

Additive Manufacturing and Combustion of Reduced Graphene Oxide Based Nanothermite Aerogels

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 consists in part of a manuscript written for publication, and a manuscript that is currently being prepared for publication. Each manuscript is co-authored by Connor MacRobbie and Dr. Anqi Wang. The breakdown of the primary work done is as follows:

Introduction presented in Chapter 1:

Connor MacRobbie was the primary author for background related to additive manufacturing, reaction mechanisms of nanothermite material, and identifying the objectives of the work completed throughout the projects. Dr. Anqi Wang was responsible for the background related to nanothermite material, as well as the background related to the graphene structure of the aerogel used in this project. Dr. Wang was also responsible for the initial project ideation and conceptualization.

Methods presented in Chapter 2:

Connor MacRobbie was the primary author for the sections on aerogel ink preparation, the direct ink writing of these inks, and the characterization methods used in this work. Connor MacRobbie was also the lead designer of the additive manufacturing device. Dr. Wang was the primary author of the section describing the synthesis of graphene oxide.

Results presented in Chapter 3:

Connor MacRobbie was the primary author for sections on the print quality of the energetic aerogel, the combustion analysis, and the analysis of post combustion products. Connor MacRobbie was also the lead in conducting combustion experiments. Dr. Wang was the primary author of the sections describing the results of XRD, DSC-TGA, and supported the analysis of post combustion products. Dr. Wang also conducted the XRD, DSC-TGA, SEM, and EDS experiments.

Discussion presented in Chapter 4:

Connor MacRobbie was the primary author of the sections discussing thermal analysis, reaction mechanisms, and applications of the product. Dr. Anqi Wang was the primary author of the section describing the effect of graphene oxide on the material.

Conclusion presented in Chapter 5 and future work presented in Chapter 6:

These sections are written solely by Connor MacRobbie

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Abstract

Nanothermites are a key material for engineering applications related to energy and heat release, such as welding, heating, and pyrotechnics. The ability to additively manufacture energetic nanothermite structures with desired combustion properties is severely limited by current technology. The reactions are often slow to propagate and release less energy than desired due to polymer binders that act as an energy sink for the reaction but are required to support the energetic material. Additionally, the controllability and tuning of nanothermite reactions are limited by the lack of a conclusive understanding of the reaction mechanisms that govern the reactions of these materials. Several different reaction mechanisms have been proposed without any conclusive evidence to support the claims. In this work we fabricate a polymer-free, reduced graphene oxide (rGO)-based nanothermite aerogel with a range of nanoparticle loadings using a novel additive manufacturing process. The nanothermites analyzed in this work are aluminum iron-oxide ($\text{Al}/\text{Fe}_2\text{O}_3$), aluminum copper-oxide (Al/CuO), and aluminum bismuth-oxide ($\text{Al}/\text{Bi}_2\text{O}_3$). SEM images demonstrate the unique porous structure formed by the thin rGO sheets which form a skeletal structure that wraps the nanoparticles into individual nanothermite clusters. EDS confirms the homogeneity of the overall structure of the aerogel and the nanothermite clusters, demonstrating that the particles are well dispersed when printing. DSC-TGA results and high-speed combustion videos confirmed the enhanced energetic performance of the printed specimen, suggesting the important role of rGO compared to conventional printing methods. A relatively high linear burn rate of 5.8m/s was demonstrated for rGO/Al/metal oxide samples with a diameter of 1.6mm at 95% nanothermite loading by mass. It was also shown that the propagation rate of the reaction was independent of the print direction. Thermal camera footage clearly indicated the generation of the pre-heating zone, reaction front, and cooling zone during the propagation. SEM, EDS, and TEM are used to analyze the post-combustion material, whose collection is enabled by the novel graphene structure of the material. By analysing the combustion product within the skeletal fragments of the sample the reaction mechanisms for three nanothermite pairings are found and discussed. It is found that in the small nanothermite clusters several previously proposed reaction mechanisms occur concurrently. Diffusion and melt dispersion, which appear to be mutually exclusive in literature, are shown to be occurring concurrently. Overall, this method allows for complex 3D printing fabrication of various rGO/nanoparticle aerogels, while giving insights as to how the reactions propagate via a series of reaction mechanisms depending on the metal oxide used for the reaction.

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Chapter 1

Introduction

1.1 Nanothermites

Nanothermites are a group of energetic metallic materials that react to produce large amounts of energy. Also known as metastable intermolecular composites, these materials are composed of solid metal fuel and metal oxide particles with one or both components at the nanoscale. Nanothermites show enhanced combustion properties, including a faster burn rate compared to conventional thermites due to the increased reactive surface area between the fuel and oxidizing particles [1, 2]. The most common and widely investigated metal fuel used in nanothermites is aluminum, as it is easier to produce than other metal fuels, lower in cost, and has an extremely high combustion enthalpy at 31 kJ/kg. Significant research has focused on the development of Al/metal oxide nanothermites, the the manufacturability with various oxidizers, compositions, and micro/meso structures to

optimize their energetic performance for specific applications, such as burning rates on the order of 1 km/s and pressurization rates on the order of 100 GPa/s [3, 4, 5, 6]. Maximum burn and pressurization rates are common quantitative parameters to compare the quality of nanothermite materials. However, there are uncertainties about the reactions of these materials that limit their use in practical applications. Some disadvantages include reactivity control and issues associated with safe production and handling, due to the occurrence of phase separation, reactive sintering, the spontaneous formation of alumina shell, and its sensitivity to external stimuli [7, 8, 9, 10, 11, 12, 13]. Additionally, the limited manufacturing methods of energetic materials limit the number of applications for the use of these materials. Lastly, one fundamental issue for the use of nanothermites is that the reaction mechanisms that govern their combustion are still unclear, especially for aluminum based nanothermites. This limits the engineer’s ability to tailor these nanothermites for specific applications as their behavior is not fully known. Overall, if the critical disadvantages of using nanothermites can be addressed and a better understanding of the reaction mechanisms can be found, engineers could better design materials with great controllability for specific applications, and handle these materials in a safer manner.

1.2 Additive Manufacturing of Energetic Materials

In recent years, researchers have been investigating the potential of using additive manufacturing for the rapid and convenient production of customizable energetic nanothermites [14]. Extrusion-based printing methods, and more specifically direct ink writing methods, have demonstrated the capability to fabricate multi-component, energetic structures with

controlled mechanical and physical properties [15]. Direct ink writing is also considered a crucial tool for the development of novel and flexible thermite-based reactive interfaces and structures [14]. A common additive to these DIW printed energetic materials is a polymer binder to obtain a desirable viscosity for extrusion and to improve the physical structure of the printed parts. The viscosity of the ink is optimized to allow consistent and accurate direct writing to occur. Additionally, polymers act as a binder to hold the loose nanoparticles together within the polymer structure, known as a polymer matrix composite, and increase the mechanical strength of the final printed structure [16]. Shen et al. demonstrated a DIW process of energetic material with 10% polymer by weight including a combination of polymers including hydroxypropyl methylcellulose, nitrocellulose, and polystyrene to print Al/CuO nanothermite with a maximum linear burn rate of 25 cm/s [17]. Mao et al. utilized a fluororubber F₂₃₁₁ at 5-25 wt%, to obtain an Al-CuO printed nanothermite with a maximum linear burning rate of 1.5 m/s [18]. Although polymers possess desirable mechanical properties, they often have undesirable combustion properties as they do not actively enhance the reaction and often consume some amount of energy produced by the reacting particles themselves. They also typically limit the thermal conductivity of the material, which significantly reduces the reaction rate of the material [16]. The printed, polymer-assisted, energetic material often has a high density, which is not ideal for maximizing the propagation rate but is required for adequate viscosity of ink during printing and final mechanical strength. Due to these factors, the typical burning rates of nanothermite materials reduce from hundreds of meters per second to below one meter per second. Therefore, an easy and adaptive fabrication method for additively manufacturing nanothermite material without significant loss in reactivity is desired.

1.3 Graphene and Aerogels

Graphene and functionalized graphene have been utilized in past research as an additive in nanothermite composites to improve their performance by reducing large agglomerations in the material [19]. Graphene has also been used in the past to improve the safety of nanothermite material by reducing the electrostatic discharge sensitivity and the chance of accidental ignition [20]. While the participative roles of graphene in thermite reactions are not yet well understood, the graphene sheets allow for a large surface area for metal and metal oxide nanoparticles to assemble on [21]. Additionally, the ability to use functionalized graphene to varying degrees can allow for the control of desired reaction behaviors [22, 23].

Graphene-based aerogels are a promising candidate to replace the polymer materials in the additive manufacturing of energetic materials. Functional graphene aerogels possess a skeletal structure that can be loaded with nanothermite particles that, combined with its considerably higher conductivity when reduced than polymers, can lead to the creation of useful energetic materials. Graphene aerogels are prepared via sol-gel methods using molecular precursors and the subsequent removal of the solvent under freeze-drying or supercritical drying, and demonstrate a tunable porous structure with a high surface area [24]. The gelation process during fabrication typically involves the reduction of graphene oxide using a chemical reducer or a hydrothermal method [25]. The porous structure allows for the loading of nanoparticles within the reduced, interwoven graphene sheets, which can have applications in supercapacitors [26], electrodes [27], catalysts [28], etc. Previous research has shown that energetic nanoparticles can be loaded into a graphene-based aerogel using a chemical reducer [29]. Within the graphene skeleton of the material,

small metal/metal oxide clusters are created when the graphene sheets wrap around the nanoparticles during reduction. This packing of the nanoparticles minimizes the phase separation between the fuel and oxidizer, enhancing the surface contact and shortening the diffusion length of the reaction. This research presented material with a burn rate near 1000 m/s with 3 times the electrostatic threshold, demonstrating enhanced combustion rates and a safer material to handle. The structure presents the opportunity for a wide variety of particle loading types and amounts.

The fabrication of reduced graphene oxide nanothermite aerogels has the potential to be conducted using a direct ink writing additive manufacturing method. The graphene oxide and nanoparticles have the potential to be loaded into an ink before being reduced to form a gel and printed onto a substrate to form a final product. A key factor in this process will be the rheological properties of the ink before and after the gelation process during extrusion. The ink must be an appropriate viscosity to be easily extruded from the printer, while also being mechanically strong enough to support its as-printed structure. Current 3D printing methods of rGO aerogel typically require a series of processes that are not compatible with nanothermites to achieve successful prints [30, 31, 32, 33]. Water is typically used as a solvent during this process to modify the viscosity of the printing ink. Additionally, to enhance the reduction process of the graphene oxide sheets and solidification of the gel structure a chemical reducer or heat treatment process is typically used. These additional processes significantly limit the use of various nanoparticles that have a sensitivity to water or high temperature. For example, Aluminum, one of the most common metal fuels, is sensitive to water as it will become less reactive due to hydroxide production within the aluminum, and sensitive to high temperatures due to its reactivity

with air creating aluminum oxide. Very few successful additive manufacturing processes have been reported using rGO loaded with nanoparticles [34]. Therefore, an innovative direct ink writing method that does not require the use of water or heat treatment is desired for the production of nanothermite graphene aerogel. It is desirable for this material to be very reactive, while controllable, and allow for a wide range of particle loadings and types.

1.4 Reaction Mechanisms of Nanothermites

The difficulty in determining the reaction mechanism is due to the variable reaction rates that researchers have been able to analyze in nanothermites, based on the heating conditions of the experiments. Experimental heating rates range from <50 K/s in DSC-TGA in an equilibrium state to an extremely rapid heating rate of over 10^9 K/s during combustion, which leads to complex physical and chemical processes [35]. These complex processes include the crystallization and cracking of the Al_2O_3 shell, reactive sintering, melting and boiling of the Al reactive core, and the chemical redox reaction between fuel and oxidizer [36, 37]. In the past researchers have proposed several reaction mechanisms including quiescent shell rupture due to phase change[38], reactive sintering via diffusion[39], and melt dispersion[40]. However, no definitive conclusion has been reached at this time.

While the slower heating tests are not a great representative of the combustion of nanothermites they can offer insight into how rapid combustion reactions are occurring. Several research groups have investigated the reaction mechanisms of nanothermite materials in an equilibrium, slow-heating environment with great consistency [1, 41]. Under slow heating conditions, individual physical and chemical processes can occur sequentially and

to completion before the proceeding process, based on the slowly increasing temperature. In the case of aluminum nanoparticles, the amorphous aluminum oxide shell crystallizes and cracks near 350°C, which allows pathways for oxygen to penetrate the particle’s pure aluminum core leading to a redox reaction as the temperature approaches the melting point of aluminum near 660°C due to its increased diffusivity.

At higher heating rates, different reaction mechanisms have been observed in nanoparticle and nanothermite reactions. A diffusion-based reaction mechanism, involving a condensed phase reaction and reactive sintering of aluminum nanoparticles with nanoscale metal oxide particles, has been observed in many publications with a wide range of metal oxide particles, including Al/CuO, Al/WO₃, and Al/Bi₂O₃ [42, 43]. During the diffusion-driven reaction mechanism heat is transferred from the presently reacting particles in the reaction front to the unreacted material surrounding it, leading to an increase in temperature in the unreacted material and subsequently its ignition, propagating the reaction. In this case, the combustion rate is governed by the rate of heat transfer through the material. It has been shown in the past that the thermal conductivity of the nanothermites decreases during this type of combustion due to air gaps that form when particles sinter together, creating inconsistencies in combustion and propagation rates on the microscopic level [44]. The diffusion based reaction mechanism has been demonstrated and is useful in explaining the behavior of nanothermite combustion under uniform heating or under slower propagation rates on the order of cm/s. However, this diffusion-based reaction mechanism does not provide a conclusive explanation for extremely rapid nanothermite combustion near 1 km/s due to the limited diffusion rate within the material.

Melt dispersion is a proposed reaction mechanism that offers a more convincing ex-

planation for the extremely rapid nanothermite combustion at high heating rates, This reaction mechanism hypothesizes that the high heating rate causes a rapid increase in temperature of the aluminum nanoparticles leading to the melting and potentially boiling of the aluminum core, which subsequently causes a rapid pressure increase within the aluminum nanoparticles. The high pressure then leads to a high stress on the aluminum oxide shell causing it to shatter. Small, high-temperature aluminum droplets are then ejected from the shell at high speeds and rapidly propagate through the material. This reaction mechanism provides a possible explanation for the supersonic propagation of nanothermites. One problem with this proposition is that at such rapid heating rates, it is nearly impossible to conduct microscopic imaging during propagation to observe the local behavior and prove this hypothesis. Collection and analysis of post-combustion material is also very difficult as the material is consumed and ejected, typically leaving very little material behind. At this time, there has been very little experimental evidence to support the melt-dispersion reaction mechanism hypothesis. One group reported a significant reduction in particle diameter after combustion with propagation rates between 10 and 1000 m/s for nano- and micro-scale Al/MoO₃, which is contradictory to reactive sintering where the particle sizes will increase. However, detailed composition information of these tiny particles was not reported, and more common nanothermite pairs in industry such as Al/CuO and Al/Fe₂O₃ were not covered [45]. Additionally, one group has reported the observation of the spallation of aluminum nanoparticles at high laser-induced heating rates, but without nanothermite reaction [46].

Due to the drastic differences between the diffusion-based reactive sintering and the melt dispersion mechanisms there is a significant debate concerning the real reaction mechanisms

that propagate aluminum based nanothermite reactions. In order to accurately address this debate, it is desired to produce a nanothermite combustion with a controllable reaction rate, while retaining the combustion product. This will allow for further analysis to better hypothesize how the reactions are occurring. Additively manufactured, reduced graphene oxide aerogel loaded with nanothermite particles promises to enable this work. This technology could provide a range of particle loadings and types to give a range of reactions. The potential to analyze the discrete nanothermite clusters within wrapped graphene sheets could provide extremely beneficial information. Also, the skeletal structure may also allow for a simple collection of post combustion debris for further analysis.

1.5 Objectives

The primary objective of this work was to create a novel additive manufacturing device to print energetic aerogels loaded with nanothermites and demonstrate the capabilities and benefits of such a material. The secondary objective is to use the novel additive manufacturing method to evaluate the fundamental reactions that occur in a nanothermite reaction to better understand them, as they are not well known at this time.

Chapter 2

Methodology

The objectives of this thesis are met over the course of two primary projects. The first of which will address the first objective of creating a novel additive manufacturing device to print energetic aerogels and demonstrate the capabilities and benefits. This project uses Al/Fe₂O₃ and Al/Bi₂O₃ nanothermites of various loadings with graphene and nanoparticles. The second project uses Al/Fe₂O₃, Al/Bi₂O₃, and Al/CuO nanothermites with set loading criteria to address the second objective of evaluating the reaction mechanisms of the nanothermites. Both of these projects share a similar methodology that is explained in this section. The few differences in methods between the two projects are also discussed.

2.1 Graphene Oxide Synthesis

The preparation of the energetic aerogel involves several processes to generate an ink that can be loaded into the direct ink writing printer. Graphene oxide (GO) sheets were first

synthesized using a modified Hummer’s method that has been reported in previous research [8, 29]. A brief description of the synthesis is given here. To synthesize the graphene oxide sheets, 1 g of graphite (XGSciences, Grade H-5, Lansing, MI) and 1 g of sodium nitrate (NaNO_3 , Sigma-Aldrich, St. Louis, MO) were added to 46 mL of sulfuric acid (H_2SO_4 , 95–98% Sigma-Aldrich, St. Louis, MO). This solution was stirred for 10 minutes in an ice-water bath. After stirring, 6 g of potassium permanganate (KMnO_4 , Fisherbrand, Waltham, MA) was slowly added to the mixture. The water bath was heated to 35°C and left at this temperature for 1 hour to allow for the oxidation of the graphite. Once the graphite was oxidized 80 mL of deionized water was added to the mixture in small increments using a dropper, and the bath temperature was increased to 90°C and left for 30 minutes. The mixture was then allowed to cool to room temperature before 200mL of deionized water and 6mL of hydrogen peroxide solution (H_2O_2 , 30% by weight, Sigma-Aldrich, St. Louis, MO) were added to the mixture to terminate the oxidation process. The purification of the GO was done by repeated centrifugation and dissolution using deionized water until the pH value of the supernatant reached 5. After 1 hour of sonication and final centrifugation, GO sheets were obtained after drying the viscous aqueous solution overnight at 65°C .

2.2 Aerogel Ink Preparation

Following the preparation of the GO sheets, the nanothermite inks were prepared for printing. The inks selected for this study included GO/Al/ Fe_2O_3 , GO/Al/ CuO , and GO/Al/ Bi_2O_3 . These nanothermite pairings were selected due to their unique physical

properties such as different melting and boiling points which could affect their combustion and reaction mechanisms. The nanoparticles used in this study included Al nanoparticles (100 nm, 83% active), Fe_2O_3 nanoparticles (100 nm), CuO nanoparticles (40 nm), and Bi_2O_3 nanoparticles (120 nm), all of which were purchased from US Research Nanomaterials, Houston, TX. Each ink had an identical synthesis procedure, with the sole variants being the metal oxide particle in the ink and the amount of each aluminum/metal oxide to match the desired loading percentages. The calculated amounts of the prepared GO sheets, aluminum nanoparticles, and oxidizing nanoparticles were first dispersed in 5 mL, 2.5 mL, and 2.5 mL of propylene carbonate (PC) (Sigma-Aldrich, St. Louis, MO), respectively. The three dispersed solutions were then sonicated for 3 hours. The solutions containing aluminum nanoparticles and metal oxide nanoparticles were then combined into one 5mL solution and sonicated for 1 hour to ensure homogeneous mixing. The mixed nanoparticle solution and the GO solution were then combined into a final 10mL solution and stirred for 10 minutes to ensure the GO sheets and nanoparticles were well mixed. The final ink solution was then left to rest for 12 to 16 hours to ensure that all of the negatively charged GO sheets and nanoparticles were dispersed in the solution. While no precipitation was observed in the mixture after resting overnight, immediately prior to printing the energetic ink solution was stirred for 5 minutes to ensure homogeneity and avoid any agglomerations that could disrupt the printing process.

The calculated mass amounts of GO, aluminum nanoparticles, and metal oxide nanoparticles for each nanothermite pairing based on the desired loading are summarized in Table 2.1. For 10mL of ink, it was found that 100 mg of GO was able to create a reliably strong structure, capable of containing the nanoparticles within the aerogel skeleton structure.

Table 2.1: Mass Amounts of Particles in Nanothermite Ink (mg)

Mixture	GO%	Al	Fe ₂ O ₃	Bi ₂ O ₃	CuO
GO/Al/Fe ₂ O ₃	20	152	248	-	-
	10	341	559	-	-
	5	720	1180	-	-
GO/Al/Bi ₂ O ₃	20	69	-	331	-
	10	155	-	745	-
	5	329	-	1571	-
GO/Al/CuO	20	86	-	-	314

Therefore, 100mg of graphene was consistently used across all samples. An equivalence ratio of 1.5 was used for each sample as previous research determined that this was the optimal composition for these thermites. It is of note that the Go/Al/CuO was not selected to be used in the first set of experiments examining the relation between the GO loading percentage and combustion properties. Therefore, only samples with 20%GO/Al/CuO were used during these works to analyze the reaction mechanisms of nanothermite pairings as this was the set loading condition for the second set of experiments.

2.3 Direct Ink Writing of Energetic Aerogel

The printing of the nanothermite aerogels is facilitated by the gelation that occurs when the graphene oxide sheets turn into reduced graphene oxide (rGO) via a chemical reaction with ethylenediamine (EDA). The reduction of the graphene sheets causes the sheets to wrap and interconnect such that a solid structure is formed with nanoparticles and propylene carbonate homogeneously spread through the material in small microscopic clusters. A more detailed discussion of the chemical reaction mechanism between GO sheets and EDA

and analysis of the reduction capabilities can be found in previously published research [29].

The physical 3D printing was performed using a novel direct ink writing (DIW) setup, enabled by two syringe pumps used to control the flow rates of the nanothermite inks and the EDA, respectively. The flow of EDA was connected to the flow of the nanothermite ink via a 27-gauge needle. The tubing used for extrusion was a 1/16" PVC tube. The flow rates of the syringe pumps were set to fix the volumetric flow rate between Go/Al/MO_x ink and EDA at 20:1, with a bulk flow velocity and extrusion of 10mm/s. Additionally, the distance between the needle injection point of EDA and the end of the extrusion tube was set to 7-8 cm. The most critical factors in printing were the selection of an appropriate gelation duration and printing velocity such that the reaction between the ink and EDA would cause the graphene sheet to reduce homogeneously before extrusion to provide the aerogel structure, while also printing accurately without defects. The large difference in diameter between the needle and the tube causes a large amount of turbulence at the EDA injection point, even though the volumetric flow rate was set to 20:1, leading to a good initial mixing and homogeneous printing structure after continuing to mix in the extrusion tube. The aerogel samples were printed onto 6.1cm x 6.1cm pieces of acrylic on top of a linear XY stage where the print pattern was dictated by an external microcontroller. A series of parallel gel strands were printed on the acrylic base to be used in a series of experiments to characterize the material. Additionally, a lattice structure was printed using a selection of sample gels to demonstrate the 3D printing capabilities of the gel. Figure 2.1 demonstrates a model and actual photo of the 3D printer setup to produce the energetic aerogels.

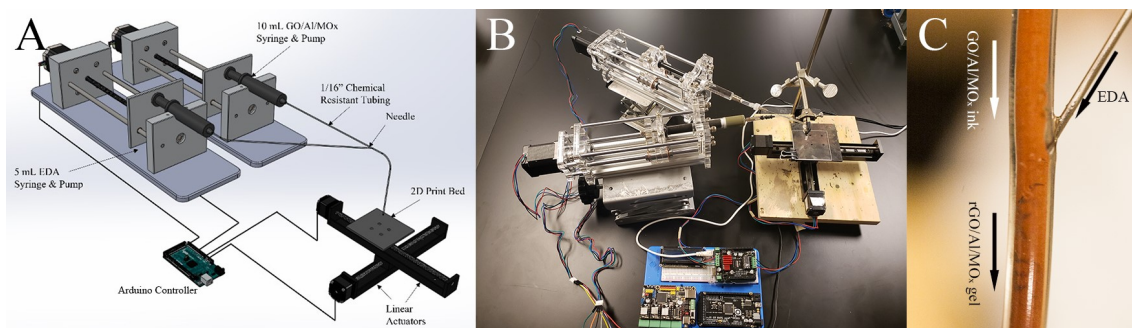


Figure 2.1: Scheme (A) and actual photo (B) of printing setup and photo (C) of the gelation junction.

Immediately after printing, each acrylic base and sample was placed in a petri dish and immersed in tert-butanol (99%, Sigma-Aldrich, St. Louis, MO) to allow the reaction to terminate. Additionally, the propylene carbonate and EDA were exchanged by tert-butanol via solvent change under stirring and heat at 35°C for 3 days. The tert-butanol was renewed every 12 hours to remove all of the PC and EDA. After the solvent exchange process was completed, the gel was freeze-dried for 1 day to remove the tert-butanol and obtain the final nanothermite aerogel samples.

2.4 Characterization

A series of experiments were conducted to analyze both the combustion properties and the reaction mechanisms of the three nanothermite aerogels. Optical images were captured using a 10X microscopic lens with the Phantom v2012 monochrome fast camera and the pixel resolution is 2.8 μm per pixel. The microstructure of the gel prior to combustion was observed using a Hitachi Su-5000 SEM (Scanning Electron Microscopy) and an Oxford

EDS (Energy Dispersive Spectroscopy). XRD (X-ray Diffraction) spectrum analysis was performed by PANalytical X'pert Pro MRD and from 10 to 80° at a step of 0.1° at GI-XRD mode. DSC-TGA (Differentiative Scanning Calorimetry and Thermogravimetric Analysis) was completed using a Netzsch STA 449 F1 from room temperature to 800 °C at a heating rate of 20 °C/min under the protection of Argon gas flow at 200 mL/min. Combustion tests were performed in open air to determine the linear burn rate and temperature of the reacting samples. Depending on the test, ignition was completed using either a Ni-alloy hot wire (Parr Instrument) connected to a DC power supply at 30V and 3A, or a 5 W 532 nm continuous laser. High-speed video was captured at 100,000 frames per second with a 5 μ s exposure time using a Phantom v2012 monochrome fast camera, and thermal video was captured at 500 frames per second at 20 μ s exposure using a Telops M350 with a 1x lens. Figure 2.2 demonstrates the combustion setup for synchronous high-speed and thermal video capture with laser ignition. This is enabled by mounting the samples in a holding fixture open to the thermal camera side and backed by acrylic on the fast camera side. This ensures that both cameras will be able to record accurate video while keeping the sample in place. Additionally, there is a slot in the sample holder such that the laser may ignite the sample. The microstructure of the gel after combustion tests was first attempted using the same SEM and EDS equipment as pre-combustion. However, greater detail of the images was desired. Therefore, a Talos 200x was used to analyze the post-combustion samples using TEM (Transmission Electron Microscopy).

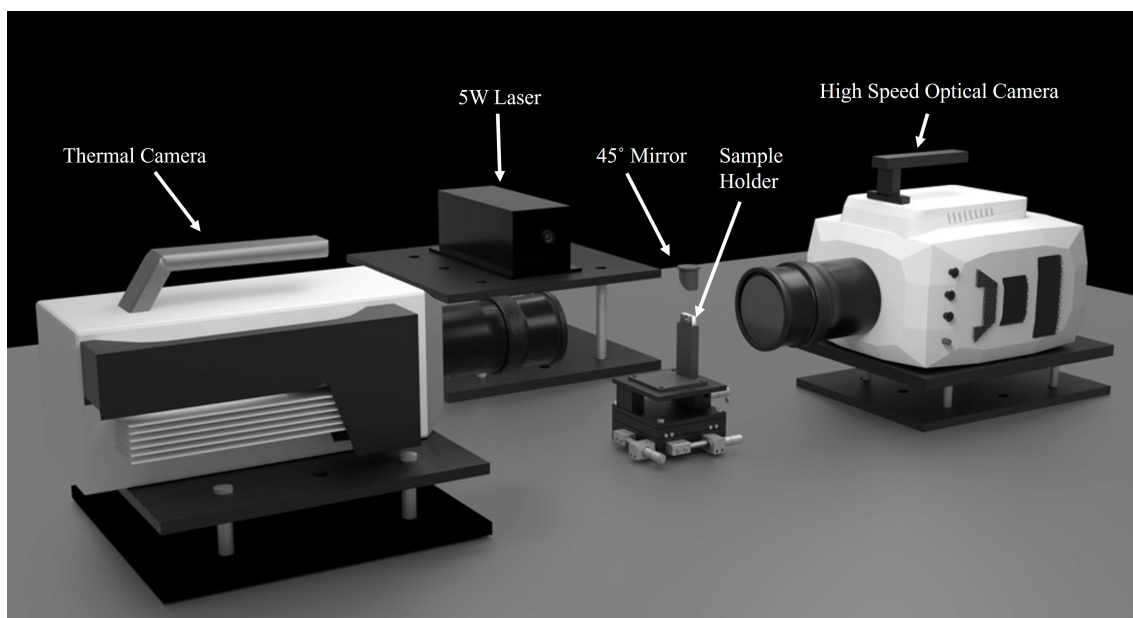


Figure 2.2: Modeled Image of Combustion Setup

Chapter 3

Results

3.1 Pre-Combustion Analysis

Pre-combustion tests were completed to characterize the nanothermite aerogel structure after it had been printed. This will help to determine how the various constituents of the aerogel affect the combustion process. The microstructure and elemental distribution of the nanoparticles will be critical to understanding the combustion of the energetic aerogel.

3.1.1 Print Quality

Several factors affect the quality of the as printed product when using the novel direct ink writing method. These factors then also affect the final aerogel quality. During the printing process the most important printing parameters that could be adjusted were the duration of gelation before the ink is extruded, the print speed, the loading % of nanoparticles which

affected the viscosity of the nanothermite ink, the distance between the extruder tip and the print bed, and finally. the distance between the printed parallel lines.

The most critical factor in the printing process is the gelation duration. Gelation began immediately after the introduction of EDA to the system. If the gelling time was too short, the ink would be extruded as a liquid and would not hold its cylindrical shape on the acrylic substrate. If the gelation time was too long, the viscosity of the ink would increase to a point where the gel would stop and start in the extrusion tube as the syringes pumped the ink through the system. This would lead to inconsistent prints as the extrusion speed varied around 10mm/s depending on the pressure being exerted on the solidifying gel as it was extruded. It was found that the optimal time for gelation given the equipment and setup used was between 7 to 8 seconds. Therefore, the length of the extrusion tube was selected based on the print speed to match this value,

The print speed that was found to be optimal for this process was 10mm/s. This speed was found to be slow enough to accurately lay the printed material on the substrate while being fast enough such that the syringes applied a consistent pressure to the nanothermite ink to allow it to print at a constant rate without the friction being a problem in the extrusion tube as the aerogel formed. Based on the gel duration and print speed the distance between the EDA injection point and the extruder tip was required to be between 70 and 80 mm.

Another important factor that dictated the print quality and consistency was the loading % of nanothermite particles. This was the reason for the change in viscosity between the samples. Since the amount of graphene used in each sample remained the same across

each trial, the only variant was the loading of nanoparticles. It was seen in the trials that the inks with a higher nanoparticle loading printed with greater consistency. The reason for this is the smaller change in viscosity between the unreacted ink and reacted ink with EDA. For the inks with a higher loading of nanoparticles, the EDA is injected into the stream and the material begins to gel. Since this gel is relatively similar in viscosity to the ink the unreacted material is pushed through the extrusion tube with the EDA and already gelled material, completing the gelation process by the end. For the samples with a lesser nanoparticle loading, and lesser viscosity, it was seen that as the material began to gel and increase in viscosity, the unreacted, low viscosity ink would rapidly bypass the gelling material. As the gelling material became stuck in the extrusion tube and EDA was not able to properly mix, Overall, all sample loadings tested were able to print, however, the consistency was better with samples of higher nanoparticle loading.

Two physical parameters that affected the quality of the prints were the distance between the extruder tip and the print bed and the distance between the printed parallel lines. The distance from the extrusion tip to the print bed was selected to be 5 mm. This distance allowed the nanothermite gel to bend and lay on the surface of the print bed without much fracturing due to bending stresses, while also being close enough to the print bed such that the printing material did not collapse under its own weight. The distance between the printed lines was selected to be 10 mm because at this distance the printed sample would minimize any fracture due to the curvature of the gel.

Overall with all of these factors taken into consideration, the printer created for this project was able to reliably print strands of about 30 to 40 mm without fracturing that could be used for a variety of combustion and optical tests to achieve the objectives of



Figure 3.1: Stages of the printing process: Energetic $\text{GO}(20\%)/\text{Al}/\text{Bi}_2\text{O}_3$ nanothermite ink (A) as printed $\text{rGO}(20\%)/\text{Al}/\text{Fe}_2\text{O}_3$ organogel (B) and post-freeze dried $\text{rGO}(20\%)/\text{Al}/\text{Bi}_2\text{O}_3$ aerogel (C).

this project. Figure 3.1 demonstrates optical images taken throughout the stages of the printing process. The mixed, homogeneous nanothermite ink can be seen in Figure 3.1 A. The as printed $\text{rGO}/\text{Al}/\text{MO}_x$ organogel with propylene carbonate and nanoparticles trapped inside is seen in Figure 3.1 B. After the solvent change process, leaving a dry brittle material, the final aerogel sample can be seen in Figure 3.1 C.

It should be noted that the focus of this work is on the feasibility of printing $\text{rGO}/$ nanothermite aerogels without requiring a polymer binder, and the analysis of its combustion properties. The system built for this study was able to reliably print samples of sufficient stability and uniformity to conduct the desired tests. The accuracy and structure of the printed gels are expected to improve with continuous development and optimization of the additive manufacturing system. This will be a larger engineering challenge for the commercial development of a graphene aerogel based nanothermite additive manufacturing system.

It is important to note that the entire manufacturing process of additively manufactured nanothermite aerogels is conducted at a room temperature of 22°C , including the

freeze drying process since the melting point of tert-butanol is 25°C. This ensures the safe handling of temperature-sensitive nanothermite, which could react and explode at higher temperatures. An alternative method to freeze drying that could be used to shorten the post-processing time is supercritical drying. Alternative carrier fluids and drying methods could also be used to shorten the drying time, however they will predominantly require an elevated temperature process which was undesired for this project.

Once the rGO/Al/MO_x aerogel had been dried it was able to be self supporting and could hold several layers of its own weight. Figure 3.2 A and B present a printed 2 layer structure immediately before and after freeze drying, respectively. Two perpendicular series of parallel lines form a lattice structure that other layers could also then be built off of. The distance between each parallel strand in this case was 5 mm to ensure that the second layer of the sample would be adequately supported. This test confirmed the potential to use this 3D printer for the fabrication of 3D structures. While some defects were present among the aerogel strands the structure was sufficiently stable to conduct the desired tests for this study. Future developments will focus on the additive manufacturing properties and focus on the final quality of the 3D printed material itself.

Figure 3.3 presents a cross-sectional view of the microstructure of the freeze-dried aerogels. Although the aerogel was extruded from a PVC tube with an inner diameter of 1.6mm (1/16”), the cross section of the final freeze-dried aerogel was not perfectly circular. It can be seen that during the freeze drying process, the sample was flattened slightly due to gravity. Quicker supercritical drying could be used to mitigate this in the future. It was shown that aerogels with higher particle loading experienced less gravity flattening during the freeze drying process, indicating that the nanoparticles assisted in supporting

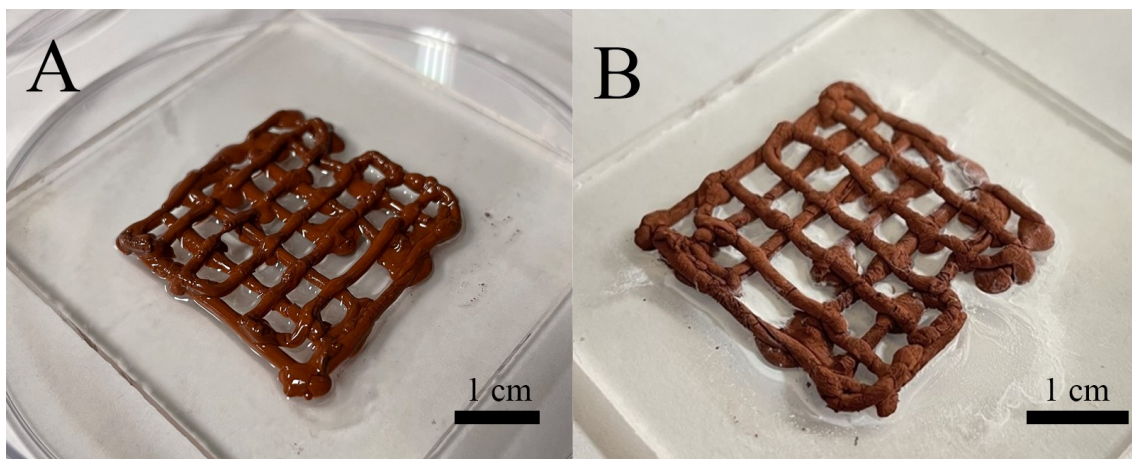


Figure 3.2: Multi-layer print before (A) and after (B) freeze drying

the graphene skeleton of the aerogel. The reduced cross sectional area of certain samples, shown in Table 3.1, was caused by gravity and potentially some minor shrinkage during the freeze drying process. In a fully developed 3D printing system this would need to be a design consideration and be accounted for. Sections of the samples were cut and weighed to determine the density of the aerogel. Based on the known particle amounts in the aerogel, the weight of a cut section, and the measured cross sectional area, the ratio of density to the theoretical maximum density of a sample with the same loading with no porosity can be calculated. From this the porosity can then be calculated. The aerogels all had extremely low densities, ranging from theoretical maximum densities of 1.8% to 7.3%, indicating the formation of a highly porous structure. It is of note that as long as the concentration of GO in the ink is high enough to form gel with the EDA, the content of GO can be adjusted, increasing the potential range of densities for printing.

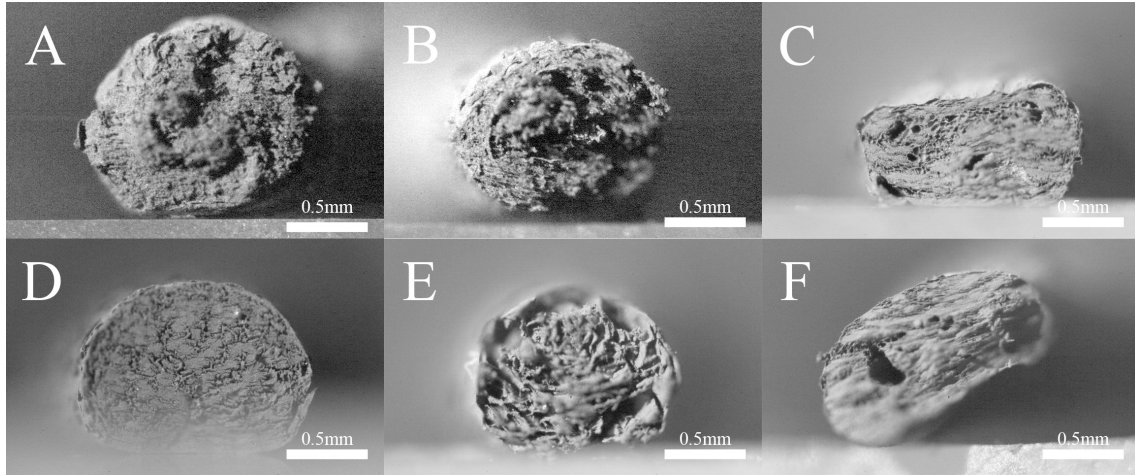


Figure 3.3: Cross sectional images of rGO/Al/Bi₂O₃ at 5% GO (A), 10% GO (B), 20% GO (C) and rGO/Al/Fe₂O₃ at 5% GO (D), 10% GO (E), 20% GO (F)

Table 3.1: Calculated cross-section area and density of the freeze-dried 3D printed aerogel

Sample	Cross Sectional Area (mm ²)	Density (mg/mm ³)	TMD%	Estimated Porosity
Ref: Ideal 1/16 inch tube	1.98	N/A	N/A	N/A
rGO(5%)/Al/Bi ₂ O ₃	1.34	0.27	4.7%	95.3%
rGO(10%)/Al/Bi ₂ O ₃	1.20	0.18	3.5%	96.5%
rGO(20%)/Al/Bi ₂ O ₃	0.99	0.081	1.8%	98.2%
rGO(5%)/Al/Fe ₂ O ₃	1.32	0.27	7.3%	92.7%
rGO(10%)/Al/Fe ₂ O ₃	1.12	0.16	4.5%	95.5%
rGO(20%)/Al/Fe ₂ O ₃	1.04	0.092	2.8%	97.2%

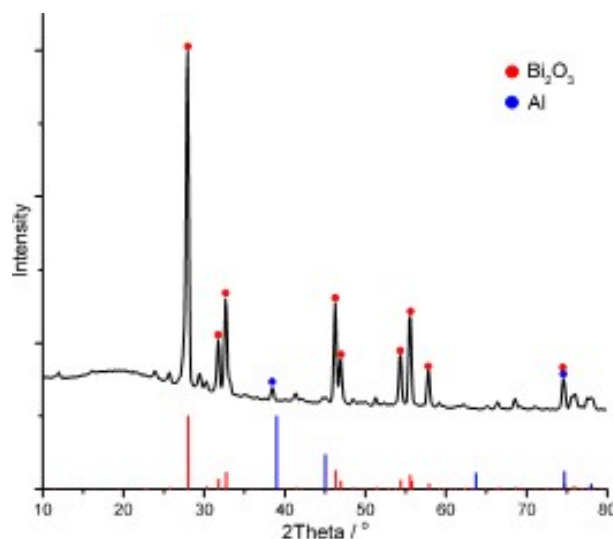


Figure 3.4: XRD spectrum of rGO(10%)/Al/Bi₂O₃

3.1.2 XRD

Figure 3.4 presents the XRD spectrum for freeze dried rGO/Al/Bi₂O₃ and the standard spectra of related components. Both Al and Bi₂O₃ were found in the final product. The XRD peak of rGO is at about 24°, however, it is indistinguishable in the XRD curve. This is partially due to the relatively low mass and well distributed mass of rGO in the sample and also due to its unique thin sheet structure. This structure is further confirmed by SEM images in the following section. The GO/Al/Fe₂O₃ sample displayed identical results, and the XRD test was not performed for rGO/Al/CuO.

3.1.3 SEM & EDS

The microstructure of the aerogels was observed using SEM and EDS. Figure 3.5 shows the microstructure images of the printed rGO(10%)/Al/Bi₂O₃. Figure 3.5 A demonstrates

an overall microscopic view of the porous structure with nanoparticles embedded within intertwined graphene sheets. Figure 3.5 B shows that the size of the pores within the structure are on the order of micrometers. The interconnected rGO sheets that constitute the framework of the aerogel and hold the nanoparticles in place can be seen in Figure 3.5 B and C. These images demonstrate that the GO sheets were well sonicated prior to being dispersed in PC and printing, leading to the formation of the extremely thin rGO layers via reduction with EDA. The reduction of graphene using EDA was confirmed via EDS using the rGO(10%)/Al/Bi₂O₃ as a representative sample. This sample showed an increase in the ratio of carbon to oxygen from 1.8 in GO sheets to 5.2 after the reduction. The amount of oxygen associated with the rGO sheets is the difference between the total amount of oxygen present and the oxygen present in the metal oxide. The results of this test are shown in Table 3.2. Figure 3.5 B also shows the pores, highlighted with white ellipses, and cluster structures of the aerogel, highlighted with blue ellipses. Figure 3.5 D, E, and F show the elemental mapping of Al, Bi, and C within the sample, respectively. It demonstrates a homogeneous distribution of Al and Bi₂O₃ nanoparticles with no phase separation. It also shows that the distribution of reduced graphene (Carbon) is more even compared to that of the nanoparticles across the structure as it plays the role of the supportive structure.

The SEM and EDS images of the other nanothermite aerogels with varying loading percentages demonstrate that the loading amount does not change the general microstructure of the material. The nanoparticles are consistently wrapped in reduced graphene sheets of the same size. However, when the loading is 95% nanoparticles the graphene sheets become more difficult to see due to the number of nanothermite clusters that are formed at this loading, as shown in Figure 3.6. When the graphene oxide loading is 20%, the graphene

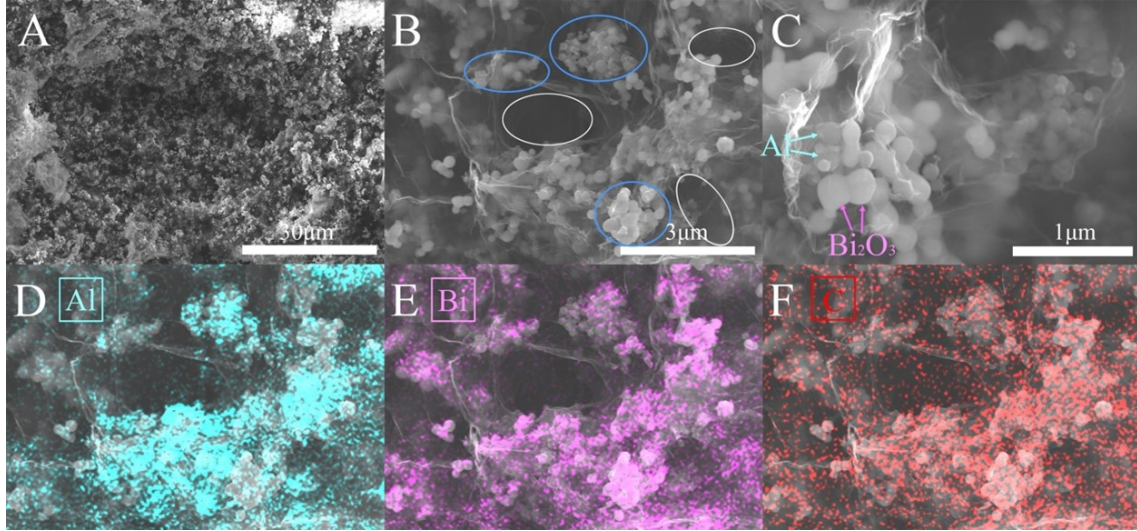


Figure 3.5: SEM images (A-C) and EDS images (D-F) and rGO(10%)/Al/Bi₂O₃

Table 3.2: Measured elemental composition in GO sheets and rGO(10%)/Al/Bi₂O₃

Sample	Elements	Atomic Percentage	C/O ratio in GO/rGO
GO Sheets	C	63.8±1.2%	1.81
	O	35.3±2.4%	
rGO(10%)/Al/Bi ₂ O ₃	C	45.2±2.4%	5.20
	O (Total)	24.6±2.1%	
	Bi	8.6±1.7%	
	Al	20.6±2.9%	
	O (rGO only)	8.7%	

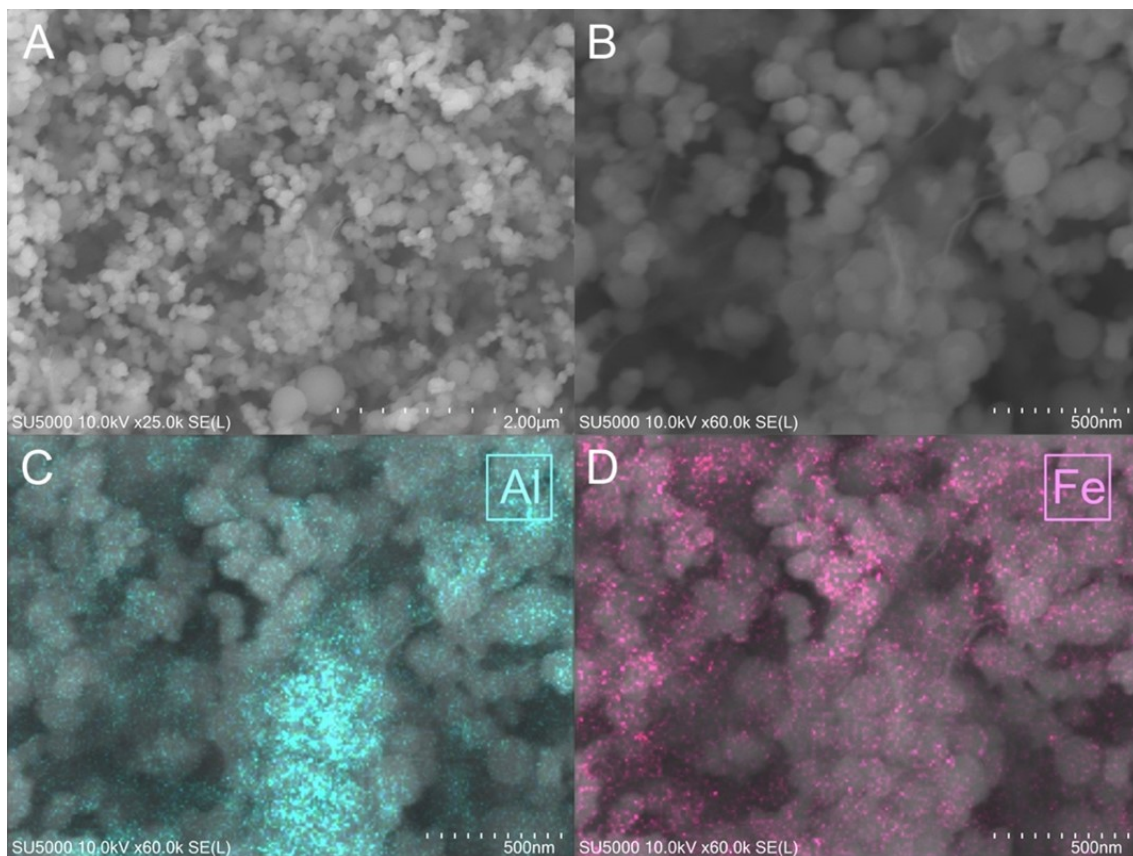


Figure 3.6: SEM images (A,B) and EDS images (C,D) and rGO(5%)/Al/Fe₂O₃

sheets are easily seen due to the limited number of nanoparticles and the cluster size, as seen in Figure 3.7.

Overall, a porous rGO skeleton was formed and a homogeneous distribution of both fuel (Al) and oxidizer (Bi₂O₃ or Fe₂O₃ or CuO) nanoparticles can be found across the samples regardless of the GO percentage in the precursor mixture. It is of note that rGO(10%)/Al/Fe₂O₃ aerogel printed with the greatest consistency, and was therefore used as an example for select experimental tests.

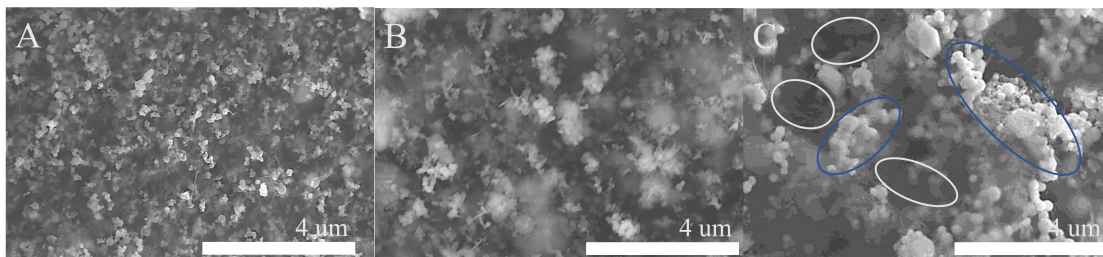


Figure 3.7: SEM images of rGO(20%)/Al/Fe₂O₃ (A), rGO(20%)/Al/CuO (B), and rGO(20%)/Al/Bi₂O₃ (C)

3.1.4 DSC-TGA

DSC-TGA tests were completed during the first set of experiments with Al/Fe₂O₃ and Al/Bi₂O₃ of varied composition. The results of these tests, as shown in Figure 3.8, demonstrate the heat exchange and mass change of the samples during a slow heating process. Exothermic and endothermic peaks are seen between 160 °C and 300°C respectively and are the result of the decomposition of the remaining oxygen containing functional groups in the rGO, which corresponds to the mass loss at the same temperatures. For the samples with higher GO %, and lower nanothermite loading, the weight loss caused by this decomposition is more significant. The main reaction between Al and the metal oxides occurs around 500-750 °C. The rGO/Al/Bi₂O₃ samples clearly show reactions before and after the melting of aluminum at 660 °C. The condensed phase reaction, with an onset temperature of about 515 °C, which is lower than the melting point of Al, represents the reaction between Al and Bi₂O₃ particles that are in direct contact. This onset temperature is also lower than that of Al/Bi₂O₃ loose powder, which is near 525 °C [29], indicating that the Al and Bi₂O₃ particles are more closely packed inside the graphene wrapped clusters compared to loose powder. The second thermite reaction peak, which was more evident

in samples with higher nanoparticle loading, indicated the reaction between the Al and metal oxide. Once a higher temperature was reached, Al was able to melt and flow freely to react with Bi_2O_3 . A significant weight loss was also demonstrated during this thermite reaction, which is likely due to the evaporation of Bi_2O_3 , or Bi due to local high temperatures during the thermite reaction. In the Al/ Fe_2O_3 samples, the curves possess a few key differences. During this reaction only one major exothermic peak is seen before the melting of aluminum, demonstrating the dominance of a condensed-phase reaction. No significant weight loss was seen in these samples due to the much higher boiling point of Fe and Fe_2O_3 . The onset temperature of this reaction was found to be around 525 °C, which is slightly less than that found in literature [47]. The reduction in onset temperature once again indicates an improved reactivity as a result of the proximity of the metal and metal oxide particles within the sample clusters. The proximity of the fuel and oxidizing nanoparticles in the aerogel structure enhances the condensed-phase reaction, which is the main reaction pathway of these materials under slow heating due to the high decomposition point of the oxides. A weight gain was found in the samples with 95% nanoparticle loading, indicating their exposure to residual oxygen in the system. This has been reported in previous publications [48]. This weight gain was not seen in samples with less nanoparticle loading due to the larger rGO barrier wrapping around the nanoparticles, further confirming the condensed phase reaction between the Al and metal oxides.

In the samples with a higher GO percentage, the decrease in energy was significantly larger than the expected change in energy release based on the decrease in nanoparticle loading. This indicates that the structure plays a significant role in the reaction, especially at low nanoparticle loading. As the concentration of GO in the nanothermite ink and the

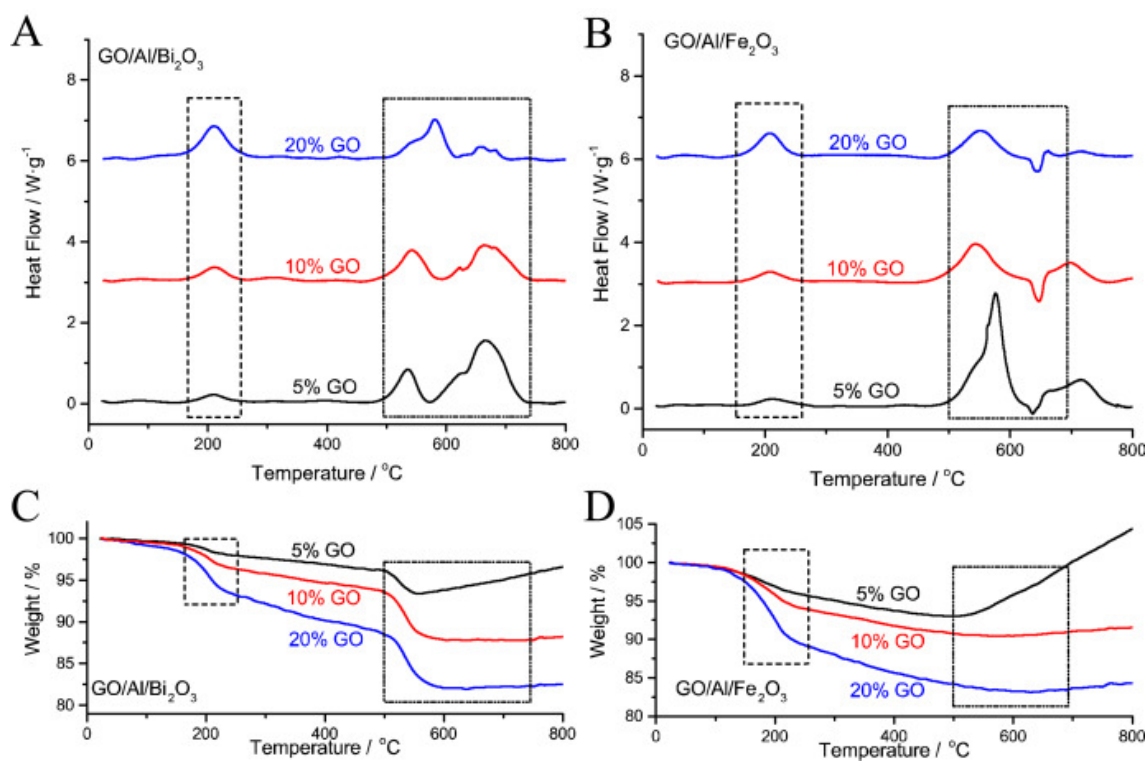


Figure 3.8: DSC-TGA of energetic rGO/Al/Bi₂O₃ and rGO/Al/Fe₂O₃

Table 3.3: DSC-TGA Data

Sample	Onset Temp. (°C)	Peak Temp. (°C)	Energy Release of Thermite Reaction (J/g)
rGO(20%)/Al/Fe ₂ O ₃	526	557	136±12
rGO(10%)/Al/Fe ₂ O ₃	521	549	228±3
rGO(5%)/Al/Fe ₂ O ₃	523	577	291±21
rGO(20%)/Al/Bi ₂ O ₃	513	552	158±34
rGO(10%)/Al/Bi ₂ O ₃	518	554	252±16
rGO(5%)/Al/Bi ₂ O ₃	516	558	328±7

ratio between the ink to EDA were kept constant between trials, it is reasonable to assume that the degree of cross-linking and number of clusters were similar among samples with different nanoparticle loading. Therefore, the samples with lower nanoparticle loading had both a larger mass of unreacting rGO and smaller nanothermite clusters. The reaction nature of equilibrium states in DSC-TGA and the limited diffusion length caused by the unique nanothermtie cluster structure limited the reaction of fuel and oxidizer within a single cluster wrapped by the rGO sheets. Therefore the completeness of the reaction is reduced when smaller clusters form with higher GO percentages. As a result, compared to the energy release values of physically mixed Al/Fe₂O₃ and Al/Bi₂O₃ (1100J/g and 700J/g respectively) the energy release values of the printed nanoenergetic aerogel from DSC-TGA are comparatively small. The energetic data from DSC-TGA is summarized in Table 3.3.

3.2 Combustion Analysis

While slow heating tests such as DSC-TGA may support the investigation of reaction mechanisms, they may not fully represent the combustion performance and mechanisms

due to the differences in reaction completeness and heating rate. For both sub projects completed during this thesis, combustion tests were completed to gather high speed and thermal imaging of the nanothermite aerogel combustion.

3.2.1 High Speed Imaging

The first set of samples, rGO/Al/Fe₂O₃ and rGO/Al/Bi₂O₃ with nanoparticle loadings of 80-95% were ignited to analyze their energetic performance. To do this, a straight piece of each sample ranging from 12 - 20 mm was cut from each printed sample and ignited. Ignition for this test was done using a 40-gauge nickel-chromium hot wire. The key frames of the combustion are shown in Figure 3.9. The combustion of each sample is seen propagating from left to right in each image set. As seen in the images, when the nanoparticle loading was greater than or equal to 90% the reaction was rapid and violent. The samples of less than 90% loading demonstrated a more controlled combustion. The propagation rates are summarized in Table 3.4. The combustion of the high particle loading samples at 95% propagated at a rate of 4.5-6 m/s, which is faster than polymer-assisted additively manufactured nanothermites of similar loading, which propagate at rates of less than 1.5m/s, typically on the order of tens of centimeters per second [16, 17, 18]. This confirms that the aerogel structure has a significant effect on the combustion properties of the nanothermites. There are several potential contributions to the improved propagation of both sample sets including the hot-spot formation due to the material's unique porous structure [29], the increased thermal conductivity due to the presence of rGO [25], and the enhanced condensed phase reaction due to the closely packed nanothermite clusters

held together by the rGO skeleton [49]. A high temperature flame and eject particles are also seen expanding toward the outer environment during the combustion further demonstrating the violence of the reaction. This is especially seen in the rGO(10%)/Al/Fe₂O₃ and rGO(10%)/Al/Bi₂O₃ shown in Figure 3.9 B and E, where the samples were self propelled from their initial position due to their light weight and reaction violence. This demonstrates the potential to use this material as a propellant in the future. When the nanoparticle loading was set to 95% the reaction propagated at such a rate that the sample combusted quicker than it could be displaced, and it remained in the same initial position. When the nanoparticle loading was set to 80% the energy released from the reaction was sufficient to self propagate, but not sufficient enough to displace the samples. Unlike other nanothermite reactions, the combustion of rGO(20%)/Al/MO_x did not break down the 3D sample structure, which can be observed in Figure 3.9 A. The higher concentration of rGO in the samples is able to better support the structure while also improving the heat transfer throughout the samples. It is also worth noting that the reaction rates of both sample sets were similar at each nanoparticle loading percent. The unique structure of the porous 3D rGO skeleton was able to govern the macroscale properties of the combustion, rather than the different reaction characteristics of each nanothermite pair.

A 2D planar combustion test was then completed to compare the propagation rate of the nanothermite aerogel with and against the print direction of the energetic ink. Figure 3.10 shows the propagation of the reaction through the sample with the flame front highlighted by the red line. The 2D sample consisted of parallel lines of rGO(10%)/Al/Fe₂O₃ aerogel with no lateral spacing between the printed lines. The average calculated flame speed was 1.68 m/s, which is almost identical to the flame speed from the linear combustion tests. It

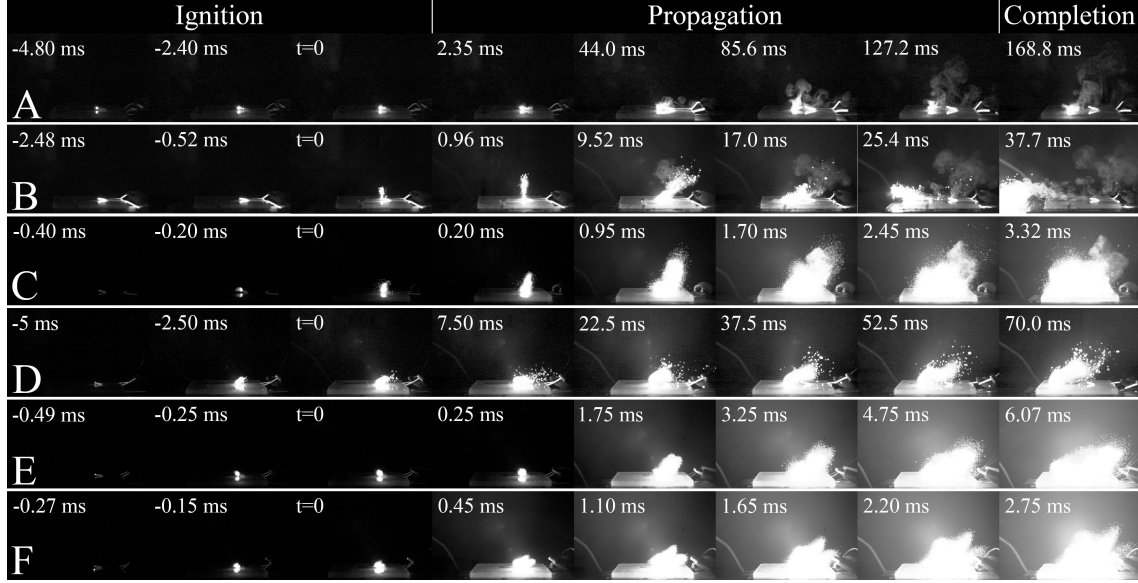


Figure 3.9: High speed images of rGO/Al/Bi₂O₃ at 20% GO (A), 10% GO (B), 5% GO (C) and rGO/Al/Fe₂O₃ at 20% GO (D), 10% GO (E), 5% GO (F)

Table 3.4: Linear Burn Rates

Sample	Burn Rate Trial 1 (m/s)	Burn Rate Trial 2 (m/s)
rGO(20%)/Al/Fe ₂ O ₃	0.30±0.036	0.165±0.037
rGO(10%)/Al/Fe ₂ O ₃	1.59±0.221	-
rGO(5%)/Al/Fe ₂ O ₃	4.73±0.068	-
rGO(20%)/Al/Bi ₂ O ₃	0.12±0.029	0.186±0.034
rGO(10%)/Al/Bi ₂ O ₃	0.64±0.128	-
rGO(5%)/Al/Bi ₂ O ₃	5.85±0.238	-
rGO(20%)/Al/CuO	-	0.60±0.102

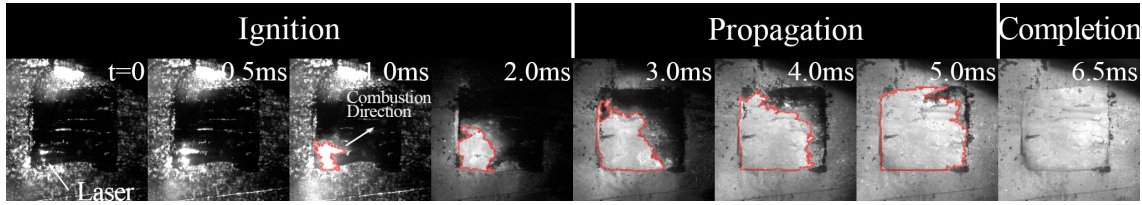


Figure 3.10: 2D planar combustion of rGO(10%)/Al/Fe₂O₃

was observed that the reaction propagates at approximately the same rate both with and against the print direction. As shown in Figure 3.10 the reaction reaches the top and right side of the square reaction zone at approximately the same time. The combustion of one piece of energetic nanothermite aerogel can easily trigger a reaction in adjacent pieces, due to the hot, rapidly ejected particles. It was also seen that the sample began to self propel towards the edges of the container during combustion due to its high energy release and light weight.

High speed videos were also taken of the second set of samples that were combusted for the purpose of analyzing post combustion material. These samples were combusted in the synchronous high speed and thermal video configuration. Figure 3.11 demonstrates the propagation of the nanothermite reaction of an rGO(20%)/Al/Fe₂O₃ sample. It was found that the burn rates of the rGO(20%)/Al/Fe₂O₃ and rGO(20%)/Al/Bi₂O₃ samples were very similar to the values as found in the first set of experiments. Additionally, the burn rate of the rGO(20%)/Al/CuO sample was found to be over three times faster than the other nanothermite aerogels. Table 3.4 summarizes the linear burn rates of the sample combusted in each experiment. All of these values are once again much faster than polymer-assisted additively manufactured nanothermite composites of similar loading [18, 50].

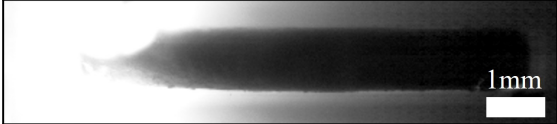
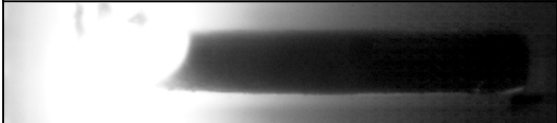
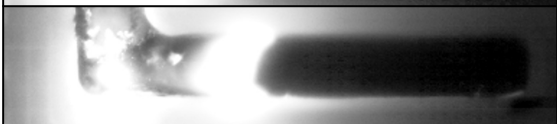
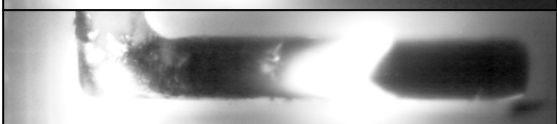
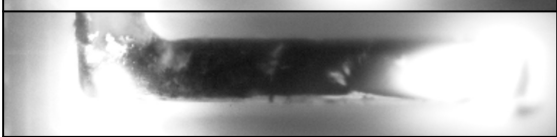
High Speed Images	Time (ms)	Reaction Stage
	0	Ignition
	15	Propagation
	30	
	45	
	60	Completion

Figure 3.11: Propagation of rGO(20%)/Al/Fe₂O₃ sample in second test set

3.2.2 Thermal Imaging

Thermal measurements can provide information regarding the combustion of nanothermite materials and demonstrate the quality of such materials. Combustion temperature could dictate the applicability of the material as well as provide insight into the fundamental physics of the reaction itself. When processing the results of the thermal camera, emissivity is a key parameter that affects the temperature measurement. However, no research has been published on the emissivity of nanothermite, largely due to its extremely high reaction rate. In some simulation based research, a value of 0.1 is used as the assumed emissivity for nanothermite reactions [51, 52]. However, if 0.1 is used as the emissivity in the case of these trials the maximum temperature is measured to be over 6000°C, much higher than the adiabatic flame temperature of Al at 3732°C. The carbon in the reduced graphene structure is likely the cause of the need for a higher emissivity value. Considering the possible role of rGO changing the emissivity, the samples were separated into three groups based on their percent graphene loading and assigned a consistent emissivity for that loading such that none of the maximum temperatures surpassed the adiabatic flame temperature of aluminum. It is expected that the local maximum temperature will closely approach the adiabatic flame temperature of aluminum and oxygen as shown in a previous study where a polymer binder was used [13]. The emissivity was assigned during the first set of experiments and used during both the first and second sets of thermal combustion experiments. It is of note that the emissivity value only changes the absolute temperature reading, and the relative temperature distribution among the samples will not change. Future research is required to accurately measure the emissivity values associated with

Table 3.5: Emissivity Values by Nanoparticle Loading

Graphene Loading	Emissivity
20% GO	0.23
10% GO	0.22
5% GO	0.19

Table 3.6: Maximum Combustion Temperature

Sample	Peak Temp. Trial 1 (°C)	Peak Temp. Trial 2 (°C)
rGO(20%)/Al/Fe ₂ O ₃	3614	3540
rGO(10%)/Al/Fe ₂ O ₃	2962	-
rGO(5%)/Al/Fe ₂ O ₃	3669	-
rGO(20%)/Al/Bi ₂ O ₃	3630	3278
rGO(10%)/Al/Bi ₂ O ₃	3710	-
rGO(5%)/Al/Bi ₂ O ₃	3029	-
rGO(20%)/Al/CuO	-	3631

nanothermite combustion. The determined emissivity values for each graphene loading percentage are summarized in Table 3.5.

Selected frames of the thermal footage of the propagation of rGO/Al/Fe₂O₃, rGO/Al/CuO, and rGO/Al/Bi₂O₃, all with a GO loading percentage of 20% are shown in Figure 3.12. It is of note that due to the propagation rate and limited frame capture rate of the thermal camera, only samples containing at least 20% GO were able to capture a reasonable number of frames for the combustion of the samples. Figure 3.13 demonstrates the combustion of the 5% and 10% GO samples which are qualitatively analyzed and discussed. In all samples, a hot flame can be seen propagating, following a thin preheating zone, and followed by a thicker cooling zone. The maximum temperatures from the thermal measurements are summarized in Table 3.6.

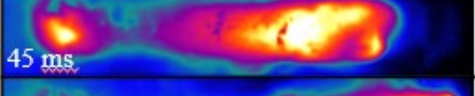
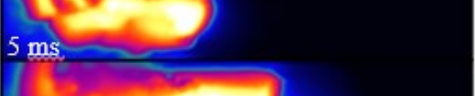
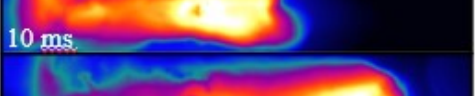
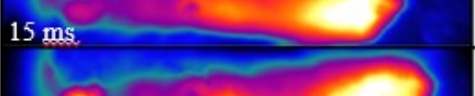
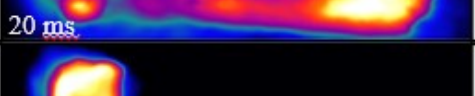
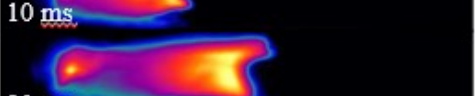
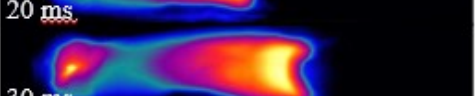
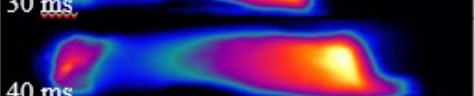
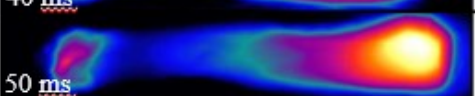
rGO/Al/Fe ₂ O ₃		Ignition
		Propagation
		
		
		Completion
rGO/Al/CuO		Ignition
		Propagation
		
		
		Completion
rGO/Al/Bi ₂ O ₃		Ignition
		Propagation
		
		
		
		Completion

Figure 3.12: Thermal propagation images for 20% GO samples

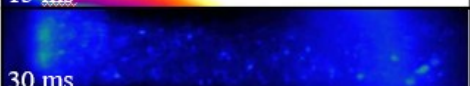
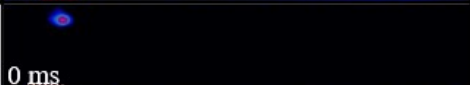
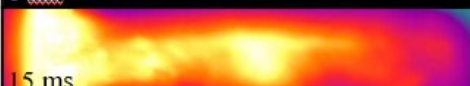
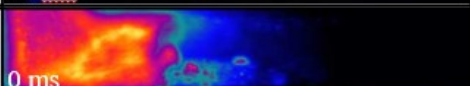
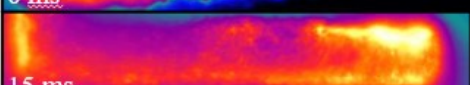
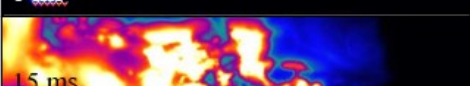
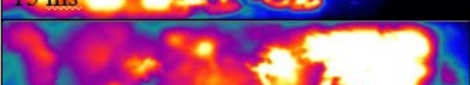
rGO(5%) /Al/Fe ₂ O ₃	 0 ms	Ignition
	 15 ms	Propagation
	 30 ms	Completion
rGO(5%) /Al/Bi ₂ O ₃	 0 ms	Ignition
	 15 ms	Propagation
	 30 ms	Completion
rGO(10%) /Al/Fe ₂ O ₃	 0 ms	Ignition
	 15 ms	Propagation
	 30 ms	Completion
rGO(10%) /Al/Bi ₂ O ₃	 0 ms	Ignition
	 15 ms	Propagation
	 30 ms	Completion

Figure 3.13: Thermal propagation images for 5% and 10% GO samples

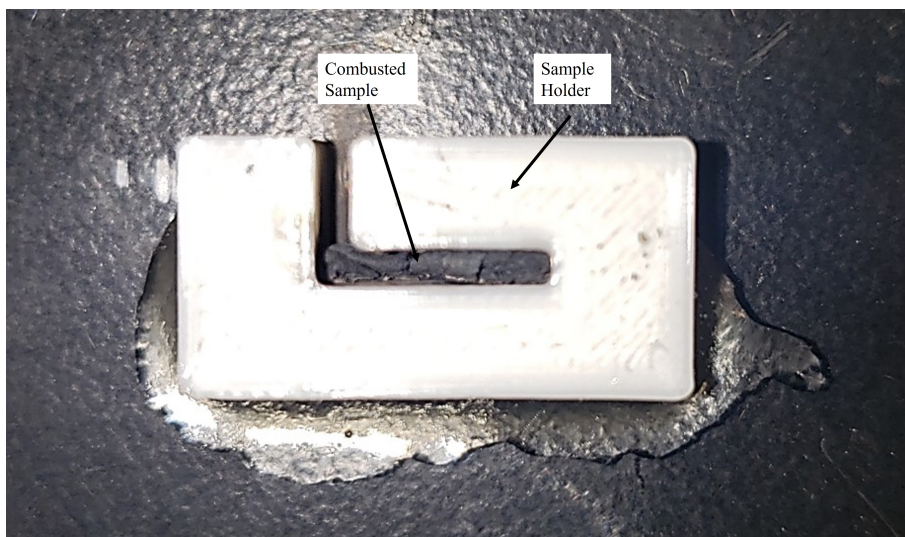


Figure 3.14: Residue of rGO/Al/CuO Sample

3.3 Post-Combustion Analysis

Figure 3.14 shows an image of the energetic aerogel material after combustion has occurred. In a typical nanothermite combustion the post-combustion residue is very difficult to obtain due to the near-detonation during combustion. The material is scattered from the ignition point or vaporized, depending on the reacting metals and metal oxides. However, for the energetic aerogel developed in this research, the controlled combustion of relatively low particle loading, and the structure of the graphene skeleton facilitated the recovery of the post-combustion material. This allows for a thorough analysis of the combusted aerogel products. The goal of the analysis is to determine how the metal fuel and metal oxides react with each other within the graphene structure and thermite clusters.

3.3.1 SEM, EDS, & TEM

SEM was first used to evaluate the microstructure of the samples after combustion. It can be seen that there are significant differences in the morphology of all of the samples after the high-temperature reactions. In rGO/Al/Fe₂O₃, seen in Figure 3.15 A, several large particles on the order of hundreds of nanometers to one micron in diameter, are seen throughout the sample. This is much larger than the initial particle sizes of the raw materials used in the fabrication of the aerogel, 100 nm Al and 100 nm Fe₂O₃. These large particles are formed due to reactive sintering due to a diffusive reaction, causing the nanoparticles to lose their nanostructure within nanoseconds as the temperature increases during combustion [9]. Reactive sintering is also seen in the rGO/Al/CuO sample as shown in 3.15 C, corresponding well with previously published data [13]. The different levels of brightness in these images indicate the different elements that have sintered together in this reaction such as Al and Fe, or Al and Cu. Additionally, the size of the sintered particles is similar to the size of the nanoclusters as shown in the SEM images before combustion, indicating that it is highly likely that the origin of the sintered particles is the original clusters. In the high-magnification images of Figure 3.15 B, D, and F it can be seen that there are small, densely packed nanoparticles attached to a substrate, the rGO structure. The particles are nearly spherical and evenly distributed on the rGO sheets. The sizes of these nanoparticles range from 5 to 50 nm in diameter, much smaller than the raw nanoparticles sizes used in fabrication. Therefore, these tiny particles must be generated as a product during the combustion of the nanothermite aerogel, along with the larger reactively sintered particles.

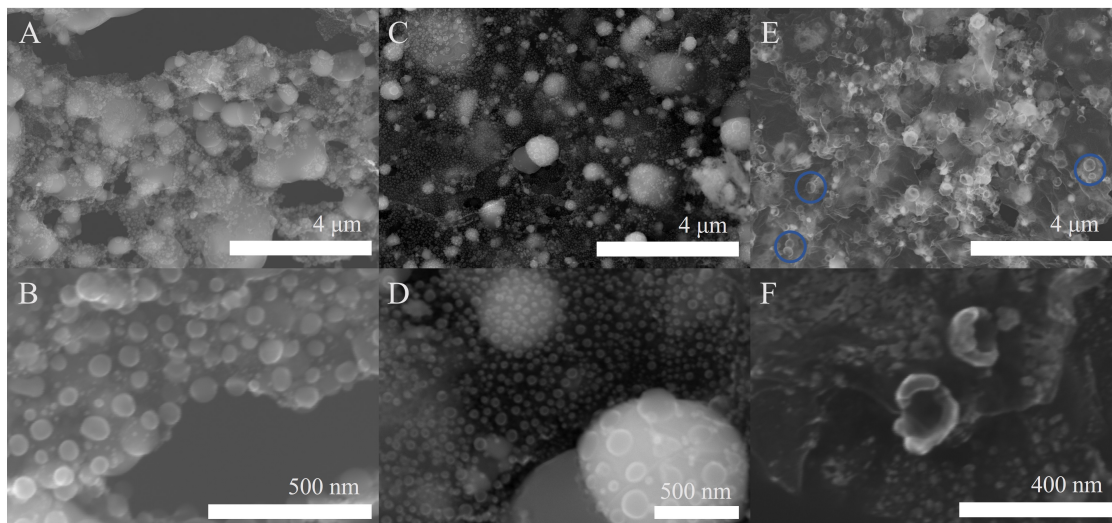


Figure 3.15: SEM of rGO/Al/Fe₂O₃ (A,B), rGO/Al/CuO (C,D), and rGO/Al/Bi₂O₃ (E,F) post-combustion

The residue material of rGO/Al/Bi₂O₃ however, presents a different structure after combustion. In 3.15 E it can be seen that there are no large sintered Al or Bi particles. The same graphene skeleton seen in the previous samples is also seen in combusted rGO/Al/Bi₂O₃, holding the reacted particles on its surface. EDS results were analyzed to show that the Bi content post-combustion is 25wt%, which is much less than the 59wt% of Bi in the raw material used in the nanothermite ink. This demonstrates that there is a significant loss of Bi during the reaction. This loss may be attributed to the boiling of Bi and Bi₂O₃, as their boiling points are 1564 °C and 1890°C respectively. These boiling points are notably lower than those of Fe and Cu at 2862°C and 2562°C, respectively. The Al content measured in EDS was measured to be approximately 50%, indicating that the Al was well preserved during the reaction. Since no large Al or Bi sintered particles are observed, the reaction mechanism for Al/Bi₂O₃ was different than those samples that un-

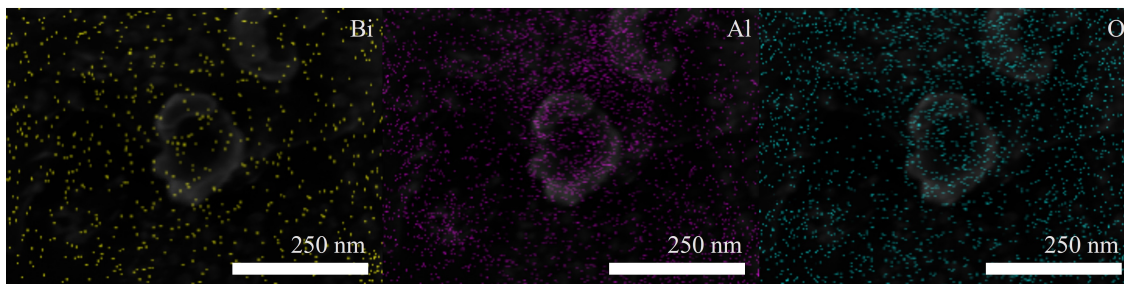


Figure 3.16: EDS of rGO/Al/Bi₂O₃ post-combustion

derwent reactive sintering. On the surface of the graphene skeleton of the rGO/Al/Bi₂O₃ sample, many small circular objects can be seen in 3.15 E highlighted with blue ellipses. These circular objects have diameters of approximately 100 nm and appear hollow in the images. A magnified view of the objects is seen in 3.15 F, confirming a hollow structure with some defects on the shell surface. 3.15 F also demonstrates some very small particles, less than 50 nm in diameter, similar to the particles observed in 3.15 B and D. Figure 3.16 demonstrates the EDS measurement of rGO/Al/Bi₂O₃. The accuracy of the EDS measurement is limited by the maximum resolution of the image. This makes it difficult to determine the elemental composition of the structures seen at this magnitude.

While the SEM and EDS provided interesting information that has not previously been seen, such as the tiny particles on the rGO sheets and the hollow shell structures in rGO/Al/Bi₂O₃, finer details were desired. Therefore TEM and EDS measurements were carried out for each of the three post combustion samples. Figure 3.17 demonstrates the TEM and EDS images of rGO/Al/Fe₂O₃ after combustion. Similar to the SEM shown previously, it is observed that there is a mixture of sintered particles and smaller scattered particles. The large sintered particles have sizes on the order of 1 μ m in diameter. The smaller particles are much smaller than 100 nm as seen in Figure 3.17 B. EDS results show

that Al and O have a nearly identical distribution, indicating the formation of Al_2O_3 , while Fe appears to be reduced to a near pure composition due to the oxidation of aluminum. EDS also demonstrates that the small particles consist of Al and O, indicating the oxidation of aluminum. As seen previously, the size of the small Al particles is much smaller than the raw aluminum that was apparent prior to combustion and must have been generated during the combustion process. This demonstrates that reactive sintering alone cannot fully explain the reaction mechanism occurring in this thermite reaction. It is hypothesized that melt dispersion occurs during the rapid heating of the Al nanoparticles. In this case, the temperature of the Al nanoparticles increases rapidly, causing the inner Al core to melt and potentially vaporize causing a high pressure within the aluminum oxide shell due to expansion. This high pressure causes the outer aluminum oxide shell to burst and eject small particles of melted or vaporized aluminum. The spallation of tiny Al droplets could either react with the surrounding particles or solidify as smaller particles on the surface of the rGO structure. The oxidation of the solidifying particles on the surface could be due to the thermite reaction or oxidation from environmental oxygen.

Figure 3.18 demonstrates the TEM and EDS images of rGO/Al/CuO post combustion. Similar to rGO/Al/ Fe_2O_3 , both sintered particles and scattered smaller particles are present in the image. The sintered particles seen in the rGO/Al/CuO sample are on the order of a few hundred nanometers, smaller than those of rGO/Al/ Fe_2O_3 , and smaller than sintered Al/CuO samples reported in previous literature [13]. This indicates that the sintering process typically includes fewer nanoparticles than previously shown. This is likely caused by the unique structure of the rGO skeleton and the subsequent reaction process of the thermite. In the previously reported polymer-assisted printing [13] the theoretical

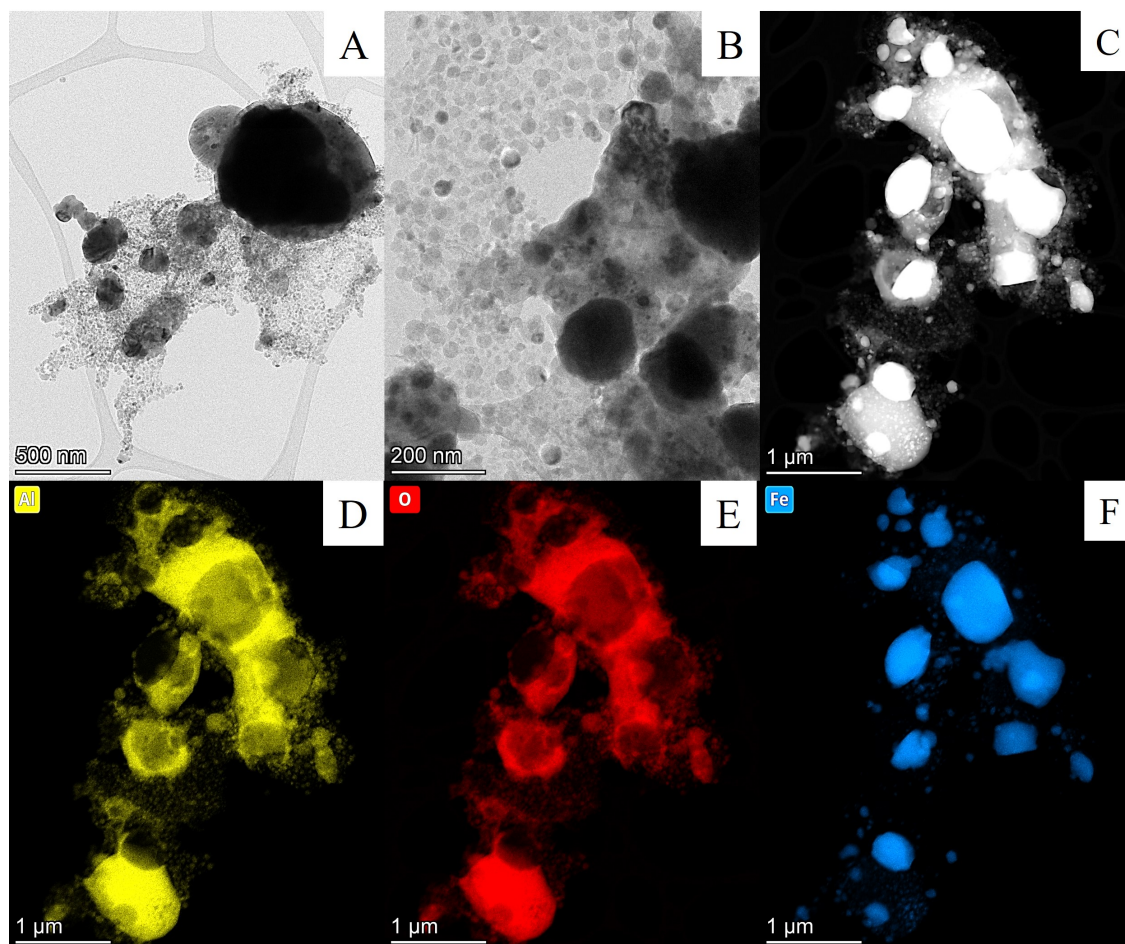


Figure 3.17: TEM of rGO/Al/Fe₂O₃ Sample

maximum density was approximately 10%, much higher than that of this study, leading to larger agglomerations and subsequent sintered particles. The high porosity structure used in this experiment limits the number of nanoparticles that can reach each other during the reaction to sinter together. The tightly wrapped rGO/nanoparticle clusters form small reaction units, leading to the redox reaction occurring within its own structure. The sintered particles of rGO/Al/CuO are likely smaller than those of rGO/Al/Fe₂O₃ due to the higher reactivity and lower ignition temperature of Al/CuO compared to Al/Fe₂O₃. The higher reaction rate of Al/CuO allows the redox reaction to complete within a larger number of small reaction clusters compared to Al/Fe₂O₃. The lower ignition temperature results in a more even flame front with more ignition sites, thus forming smaller sintered particles. Also, similar to the rGO/Al/Fe₂O₃ sample, there are many small particles attached to rGO sheets composed of Al and O in the combustion residue, significantly smaller than the original material. Once again, this is an indication of a melt dispersion reaction mechanism that contributes to the reaction of Al and CuO as well as reactive sintering.

Figure 3.19 demonstrates the TEM and EDS images for the rGO/Al/Bi₂O₃ sample post combustion. The microstructures seen in the rGO/Al/Bi₂O₃ sample are clearly different than those in the rGO/Al/Fe₂O₃ and rGO/Al/CuO samples. It can be seen that there are no large, solid sintered particles in the resultant material from the combustion. Many tiny particles are seen in the background of the image, attached to the reduced graphene sheet skeleton. Similar to the other two samples these particles are oxidized aluminum. These small oxidized aluminum particles are around 30 nm in size, much smaller than the 100 nm aluminum used in the ink solution, and are not perfectly spherical. It is hypothesized that these tiny particles are produced during the spallation of aluminum from the reactive

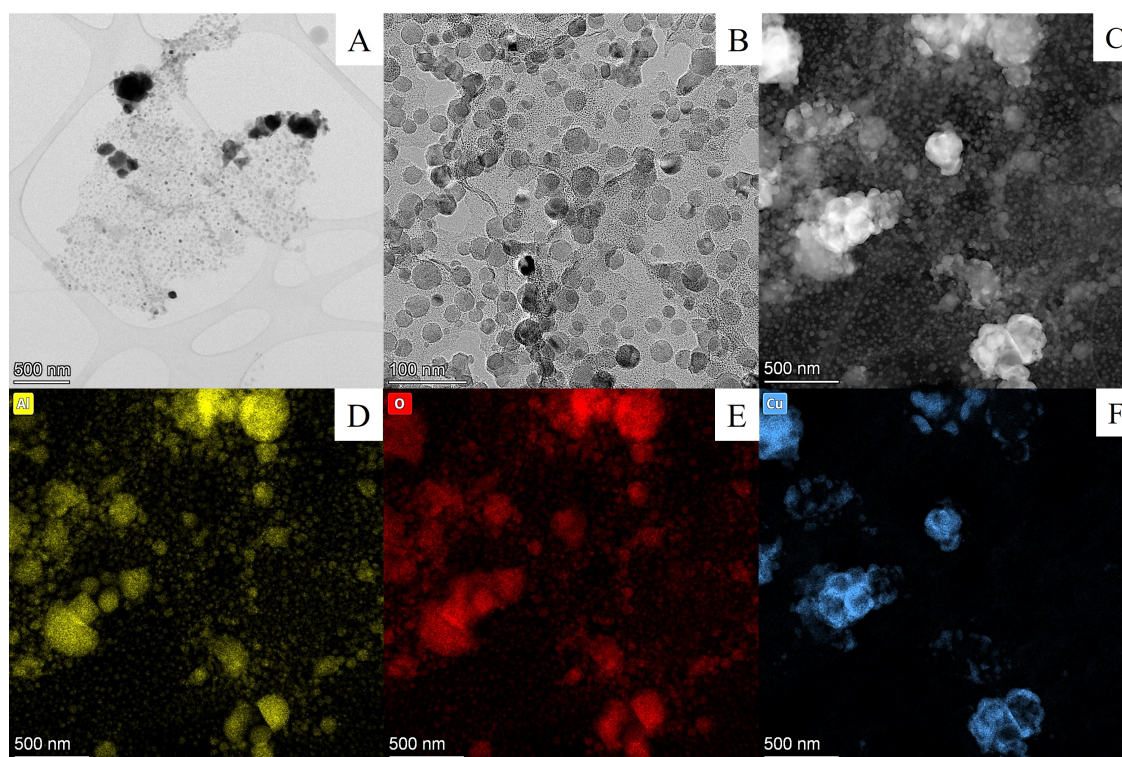


Figure 3.18: TEM of rGO/Al/CuO Sample

aluminum core, indicating that melt dispersion is occurring during this thermite reaction. Additionally, hollow shell structures in the size range of 100 to 400 nm in diameter are seen throughout the sample shown in 3.19 A and B. EDS results in 3.19 confirm that these hollow structures are composed of aluminum oxide. The size and shape of the shell structures indicate that they were likely produced during the rapid heating and spallation of the reactive aluminum core, leaving behind the hollow spherical aluminum oxide shell. it is of note that the post-combustion aluminum oxide shells are approximately 20 nm in thickness, which is much thicker than the original amorphous aluminum oxide shells, which are typically less than 4nm thick [53]. The significant growth of the aluminum oxide shell reveals the occurrence of a redox chemical reaction between the interfacial contact of Al and Bi_2O_3 likely caused by diffusion. The reduced bismuth, however, presents a drastically different distribution compared to the Fe and Cu in the previous samples. As summarized in EDS statistical data from SEM, a significant loss of Bi occurred during the combustion of the sample due to its evaporation. The TEM-EDS results shown in 3.19 F confirm this. The bismuth is seen to be evenly distributed across the sampled region in the image rather than sintering together into larger particles. This is a clear result of the vaporization and subsequent condensation of Bi or Bi_2O_3 . Therefore, this is the reason why Bi is not seen directly in the SEM images but is seen as a distribution in the EDS images. The slightly more concentrated areas of Bi overlap with the hollow Al_2O_3 structure indicating a reaction on the surface of these particles, further confirming the reaction driven by diffusion on the shell surface. A few extremely small particles, no larger than 10nm are also seen in this sample, which is also representative of the solidification of evaporate Bi, with minor crystal growth.

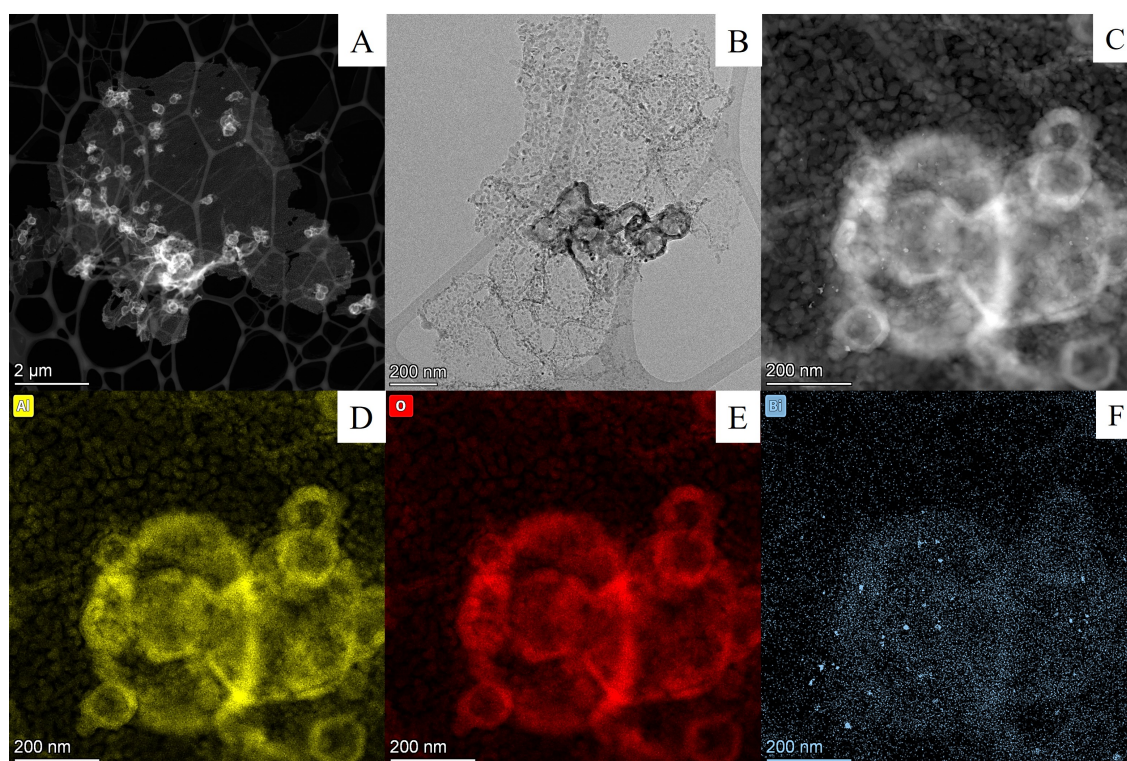


Figure 3.19: TEM of rGO/Al/Bi₂O₃ Sample

Chapter 4

Discussion

4.1 Thermal Propagation Analysis

Thermal propagation during combustion is a key factor in the evaluation of the energetic aerogel for select applications. The heating and cooling zones can give a lot of information on the behavior of the material. Due to limitations in the frame capture rate of the thermal camera at 750fps, thermal analysis could only be completed on the samples made with 20% GO. For the samples containing 5% and 10% GO, only a few frames were able to be captured during combustion. Selected frames of the thermal footage of the combustion of rGO(20%)/Al/Bi₂O₃ and rGO(20%)/Al/Fe₂O₃ along with their respective center line temperature profiles over time are shown in Figure 4.1. The center line location where temperature is measured for this analysis is shown in Figure 4.1 A and C. It is of note that the high peak temperature at 1.5mm is caused by the laser used for ignition and is

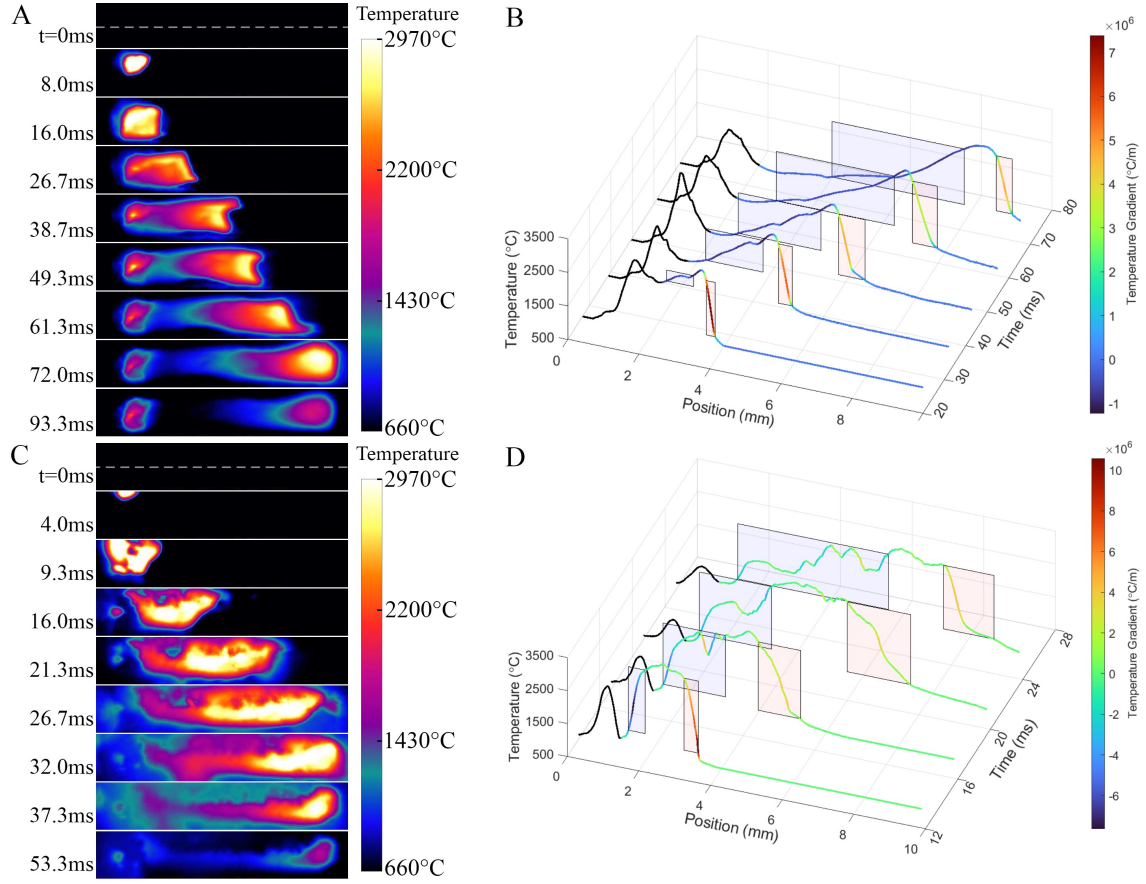


Figure 4.1: Thermal propagation of rGO(20%)/Al/MO_x samples

disregarded in the analysis of this experiment.

Clearly visible in Figure 4.1 A and C a hot flame is seen propagating, led by a thin pre-heating zone and followed by a thick cooling zone. The pre-heating zone is defined as the zone in front of the peak temperature ranging from 90% to 10% of the difference between peak temperature and the lowest temperature ahead of the flame front. Similarly, the cooling zone is defined as the zone behind the flame front, ranging from 90% to 10% of the difference between the peak temperature and the lowest temperature measured behind

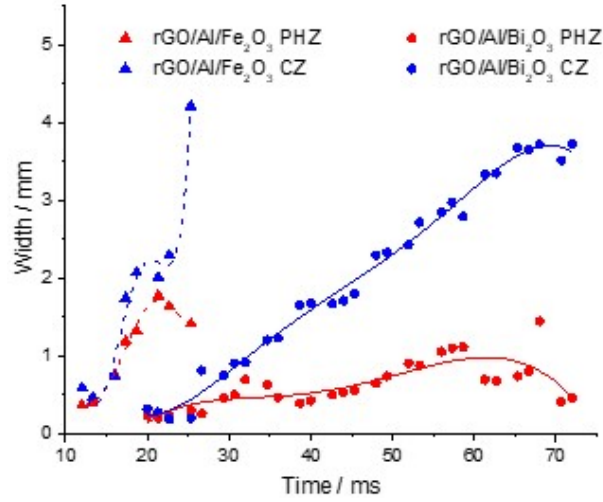


Figure 4.2: Pre-heating and cooling zone widths of rGO(20%)/Al/Bi₂O₃ and rGO(20%)/Al/Fe₂O₃

the peak temperature. Both the pre-heating and cooling zones can be easily distinguished and labeled for the rGO(20%)/Al/Bi₂O₃ sample due to its slow and steady propagation. Therefore the rGO(20%)/Al/Bi₂O₃ sample was primarily used for the thermal analysis of the aerogel material. A pre-heating zone, ranging from roughly 200-1000 μm in width can be seen as red boxes in Figure 4.1 B, and a cooling zone up to 4mm in width can be seen as blue boxes in Figure 4.1 B. The change in pre-heating and cooling zone widths over time can be seen in 4.2. It is clearly seen that the widths of both zones increased with propagation until 60-65 ms. As the reaction approached its end, the width of the preheating zone reduced due to the limited remaining sample and more irregular propagation, possibly due to convection. At the same time, the cooling zone width reached a plateau, indicating that a possible equilibrium had been reached between the heat generation, heat transfer, and heat loss to the environment.

Within the preheating zone, a highly linear temperature rise can be seen between 1000°C and the peak temperature. It can be calculated that the thermal gradient, represented by the slope in the graph, can be calculated to be between $3\text{-}6\times 10^6$ K/m. This is a much lower thermal gradient than reported values for the reaction front at 10^{10} [54], and the sintering zone at 3×10^7 K/m [13]. The reduction in thermal gradient is likely caused by the increased thermal conductivity of rGO. The calculated overall heat transfer rate in the preheating zone is calculated to be around $3\text{ Wm}^{-1}\text{K}^{-1}$. This is higher than the thermal conductivity values reported in literature for Al/Fe₂O₃ nanothermite with 0.7-0.9 porosity at 0.4-2 W/mK [55] or a consolidated aluminum pellet with 0.2-0.6 porosity at 0.2-1 W/mK [56]. Both previous works used samples with lower porosity than the tested samples in this experiment, further indicating the enhanced conductivity of the aerogel. A recent publication indicated that increasing the thermal conductivity of nanothermite material can enhance the heat transfer modes to the unreacted nanothermite region and subsequently increase the combustion rate [57]. It should be noted that the possibility of thermal convection carried by hot gas or hot ejections as well as thermal radiation cannot be ruled out from the thermal measurements. However, the convection effect would have to account for 90% of heat transfer for the conductivity to be on the same magnitude as previously published results of nanothermite with similar porosity. Additionally based on the linear temperature gradient in the preheating zone, it is hypothesized that the primary mode of heat transfer is conduction. Considering the high porosity of the sample, 98%, and lower thermal conductivity of Bi₂O₃ at around 1 W/mK [58], it is reasonable to believe that the great heat transfer rate can be mainly attributed to the highly conductive rGO skeleton. Moreover, the measured value here is one of the first few reported experimentally

in nanothermite research and can be used for modeling such systems with a low theoretical maximum density.

The cooling zone can also be used to analyze the heat transfer properties of the nanothermite aerogel samples. The plateau of the cooling zone of the rGO(20%)/Al/Bi₂O₃ sample settled around 3.6mm, which is much thicker than what has been reported in polymer assisted nanothermite [13]. It is hypothesized that the heat from the reaction was well dissipated throughout the sample due to the addition of the thermally conductive rGO.

The thermal camera footage and temperature profile of rGO(20%)/Al/Fe₂O₃ can be seen in Figure 4.1 C and D. Immediately it can be seen that the reaction of this sample was far more violent and irregular than that of the rGO(20%)/Al/Bi₂O₃ sample. The boundary between the flame front, preheating zone, and cooling zone are also less evident, However, the same 90%-10% analysis can be implemented with some confidence. Similar to the rGO(20%)/Al/Bi₂O₃ sample the rGO(20%)/Al/Fe₂O₃ sample both the preheating and cooling zones increased in width as the reaction propagated. Additionally, the preheating zone began to plateau and reduce as previously seen. One difference is that the cooling zone did not reach equilibrium. This is possibly due to the violence of the reaction from the higher aluminum percentage and lower activation energy of Al/Fe₂O₃ at 145 kJ/mol, compared to that of Al/Bi₂O₃ at 210 kJ/mol [59, 60]. The more violent reaction could cause the material to be ejected from the sample holder or shift the material out of the camera's focus.

4.2 Effect of Graphene

Combining the DSC/TGA and combustion test results, it can be concluded that the rGO used in the printed aerogel plays many roles in the structure of the gel, both enriching and diminishing the reactivity at the same time. The rGO skeleton allowed nanoparticles to assemble and form a unique porous structure which was able to accelerate the reaction. In polymer assisted 3D printed nanothermite materials, the polymer forms a continuous phase with metal fuel and metal oxide particles dispersed throughout the material, significantly reducing the amount of contact between reacting particles [17]. Although some polymers used in 3D printing are considered oxidizers themselves, such as fluoropolymers [13, 18], the slow decomposition of these polymers is the rate-determining step of the combustion. However, in the 3D printed rGO/Al/MO_x samples, no polymer was involved, and more importantly, the metal fuel and metal oxide particles were tightly packed together into clusters. A recently proposed reaction mechanism of nanothermite combustion based on reactive sintering and heat transfer can help explain this improvement [13]. In micro-scale visualization of Al/CuO nanothermite combustion, it was almost always observed that the thermite reaction happened locally within an agglomerate of Al and CuO nanoparticles, accompanied by the sintering of the fuel and oxidizer particles within its volume. As a result, an individual particle assembly of a micro-sized Al₂O₃ particle covered by Cu is formed. The propagation rate within the sintered particle was around 50 cm/s. However, the sintered particle significantly limited the heat transfer to neighboring areas, reducing the macroscale flame velocity to only 3 cm/s. In the 3D printed nanothermite aerogel structure presented in this thesis, the formation of clusters during the 3D printing process is

expected to facilitate the agglomeration of reactive nanoparticles and subsequently enhance the reactivity. The significantly reduced diffusion length between the metal fuel and the metal oxide allows for a much faster condensed phase reaction [43]. Meanwhile, the rGO skeleton efficiently transfers heat from one agglomerate to the next, further enhancing the reaction rate. Lastly, the micron-sized pores within the rGO skeleton allowed hot combustion products to better propagate inside the structure, leading to the local formation of hot spots in the scaffold [29].

It is possible that the rGO skeleton also hindered the propagation of the nanothermite reaction. When the nanoparticle loading was lower, and the GO loading was higher, the combustion enthalpy per unit mass for the thermite reaction was less. The greater amount of rGO is likely acting as a barrier, effectively reducing the contact between the metal Al and metal oxide particles, therefore reducing the activity. Also, the thermally conductive rGO structure could be dissipating the heat generated during the reaction, hindering combustion progress. Therefore, the nanoparticle loading percentage must be higher than a certain threshold to guarantee the accelerating effect of rGO in the final aerogel. This value is dependent on several parameters, including the topology of the printed aerogel, the properties of the nanothermite materials, and the amount of EDA used in the gelation reaction when printing. The results observed in this study suggest that increasing the nanoparticle loading beyond 95% may produce even faster and more energetic combustion and would also reduce the effects of rGO in forming localized clusters.

4.3 Reaction Mechanisms

The micro-morphology of each of the three rGO/Al/Metal oxide samples after combustion offers great insights into the chemical reactions and physical processes that dictate the reaction mechanisms and propagation of the combustion. Overall, the reaction mechanism is highly dependent on the metal oxide chosen for the combustion as evident by the very different morphologies of the sample residue post-combustion. For non-volatile metal oxides, of which both the metal oxides and its corresponding metal (ex. Fe_2O_3 and Fe) have very high boiling points, the post combustion debris confirmed the co-occurrence of both reactive sintering and melt dispersion. However, in rGO/Al/ Bi_2O_3 where Bi and Bi_2O_3 have relatively low boiling points, the reactive sintering is absent while the reaction diffusion and melt dispersion are seen.

The major difference between the samples is whether or not reactive sintering is observed. In the rGO/Al/ Fe_2O_3 and rGO/Al/CuO samples, both sintered Al and sintered Fe/Cu are seen. This indicates that the temperature of the flame front is higher than the melting points of Fe and Cu at 1538°C and 1085°C , respectively, but may be lower than the boiling point of Fe or Cu at 2662°C and 2562°C , respectively. These temperatures correspond fairly well with the measured median flame front temperature of Al/CuO from two color pyrometry data at about 2700°C as seen in previous research [13]. This also indicates that the approximation for the emissivity of the samples may be incorrect as the boiling of Fe and Cu are not seen. However, the maximum temperature of the combustion could locally reach temperatures above the boiling points of Fe and Cu throughout the sample without having the time to boil a significant amount of the material, with the heat

potentially being dispersed throughout the sample via the graphene structure. Overall, due to technological constraints, this is an approximation that all research groups working with the combustion of nanothermite must make.

In the rGO/Al/Bi₂O₃ sample, the boiling of Bi₂O₃ and Bi causes a significant amount of heat consumption during the combustion, leading to a significantly lower maximum temperature at the flame front. Looking at the samples with 20% GO by weight the maximum temperatures for rGO/Al/Bi₂O₃, rGO/Al/Fe₂O₃, and rGO/Al/CuO were 3278°C, 3540°C, and 3632°C, respectively. Although there is still limited certainty of the maximum temperature during combustion, the temperature of rGO/Al/Bi₂O₃ is conclusively about 300°C lower than the other two samples. Therefore, it is reasonable to hypothesize that reactive sintering of Al nanoparticles has a high temperature threshold to trigger and complete during the combustion. Past research has shown that the reactive sintering of Al in Al/CuO finishes within 10 ms at 1200°C [9], while the extremely fast heating (10¹¹K/s) caused the reactive sintering of Al within 0.5 μs[61]. While the combustion temperature is definitely considerably higher than 1200°C, considering the boiling point of Bi₂O₃ and Bi, the duration of the locally high temperature may not be sufficient to allow Al nanoparticles to sinter. Therefore, although reactive sintering of Al is clearly a well-established and confirmed reaction mechanism for high temperature nanothermite combustion with relatively low speed, it may not be universal to all energetic nanomaterials.

The occurrence of melt dispersion is consistently observed in all of the tested samples. In each of the three sample cases, the small oxidized aluminum particles of less than 100nm in diameter are densely attached to the surface of the rGO sheets. The spallation of Al, as described by previous research [40, 45], is the most reasonable explanation for

this phenomenon. The Al-O particles formed on the rGO skeleton in the rGO/Al/Fe₂O₃ and rGO/Al/CuO samples are very spherical as seen in the TEM images, whereas the Al-O particles present in the rGO/Al/Bi₂O₃ sample are more irregular in shape. This is likely caused by the difference in reaction temperature and subsequent reaction violence during combustion. The higher temperature of the rGO/Al/Fe₂O₃ and rGO/Al/CuO combustion may cause a stronger ejection of molten or vaporized Al due to the more rapid pressurization of the Al₂O₃ shell. This more rapid and hotter material travels to the rGO sheets and condenses into spherical particles in cooling. On the other hand, for rGO/Al/Bi₂O₃, the melt dispersion effect is weaker at lower temperatures, resulting in lower temperature Al to be ejected which can condense quicker into irregular forms upon contact with the graphene sheets. Additionally, in the rGO/Al/Bi₂O₃ sample, the presence of the hollow Al₂O₃ shell strongly supports the melt dispersion case. The hollow shell with partial openings indicates that it is cracking and breaking during the reaction, and the fragments confirm high stress is generated within the core of the particle. The presence of melt dispersion in the rGO/Al/Bi₂O₃ sample also suggests that melt dispersion will occur before reactive sintering under low temperatures or at faster heating rates.

Overall, it is critical to analyze all of the possible pathways for the chemical redox reaction and physical processes that occur during combustion. Although reactive sintering is not observed in rGO/Al/Bi₂O₃ post-combustion material, the thickened layer of Al₂O₃ clearly indicates that a diffusion based reaction occurred at the interface of the fuel and oxidizer nanoparticles. Therefore, a diffusion reaction, including at least partial reactive sintering, plays a significant role in all three samples during the reaction. It is reasonable to believe that both reactive sintering and melt dispersion exist during the combustion of

all samples with a propagation speed between 15 - 60 cm/s. The high boiling point and decomposition temperatures of Fe_3O_3 make $\text{rGO}/\text{Al}/\text{Fe}_2\text{O}_3$ a great reference sample with the simplest process. The exothermic reaction is likely triggered by both interfacial diffusion between fuel and oxidizer and reactive sintering, and the propagation is caused by mass diffusion, heat transfer, and melt dispersion. In $\text{rGO}/\text{Al}/\text{CuO}$, another major process occurs. Between 850°C and 1000°C CuO decomposes into Cu_2O [62], which can provide additional oxygen for the reaction with aluminum. While the additional oxygen is not required for the ignition of nanothermite [49], the formation of this oxygen gas can contribute to the higher propagation rate seen in the $\text{rGO}/\text{Al}/\text{CuO}$ sample. In $\text{rGO}/\text{Al}/\text{Bi}_2\text{O}_3$, the low boiling points of Bi_2O_3 and Bi significantly reduced the reaction temperature of this material, hindering the occurrence of reactive sintering. However, the combustion speed was only slightly lower than that of $\text{rGO}/\text{Al}/\text{Fe}_2\text{O}_3$. It is hypothesized that the boiled Bi_2O_3 or Bi vapor may travel across the sample similar to the gaseous oxygen of $\text{rGO}/\text{Al}/\text{CuO}$, heating up or igniting the unreacted sample, accelerating the flame propagation. Overall, the combustion behavior of nanothermite is therefore governed by the physical properties of the metal fuel and metal oxide selected for the reaction.

4.4 Applications

There is a wide range of applications for the additively manufactured energetic aerogel developed in this project. The great variability and controllability of the combustion behavior allow it to be suited for several applications. Slower burning materials with lower energetic nanoparticle loading could be well suited for propellant, soldering, or welding.

The high temperature combustion is expected to aid in applications where a lot of heat is required such as welding. The faster burning samples with higher energetic nanoparticle loading could be used for explosives, pyrotechnics, and triggering mechanisms. Based on the direct ink writing method if the loading percentage of the aerogel could be controlled during the print, a functionally graded material could be created. The functional grading of a solid energetic material could be used in several applications including solid rocket motors, which typically require complex manufacturing methods [60]. If a solid rocket could be functionally graded a less complex grain geometry could be used as the combustion of the fuel could be controlled via other means such as the loading of reactive components in the fuel. It is important to note that the applications of this direct ink writing additive manufacturing method are not limited to combustible materials. The wide range of particle loading and unique porous graphene structure could have benefits for applications in supercapacitors, electrodes, and catalysts.

Chapter 5

Conclusions

This work investigated the structural, thermochemical, and combustion properties of a novel, polymer-free nanothermite aerogel fabricated by an innovative direct ink writing method. An rGO/Al/MO_x nanothermite aerogel with flexible nanoparticle loading was fabricated at room temperature by reducing graphene oxide sheets in-line in a direct ink writing system via a reaction with EDA. The printed nanothermite aerogel presented a unique porous structure of interconnected reduced graphene oxide sheets and independently wrapped nanothermite clusters within the sheets. The nanoparticles showed no sign of phase separation and showed great dispersion and homogeneity within the reduced graphene oxide skeleton. The tightly packed metal fuel and metal oxide nanoparticles within each cluster enclosed by graphene sheets significantly shortened the required diffusion length for the occurrence of an energetic reaction. This reduced the reaction temperature and promoted the occurrence of condensed-phase reactions, accelerating the reaction propagation. With a nanoparticle loading of over 90%, the material showed a linear burn

rate on the order of meters per second, which is much higher than the polymer assisted 3D printed nanothermite composites, highlighting the merit of the polymer-free structure developed over the course of this project. The nanothermite aerogel also demonstrated a high combustion temperature, comparable to other alternative 3D printed energetic materials. It was confirmed that while rGO helped to form local reactive clusters to facilitate nanothermite reactions, a relatively high nanoparticle loading was favored to achieve a high combustion rate. It was also shown that rGO played both a role in primarily catalyzing, but also likely hindering the propagation of combustion, ultimately leading to a high combustion rate of the aerogel compared to polymer based nanothermite 3D printing methods.

This work also investigated the reaction mechanisms of the three nanothermite pairings using the unique structure of the rGO aerogel to analyze the post-combustion residue. The strong, porous graphene structure of the aerogel allowed for the effective collection of post-combustion materials for deeper analysis using electron microscopy to gain an improved understanding of the nanothermite reactions. The melt dispersion and diffusion mechanisms, which were previously thought to be contradictory, have been shown to appear simultaneously in the reactions depending on the metal and metal oxide pairing. Reactive sintering required a relatively higher temperature to take place, thus was absent in the rGO/Al/Bi₂O₃ sample due to the lower temperature of combustion caused by the boiling of Bi and Bi₂O₃. Reaction via general diffusion is observed in all samples regardless of the temperature. Melt dispersion was also shown to have occurred across all samples, especially under the circumstances of lower reaction temperature. This was confirmed by the densely scattered Al-O nanoparticles that were smaller than the raw material used

in printing and by the fragmented Al_2O_3 shells. The elevated temperature caused the Al nanoparticles to melt or evaporate as seen by the very spherical condensed particles. The reactivity and rate at which aluminum is ejected from the aluminum oxide shell can be an important factor that boosts the propagation rate of combustion. Other contributors such as the generation of gaseous oxygen due to decomposition will also change the macroscopic reaction properties of the nanothermite material. In summary, the choice of metal oxide plays a critical role in the reaction performance of nanothermite, and the occurrence of different reaction pathways can be used to achieve desired behaviors for various materials.

Chapter 6

Future Work

The primary focus of this project moving forward will be the continuous development of the additive manufacturing system to improve and optimize the system. This rGO nanoparticle aerogel has promise for both fundamental scientific research and a variety of industrial applications, with and beyond nanoenergetic materials. The objective moving forward will be to improve the consistency and accuracy of the prints such that more complex and detailed structures can be printed with better controllability. It is desired to have printed material of complex shapes with no breakages, deformities, or inconsistencies. Potential improvements also lie in the mixing of nanoparticles and reducing agents in the direct ink writing method. One major improvement that could be made with the nanothermite ink creation is the variability in loading of the ink in-situ. This would mean that while printing, based on fluid flow rate the loading of graphene oxide, metal fuel, and metal oxide could be varied throughout the print. It would also be beneficial to test other additives that could help the print depending on the desired application. For example,

a gasifying agent could be included for the application of a propellant. Additionally, if a greater level of automation could be implemented into the system, the product would be more viable for commercial applications as less human intervention would be required. Overall, the development of this project and product will be a large engineering endeavor and could suit many purposes.

The secondary focus of this project will be continuing to use the additively manufactured graphene aerogel structure to gain a better understanding of the reaction mechanisms of nanothermite. The reaction mechanisms of other common nanothermite metal/metal oxide combinations can be analyzed to gain a deeper understanding of how their reactions propagate, which can lead engineers to better design thermite compositions based on the application.

References

- [1] M. L. Pantoya and J. J. Granier. Combustion behavior of highly energetic thermites: Nano versus micron composites. *Propellants, Explosives, Pyrotechnics*, 30:53–62, 2005.
- [2] S. Bhattacharya, A. K. Agarwal, T. Rajagopalan, and V. K. Patel. Nano-energetic materials. *Energy, Environment, and Sustainability*, Springer, 2019.
- [3] R. Thiruvengadathan, A. Bezmelnitsyn, S. Apperson, C. Staley., P. Redner, W. Balas, S. Nicolich, D. Kapoor, K. Gangopadhyay, and S. Gangopadhyay. Combustion characteristics of novel hybrid nanoenergetic formulations. *Combustion and Flame*, 158, 2011.
- [4] V. E. Sanders, B. W. Asay, T. J. Foley, B. C. Tappan, A. N. Pacheco, and A. F. Son. Reaction propagation of four nanoscale energetic composites (al/moo3, al/wo3, al/cuo, and b12o3). *Journal of Propulsion and Power*, 23, 2007.
- [5] D. K. Smith, D. K. Unruh, C. Wu, and M. L. Pantoya. Replacing the al2o3 shell on al particles with an oxidizing salt, aluminum iodate hexahydrate. part i: Reactivity. *The Journal of Physical Chemistry C*, 121, 2017.

- [6] R. Thiruvengadathan, C. Staley, J. M. Geeson, S. Chung, K. E. Raymond, K. Gangopadhyay, and S. Gangopadhyay. Enhanced combustion characteristics of bismuth trioxide-aluminum nanocomposites prepared through graphene oxide directed self-assembly. *Propellants, Explosives, Pyrotechnics*, 4, 2015.
- [7] J. A. Puszynski, C. J. Bulian, and J. J. Swiatkiewicz. Processing and ignition characteristics of aluminum-bismuth trioxide nanothermite system. *Journal of Propulsion and Power*, 23, 2007.
- [8] R. Thiruvengadathan, S. Chung and S. Basuray, B. Balasubramanian, C. Staley, K. Gangopadhyay, and S. Gangopadhyay. A versatile self-assembly approach toward high performance nanoenergetic composite using functionalized graphene. *Langmuir*, 30, 2014.
- [9] K. T. Sullivan and 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, 2012.
- [10] G. C. Egan, K. T. Sullivan, T. LaGrange, B. W. Reed, and M. R. Zachariah. In situ imaging of ultra-fast loss of nanostructure in nanoparticle aggregates. *Journal of Applied Physics*, 115, 2014.
- [11] M. Pantoya and S. W. Dean. The influence of alumina passivation on nano-al/teflon reactions. *Thermochimica Acta*, 493:109–110, 2009.
- [12] V. I. Levitas, B. W. Asay, S. F. Son, and M. Pantoya. Melt dispersion mechanism for fast reaction of nanothermites. *Applied Physics Letters*, 89, 2006.

- [13] H. Wang, D. J. Kline, and M. R. Zachariah. In-operando high-speed microscopy and thermometry of reaction propagation and sintering in a nanocomposite. *Nature Communications*, 10, 2019.
- [14] N. V. Muravyev, K. A. Monogarov, U. Schaller, I. V. Fomenkov, and A. N. Pivkina. Progress in additive manufacturing of energetic materials: Creating the reactive microstructures with high potential of applications. *Propellants, Explosives, Pyrotechnics*, 44, 2019.
- [15] V. G. Rocha, E. Saiz, I. S. Tirichenko, and E. García-Tuñón. Direct ink writing advances in multi-material structures for a sustainable future. *Journal of Materials Chemistry A*, 8, 2020.
- [16] H. Wang, J. Shen, D. J. Kline, N. Eckman, N. R. Agrawal, T. Wu, P. Wang, and M. R. Zachariah. Direct writing of a 90 wt% particle loading nanothermite. *Advanced Materials*, 31, 2019.
- [17] J. Shen, H. Wang, D. J. Kline, Y. Yang, X. Wang, M. Rehwoldt, T. Wu, S. Holdren, and M. R. Zachariah. Combustion of 3d printed 90 wt% loading reinforced nanothermite. *Combustion and Flame*, 215:86–92, 2020.
- [18] Y. Mao, L. Zhong, X. Zhou, D. Zheng, X. Zhang, T. Duan, F. Nie, B. Gao, and D. Wang. 3d printing of micro-architected al/cuo-based nanothermite for enhanced combustion performance. *Advanced Engineering Materials*, 21, 2019.
- [19] J. Wang, J. Wang, S. Wang, H. Li, Q. Yan, and K. Xu. High-energy al/graphene oxide/cufe₂o₄ nanocomposite fabricated by self-assembly: Evaluation of heat release,

- ignition behavior, and catalytic performance. *Energetic Materials Frontiers*, 2(1):22–31, 2021.
- [20] A. Wang, S. Bok, C. J. Mathai, K. Gangopadhyay, J. McFarland, M. R. Maschmann, and S. Gangopadhyay. Stability study of iodinated reduced graphene oxide and its application in self-assembled al/bi₂o₃ nanothermite composites. *Nano Futures*, 4(4):045002, nov 2020.
- [21] Y. Chen, G. Egan, J. Wan, S. Zhu, R. Jacob, W. Zhou, J. Dai, Y. Wang, V. Danner, Y. Yao, K. Fu, Y. Wang, W. Bao, T. Li, M. Zachariah, and L. Hu. Ultra-fast self-assembly and stabilization of reactive nanoparticles in reduced graphene oxide films. *Nature Communications*, 2016.
- [22] Y. Wang, F. Li, Y. Shen, C. Wang, Z. Zhang, J. Xu, Y. Ye, and R. Shen. Fabrication of high electrostatic safety metastable al/cuo nanocomposites doped with nitro-functionalized graphene with fast initiation ability and tunable reaction performance. *Combustion and Flame*, 233:111580, 2021.
- [23] A. Wang, S. Bok, C. Mathai, R. Thiruvengadathan, C. Darr, H. Chen, M. Zachariah, K. Gengopadhyay, J. McFarland, M. Maschmann, and S. Gangopadhyay. Synthesis, characterization and nanoenergetic utilizations of fluorine, oxygen co-functionalized graphene by one-step xef₂ exposure. *Combustion and Flame*, 215:324–332, 2020.
- [24] I. Smirnova and P. Gurikov. Aerogel production: Current status, research directions, and future opportunities. *The Journal of Supercritical Fluids*, 134:228–233, 2018. 30th Year Anniversary Issue of the Journal of Supercritical Fluids.

- [25] G. Gorgolis and C. Galiotis. Graphene aerogels: a review. *2D Materials*, 4, 2017.
- [26] K. Ghosh, C. Y. Yue, M. Moniruzzaman, R. K. Jena, and S. Bi. Development of a 3d graphene aerogel and 3d porous graphene/mno₂@polyaniline hybrid film for all-solid-state flexible asymmetric supercapacitors. *Sustainable Energy Fuels*, 2, 2017.
- [27] X. Tian, Y. Zhou, X. Tu, Z. Zhang, and G. Du. Well-dispersed lifepo₄ nanoparticles anchored on a three-dimensional graphene aerogel as high-performance positive electrode materials for lithium-ion batteries. *Journal of Power Sources*, 340:40–50, 2017.
- [28] B. Cai and A. Eychmuller. Promoting electrocatalysis upon aerogels. *Advanced Materials*, 31, 2018.
- [29] A. Wang, S. Bok, R. Thiruvengadathan, K. Gangopadhyay, J.A. McFarland, M.R. Maschmann, and S. Gangopadhyay. Reactive nanoenergetic graphene aerogel synthesized by one-step chemical reduction. *Combustion and Flame*, 196, 2018.
- [30] E. Brown, P. Yan, H. Tekik, A. Elangovan, J. Wang, D. Lin, and J. Li. 3d printing of hybrid mos₂-graphene aerogels as highly porous electrode materials for sodium ion battery anodes. *Materials Design*, 170:107689, 2019.
- [31] Q. Zhang, F. Zhang, S. Medarametla, H. Li, C. Zhou, and D. Lin. 3d printing of graphene aerogels. *Nano Micro Small*, 12, 2016.
- [32] C. Zhu, T. Han, E. Duoss, A. Golobic, J. Kuntz, C. Spadaccini, and M. Worsley. Highly compressible 3d periodic graphene aerogel microlattices. *Nature Communications*, 6, 2015.

- [33] Y. Jiang, Z. Xu, T. Huang, Y. Liu, G. Guo, J. Xi and W. Gao, and C. Gao. Direct 3d printing of ultralight graphene oxide aerogel microlattices. *Advanced Funtional Materials*, 28, 2018.
- [34] A. Tsang, K. N. Hui, K. S. Hui, B. Liu, L. Yu, B. Shi, and H. Huang. Ink-printed metal/graphene aerogel for glucose electro-oxidation. *Battery Energy*, 1, 2022.
- [35] V. I. Levitas. Burn time of aluminum nanoparticles: Strong effect of the heating rate and melt-dispersion mechanism. *Combustion and Flame*, 156, 2009.
- [36] M. A. Trunov, M. Schoenitz, and E. L. Dreizin. Ignition of aluminum powders under different experimental conditions. *Propellants, Explosives, Pyrotechnics*, 30, 2005.
- [37] K. Park, D. Lee, A. Rai, D. Mukherjee, and M. R. Zachariah. Size-resolved kinetic measurements of aluminum nanoparticle oxidation with single particle mass spectrometry. *Journal of Chemical Information and Modeling*, 109, 2005.
- [38] A. Rai, D. Lee, K. Park, and M. R. Zachariah. Importance of phase change of aluminum in oxidation of aluminum nanoparticles. *Journal of Physical Chemistry B*, 108, 2004.
- [39] A. Rai, K. Park, L. Zhou, and M. R. Zachariah. Understanding the mechanism of aluminium nanoparticle oxidation. *Combustion Theory and Modelling*, 10, 2006.
- [40] V. I. Levitas, B. W. Asay, S. F. Son, and M. Pantoya. Melt dispersion mechanism for fast reaction of nanothermites. *Applied Physics Letters*, 89, 2006.

- [41] Ahmed Fahd, Charles Dubois, Jamal Chaouki, and John Z. Wen. Combustion behaviour and reaction kinetics of go/al/oxidizing salts ternary nanothermites. *Journal of Thermal Analysis and Calorimetry*, 147, 2022.
- [42] J. Shen, Z. Qiao, J. Wang, G. Yang, J. Chen, Z. Li, X. Liao, H. Wang, and M. R. Zachariah. Reaction mechanism of al-cuo nanothermites with addition of multilayer graphene. *Thermochimica Acta*, 666:60–65, 2018.
- [43] R. J. Jacob, G. Jian, P. M. Guerieri, and M. R. Zachariah. Energy release pathways in nanothermites follow through the condensed state. *Combustion and Flame*, 162:258–264, 2015.
- [44] H. Wang, D.J. Kline, and M.R. Zachariah. In-operando high-speed microscopy and thermometry of reaction propagation and sintering in a nanocomposite. *Nature Communications*, 10:3032, 2019.
- [45] V. I. Levitas, M. L. Pantoya, and S. Dean. Melt dispersion mechanism for fast reaction of aluminum nano- and micron-scale particles: Flame propagation and sem studies. *Combustion and Flame*, 161:1668–1677, 2014.
- [46] N. Zakiyyan, C. Mathai, J. McFarland, S. Gangopadhyay, and M. R. Maschmann. Spallation of isolated aluminum nanoparticles by rapid photothermal heating. *Applied Materials and Interfaces*, 14:55277–55287, 2022.
- [47] T. Zhang, Z. Wang, G. Li, and Y. Luo. Tuning the reactivity of al/fe₂o₃ nanoenergetic materials via an approach combining soft template self-assembly with sol–gel process. *Journal of Solid State Chemistry*, 230:1–7, 2015.

- [48] E. Lebedev, L. Sorokina, A. Trifiniv, R. Ryazanov, S. Pereverzeva, S. Gavrilov, and D. Gromov. Influence of composition on energetic properties of copper oxide – aluminum powder nanothermite materials formed by electrophoretic deposition. *Propellants, Explosives, Pyrotechnics*, 47, 2021.
- [49] G. 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.
- [50] Fidel D. Ruz-Nuglo and Lori J. Groven. 3-d printing and development of fluoropolymer based reactive inks. *Advanced Engineering Materials*, 20, 2017.
- [51] 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.
- [52] 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.
- [53] Renita K. Walzel, Valery I. Levitas, and Michelle L. Pantoya. Aluminum particle reactivity as a function of alumina shell structure: Amorphous versus crystalline. *Powder Technology*, 374:33–39, 2020.
- [54] B. Julien, H. Wang, E. Tichtchenko, S. Pelloquin, A. Esteve, M. Zachariah, and C. Rossi. Elucidating the dominant mechanisms in burn rate increase of thermite nanolaminates incorporating nanoparticle inclusions. *Nanotechnology*, 32, 2021.

- [55] J. Puszynski. Processing and characterization of aluminum-based nanothermites. *Journal of Thermal Analysis and Calorimetry*, 96, 2009.
- [56] S. C. Stacy, X. Zhang, M. Pantoya, and B. 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.
- [57] H. Wang, D. J. Kline, M. C. Rehwoldt, and M. R. Zachariah. Carbon fibers enhance the propagation of high loading nanothermites: In situ observation of microscopic combustion. *Advanced Engineering Materials*, 13, 2021.
- [58] V I Fedorov and I Y Davydov. Thermoelectric properties of vanadium, bismuth, and antimony oxides in the temperature interval 500–1500/sup 0/k. *High Temp. (USSR) (Engl. Transl.); (United States)*, 16:1, 7 1978.
- [59] S. Li, T. Gao, M. Yao, W. Ding, J. Chen, J. Song, S. Zhang, and R. Zhu. Thermal behavior and combustion performance of al/bi₂o₃ nano thermites with the effect of potassium perchlorate. *Materials Research Express*, 8, 2021.
- [60] Run-Hua Fan, Hong-Liang Lü, Kang-Ning Sun, Wan-Xia Wang, and Xin-Bing Yi. Kinetics of thermite reaction in al-fe₂o₃ system. *Thermochimica Acta*, 440(2):129–131, 2006.
- [61] G. C. Egan, T. LaGrange, and M. R. Zachariah. Time-resolved nanosecond imaging of nanoscale condensed phase reaction. *Journal of Physical Chemistry C*, 119, 2015.
- [62] W. Hu, F. Donat, S. A. Scott, and J. S. Dennis. The interaction between cuo and al₂o₃ and the reactivity of copper aluminates below 1000 °c and their implication on

the use of the cu–al–o system for oxygen storage and production. *The Royal Society of Chemistry*, 6, 2016.