that would expel the particles.

Taking a look at the CS thermal data, Figure 5.6(a,b) shows a more consistent banding of the temperature contours with little to no irregularities along the flame front. Here, the conduction distance was measured to be ~ 600 μm . Again, it is noted and even more

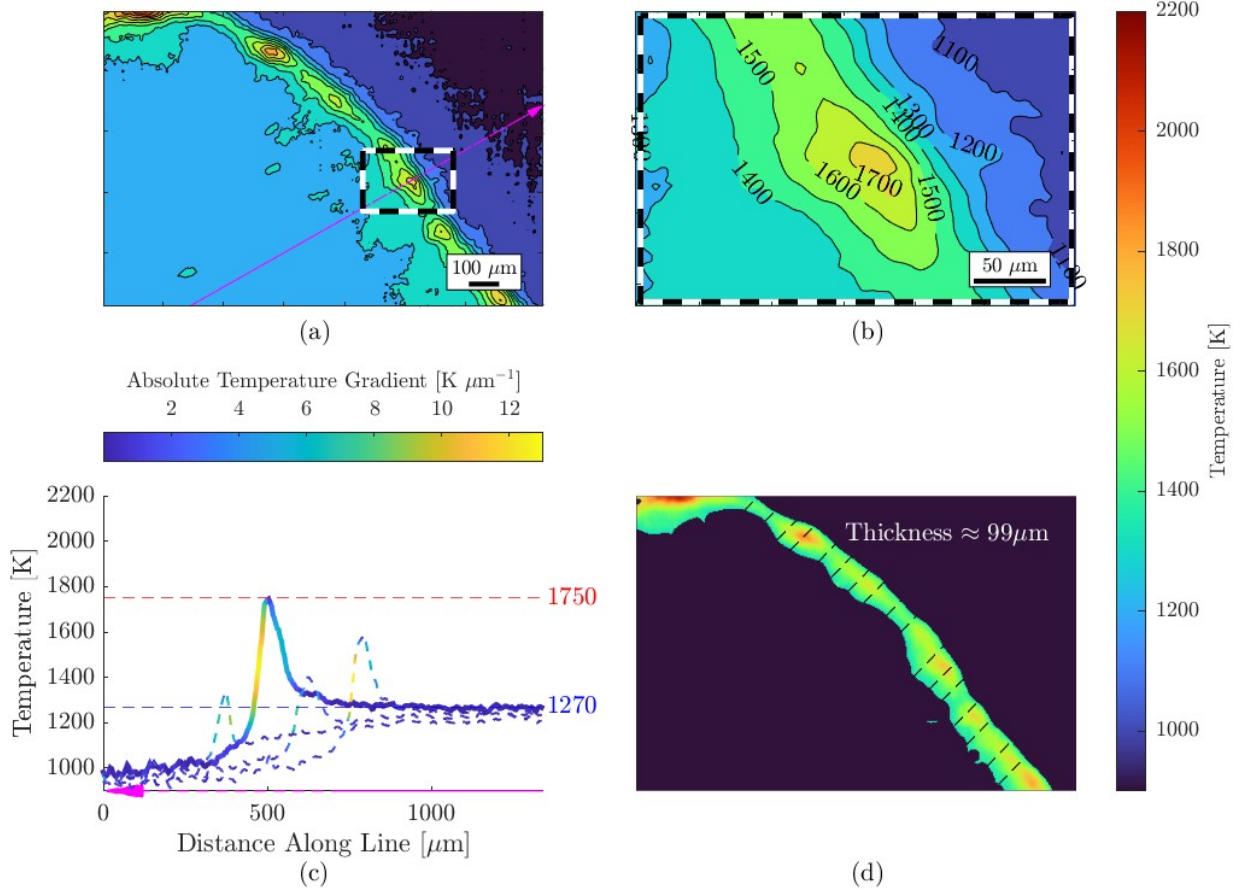


Figure 5.6: A closer look at one of the thermal images of the PM film (propagation direction indicated by magenta arrow): (a) the full-sized image, contoured at 200 K intervals; (b) contours zoomed into the 300 μm $\times$ 200 μm rectangle found in **a**; (c) temperature profile measured along the magenta arrow found in **a**; (d) Masked flame front displaying approximate thickness

apparent here that the hot regions appear to spread out and travel along the flame front itself, The contours illustrate the temperature “strata” that are formed along the flame front, which are reminiscent of a shock wave. Once more, this will be discussed in further detail in the next section.

With regards to the temperature profile of the [PM](#) sample, [Figure 5.5\(c\)](#) shows a sharp jump ($\frac{dT}{ds} \sim 25 \text{ K } \mu\text{m}^{-1}$) followed by a nearly equally sharp descent into the post-combustion space. The [CS](#) film's temperature profile also shows a jump ($\frac{dT}{ds} \sim 12 \text{ K } \mu\text{m}^{-1}$), but descends at a much lower rate ($\sim 7 \text{ K } \mu\text{m}^{-1}$). This seems to indicate that some of the combustion energy is remaining local to the reaction zone.

5.3 Particle Ejection

One interesting observation from the [PM](#) combustion is the size of the ejected particles, which was estimated to be at most $20 \mu\text{m}$, as can be seen in the [UHS](#) images in [Figure 5.7](#). This size is similar to the size of the hot spots, suggesting that the ejections are particles that have undergone reactive sintering and were subsequently ejected when the thermite reaction occurred and gas was generated.

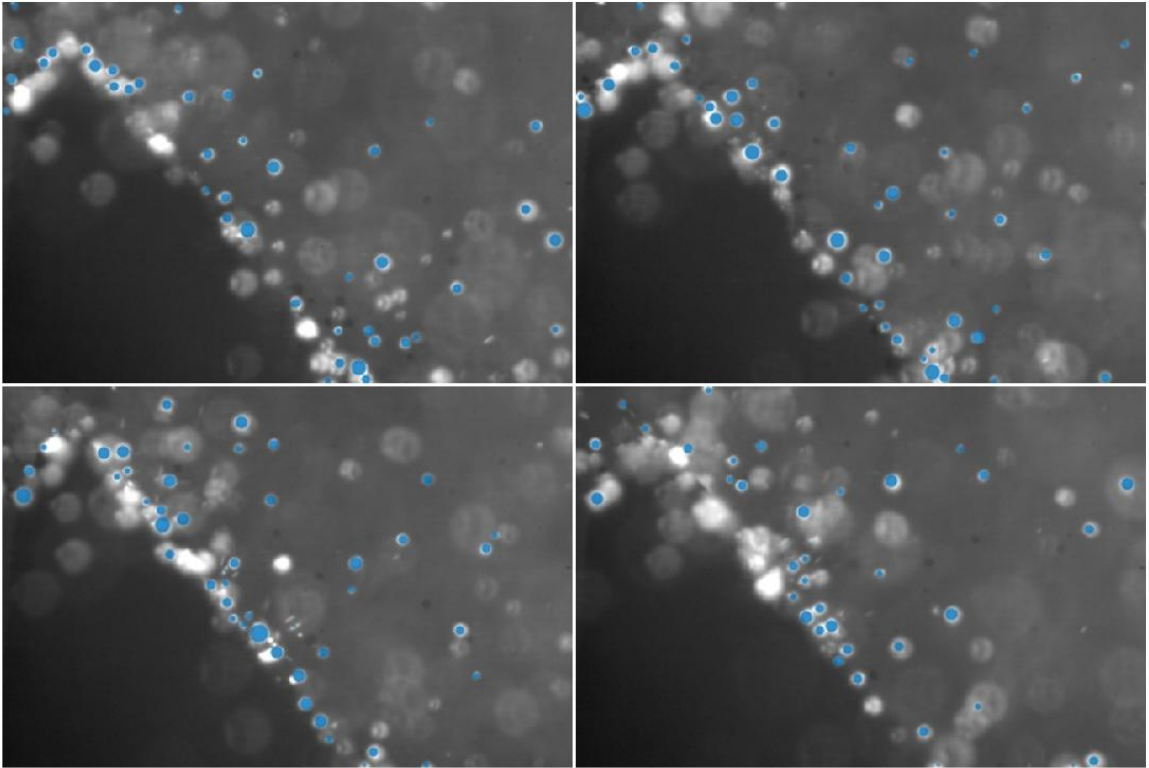


Figure 5.7: [PM](#) particle ejection

In contrast, the images for the [CS](#) sample can be seen in [Figure 5.8](#).

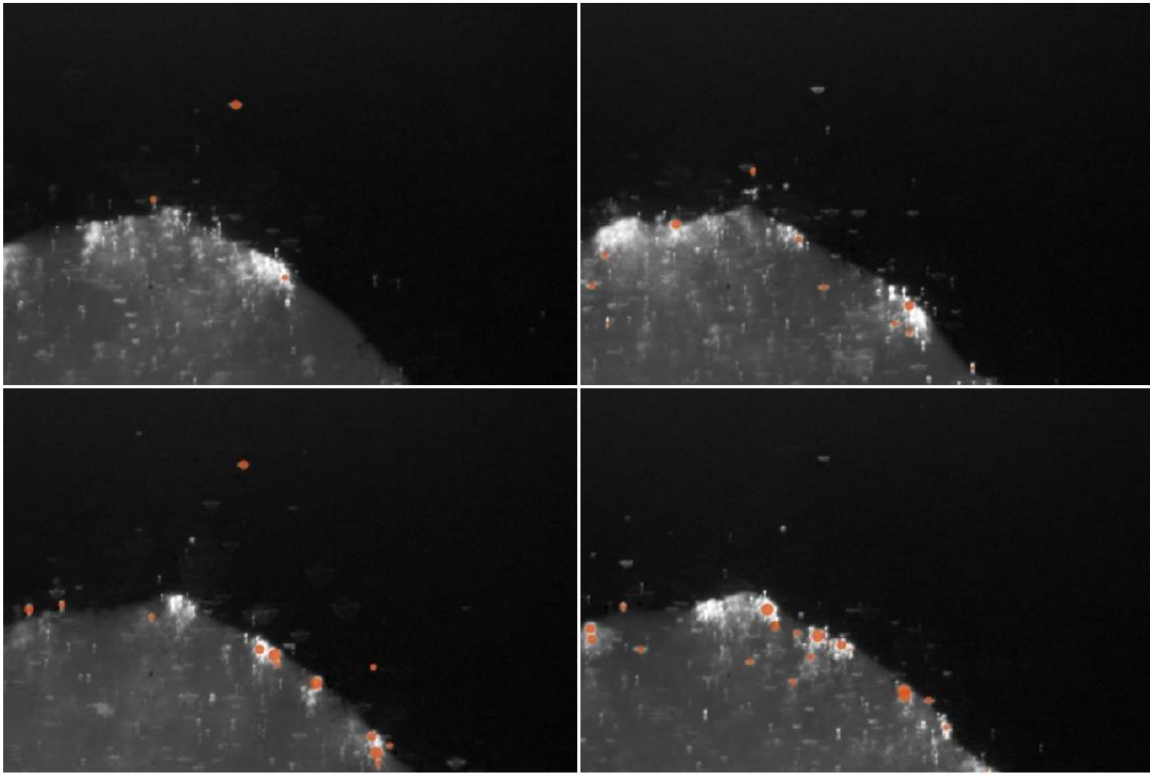


Figure 5.8: [CS](#) particle ejection

The major differences between the images seen here and in [Figure 5.7](#) are threefold:

- The particle ejection seen in the [CS](#) footage may more aptly be characterized as an “exhaust” rather than an “ejection” of aggregated particles as displayed by the [PM](#) film, resulting in the hotter post-combustion region of space seen in the previous section
- The combustion events seem to occur somewhat sequentially along the flame front, showing dark spots in areas where combustion is not occurring
- In the locations where the combustion is occurring (henceforth referred to as “reaction front”), the particles behave as if they were exploding, spraying out the exhausted particles

As was alluded to in previous sections, the driving force for the propagation of the flame

front appears to come from the “racing” of the reaction front up and down the edge of the film (the aforementioned tangential propagation). Analysis of the footage shows that the racing is too rapid to observe going from one end to the other. The edge of the film advances in every frame, implying that the reaction front is traveling at least the width of the film in one duration of the frame ($\gtrsim 100 \text{ m s}^{-1}$). These observations seem to corroborate the melt dispersion model, which is characterized by high velocity explosions and very fine particle sizes.

A note regarding the measured particle sizes: MATLAB has a limited ability to detect particles with diameters under $37.5 \text{ }\mu\text{m}$ (10 px), which renders measurements under approximately $8 \text{ }\mu\text{m}$ impossible (the size distribution histograms may be seen in [Appendix A](#)). Therefore, the median particle size gives an upper limit for the actual size of ejected particles. Nonetheless, the number of larger diameter particles in the footage (importantly, the lack thereof) indicates that the [CS](#) particles are generally much smaller than their [PM](#) counterparts in the vicinity of the flame front. Indeed, this is further evidenced by the SEM/EDS composite images seen in [Section 5.5](#) and will be discussed there in further detail.

5.4 Fuel-Rich Particles

Additional combustion events were recorded for samples with an [Equivalence Ratio \(ER\)](#) of $\phi = 2.5$ as this ratio was found to give the most significant energy release for both [PM](#) and [CS](#) structure samples [[65](#), [56](#)]. It is important to note that the size of the particles stayed relatively the same between the two ratios. As expected, the same aspects of combustion were seen in the fuel-rich particles as in the stoichiometric particles, just to greater extremes. For both cases, the local propagation speed was seen to faster than their stoichiometric counterparts, temperatures were greater (both at maximum and in the post-combustion spaces), while the shape of the flame front stayed relatively consistent. The most interesting deviations from their stoichiometric counterparts can be seen in the [SEM/EDS](#) analysis in the following section.

5.5 SEM/EDS Analysis

Analyzing the debris collected after a combustion event for both samples, the size of the cooled particles were found to be around 10 and 6 μm for the PM (Figure 5.9) and CS (Figure 5.10) particles, respectively.

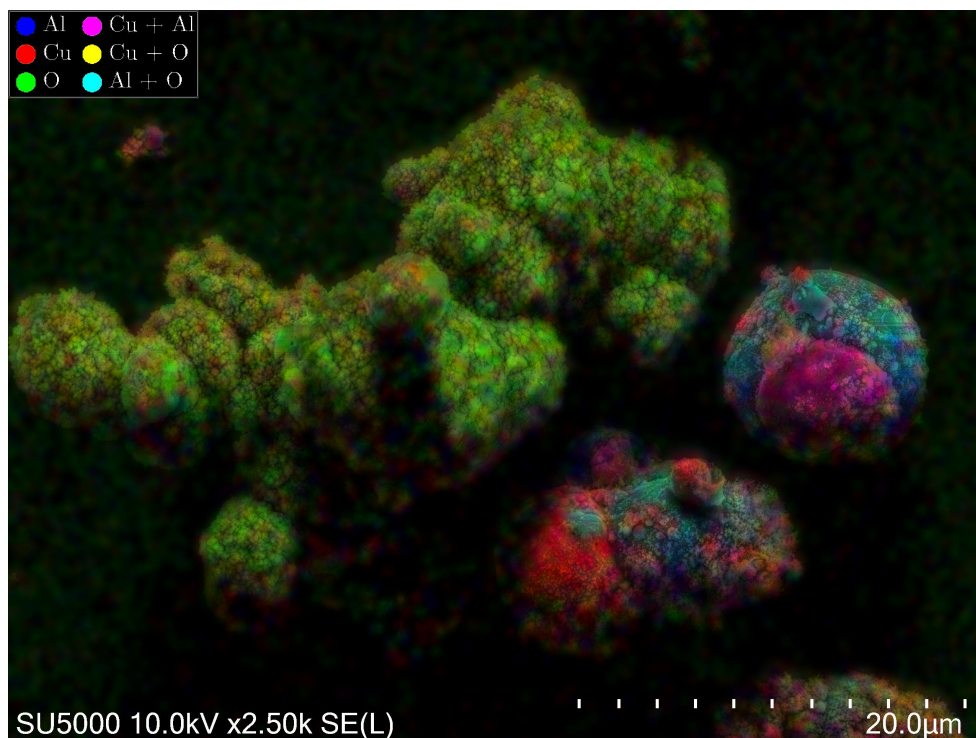


Figure 5.9: SEM/EDS composite images of post-combustion debris of PM particles. The large oxygen-rich structure in is presumed to be SiO_2 from the glass substrate used to collect the debris

Note that the color brightness shown in the image are a product of the processing algorithm and are not necessarily representative of anything. These composite images were generated by layering the elemental compositions (weight percentages) given by the EDS results into RGB channels (red = Cu, green = O, blue = Al) and merging it with an “edge-aware” Laplacian filter of the SEM image. Hence, the colors (hues) reveal the relative compositions of each element of interest at the surface of the particles. The legend makes additional note of binary overlaps between the three elements, indicating what the color would be if the weight percentages were equivalent between two elements. Noting this, it is clearly shown that the CS particles exhibit a high degree of combustion completeness,

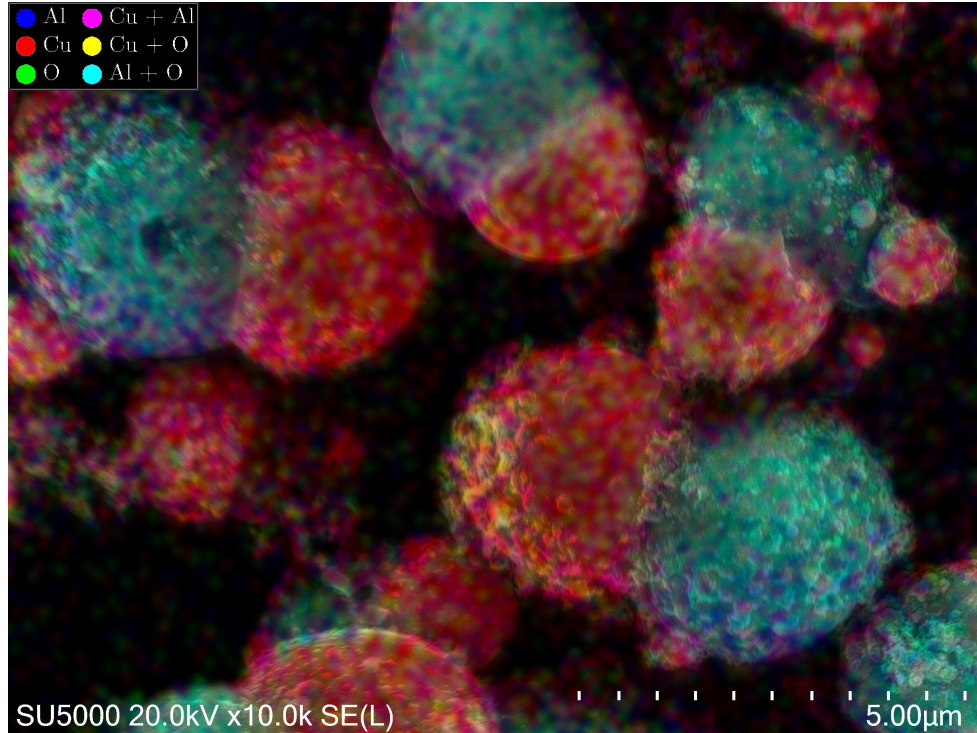


Figure 5.10: SEM/EDS composite images of post-combustion debris of [CS](#) particles

illustrated by the purity and phase separation of Cu and Al_xO_y . In contrast, the [PM](#) image shows a surprising level of alloying between Cu and Al as well as oxygen-rich regions of Al_xO_y —all within the same particle. Thus, it can be said that the [CS](#) particles not only combust faster than the [PM](#) particles, but combust more completely as well.

These observations suggest a few things for [CS](#) particles:

- The energy that would normally be carried away by large, ejected particles remains relatively local to the reaction zone
- The propagation speed is being enhanced by the heat contained in the exhaust
- The ejected particles have undergone a more complete combustion

This highlights the importance of optimizing the combustion process to ensure complete combustion.

With regards to the fuel-rich particles, the same SEM/EDS analysis as before is shown in [Figure 5.11](#) and [Figure 5.12](#). As indicated, both particles show greater degrees of phase

separation between Cu and Al_xO_y than their stoichiometric counterparts. The increased phase separation in the PM particles may be due to the presumed increase in the energy injected by reactive sintering, given the 2.5-fold increase in the amount of fuel particles.

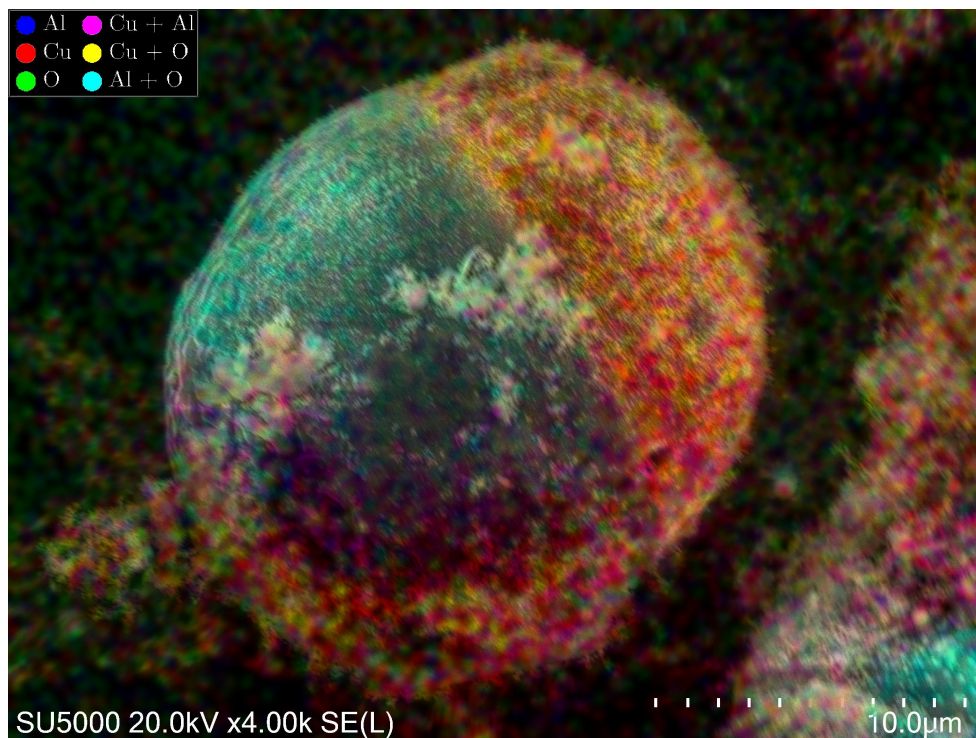


Figure 5.11: SEM/EDS composite images of post-combustion debris from fuel-rich PM particles

The high saturation (“bleached” coloration) seen in the PM particles indicate an overlap of the three elements (equal weight percentages would appear as monochrome). As such, it is shown that while the phase separation for both particles increases by increasing the amount of fuel, the CS particle combustion proves to be significantly more efficient. Interestingly, while the combustion efficiency increased for the PM particles, the post-combustion debris shows a twofold increase in the diameter to approximately $20\ \mu\text{m}$, which is even larger than the medians measured by MATLAB. This is presumed to be due to a kind of survivorship bias, in that one can expect that the subset of *collected* combusted particles would not contain the particles that were *distantly ejected*; i.e., the largest particles with the smallest ejection distance would make up the majority of the particles collected.

Perhaps unsurprisingly, the post-combustion CS particles shrunk by more than half

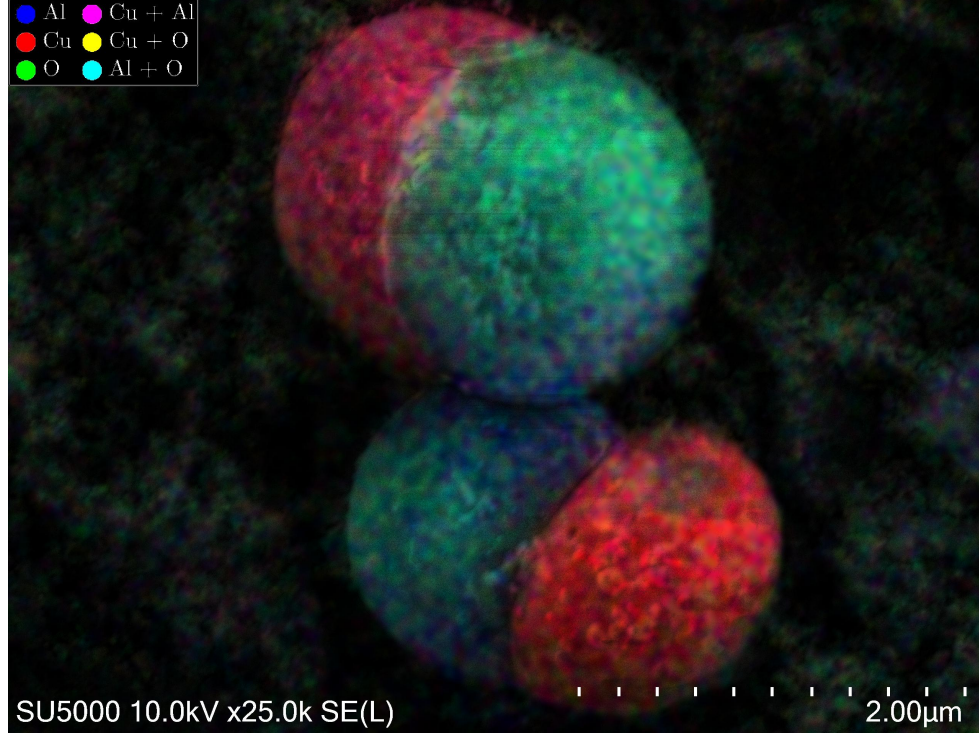


Figure 5.12: SEM/EDS composite images of post-combustion debris from fuel-rich [CS](#) particles

compared to their stoichiometric equivalents. However, the coloration seems to indicate a greater-than-stoichiometric level of oxidation of the Al, which is assumed to also be caused by the interaction with the oxygen in the air.

5.6 Discussion

In [Section 5.1](#), it was found that the [PM](#) sample showed an irregularity in the shape of the flame front caused by localized hot spots. Furthermore, the spacing of the contours seen in the [PM](#) velocity map show that the flame front actually oscillates between fast and slow propagation in some areas (small spacing to large spacing), which corroborates the heating/combustion/cooling cycle reported by Wang et al. [57], who also noted the appearance of “stochastic bright spots” with temperatures of over 3000 K. The temperature gradient we observed was also similar to what they found, both being around $30 \text{ K } \mu\text{m}^{-1}$. Additionally, the [SEM/EDS](#) composite image of the combusted [PM](#) debris showed a highly spherical morphology indicative of the reactive sintering mechanism [45]; not to mention

the discontinuous regions of Cu attached to the debris seen in both [PM](#) composite images, which are in agreement with the images presented by Wang et al. [57] However, the presence of alloyed Al/Cu and bleached coloration in the stoichiometric and fuel-rich samples, respectively, shows the relative inefficiency of the reaction. Further commenting on the hot spots seen at the flame front, the temperatures observed may be greater than even the T_{af} of the Al/CuO reaction. While this would not make sense in purely diffusion-controlled reaction, it would be possible under the reactive sintering mechanism, given that the sintering of Al would inject additional energy into the system. Since T_{af} is calculated from the thermochemical energy balance of the bulk reaction, it would indeed neglect the transfer of surface energy as the nanoparticles sinter together. It should also be noted that while the discussion of reactive sintering has been focused on the sintering of Al, the reactive sintering of CuO has also been observed by Sullivan et al. [45] at a temperature of 1250 K with a heating rate of 10^6 K s^{-1} , which could also have provided supplemental energy. Finally, it would be remiss to completely rule out the role of atmospheric oxygen in the reaction. While the exposure of Al to oxygen is expected to be limited due to the packing of the particles, the T_{af} of the Al/O reaction has been noted to be as high as 4000 K [47].

In contrast to the [PM](#) sample, the [CS](#) sample displayed high uniformity in not only the shape of the flame front and distribution of heat but the spacing of the velocity map contours as well. Hot spots are generally unseen on the flame front, the temperatures seem to be well under T_{af} , and the reaction does not appear to undergo a heating/combustion/cooling cycle as noted by both Wang et al. [57] and Kim et al. [23]. Thus it may be inferred that reactive sintering is not a dominant reaction mechanism for the [CS](#) sample. The temperature profile also showed a relatively small temperature gradient leading up to the flame front ($\sim 12 \text{ K } \mu\text{m}^{-1}$) and an even smaller gradient after the flame front passes ($\sim 7 \text{ K } \mu\text{m}^{-1}$). This fact coupled with the uniformly-shaped temperature banding seen in the temperature map and a slightly larger conduction distance and flame front thickness indicate that the [CS](#) film exhibited greater heat conduction. While Kline et al. [24] noted a similar effect, in that higher thermal conduction is linked to a more homogeneous thermal profile and flame front, they also found that in their case, this actually caused a slowing of the propagation rate, rather than the acceleration that is seen

here. With regards to the SEM/EDS composite image of the CS debris, it was seen that the particles also showed a spherical morphology, with the added observation that the Cu was found to be highly spherical as well. This comes as no surprise since the flame front temperatures were seen to reach the melting temperature of Cu (1358 K). Given the purity of the Cu seen in the image, it makes sense that it would be able to melt to form a sphere just like the Al_2O_3 . A similar morphology was seen in Figure 2.4 from the observations of Egan et al. [10], who attributed it to reactive sintering. However, it is still unclear how the combusted debris grew to be 20–50 times the original size of the original particles if reactive sintering had a limited role in its combustion. While the melt dispersion model does not indicate what the post-combustion particles should look like, the reaction products seen in the CS composite images may provide further evidence of it. It is hypothesized that the following events occurred:

1. In the reaction front, the CS particle explodes and ternary Al/ Al_2O_3 /CuO particles are ejected. The explosion of particles was seen in the particle ejection images in Section 5.3
2. As the ternary particles travel, the thermite reaction occurs and oxygen diffuses from the CuO side to the Al side. The speed of the chain reaction at the reaction front was estimated to be $\gtrsim 100 \text{ m s}^{-1}$, which is in agreement with what Levitas et al. [27] estimated. Additionally, this could explain why temperatures near T_{af} were not seen along the flame front—because the thermite reaction occurred *after* the particles had been ejection/spallated
3. Additionally, as the particles travel, they may collect mass either by sintering, condensation, or collisions with other particles
4. Phase separation of Al_2O_3 and Cu causes the distinct hemispherical sides seen in the composite images

A diagram of the hypothesized model is seen in Figure 5.13

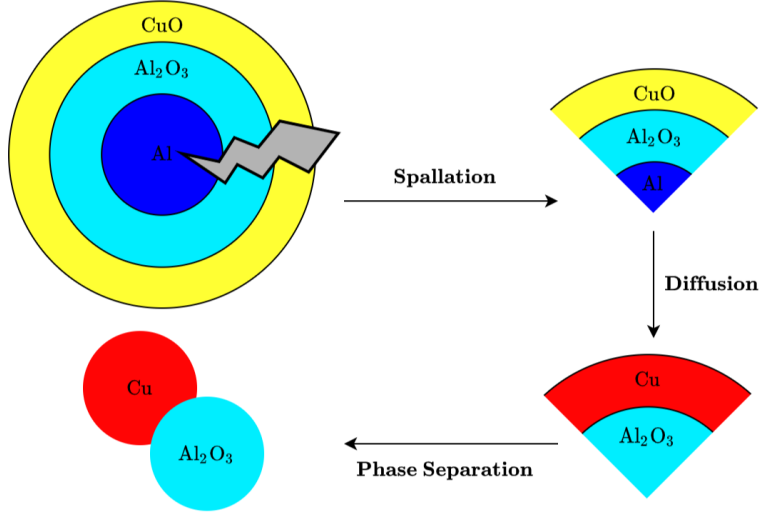


Figure 5.13: Proposed melt dispersion model for CS particles: 1) Particle undergoes spallation and forms ternary Al/Al₂O₃/CuO particles; 2) Ternary particles inter-diffuse and form the binary Al₂O₃/Cu particle; 3) Phase separation of Al₂O₃ and Cu

In this model, the very smallest of the particles are unable to be collected, but the ones that are analyzed are still about 50 times larger than they were originally, as compared to the three orders of magnitude increase reported by Wang et al. [57]. With regards to the fuel-rich particles, the size increase was even smaller at about a 20-fold increase. Since increasing the amount of fuel also increases the thickness of the outer shells (decreasing $M = \frac{R}{\delta}$, from [27]), it is reasonable that the ejection speed also increases in proportion to the pressure gain that this would cause. Thus, the particles have less time to accumulate mass as it travels. Under these circumstances, it seems plausible that the melt dispersion mechanism has been observed in the combustion of the CS particles.

Chapter 6

Conclusion

MICs are a relatively new, exciting topic of research that follows the modern trend of taking a well-explored technology and miniaturizing it. This change of scale comes with additional hardships—observation and analysis techniques have yet to fully catch up with the technology, leaving researchers burdened with questions that cannot yet be robustly answered. Using high-speed cameras, ratio pyrometry is one of the ways in which combustion reactions may be observed thermographically at both the spatial and temporal micro-scale.

In this work, the design for a ratio pyrometry setup was presented along with the theory behind it and its operating procedure. Additionally, an in-depth thermographic analysis of the combustion of both Physically-Mixed (PM) and Core-Shell (CS) Al/CuO nanothermites is reported. Samples mixed with 10% polymer were formed into 25- μ m-thin sheets and ignited with a fuse wire. Observations were made involving the reaction pathways of MICs and crucial reaction parameters, such as propagation rate, peak temperature, and thermal gradient were investigated to understand them. Table 6.1 summarizes the overarching observations made between the two sample types.

It was found that the while the PM film burned at much higher temperatures than the CS film did—with over double the maximum temperature gradient—the CS film burned at about 1.4 times the rate of the PM film. SEM/EDS analysis showed that the post-combustion CS debris was about half the size of and displayed a greater degree of combus-

	Physically-Mixed	Core-Shell
Max T [K]	3405	2156
Max T Grad. [K μm^{-1}]	105	55
Bulk / Mean Speed [cm s $^{-1}$]	3.97 / 7.44	5.44 / 10.80
Particle Ejection	Large, ongoing combustion	Exhaust-like, explosive

Table 6.1: Summary of results for entire dataset

tion completeness than did the [PM](#) debris.

It has been hypothesized that the reaction mechanism for the [PM](#) structured Al/CuO sample is reactive sintering-dominated, leading to the formation of local hot spots across the flame front. Conversely, it is believed that the combustion behavior of the [CS](#) sample is characteristic of the theorized melt dispersion mechanism. A model for the melt dispersion mechanism is hypothesized for [CS](#) nanothermites that may apply for other ordered-structure [MICs](#) as well.

6.1 Recommendation for Future Work

To better our understanding of the reaction pathways of [MICs](#), it is suggested that the combustion using other ordered-structures, such as [3DOM](#) structures, be investigated as well. In addition, it is proposed that a nanosecond or faster laser be used in conjunction with ordered-structure [MICs](#) to combust particles at high heating rates in order to further explore the theorized melt dispersion mechanism. While utilization of a nanosecond laser was demonstrated with [PM](#) nanoparticles by Egan et al. [10], it has yet to be seen in an environment where reactive sintering may play a limited role in the reaction. Such experiments are recommended to be performed in an inert environment to rule out the participation of atmospheric oxygen in any of the reactions. Finally, particle ejection velocities may be measured at the flame front in order to consider all of the energy leaving the system during combustion.

References

- [1] C. E. Aumann. Oxidation behavior of aluminum nanopowders. *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures*, 13(3):1178, May 1995. doi:[10.1116/1.588232](https://doi.org/10.1116/1.588232).
- [2] Shantanu Bhattacharya, Avinash K. Agarwal, Thiruvengadathan Rajagopalan, and Vinay K. Patel. *Nano-Energetic Materials*. Energy, Environment, and Sustainability. Springer, Singapore, 2019. doi:[10.1007/978-981-13-3269-2](https://doi.org/10.1007/978-981-13-3269-2).
- [3] Carlos D. S. Brites, Patricia P. Lima, Nuno J. O. Silva, Angel Millán, Vitor S. Amaral, Fernando Palacio, and Luís D. Carlos. Thermometry at the nanoscale. *Nanoscale*, 4(16):4799, 2012. doi:[10.1039/c2nr30663h](https://doi.org/10.1039/c2nr30663h).
- [4] P. Chakraborty and M. R. Zachariah. Do nanoenergetic particles remain nano-sized during combustion? *Combustion and Flame*, 161(5):1408–1416, 2014. doi:[10.1016/j.combustflame.2013.10.017](https://doi.org/10.1016/j.combustflame.2013.10.017).
- [5] Kesiany M. de Souza and Marcelo J. S. de Lemos. Detailed numerical modeling and simulation of fe₂o₃-al thermite reaction. *Propellants, Explosives, Pyrotechnics*, 46(5):806–824, 2021. doi:[10.1002/prop.202000290](https://doi.org/10.1002/prop.202000290).
- [6] Sili Deng, Yue Jiang, Sidi Huang, Xinjian Shi, Jiheng Zhao, and Xiaolin Zheng. Tuning the morphological, ignition and combustion properties of micron-al/cuo thermites through different synthesis approaches. *Combustion and Flame*, 195:303–310, 2018. doi:[10.1016/j.combustflame.2018.04.028](https://doi.org/10.1016/j.combustflame.2018.04.028).

- [7] John M. Densmore, Barrie E. Homan, Matthew M. Biss, and Kevin L. McNesby. High-speed two-camera imaging pyrometer for mapping fireball temperatures. *Applied Optics*, 50(33):6267, November 2011. [doi:10.1364/AO.50.006267](https://doi.org/10.1364/AO.50.006267).
- [8] David M. B. Dombroski, Anqi Wang, John Z. Wen, and Marco Alfano. Joining and welding with a nanothermite and exothermic bonding using reactive multi-nanolayers – a review. *Journal of Manufacturing Processes*, 75:280–300, 2022. [doi:10.1016/j.jmapro.2021.12.056](https://doi.org/10.1016/j.jmapro.2021.12.056).
- [9] L. Jonathan Dowell. Fluorescence Thermometry. *Applied Mechanics Reviews*, 45(7):253–260, July 1992. [doi:10.1115/1.3119756](https://doi.org/10.1115/1.3119756).
- [10] G. C. Egan, T. LaGrange, and M. R. Zachariah. Time-resolved nanosecond imaging of nanoscale condensed phase reaction. *Journal of Physical Chemistry C*, 119(5):2792–2797, 2015. [doi:10.1021/jp5084746](https://doi.org/10.1021/jp5084746).
- [11] Garth C. Egan and Michael R. Zachariah. Commentary on the heat transfer mechanisms controlling propagation in nanothermites. *Combustion and Flame*, 162(7):2959–2961, 2015. [doi:10.1016/j.combustflame.2015.04.013](https://doi.org/10.1016/j.combustflame.2015.04.013).
- [12] Joseph Mark Epps, Jean-Pierre Hickey, and John Z. Wen. Modelling reaction propagation for al/cuo nanothermite pellet combustion. *Combustion and Flame*, 229:111374, 2021. [doi:10.1016/j.combustflame.2021.02.020](https://doi.org/10.1016/j.combustflame.2021.02.020).
- [13] Ahmed Fahd, Alex Baranovsky, Charles Dubois, Jamal Chaouki, and John Z. Wen. Superior performance of quaternary nc/go/al/kclo4 nanothermite for high speed impulse small-scale propulsion applications. *Combustion and Flame*, 232:111527, 2021. [doi:10.1016/j.combustflame.2021.111527](https://doi.org/10.1016/j.combustflame.2021.111527).
- [14] S.H. Fischer and M.C. Grubelich. Theoretical energy release of thermites, intermetallics, and combustible metals. Technical Report SAND–98-1176C, CONF-980728–, 658208, Sandia National Laboratory, June 1998. [doi:10.2172/658208](https://doi.org/10.2172/658208).
- [15] Jing Gao, Jingyuan Yan, Beikai Zhao, Ze Zhang, and Qian Yu. In situ observation of temperature-dependent atomistic and mesoscale oxidation mechanisms of

- aluminum nanoparticles. *Nano Research*, 13(1):183–187, 2020. doi:[10.1007/s12274-019-2593-3](https://doi.org/10.1007/s12274-019-2593-3).
- [16] Ludovic Glavier, Guillaume Taton, Jean-Marie Duc  r  , Vincent Baijot, St  phane Pinon, Theo Calais, Alain Est  ve, Mehdi Djafari Rouhani, and Carole Rossi. Nanoenergetics as pressure generator for nontoxic impact primers: Comparison of al/bi₂o₃, al/cuo, al/moo₃ nanothermites and al/ptfe. *Combustion and Flame*, 162(5):1813–1820, 2015. doi:[10.1016/j.combustflame.2014.12.002](https://doi.org/10.1016/j.combustflame.2014.12.002).
- [17] Jennifer L. Gottfried, Dylan K. Smith, Chi-Chin Wu, and Michelle L. Pantoya. Improving the explosive performance of aluminum nanoparticles with aluminum iodate hexahydrate (aih). *Scientific Reports*, 8(1):8036, 2018. doi:[10.1038/s41598-018-26390-9](https://doi.org/10.1038/s41598-018-26390-9).
- [18] Travis Goulette, Charles D. Howard, and Michael W. Davidson. Infinity Optical Systems. URL: <https://www.microscopyu.com/microscopy-basics/infinity-optical-systems>.
- [19] Mitio Inokuti and Fumio Hirayama. Influence of Energy Transfer by the Exchange Mechanism on Donor Luminescence. *The Journal of Chemical Physics*, 43(6):1978–1989, September 1965. doi:[10.1063/1.1697063](https://doi.org/10.1063/1.1697063).
- [20] R. J. Jacob, G. Q. Jian, P. M. Guerieri, and M. R. Zachariah. Energy release pathways in nanothermites follow through the condensed state. *Combustion and Flame*, 162(1):258–264, 2015. doi:[10.1016/j.combustflame.2014.07.002](https://doi.org/10.1016/j.combustflame.2014.07.002).
- [21] G. Q. Jian, S. Chowdhury, K. Sullivan, and M. R. Zachariah. Nanothermite reactions: Is gas phase oxygen generation from the oxygen carrier an essential prerequisite to ignition? *Combustion and Flame*, 160(2):432–437, 2013. doi:[10.1016/j.combustflame.2012.09.009](https://doi.org/10.1016/j.combustflame.2012.09.009).
- [22] Boris Khasainov, Marc Comet, Bernard Veyssiere, and Denis Spitzer. Comparison of Performance of Fast-Reacting Nanothermites and Primary Explosives. *Propel-*

- lants, Explosives, Pyrotechnics*, 42(7):754–772, July 2017. doi:[10.1002/prop.201600181](https://doi.org/10.1002/prop.201600181).
- [23] Suyong Kim, Averitt A. Johns, John Z. Wen, and Sili Deng. Burning structures and propagation mechanisms of nanothermites. *Proceedings of the Combustion Institute*, 39(3):3593–3604, 2023. doi:[10.1016/j.proci.2022.07.113](https://doi.org/10.1016/j.proci.2022.07.113).
- [24] Dylan J. Kline, Miles C. Rehwoldt, Haiyang Wang, Noah E. Eckman, and Michael R. Zachariah. Why does adding a poor thermal conductor increase propagation rate in solid propellants? *Applied Physics Letters*, 115(11):114101, September 2019. doi:[10.1063/1.5113612](https://doi.org/10.1063/1.5113612).
- [25] V Levitas. Burn time of aluminum nanoparticles: Strong effect of the heating rate and melt-dispersion mechanism. *Combustion and Flame*, 156(2):543–546, 2009. URL: <https://linkinghub.elsevier.com/retrieve/pii/S001021800800360X>, doi:[10.1016/j.combustflame.2008.11.006](https://doi.org/10.1016/j.combustflame.2008.11.006).
- [26] Valery I. Levitas, Blaine W. Asay, Steven F. Son, and Michelle Pantoya. Melt dispersion mechanism for fast reaction of nanothermites. *Applied Physics Letters*, 89(7):071909, 2006. doi:[10.1063/1.2335362](https://doi.org/10.1063/1.2335362).
- [27] Valery I. Levitas, Michelle L. Pantoya, and Birce Dikici. Melt dispersion versus diffusive oxidation mechanism for aluminum nanoparticles: Critical experiments and controlling parameters. *Applied Physics Letters*, 92(1):011921, 2008. doi:[10.1063/1.2824392](https://doi.org/10.1063/1.2824392).
- [28] Zhichao Liu and John Z. Wen. Role of redox reactions involving interfacial oxygen migration in ignition of nanolayered al/a-al₂ox/cuo energetic composite. *Chemical Engineering Journal Advances*, 11:100322, 2022. doi:[10.1016/j.cej.2022.100322](https://doi.org/10.1016/j.cej.2022.100322).
- [29] Patrick Llull, Xuejun Liao, Xin Yuan, Jianbo Yang, David Kittle, Lawrence Carin, Guillermo Sapiro, and David J. Brady. Coded aperture compressive temporal imaging. *Optics Express*, 21(9):10526, May 2013. doi:[10.1364/OE.21.010526](https://doi.org/10.1364/OE.21.010526).

- [30] Karen S. Martirosyan, Maxim Zyskin, Charles M. Jenkins, and Yasuyuki Horie. Fluid dynamic modeling of nano-thermite reactions. *Journal of Applied Physics*, 115(10), 2014. doi:[10.1063/1.4867936](https://doi.org/10.1063/1.4867936).
- [31] Kevin McNesby, Steven Dean, Richard Benjamin, Jesse Grant, James Anderson, and John Densmore. Imaging pyrometry for most color cameras using a triple pass filter. *Review of Scientific Instruments*, 92(6):063102, June 2021. doi:[10.1063/5.0037230](https://doi.org/10.1063/5.0037230).
- [32] K. A. Monogarov, D. B. Meerov, Yu V. Frolov, and A. N. Pivkina. Combustion features of nanothermites in pyrotechnic heaters. *Russian Journal of Physical Chemistry B*, 13(4):610–614, 2019. doi:[10.1134/S1990793119040250](https://doi.org/10.1134/S1990793119040250).
- [33] Nikita V. Muravyev, Konstantin A. Monogarov, Uwe Schaller, Igor V. Fomenkov, and Alla N. Pivkina. Progress in additive manufacturing of energetic materials: Creating the reactive microstructures with high potential of applications. *Propellants, Explosives, Pyrotechnics*, 44(8):941–969, 2019. doi:[10.1002/prop.201900060](https://doi.org/10.1002/prop.201900060).
- [34] Eric Nixon, Michelle Pantoya, and Daniel Prentice. Quantification of Heat Flux From a Reacting Thermite Spray. In *Volume 3: Combustion, Fire and Reacting Flow; Heat Transfer in Multiphase Systems; Heat Transfer in Transport Phenomena in Manufacturing and Materials Processing; Heat and Mass Transfer in Biotechnology; Low Temperature Heat Transfer; Environmental Heat Transfer; Heat Transfer Education; Visualization of Heat Transfer*, pages 73–80, San Francisco, California, USA, January 2009. ASMEDC. doi:[10.1115/HT2009-88219](https://doi.org/10.1115/HT2009-88219).
- [35] Kok S. Ong, Liben Jiang, and Koon C. Lai. 4.20 Thermoelectric Energy Conversion. In *Comprehensive Energy Systems*, pages 794–815. Elsevier, 2018. doi:[10.1016/B978-0-12-809597-3.00433-8](https://doi.org/10.1016/B978-0-12-809597-3.00433-8).
- [36] N. W. Piekiel, K. T. Sullivan, S. Chowdhury, and M. R. Zachariah. The role of metal oxides in nanothermite reactions: Evidence of condensed phase initiation. *DEFENSE TECHNICAL INFORMATION CENTER*, 2016.

- [37] C. Rossi, K. Zhang, D. Esteve, P. Alphonse, P. Tailhades, and C. Vahlas. Nanoenergetic materials for mems: A review. *Journal of Microelectromechanical Systems*, 16(4):919–931, 2007. doi:[10.1109/jmems.2007.893519](https://doi.org/10.1109/jmems.2007.893519).
- [38] Carole Rossi. Engineering of al/cuo reactive multilayer thin films for tunable initiation and actuation. *Propellants, Explosives, Pyrotechnics*, 44(1):94–108, 2019. doi:[10.1002/prop.201800045](https://doi.org/10.1002/prop.201800045).
- [39] Sergio Rossi, Edward L Dreizin, and Chung K. Law. Combustion of Aluminum Particles in Carbon Dioxide. *Combustion Science and Technology*, 164(1):209–237, March 2001. doi:[10.1080/00102200108952170](https://doi.org/10.1080/00102200108952170).
- [40] Morgan D. Ruesch, Austin J. McDonald, Garrett C. Mathews, Steven F. Son, and Christopher S. Goldenstein. Characterization of the influence of aluminum particle size on the temperature of composite-propellant flames using CO absorption and AlO emission spectroscopy. *Proceedings of the Combustion Institute*, 38(3):4365–4372, 2021. doi:[10.1016/j.proci.2020.06.163](https://doi.org/10.1016/j.proci.2020.06.163).
- [41] Florin Saceleanu, Mahmoud Idir, Nabiha Chaumeix, and John Z. Wen. Combustion characteristics of physically mixed 40 nm aluminum/copper oxide nanothermites using laser ignition. *Frontiers in Chemistry*, 6, 2018. doi:[10.3389/fchem.2018.00465](https://doi.org/10.3389/fchem.2018.00465).
- [42] Ali Sheikhpour, Seyed Ghorban Hosseini, Saeed Tavangar, and Mohammad Hossein Keshavarz. The influence of magnesium powder on the thermal behavior of al–cuo thermite mixture. *Journal of Thermal Analysis and Calorimetry*, 129(3):1847–1854, 2017. doi:[10.1007/s10973-017-6343-z](https://doi.org/10.1007/s10973-017-6343-z).
- [43] Shawn C. Stacy, Xin Zhang, Michelle Pantoya, and Brandon Weeks. The effects of density on thermal conductivity and absorption coefficient for consolidated aluminum nanoparticles. *International Journal of Heat and Mass Transfer*, 73:595–599, 2014. doi:[10.1016/j.ijheatmasstransfer.2014.02.050](https://doi.org/10.1016/j.ijheatmasstransfer.2014.02.050).

- [44] Clay S. Staley, Kristofer E. Raymond, Rajagopalan Thiruvengadathan, Steven J. Apperson, Keshab Gangopadhyay, Sean M. Swaszek, Robert J. Taylor, and Shubhra Gangopadhyay. Fast-impulse nanothermite solid-propellant miniaturized thrusters. *Journal of Propulsion and Power*, 29(6):1400–1409, 2013. doi:[10.2514/1.B34962](https://doi.org/10.2514/1.B34962).
- [45] K. T. Sullivan, N. W. Piekiet, C. Wu, S. Chowdhury, S. T. Kelly, T. C. Hufnagel, K. Fezzaa, and M. R. Zachariah. Reactive sintering: An important component in the combustion of nanocomposite thermites. *Combustion and Flame*, 159(1):2–15, 2012. doi:[10.1016/j.combustflame.2011.07.015](https://doi.org/10.1016/j.combustflame.2011.07.015).
- [46] Kyle T. Sullivan, Cheng Zhu, Eric B. Duoss, Alexander E. Gash, David B. Kolesky, Joshua D. Kuntz, Jennifer A. Lewis, and Christopher M. Spadaccini. Controlling material reactivity using architecture. *Advanced Materials*, 28(10):1934–1939, 2016. doi:[10.1002/adma.201504286](https://doi.org/10.1002/adma.201504286).
- [47] D. S. Sundaram, V. Yang, and V. E. Zarko. Combustion of nano aluminum particles (Review). *Combustion, Explosion, and Shock Waves*, 51(2):173–196, March 2015. doi:[10.1134/S0010508215020045](https://doi.org/10.1134/S0010508215020045).
- [48] Dilip Srinivas Sundaram, Puneesh Puri, and Vigor Yang. A general theory of ignition and combustion of nano- and micron-sized aluminum particles. *Combustion and Flame*, 169:94–109, 2016. doi:<https://doi.org/10.1016/j.combustflame.2016.04.005>.
- [49] Cui-Ming Tang, Xiao-Xu Chen, Xin-Lu Cheng, Chao-Yang Zhang, and Zhi-Peng Lu. Ab initio molecular dynamics study of thermite reaction at al and cuo nano-interfaces at different temperatures. *Chemical physics letters*, 699:171–181, 2018. doi:[10.1016/j.cplett.2018.03.047](https://doi.org/10.1016/j.cplett.2018.03.047).
- [50] Tec Science. Planck’s law and Wien’s displacement law, March 2022. URL: <https://www.tec-science.com/thermodynamics/temperature/plancks-law-of-blackbody-radiation/>.

- [51] Emelian Tichtchenko, Alain Estève, and Carole Rossi. Modeling the self-propagation reaction in heterogeneous and dense media: Application to al/cuo thermite. *Combustion and Flame*, 228:173–183, 2021. [doi:10.1016/j.combustflame.2021.01.040](https://doi.org/10.1016/j.combustflame.2021.01.040).
- [52] M. A. Trunov, M. Schoenitz, and E. L. Dreizin. Effect of polymorphic phase transformations in alumina layer on ignition of aluminium particles. *Combustion Theory and Modelling*, 10(4):603–623, August 2006. [doi:10.1080/13647830600578506](https://doi.org/10.1080/13647830600578506).
- [53] Dieter Vollath, Franz Dieter Fischer, and David Holec. Surface energy of nanoparticles – influence of particle size and structure. *Beilstein Journal of Nanotechnology*, 9:2265–2276, August 2018. [doi:10.3762/bjnano.9.211](https://doi.org/10.3762/bjnano.9.211).
- [54] Anqi Wang, Sangho Bok, Cherian Joseph Mathai, Rajagopalan Thiruvengadathan, Charles M. Darr, H. Chen, Michael R. Zachariah, Keshab Gangopadhyay, Jacob A. McFarland, Matthew R. Maschmann, and Shubhra Gangopadhyay. Synthesis, characterization and nanoenergetic utilizations of fluorine, oxygen co-functionalized graphene by one-step xef2 exposure. *Combustion and Flame*, 215:324–332, 2020. [doi:10.1016/j.combustflame.2020.02.005](https://doi.org/10.1016/j.combustflame.2020.02.005).
- [55] Anqi Wang, Sangho Bok, Rajagopalan Thiruvengadathan, Keshab Gangopadhyay, Jacob A. McFarland, Matthew R. Maschmann, and Shubhra Gangopadhyay. Reactive nanoenergetic graphene aerogel synthesized by one-step chemical reduction. *Combustion and Flame*, 196:400–406, 2018. [doi:10.1016/j.combustflame.2018.06.034](https://doi.org/10.1016/j.combustflame.2018.06.034).
- [56] Anqi Wang, Shina Maini, Jean-Pierre Hickey, and John Z. Wen. Solution synthesis of core-shell n-al@cuo based on electrostatic self-assembly for enhanced energetic performance. *Chemical Engineering Journal Advances*, 11:100323, 2022. [doi:10.1016/j.cej.2022.100323](https://doi.org/10.1016/j.cej.2022.100323).
- [57] Haiyang Wang, Dylan J. Kline, and Michael R. Zachariah. In-operando high-speed microscopy and thermometry of reaction propagation and sintering in a

- nanocomposite. *Nature Communications*, 10(1):3032, 2019. doi:[10.1038/s41467-019-10843-4](https://doi.org/10.1038/s41467-019-10843-4).
- [58] M. R. Weismiller, J. G. Lee, and R. A. Yetter. Temperature measurements of al containing nano-thermite reactions using multi-wavelength pyrometry. *Proceedings of the Combustion Institute*, 33(2):1933–1940, 2011. doi:[10.1016/j.proci.2010.06.094](https://doi.org/10.1016/j.proci.2010.06.094).
- [59] Connor Woodruff, Steven W. Dean, and Michelle L. Pantoya. Comparison of pyrometry and thermography for thermal analysis of thermite reactions. *Applied Optics*, 60(16):4976–4985, 2021. doi:[10.1364/AO.423924](https://doi.org/10.1364/AO.423924).
- [60] Naadaa Zakiyyan, Charles M. Darr, Biyan Chen, Cherian Mathai, Keshab Gangopadhyay, Jacob McFarland, Shubhra Gangopadhyay, and Matthew R. Maschmann. Surface Plasmon Enhanced Fluorescence Temperature Mapping of Aluminum Nanoparticle Heated by Laser. *Sensors*, 21(5):1585, February 2021. doi:[10.3390/s21051585](https://doi.org/10.3390/s21051585).
- [61] Naadaa Zakiyyan, Cherian Mathai, Jacob McFarland, Shubhra Gangopadhyay, and Matthew R. Maschmann. Spallation of isolated aluminum nanoparticles by rapid photothermal heating. *ACS Applied Materials & Interfaces*, 14(49):55277–55284, 2022. doi:[10.1021/acsami.2c18678](https://doi.org/10.1021/acsami.2c18678).
- [62] Naadaa Zakiyyan, Anqi Wang, Rajagopalan Thiruvengadathan, Clay Staley, Joseph Mathai, Keshab Gangopadhyay, Matthew R. Maschmann, and Shubhra Gangopadhyay. Combustion of aluminum nanoparticles and exfoliated 2d molybdenum trioxide composites. *Combustion and Flame*, 187:1–10, 2018. doi:[10.1016/j.combustflame.2017.08.027](https://doi.org/10.1016/j.combustflame.2017.08.027).
- [63] James Zapata, Andrea Nicollet, Baptiste Julien, Guillaume Lahiner, Alain Esteve, and Carole Rossi. Self-propagating combustion of sputter-deposited Al/CuO nanolaminates. *Combustion and Flame*, 205:389–396, July 2019. doi:[10.1016/j.combustflame.2019.04.031](https://doi.org/10.1016/j.combustflame.2019.04.031).

- [64] T. F. Zhang, Z. Wang, G. P. Li, and Y. J. Luo. Tuning the reactivity of al/fe₂o₃ nanoenergetic materials via an approach combining soft template self-assembly with sol-gel process process. *Journal of Solid State Chemistry*, 230:1–7, 2015. doi:[10.1016/j.jssc.2015.06.021](https://doi.org/10.1016/j.jssc.2015.06.021).
- [65] Yiqi Zhang, Hongtao Sui, Yuning Li, and John Z. Wen. Energetic characteristics of the al/cuo core-shell composite micro-particles fabricated as spherical colloids. *Thermochimica Acta*, 689:178656, 2020. doi:[10.1016/j.tca.2020.178656](https://doi.org/10.1016/j.tca.2020.178656).
- [66] Guoqiang Zheng, Wenchao Zhang, Ruiqi Shen, Jiahai Ye, Zhichun Qin, and Yimin Chao. Three-dimensionally Ordered Macroporous Structure Enabled Nanothermite Membrane of Mn₂O₃/Al. *Scientific Reports*, 6(1):22588, March 2016. doi:[10.1038/srep22588](https://doi.org/10.1038/srep22588).
- [67] X. Zhou, M. Torabi, J. Lu, R. Q. Shen, and K. L. Zhang. Nanostructured energetic composites: Synthesis, ignition/combustion modeling, and applications. *Acs Applied Materials & Interfaces*, 6(5):3058–3074, 2014. doi:[10.1021/am4058138](https://doi.org/10.1021/am4058138).
- [68] Xiang Zhou, Daguo Xu, Guangcheng Yang, Qiaobao Zhang, Jinpeng Shen, Jian Lu, and Kaili Zhang. Highly exothermic and superhydrophobic mg/fluorocarbon core/shell nanoenergetic arrays. *ACS Applied Materials & Interfaces*, 6(13):10497–10505, 2014. doi:[10.1021/am502078e](https://doi.org/10.1021/am502078e).
- [69] Baozhong Zhu, Jinghui Wang, Qichang Wang, Yunlan Sun, Weiqi Chen, and Jiquan Wang. Promotional effect of silica on the combustion of nano-sized aluminum powder in carbon dioxide. *Chinese Journal of Aeronautics*, 35(4):245–252, April 2022. doi:[10.1016/j.cja.2021.05.020](https://doi.org/10.1016/j.cja.2021.05.020).
- [70] Xiangrui Zou, Ningfei Wang, Lijuan Liao, Qingzhao Chu, and Baolu Shi. Prediction of nano/micro aluminum particles ignition in oxygen atmosphere. *Fuel*, 266:116952, 2020. doi:<https://doi.org/10.1016/j.fuel.2019.116952>.

Appendix A

Supplementary Figures

A.1 Particle Size Histograms

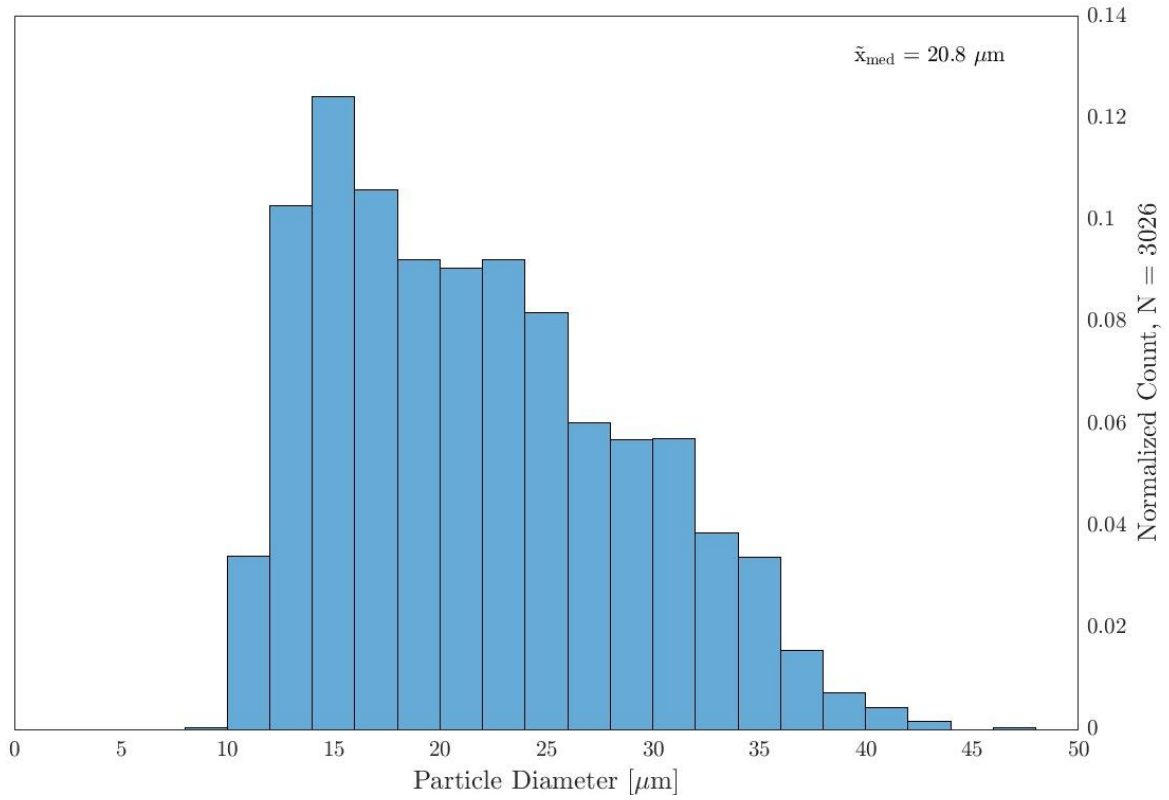


Figure A.1: [PM](#) particle size histogram, normalized to the total count

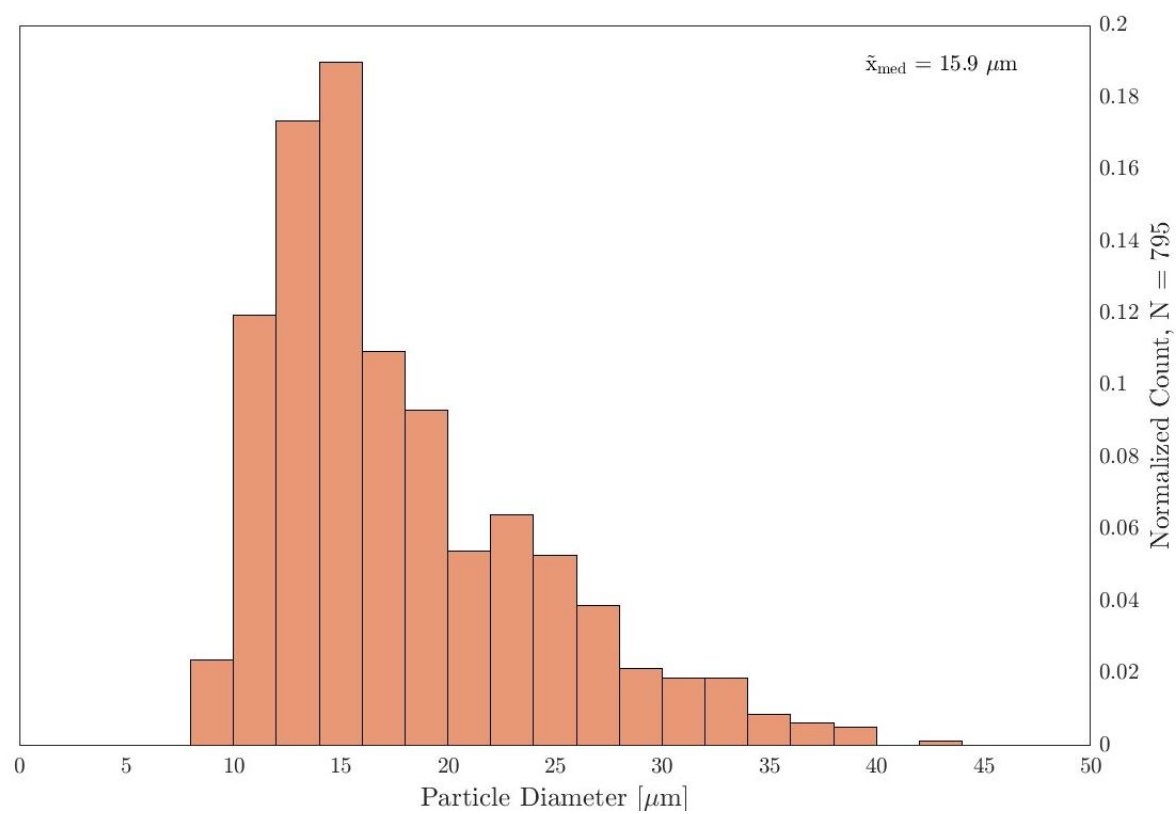


Figure A.2: CS particle size histogram, normalized to the total count